# Measurements of VOCs by passive Radiello sampling at a hydraulic fracturing site in the Surat Basin, Queensland

## Milestone of 6 of Project W.11- Air, Water and Soil Impacts of Hydraulic Fracturing

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GISERA

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The authors thank the landholders for hosting measurements on their property, SGS staff for performing the sampling and analysis, and Origin Energy.

# Glossary

## Units of measurement

$\mu g\ m^{-3}$ – micrograms per cubic metre (1 microgram = one millionth of a gram)

ppm – parts per million by volume

ppb – parts per billion by volume

## Nomenclature

Aldehyde – a class of oxygenated volatile organic compounds

Ambient air – outdoor air

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

Geogenic- of geological origin

VOC – volatile organic compound

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

## Abbreviations

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

CO – carbon monoxide

$CO_2$ – carbon dioxide

$CH_4$ - methane

GISERA – Gas Industry Social and Environmental Research Alliance

HF- Hydraulic Fracturing

$H_2S$ – hydrogen sulphide

NEPM – National Environment Protection Measure

$NO_x$ – oxides of nitrogen

$O_3$ - ozone

PM2.5 - particles with an aerodynamic diameter of < 2.5 µm

PM10 - particles with an aerodynamic diameter of < 10 µm

SBAAQ Study- Surat Basin Ambient Air Quality Study (Lawson et al 2016)

# Executive Summary

A study of the ambient concentrations of a range of VOCs, aldehydes and hydrogen sulphide by Radiello passive sampling methods was undertaken at a site within a region of intensive Coal seam gas (CSG) production in the Surat Basin in Queensland from October 2016 to September 2017. Samples were collected at 7 locations within a property where 18 CSG wells underwent Hydraulic Fracturing (HF) treatments in late 2016 and mid-2017. Sampling occurred during HF periods as well as periods when HF was not occurring. There was a range of well development operations occurring at the study site during the measurement period including well integrity testing, perforation, HF site set-up, HF treatment, and well completions. It was not uncommon to observe several different activities well development, occurring simultaneously across different well pads.

Samples were exposed for ~14 days each and  were likely to have been impacted by multiple emissions from multiple well development activities including HF as well as sources natural (e.g. smoke, vegetation) and other man-made sources (e.g. vehicles, industry, agriculture) of VOCs, aldehydes and $H_2S$ from the surrounding area.

The study was designed to address three objectives:

**Objective 1**- Provide comparisons of the VOC levels observed at the HF site with Australian federal and state and other relevant air quality objectives.

**Objective 2**- Provide comparisons of the composition of VOCs observed at a HF site with simultaneous measurements from areas within the Surat Basin not directly impacted by HF operations.

**Objective 3**- Provide comparisons of the composition of VOCs observed during HF activity with data from measurements during non- HF periods at the same site.

There were 22 compounds reported above the detection limit (DL) of the Radiello method at the HF study sites on one or more occasions. The maximum concentrations for all 22 compounds detected at the HF study sites during this study were tens to thousands of times below National (NEPM) and State (EPP) long-term (annual) air quality guidelines, and international air quality guidelines (Texas AMCV/ESL) referenced here. The maximum concentrations of the NEPM air toxics benzene, toluene, and xylenes measured at the HF study site were tens to thousands of times lower than their respective NEPM monitoring investigation levels. Only 24-hour goals are specified for formaldehyde in the Air Toxics NEPM and the Radiello data reported levels of these pollutants cannot be assessed against these short-term guidelines. Instead the data, which had a maximum of 2.12 ppb, was compared against the annual Texas AMCV value for formaldehyde of 9ppb.There were 32 compounds including $H_2S$, that were not reported above the DL at the HF sites on any occasion and the maximum DLs for these compounds were tens to thousands of times lower than their relevant air quality guideline values.

Data from the HF study site were compared data with from 6 other sampling sites operated as part of the Surat Basin Ambient Air Quality (SBAAQ) Study (Lawson et al., 2017). Overall, the range of concentrations and detection frequencies observed for each compound at the HF site were similar to those observed at regional (>10km from CSG infrastructure) and other gas field sites

which were not known to be directly impacted by HF activities, and were also equal to or less than those observed in the township of Chinchilla. However, there were some exceptions:

- Maximum concentrations of toluene and formaldehyde observed at the HF site were higher than those observed for the gas field and regional sites not known to be directly impacted by HF. The detection frequency of toluene at the HF site was also slightly higher than the detection frequencies for the regional and gas field sites
- There were two compounds detected infrequently (1-2%) at the HF study site at very low concentrations (≤ 0.03 ppb) that were not detected at any of the other sites. These were: methyl isobutyl ketone; detected at Property A on one occasion in May 2017 during the non-HF period, and; tetrachloroethylene, detected on two occasions at Property B, once in July 2017 during HF, and the other in August 2017 after the HF period.

For most species measured, the concentration range and detection frequency during HF did not differ significantly from non-HF periods. However, there were some exceptions:

- The maximum concentrations of the VOCs benzene, toluene, m&p xylenes, and ethyl acetate measured during the HF period were slightly (< 0.1 ppb) higher than maximum concentrations measured in the non-HF periods. Detection frequencies of these compounds were also 9 – 19% higher during HF periods.
- The maximum concentrations of formaldehyde, and propanal measured during the HF period were higher than the maximums observed in the non-HF periods. The detection frequency of propanal was also 41% higher during HF periods.
- The detection frequency of butanal and n-undecane were ~18% higher during HF periods but the observed maximum concentrations did not differ significantly between HF and non-HF periods.

A more detailed analysis of the concentrations of the NEPM air toxics benzene, toluene, xylenes and formaldehyde and the potential factors that may have contributed to their observed concentrations during HF at the study site was undertaken. In general, the concentrations of BTEX compounds were at or below the DL (< 0.04 ppb) for the majority (> 70%) of the measurement period. Most of the time, the observed concentrations of BTEX compounds were similar across all 7 sampling sites (Sites A 1 – 3, and Sites B 1 – 4).

However there were some exceptions to these trends including:

- A peak in benzene concentrations of ~ 0.1 ppb in December 2016 which coincided with HF at Property A but was attributed to a regional smoke event based on: the widespread nature of this peak benzene event which was observed at other sites across the Surat Basin; information of a smoke event reported as part of the SBAAQ study; and analysis of typical VOC profiles from smoke.
- A peak in toluene, xylene and ethylbenzene concentrations was observed at a single sampling location with the HF site in July 2017. The localised nature of this event and analysis of wind direction indicated, but did not conclusively show, that local emissions from activities on site may have contributed to the peak in toluene, xylene and ethylbenzene concentrations. The VOC profiles of this event are suggestive of vehicle emissions however the source remains unresolved.

- Concentrations of formaldehyde observed across the HF site and other sites in the Surat Basin were similar over the study period and showed higher concentrations during summer likely due to contributions from photochemical production of formaldehyde in the atmosphere. On occasion, slightly higher concentrations of formaldehyde were observed at one or two sampling sites which were located predominantly downwind from well pads during HF activity. Further work is required to characterise the potential sources of formaldehyde associated with HF activity which currently remain poorly understood.

In summary, measurements of VOCs and aldehydes by passive Radiello monitoring at a HF site reported levels that were well below national, state and relevant international annual ambient air quality guidelines which are designed to protect human health, wellbeing and the environment, and were similar to those measured at other regional and gas field locations in the Surat Basin not known to be directly impacted by HF during the measurement period. While a regional smoke event was most likely responsible for a small peak in benzene concentrations, there was some indication that local sources including well development activities on site may have been associated with occasional peaks in the 14-day average concentrations of toluene, xylenes, ethylbenzene and formaldehyde, as well as higher concentrations and/or detection frequencies of propanal, butanal, n-undecane, and ethyl acetate. However the specific sources of these compounds remain unresolved.

Further work to better understand the factors that influence the concentration of VOCs and aldehydes in the atmosphere during well development activities and the impact of HF on air quality more broadly is underway. VOCs and aldehydes are only one group of compounds that are relevant to air quality. The National Environment (ambient air quality) Protection Measure, like the air toxics NEPM, prescribes air quality objectives for several other air pollutants including carbon monoxide (CO), oxides of nitrogen ($NO_x$), ozone ($O_3$), sulphur dioxide ($SO_2$), airborne particles (PM) and lead (NEPM 2016).

This report was produced as part of Phase 1 of the GISERA Air, Water and Soil Impacts of Hydraulic Fracturing: Phase 2 (W.11). Phase 2 (W.12) of the project involves a more comprehensive investigation of air, water and soil quality during HF at a site in the Surat Basin based on detailed peer-reviewed study designs developed for air quality (Dunne et al., 2017) and water and soil quality (Apte et al., 2017) studies as part of Phase 1.

This comprehensive study involved measurements at another site in which 10 CSG wells underwent HF between September and October 2017. The measurement program ran from July – December 2017 covering periods prior to HF, during HF activity, and after HF had concluded. Measurements were conducted at 6 different sampling locations within the field, with 16 different air quality variables measured utilising a mixture of continuous measurement systems for CO, $NO_x$, $O_3$, and airborne particles and integrated sampling of VOCs, aldehydes and airborne particles onto specialised sample cartridges or filters. Particular highlights of the measurement program undertaken by CSIRO and project partners for this study include:

- The most comprehensive suite of measurements of air quality undertaken in an Australian gas-field to date with over 50 individual measurement systems capable of detecting ~ 100 species including all air pollutants listed in the National Environment Protection Measures for Ambient Air Quality (NEPM 2015) and Air Toxics (NEPM 2011).

- High spatial resolution with measurements taken across 6 sites within a ~600 ha site containing 10 wells. Local meteorological conditions were measured at each sampling location.
- High time resolution with the combination of continuous measurements and short duration integrated sampling (12-hour – 48-hour samples) which are in line with the duration of HF activities (~ 1 - 2 days).

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

**Objective 1:** Quantify changes in air pollutant levels above background that occur during HF operations.

**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**: 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.

CSIRO Land and Water are undertaking a parallel study of the impact of HF on surface water, groundwater and soil. The proposed measurements of surface water, groundwater and soil occurred at the same time as some of the air quality measurements described in this report and also during the Phase 2 air quality study. The data from this study will provide important information on the composition of HF fluids and flowback water, which will improve our understanding of their potential to act as sources of air pollutants on HF sites. The final report for the Phase 2 study is expected to be released in early 2018. More information and project updates can be found at: https://gisera.csiro.au/project/air-water-and-soil-impacts-of-hydraulic-fracturing-phase-2/ .

# Preface

CSIRO Climate Science Centre is leading a project within the Gas Industry Social and Environmental Research Alliance (GISERA) investigating the impact of hydraulic fracturing (HF) on air, soil and water quality. An initial phase (Phase 1) proposal was approved by the GISERA Queensland Regional Research Advisory Committee (RRAC) in late 2016. Phase 1 (GISERA Project W.11) of the project involved conducting a review of the state of knowledge of impacts of HF on air, soil and water quality and the design of study to measure these impacts in the vicinity of wells before, during and after HF (GISERA 2018). The outputs of Phase 1 included:

- *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 surface water, groundwater and soil contaminants associated with CSG extraction using HF;
- *Task 3*- Report, including: state of the knowledge about the potential sources of air pollutants associated with CSG extraction using HF;
- *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 measurements of surface water, ground water and soil made before HF commenced in October 2016;

Phase 2 of the project (GISERA Project W.12) involved undertaking *“a comprehensive monitoring campaign to measure the air, surface water, ground water, and soil impacts of hydraulic fracturing of gas production wells in the Surat Basin, Queensland*” (GISERA 2017) at a selected study site.

In October 2016 Origin Energy secured the permission of landholders, and engaged SGS Leeder to undertake passive monitoring of volatile organic compounds (VOCs) and hydrogen sulphide ($H_2S$) in air at the proposed study site. Plans were also made to engage a third party contractor, Ecotech (Brisbane, Queensland) for the provision of a fixed air quality monitoring station (AQMS) also to be located at the study site. CSIRO visited the proposed study sites in October 2016 and provided advice and oversight on the selection of sites for the passive VOC and $H_2S$ monitoring and the AQMS.

This report is the output for Task 6 from Phase 1 (W.11) of this Project. In the original project proposal the objective of this task was to analyse and summarise air quality data measured near the study site before commencement of HF activity to provide information on baseline air composition. However, the selected location for the Phase 2 study (W.12) became unviable due to a lack of access to mains power required to operate the fixed air quality monitoring station and an alternative site was secured.

The passive VOC and $H_2S$ monitoring at the original study site was continued until December 2017 and a variation to the scope of Task 6 was approved by GISERA. The revised Task 6 objective was to provide measurements of VOCs by passive Radiello sampling before, during and after HF at the original study site in the Surat Basin, Queensland. This report *Measurements of VOCs by passive Radiello sampling at a hydraulic fracturing site in the Surat Basin (Draft)* is the revised output of *Task 6* of the GISERA project.

Access to an alternative location for Phase 2 (W.12) of the project *"a comprehensive monitoring campaign to measure the air, surface water, ground water, and soil impacts of hydraulic fracturing of gas production wells in the Surat Basin, Queensland*" (GISERA 2017) was secured in Origin Energy's Combabula development area and measurements were undertaken from July- December 2017 with a final report due for release in December 2018 (Dunne et al. 2017, 2018).

# 2 Introduction

Hydraulic fracturing (HF) is a well stimulation process that involves the high pressure injection of a large volume of fluids into a well in order 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 chemicals 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:

- APLNG (2016) https://www.originenergy.com.au/content/dam/origin/about/our-approach/docs/OurApproach-2016-Hydraulic-Fracture-Stimulation.pdf
- Santos (2016) https://www.santos.com/what-we-do/production/hydraulic-fracturing/material-data-safety-sheets/
- QGC – BG Group (2017)- https://www.shell.com.au/about-us/projects-and-locations/qgc/about-onshore-natural-gas/hydraulic-fracturing-and-chemicals-used.html

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 make adjustments to 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 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 hydraulic fractured wells due to the chemicals used in HF, for example, 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, radionuclides, inorganic compounds such as hydrogen sulphide and organic compounds such as hydrocarbons, and phenols (Schinteie et al., 2015). When geogenic contaminants are mobilized 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, in on-site ponds, or captured directly at the wellhead and removed by a gathering network and transferred to a water treatment facility. Flow-back occurs over several hours to days and is ceased once the majority of solids have cleared from the fluids.

The handling and storage of HF fluids, flowback 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 flowback fluids, well failure or connections between the coal seam and overlaying strata to surface via pathways created or expanded during HF.
- Exhaust and evaporative fuel emissions from equipment and vehicles on site.

Volatile organic compounds (VOCs) and hydrogen sulphide ($H_2S$) are among multiple air pollutants that may be emitted from coal seam gas extraction activities including HF via these pathways. Once emitted to the atmosphere some of these primary air pollutants may undergo chemical transformations forming secondary reaction products which may also affect air quality. Here we present a study of the ambient concentrations of VOCs, including aldehydes a class of oxygenated VOCs, and $H_2S$ at a HF site within a region of intense CSG development in the Surat Basin in Queensland.

VOCs, aldehydes and $H_2S$ were measured by passive Radiello sampling. The gases measured using the Radiello passive samplers include 4 of the 5 gases listed in the National Environment Protection (Air Toxics) Measure (NEPC 2011) including benzene, toluene, xylenes and formaldehyde. Comparison of measured levels to these guidelines during periods of HF activity can be used to assess the ambient air quality at hydraulic fracturing sites.

Radiello sampling occurred from October 2016 – September 2017 with each sample cartridge exposed to air for approximately two weeks and the average concentration of each gas over the period exposed was reported. Samples were collected at seven locations within a ~ 5 x 6 km area in which 21 CSG wells underwent HF treatments in late 2016 and mid-2017. A range of well development operations occurred at the study site during the measurement period including but not limited to:

- **Well integrity testing** – down-hole survey of the well. Typically takes 1 day.
- **Well casing perforation** – the well is perforated at target intervals using specialised explosive charges to create connection of the coal seam to the well. Typically takes 1 day.
- **Well head changeover** – installation of specialised HF well head. Typically takes 1 day.
- **Site set-up** – HF operations require a number of pieces of equipment including above ground water storage ponds, mixing units, high pressure pumps, a coiled tubing unit to convey HF fluids down the well, crane, chemical and proppant storage trailers, flowback tanks, control vans and vehicles. The set-up of the HF spread can take 2 – 5 days.
- **Hydraulic Fracturing** – the injection of HF fluids (water, sand, chemicals) into targeted intervals at high pressure via the coiled tubing unit. Typically takes 1 – 3 days.
- **Well Completion** – the well is flowed back, production equipment installed in the well and connected to surface production equipment (pumps, separators, and pipelines).

It was not uncommon for several different activities to be occurring across different well pads at the same time and each of these activities requires specialised rigs, equipment and vehicles. Samples collected at the site during the study period may have also been impacted by sources of VOCs, aldehydes and $H_2S$ from the surrounding area including:

- Natural sources such as soil and emissions from vegetation
- Local /regional traffic emissions
- Agricultural and farming emissions
- Smoke from bushfires, prescribed burning and wood heater emissions
- Non-HF related CSG industry emissions
- Other Industrial, commercial and domestic emissions

Given the long sample exposure times of ~14 days, samples collected during activity at the study site were likely to have been impacted by multiple sources and not exclusively by HF.

## 2.1 Study objectives

The objectives of the present study were to:

**Objective 1**- Provide comparisons of the VOC levels observed at the HF site with Australian federal, state and other relevant air quality objectives.

**Objective 2**- Provide comparisons of the composition of VOCs observed at a HF site with simultaneous measurements from areas within the Surat Basin not known to be directly impacted by HF operations.

**Objective 3**- Provide comparisons of the composition of VOCs observed during HF activity with data from measurements during non- HF periods at the same site.

## 2.2 Out of Scope

There are several aspects of well development that were not within the scope of this project, namely the impacts of drilling and well construction. The wells on the proposed study site were drilled in 2015 – 2016. Likewise, the scope of the study described here does not provide the following:

**A formal risk assessment:** Prior to commencing HF activities as part of their Environmental Authority Permit, companies must update the stimulation risk assessment in their Environmental Management Plan related to HF “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 described here does not provide an assessment of risk.

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

**An assessment of representativeness and scalability:** The study presented here is specific to HF activity being carried out in the sites identified. The representative 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.

## 2.3 Air quality objectives

Air quality objectives prescribed in National and State legislation are established for use in assessing the significance of the measured levels of air toxics with respect to protection of human health, wellbeing and the environment. If the prescribed levels of pollutants are exceeded then it does not necessarily indicate a problem, but that further investigation is required by the relevant jurisdiction to determine the circumstances that led to the exceedance and its potential implications to human health and the environment. Likewise, short term exceedances of these values do not necessarily imply that adverse effects on human health will automatically occur.

Air quality guidelines referred to in this study were ranked (Tier 1, 2 3). If an air quality guideline/ value was not available from the first tier, a subsequent tier was used.

**Tier 1: National Environment Protection (Air Toxics) Measure- 2011.** The pollutants relevant to this study to which the NEPM measure applies are benzene, toluene, xylenes and formaldehyde.

**Tier 2: 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 6 of which are measurable by the Radiello methods employed in this study (1,2 dichloroethane,1,3-butadiene,dichloromethane, styrene, tetrachloroethylene, vinyl chloride monomer).

Australian Federal or State ambient air guidelines were not available for most of the VOCs measured in this study. In the absence of Australian guidelines international guidelines that covered the range of VOCs measured in this study were consulted:

**Tier 3: Texas Commission on Environmental Quality Air Monitoring Comparison Values (ACMV) and Effects Screening Levels (ESLs)**. The AMCV and ESL values are "chemical specific air concentrations set to protect human health and welfare". Where AMCV values were not available for a specific compound the appropriate ESL was used. For details on the difference between AMCVs and ESLs the reader is referred to TCEQ (2010) (https://www.tceq.texas.gov/toxicology/amcv/about). Only the "long term" values, which are based on annual data concerning chronic health and vegetation effects were used for comparison with the Radiello data in this study.

There are also measurement considerations that must be taken into account when comparing air pollutant measurements with air quality criteria:

1) **Reference Methods**- The Air Toxics NEPM lists appropriate reference methods for the measurement of prescribed air toxics. This study reports measurements by passive Radiello sampling which is not listed as a reference method in the Air Toxics NEPM.

2) **Averaging period**- Each passive Radiello sampler was deployed for ~14 days, and the results from each sample represent an average concentration over the exposure period. Given the long averaging time it is appropriate to compare the reported concentrations with longer term air quality guidelines (e.g. annual), rather than short-term guidelines (e.g. 1 h, 8 h, 24 h). Australia's Air Toxics NEPM prescribes annual air quality objectives for benzene, toluene and xylenes against which the Radiello monitoring results can be assessed. Only 24-hour goals are specified for formaldehyde in the NEPM (2011) and for $H_2S$ in the Qld EPP (2008) and the Radiello data reported levels of these pollutants cannot be assessed against these short-term guidelines. Instead, the Radiello results for formaldehyde will be compared to annual Texas AMCV values and $H_2S$ concentrations will be compared against Western Australian Dept. of Health guidelines (WA DOH 2009).

# 2 Study location

Hydraulic fracturing operations on two neighbouring properties were targeted in this study. The eastern property will be referred to here as Property A and the western property as Property B. In October 2016 a program of VOC monitoring by passive Radiello sampling was initiated at 7 locations within the two properties- 3 sample sites on the Property A and 4 sampling sites on the Property B. The sampling locations are shown on the map in Figure 1.

The properties are separated by the Leichardt Highway between the towns of Miles (population < 2000) and Condamine (population < 500) (Figure 1). The properties are predominantly flat, semi-arid open grassland with stands of native tree vegetation.

**Property A** - This property is approximately 1100 ha and contains 19 CSG wells, grid spaced at ~ 600 – 700 m intervals. The wells were drilled and constructed between December 2013 and January 2014 with two additional wells constructed in October 2015 (Source: Qld Globe). Well depths range from 706 – 822 m and target the Walloon Coal Measures. Five wells underwent HF in November 2016 after which they were completed and brought into production (Figure 1 and Table 1).

**Property B** - This property is approximately 1200 ha and also contains 19 CSG wells, grid spaced at ~ 600 – 700 m intervals. The wells were drilled and constructed between August and September 2015 with an additional well constructed in August 2016 (Source: Qld Globe). Well depths range from 740 – 860 m and target the Walloon Coal Measures. Sixteen wells underwent HF in May – August 2017 after which they were completed and brought into production (Figure 1 and Table 1).

The area to the west is dominated by farmland with a low density of CSG wells within a 5 km radius of the boundary. In contrast, the area to the east of the properties, is dominated by farmland with a high density of CSG wells (grid spaced ~ 600 – 700 m) (Figure 1). The wells in this area are serviced by a gathering network feeding into the Condabri Central Gas Processing Facility which is approximately 3 - 5 km to the south of the study sites. Miles Airport lies approximately 5 km to the south.

The Surat Basin is a sub-tropical region with winter months (April to September) mostly cool and dry, and summer months (November to February) mostly hot with higher rainfall. Wind patterns vary during the year with the months January - April dominated by easterly winds; the months May - July a mixture of easterly and south-westerly winds; the months August- October dominated by north-easterly winds with a small component of winds from the southwest; and the months November – December dominated by Northerly winds with an increasing component of winds from the northeast as summer develops.

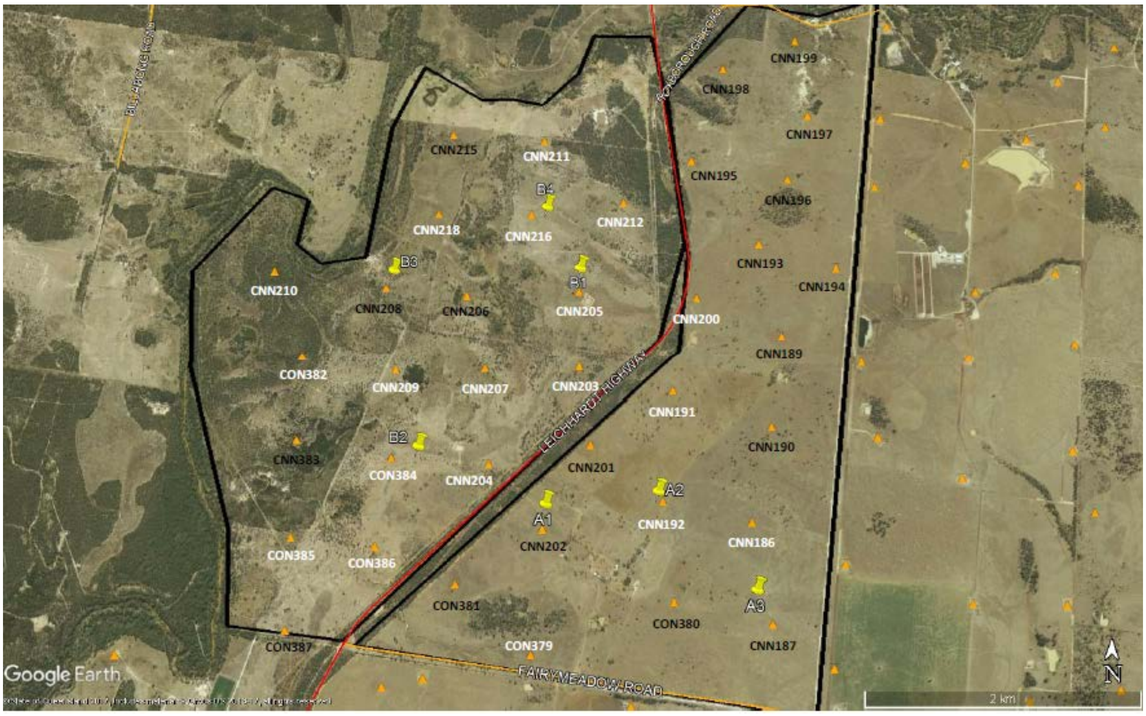


Figure 1 The study site showing passive sampling locations within each field (yellow pins). Orange triangles are the CSG wells. The ID of the wells that underwent HF are labelled in white, and wells that did not undergo HF are labelled in black.

Table 1 Well IDs (Qld Globe 2017) and HF start and end dates for Property A and Property B CSG wells.

| Well ID | HF start | HF end |
|---|---|---|
| ***Property A*** | | |
| **CNN 186** | 12/11/2016 | 16/11/2016 |
| **CNN 192** | 16/11/2016 | 21/11/2016 |
| **CON 379** | 21/11/2017 | 25/11/2017 |
| **CNN 191** | 28/11/2016 | 2/12/2016 |
| **CNN 200** | 2/12/2016 | 6/12/2016 |
| ***Property B*** | | |
| **CON 385** | 24/05/2017 | 2/06/2017 |
| **CNN 211** | 16/06/2017 | 18/06/2017 |
| **CON 384 H2** | 19/06/2017 | 23/06/2017 |
| **CNN 203** | 25/06/2017 | 30/06/2017 |
| **CNN 205 H1** | 1/07/2017 | 3/07/2017 |
| **CNN 207** | 3/07/2017 | 5/07/2017 |
| **CNN 216 H4** | 6/07/2017 | 7/07/2017 |

| Well ID | HF start | HF end |
|---|---|---|
| **CNN218** | 8/07/2017 | 18/07/2017 |
| **CNN 209** | 18/07/2017 | 21/07/2017 |
| **CON 382** | 21/07/2017 | 23/07/2017 |
| **CNN 210** | 23/07/2017 | 24/07/2017 |
| **CNN 204** | 25/07/2017 | 10/08/2017 |
| **CON 386** | 9/08/2017 | 12/08/2017 |
| **CON 387** | 11/08/2017 | 14/08/2017 |
| **CNN 212** | 14/08/2017 | 16/08/2017 |
| Property A wells that did not undergo HF: CNN 187 CNN 189, CNN 190, CNN 193, CNN 194, CNN 195, CNN 196, CNN 197, CNN 198R, CNN 199, CNN 201, CNN 202, CON 380, CON 381.<br>Site B wells that did not undergo HF: CNN 206, CNN 208, CNN 215, CON 383. | | |

## 2.4 Existing Air Quality Measurements

A major advantage of the site selected for the present study is its location within the air quality monitoring network operating as part of the current GISERA Surat Basin Ambient Air Quality (SBAAQ) Study (Lawson et al., 2017). The network comprised 10 sites at which VOCs and $H_2S$ have been monitored by passive Radiello samplers from 2014 - 2016 (indicated in red in Figure 2).

There were also 5 ambient air quality monitoring stations operated from 2015 – 2017 as part of the SBAAQ Study (indicated in green in top panel). These sites included instruments for monitoring oxides of nitrogen (NOx), ozone ($O_3$), carbon monoxide (CO), methane ($CH_4$), carbon dioxide ($CO_2$), airborne particles and meteorology.

For the purposes of comparison, data from 6 of the sampling sites operated as part of the SBAAQ study will be presented alongside data from the 7 sampling locations within the HF site deployed for this study. The sampling sites are presented as 4 types:

- **Hydraulic Fracturing (HF) Sites**- this category includes the seven sites across the two properties (Property A sites A1 to A3 and Property B sites B1 – B4) where HF activities were undertaken during the study period.
- **Gas Field Sites**- this category includes 3 sampling sites located within gas fields in the Surat Basin: Miles which has ~ 31 CSG wells within 2 km and is located ~ 8 km north of the HF study site; Wilgas which has ~ 12 CSG wells within 2 km and is located ~ 8 km South of the HF study site, and Rockwood which has ~ 27 CSG wells within 2 km and is located ~ 23 km to the south-east of the study site. Data from these sites were included in this analysis to provide comparative data from locations within CSG development areas that were not known to be directly impacted by HF.

- **Regional Sites**- this category includes 2 locations (Burncluith and Tara Region) located in areas > 10 km away from CSG infrastructure and 40 – 50 km away from the HF study site. These sites are included here to provide comparative data from a locations outside of CSG development areas.
- **Township site**- this is a single sampling site located within the largest nearby township Chinchilla, population ~6,600. These were included to provide comparative data from a location likely to be impacted by sources of VOCs and $H_2S$ typical of higher population density areas such as emissions from vehicles, commercial/industrial activities, and residences.

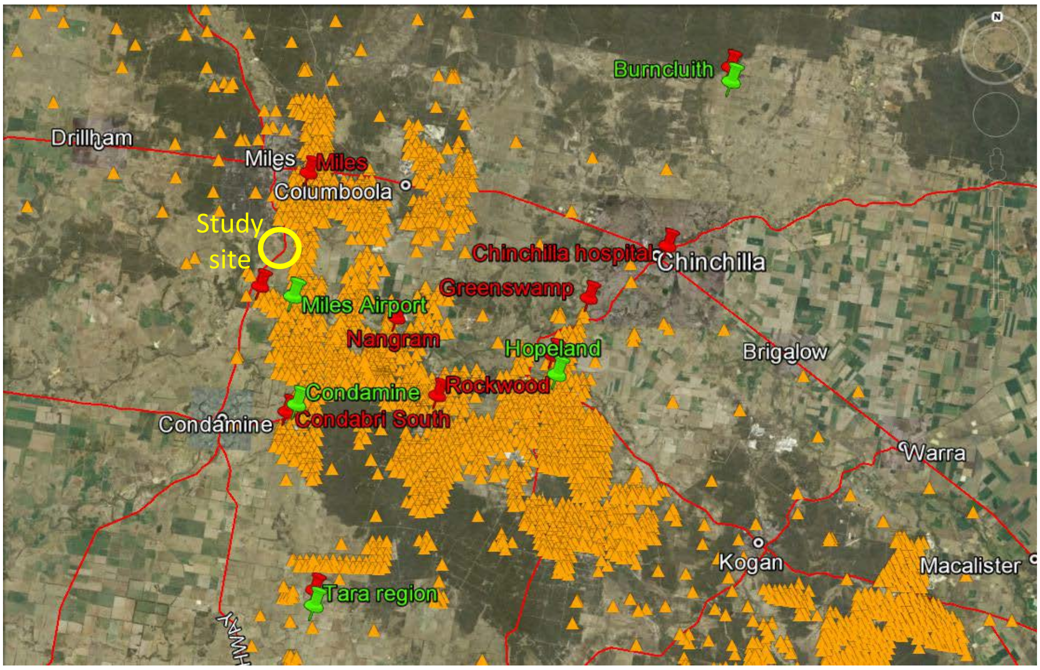


Figure 2 The study site within the Miles-Chinchilla-Condamine region of the Surat Basin. Orange triangles represent CSG wells. Red pins are the Surat Basin Ambient Air Quality (SBAAQ) Study Radiello sampling sites, green pins are the SBAAQ stations.

# 3 Methodology

## 3.1 Passive Radiello sampling and analysis

One way to measure VOCs and hydrogen sulphide in the atmosphere is known as passive Radiello sampling (Radiello Manual, 2006). In the present study the Radiello sampling and analysis was conducted by a third party contractor, SGS-Leeder, on behalf of GISERA. SGS Leeder Chinchilla Qld conducted the sampling. The cartridges were deployed on purpose built poles ~2 m height, fitted with manufacturer supplied shelters to protect the Radiello samplers from adverse weather (Figure 3). Each cartridge was exposed to air for approximately 2 weeks, and then packed in a sealed container and sent to SGS Leeder's laboratories in Notting Hill, Victoria for analysis.

**Figure 3 Passive Radiello samplers deployed in the field housed in weather proof covers and mounted on ~ 2m high poles.**

During sampling, gases passively migrate through a diffusive surface on the cartridge at a known rate (the sampling rate), and are trapped on an adsorbent surface. Different sampling and analysis methods are used to capture different types of VOCs and $H_2S$. In the present study three different Radiello methods were employed:

**VOCs chemically desorbed with carbon disulphide ($CS_2$)-** The VOC sample cartridge (Code 130, Radiello, Padova, Italy) is a stainless steel net cylinder, with 100 mesh grid opening and 5.8 mm diameter, packed with 530 ± 30 mg of activated charcoal with particle size 35-50 mesh. During sampling VOCs present in the air adsorb to the activated charcoal and are trapped. During analysis the VOCs are chemically desorbed by $CS_2$ displacement and then analysed by gas chromatography with mass spectrometer detection.

SGS –Leeder report atmospheric concentrations for 46 VOC compounds via this method. The average atmospheric concentrations over the sample exposure time are determined from the mass of the analyte detected on the cartridge (m, units: µg), the exposure time (t, units: min) and the compound specific sampling rate ($Q_K$, units: mL min-1) via Equation 1. The sampling rate of each the VOCs measurable by this method have been determined experimentally by the manufacturer (Radiello 2006).

$$C(\mu g\ m^{-3}) = \frac{m\ (ug)}{Q_K(mL\ min^{-1}) \times t(min)}$$

Equation 1

**Aldehydes by DNPH Derivatization** – The aldehyde sample cartridge (Code 165, Radiello, Padova, Italy) is a stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated Florisil®. During sampling aldehydes present in the air react with 2, 4-DNPH to give the corresponding 2,4-dinitrophenylhydrazones. During analysis. The hydrazone derivatives are extracted with acetonitrile and analysed by selected ion monitoring (SIM) mass spectrometry (MS).

SGS –Leeder report atmospheric concentrations for 9 aldehyde compounds via this method using the same quantification procedure as outlined for the VOCs above (Equation 1). One aldehyde compound, acrolein, was excluded from reporting in this study as evidence in the scientific literature has shown the 2,4-DNPH derivatisation technique used here is unsuitable for acrolein measurements (Ho et al., 2011).

**Hydrogen sulphide ($H_2S$) by zinc acetate chemi-adsorption**- The $H_2S$ sample cartridge (code 170, Radiello, Padova, Italy) is made of microporous polyethylene and impregnated with zinc acetate. During sampling, $H_2S$ is chemically adsorbed by zinc acetate and undergoes reaction to form stable zinc sulphide. The sulphide is recovered from the cartridge by extraction with water. Then the sulphide undergoes reaction with N, N-dimethyl-p-phenylendiammonium in the presence of a strong oxidizing agent (ferric chloride) in a strongly acid solution. This reaction yields methylene blue which is quantified by visible spectroscopy. SGS –Leeder report atmospheric concentrations of $H_2S$ via this method using an analogous procedure to that outlined for the VOCs above (Equation 1).

## 3.2 Detection limits

All air pollutant measurement methods have lower limits, below which the concentration of a pollutant cannot be reliably measured, which is referred to here as the Detection Limit (DL). Detection limits for each compound were determined from:

- The Practical Quantitation Limit (PQL) of the analysis method i.e. the minimum amount that can be reliably detected on a Radiello sampler (µg/tube);
- The uptake rate of the compound of interest onto the Radiello sampler (mL/min)

The DL for the Radiello samples is based on instrument performance, exposure time and the analytes' given uptake rate:

$$DL\ \mu g/m^3 = [PQL\ (\mu g/tube) \times 10^6\ (mL/m^3)] / [Exposure\ time\ (min) \times Uptake\ rate\ (mL\ min^{-1})]$$

Equation 2

For example, the uptake rate for Benzene = 80 mL $min^{-1}$ and the laboratory used in this study specified a PQL of 0.1 µg/tube. Hence, for an exposure period of 14 days (20160 min) the DL was calculated as follows:

DL (Benz) = $(0.1 \times 10^6) / (20160 \times 80) = 0.06$ µg/$m^3$

This method for calculating the DLs has several important implications when reporting, processing and analysing the Radiello data. In particular:

**Values < DL-** SGS Leeder report measurements less than the DL in the format "<(Value =DL)". e.g. given a DL for Benzene of 0.06 µg $m^{-3}$, a measurement less than 0.06 is reported as "<0.06". For the purposes of this study a conservative approach has been taken, in which values less than the DL are assumed to be equal to the DL. Therefore the data reported here may represent an upper limit of concentrations.

**Unequal sampling times** - Each sampler was deployed for a period of approximately two weeks the average exposure time was 14.1 days with a wide degree variability (8.8 – 28 days).The measured values reported represent an integrated concentration (µg/$m^3$) averaged over the exposure period. As described above, the DL is dependent on the sample exposure period and each sample may have a different DL dependent on sampling time. Detection Limits decrease with increasing exposure time. Hence a 1-week sample may have a DL (Benzene) of 0.14 µg/$m^3$, a two week sample DL = 0.06 µg/$m^3$, 3-week = 0.04 µg/$m^3$. Therefore a value of 0.05 µg/$m^3$ may be reported as a "detect" in a 3-week sample but a non-detect in a 1 or 2 week sample.

## 3.3 Quality Assurance (QA)

### Sampling Rate

All measurement methods have an uncertainty attached to their reported values based on the accuracy and precision of the method. A major source of measurement uncertainty of the Radiello method is the sampling rate - the rate the analyte is adsorbed from the air to the adsorbent cartridge (Pennequin-Cardinal et al 2004). The sampling rates applied in the measurement equation for the purposes of this study were experimentally determined by the manufacturer. The Radiello manufacturer stated uncertainties at 95% confidence for experimentally-determined sampling rates of the compounds measured in this study range from 1.1 – 23.5 % (Radiello 2006, Lawson et al., 2018).

Dodecane was excluded from reporting in this study in response to advice from the sampler manufacturer Radiello due to concerns about the accuracy of the sampling rate stated for dodecane (Lawson et al., 2018).

### Method blanks

Method blanks are Radiello samplers that are identical to those used for sampling but are not transported to the sampling location, rather they are stored in the laboratory and analysed alongside the samples. Method blanks are used to check whether there are sources of contamination in the laboratory and ideally reported values are < DL of 0.1 µg/tube for all species analysed. In this study, 98% of VOC method blanks, 86% of carbonyl method blanks and 100% of $H_2S$ method blanks reported values below the DL of 0.1 µg/tube for all species.

### Method spikes

Method spikes are Radiello samplers that are identical to those used for sampling except that they are spiked with a known amount of a set of chemicals of interest and analysed alongside the samples. Method spikes are used to determine the analytical bias and ideally reported values are within 30% of the spiked mass that was added. Average method spike recoveries for this study were:

- 92 to 103 % recovery for 7 VOC species (benzene, toluene, m & p- xylene, o-xylene, ethylbenzene, chlorobenzene, 1,4-dichlorobenzene)
- 52 to 92 % recovery for 4 aldehydes (formaldehyde, acetaldehyde, butanal, benzaldehyde)
- 102 % recovery for $H_2S$

Benzaldehyde recoveries ranged from 40 – 69% indicating consistent negative bias in the analysis of benzaldehyde by this method. Butanal recoveries ranged from 46 – 106%, with more than half of the method spikes reporting recoveries <70% indicating a frequent negative bias in the analysis of butanal by this method. Consequently, sample data for benzaldehyde and butanal should be considered lower bounds of atmospheric concentrations in this study. It is important to note that even if the maximum concentrations of butanal and benzaldehyde reported in this study were underestimated by 60% they would still be tens of times lower than the relevant air quality standard of 8.9 ppb referenced here (see section 4.1).

Formaldehyde recoveries ranged from 63 – 131% with one fifth of method spikes reporting recoveries of < 70% indicating a moderately frequent negative bias in the analysis of formaldehyde by this method. The sample data for formaldehyde was reported for this study however due to the negative analytical bias the atmospheric concentrations could have been underestimated on occasions. It is important to note that even if the maximum concentration of formaldehyde of 2.12 ppb reported in this study was underestimated by 30% it would still be around three times lower than the relevant air quality standard of 9 ppb referenced here (see section 4.1).

Typically 2 method spikes were analysed alongside each batch of samples. The agreement between the paired duplicate method spikes provides an estimate of the analytical precision. Analytical precision is expressed as the relative percent difference (RPD) and is calculated from the ratio of the absolute difference between the duplicates to the average of the duplicates and is reported as percentage. Ideally RPD values are < 20%. For this study average RPD values were:

- RPD = 4 to 6% for 7 VOC species (benzene, toluene, m & p- xylene, o-xylene, ethylbenzene, chlorobenzene, 1, 4-dichlorobenzene).
- RPD = 7 to 9% for 4 aldehydes (formaldehyde, acetaldehyde, butanal, benzaldehyde).
- RPD = 6 % for $H_2S$

Less than 3% of the paired method spike measurements had RPD values > 20%.

### Trip Blanks

For each round of sampling a trip blank was also collected. The trip blank tubes are identical to the sample tubes and are shipped with the samples to the field and returned unopened to the laboratory for analysis. The purpose of the trip blank is to identify potential sample contamination which may occur during transport, storage, handling and analysis.

There were four rounds of sampling where significant levels of one or more VOCs were detected on the trip blank:

- VOC sample from period 9 – 24 February 2017: n-hexane concentrations detected on the blank were > 30% of the maximum n-hexane concentrations detected in the HF site samples. N-hexane data from this round of sampling was excluded for this analysis.
- VOC sample from period 4 – 18 May 2017: 2-methyl pentane concentrations detected on the blank were > 30% of the maximum 2-methyl pentane concentrations detected in the HF site samples. 2-methyl pentane data from this round of sampling was excluded for this analysis.
- VOC sample for period 18 May – 1 June 2017: Concentrations of multiple VOC species including methyl cyclohexane, n-heptane, toluene and trichloroethylene were detected on the trip blank at levels > 30% of the maximum levels detected in samples from the HF site. Due to extensive nature of contamination all VOC data from this round of sampling was excluded for this analysis.
- VOC sample for period 12 – 21 September: n-hexane concentrations detected on the blank were > 30% of the maximum n-hexane concentrations detected on the HF site samples. N-hexane data from this round of sampling was excluded for this analysis.

### Field Duplicates

Field duplicates are two samplers which are co-deployed in the same location side by side, exposed for the same amount of time, and treated and analysed identically. Field duplicates were not deployed at the HF study site but were deployed during the HF study period at three other sites in the Surat Basin. The agreement between field duplicates provides an estimate of the precision of the combined sampling and analysis process and is ideally within 40%. In this study, agreement between paired measurements for a given species was only assessed when the mass reported for both duplicate samples was greater than the DL. There were 18 species which had duplicate measurements > DL one more than one occasion.

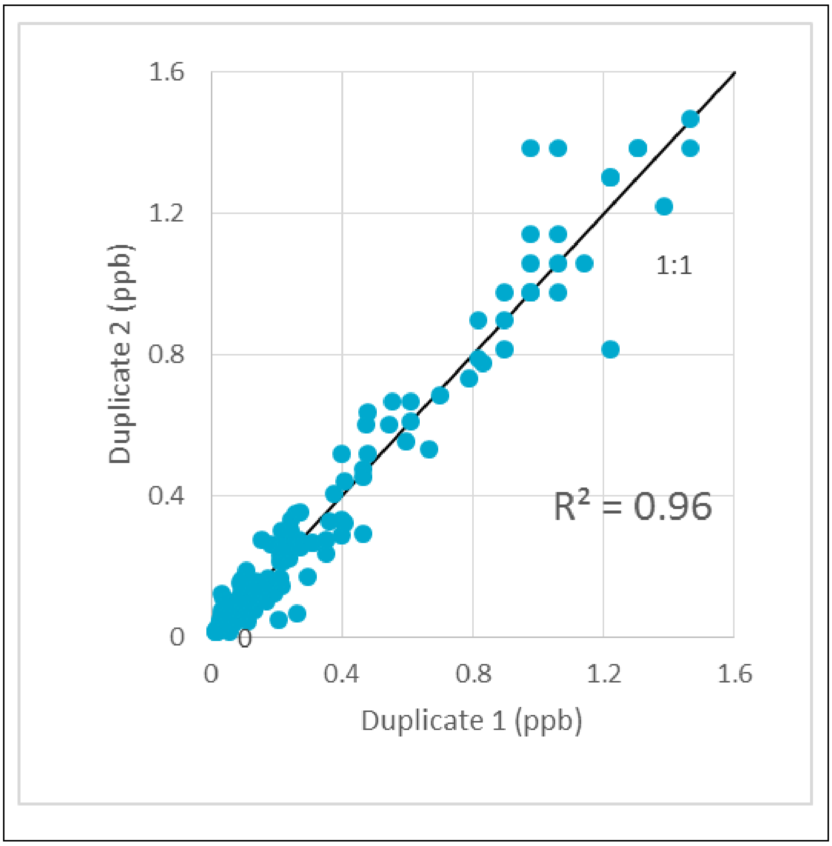


Figure 4 Comparison of field duplicates measurements. Note, only measurements in which both duplicate samples were greater than the DL were included.

Overall the agreement between the paired measurements was generally good (correlation coefficient $R^2$=0.96) and typically within 40% of each other (Figure 4). At low concentrations, there were more occasions when the relative difference between the paired measurements was > 40% but these were considered acceptable as the absolute difference (ppb) between duplicate measurements overall were very small with average absolute differences ranging from 0.00 – 0.10 ppb, and maximum absolute differences ranging from 0.00 – 0.41 ppb.

## 3.4 Data capture

Data from samples collected during the period 6 October 2016 – 21 September 2017 are included in the analysis for this report. The number of VOC, aldehyde and $H_2S$ samples successfully collected during HF and non-HF periods are listed in Table 2. Details of the number of samples collected at each sampling site during each round of sampling are provided in Appendix A.1. Across the two sampling sites (Properties A & B) a total of 134 VOC samples were successfully collected during the study period (6/10/16 – 21/9/17). A similar number of $H_2S$ samples were also collected (total = 138). Fewer aldehyde samples were collected (total = 116) due to a supply shortage of the aldehyde sample cartridges.

The measurement period contained both HF and non-HF impacted periods. HF periods are defined as periods where hydraulic fracturing activity was occurring on either site (Property A or B) and non-HF periods are defined as periods where no HF activity was occurring on either site. Under the Queensland Petroleum Regulation 2004, companies are required to submit well completion reports for each well treated with HF. These reports provide information on the well location, the timing and duration of HF, and details of the HF treatments performed. The completion reports for the wells that underwent HF at the study site were provided to CSIRO for the purpose of this report. Table 1 lists the ID of the wells that underwent HF, and the timing and duration of HF for each.

**Table 2 Number of samples successfully collected at Properties A and B for the measurement period 6 October 2016 – 21 September 2017.**

| Site & Activity period | N (%) | | |
|---|---|---|---|
| | VOC | Aldehydes | $H_2S$ |
| **Both sites All** | 134 | 116 | 138 |
| **Both sites HF period** | 48 (36%) | 54 (47%) | 54 (39%) |
| **Both sites non-HF periods** | 86 (64%) | 62 (53%) | 84 (61%) |
| **Property A All** | 48 | 37 | 49 |
| **Property A HF Period** | 12 (25%) | 14 (38%) | 14 (29%) |
| **Property A non-HF periods** | 36 (75%) | 23 (62%) | 35 (71%) |
| **Property B All** | 86 | 79 | 89 |
| **Property B HF period** | 36 (42%) | 40 (51%) | 40 (45%) |
| **Property B non-HF periods** | 50 (58%) | 39 (49%) | 49 (55%) |

The Radiello samplers were deployed for an average of ~14 days and exposure periods of individual samples often straddled HF and non-HF periods. Any sample that was exposed while HF activity was taking place was considered as a HF impacted sample. At the Site A site, ~ 25 - 40% of samples were collected during HF periods, and ~ 35- 40% of samples were collected at the Site B site during HF periods.

# 4 Results

## 4.1 Comparison with air quality guidelines

Table 3 lists the 22 compounds reported above the DL at the HF study site on one or more occasions alongside their reported concentration range and relevant air quality guideline. The maximum concentrations for all 22 compounds detected at Property A and B during this study were tens to thousands of times below their relevant long-term (annual) air quality guidelines referenced here.

The maximum concentration of benzene measured at the HF study site of 0.09 ppb was more than 30 times lower than the NEPM air toxics monitoring investigation level of 3 ppb. Likewise the maximum concentrations of the other NEPM air toxics toluene (0.18 ppb), and xylenes (0.11) measured at the HF study site were hundreds to thousands of times lower than their respective NEPM monitoring investigation levels. Only 24-hour goals are specified for formaldehyde in the Air Toxics NEPM (2011) and the Radiello data reported levels of these pollutants cannot be assessed against these short-term guidelines. Instead, the maximum of 2.12 ppb from the radiello data for formaldehyde was compared against the annual Texas AMCV value of 9ppb. Tetrachloroethylene was detected on two occasions with a maximum concentration of 0.02 ppb which is hundreds of times lower than the annual Queensland EPP air quality objective of 36 ppb.

Table 4 lists the 32 compounds that were not reported above the DL at the HF sites on any occasion, alongside their maximum DL for the study period and relevant air quality guideline. With the exception of glutaraldehyde, the maximum DLs for these compounds were tens to thousands of times lower than their relevant air quality guideline values. For these 32 compounds we can conclude that these compounds were either not present in the air at the HF study sites or present in concentrations too low to be reliably measured with the Radiello sampling method employed in this study. We can also conclude that these compounds were present at concentrations that were well below the relevant ambient air guidelines. These 32 non-detected compounds are excluded from further consideration in this report.

The maximum DL of glutaraldehyde was 0.03 ppbv which was very close to the annual Texas AMCV of 0.05 ppbv suggesting that the Radiello technique is not sensitive enough to allow for robust comparisons with the Texas AMCV values for glutaraldehyde.  While compliance with the Texas AMCV cannot be definitively demonstrated with the measurement method employed here, the available data suggests the concentration of glutaraldehyde did not exceed the Texas AMCV during the present study. As part of Phase 2 of the GISERA Hydraulic Fracturing project (W.12), sampling of glutaraldehyde was conducted by CSIRO using an active sampling method with a significantly lower DL of 0.002 ppbv, from July – November 2017. Results of this study are due to be released in December 2018 (Dunne et al., 2017).

**Table 3 The concentration ranges and detection frequencies for the HF study site and their relevant annual/ long term ambient air quality objective values. Data for the regional sites, gas filed sites and the township site are also presented for comparison.**

| | HF Sites | | Regional sites | | Gas-field sites | | Township site | | Annual/ long-term ambient air quality objective | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Properties A & B | | Tara region & Burncluith | | Wilgas, Miles, Rockwood | | Chinchilla | | ppb | Source |
| | Range (ppb) | DF (%) | Range (ppb) | DF (%) | Range (ppb) | DF (%) | Range (ppb) | DF (%) | | |
| *N (VOC samples)* | *134* | | *45* | | *67* | | *24* | | | |
| **2-methylpentane** | 0.01 - 0.11 | 5% | 0.01 - 0.07 | 9% | 0.01 - 0.08 | 3% | 0.01 - 0.21 | 27% | 100 | Texas AMCV |
| **3-methylpentane** | 0.01 - 0.03 | 1% | 0.01 - 0.04 | 7% | 0.01 - 0.04 | 1% | 0.01 - 0.10 | 48% | 100 | Texas AMCV |
| **n-Hexane** | 0.01 - 0.09 | 13% | 0.01 - 0.04 | 15% | 0.02 - 0.06 | 18% | 0.02 - 0.15 | 43% | 190 | Texas AMCV |
| **n-Decane** | 0.01 - 0.08 | 21% | 0.01 - 0.06 | 16% | 0.01 - 0.04 | 21% | 0.01 - 0.08 | 39% | 175 | Texas AMCV |
| **n-Undecane** | 0.02 - 0.08 | 15% | 0.02 - 0.10 | 18% | 0.02 - 0.07 | 15% | 0.02 - 0.10 | 39% | 55 | Texas AMCV |
| **Cyclohexane** | 0.01 - 0.06 | 1% | 0.01 – 0.05 | 0% | 0.02 - 0.06 | 0% | 0.02 - 0.07 | 17% | 100 | Texas AMCV |
| **Benzene** | 0.01 - 0.09 | 21% | 0.02 - 0.07 | 22% | 0.01 - 0.09 | 24% | 0.02 - 0.28 | 61% | 3<br>1 | NEPM/EPP<br>Texas AMCV |
| **Toluene** | 0.01 - 0.18 | 29% | 0.01 - 0.13 | 24% | 0.01 - 0.04 | 22% | 0.03 - 0.42 | 100% | 100<br>1100 | NEPM/EPP<br>Texas AMCV |
| **o-xylene** | 0.01 - 0.03 | 1% | 0.01 – 0.03 | 4% | 0.01 - 0.04 | 0% | 0.01 - 0.07 | 48% | 200 | NEPM/EPP |

| | HF Sites | | Regional sites | | Gas-field sites | | Township site | | Annual/ long-term ambient air quality objective | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Properties A & B | | Tara region & Burncluith | | Wilgas, Miles, Rockwood | | Chinchilla | | ppb | Source |
| | Range (ppb) | DF (%) | Range (ppb) | DF (%) | Range (ppb) | DF (%) | Range (ppb) | DF (%) | | |
| | | | | | | | | | 140 | Texas AMCV |
| **m & p-xylenes** | 0.01 - 0.08 | 9% | 0.01– 0.11 | 16% | 0.01 - 0.06 | 7% | 0.02 - 0.22 | 91% | 200<br>140 | NEPM/EPP<br>Texas AMCV |
| **Sum xylenes** | 0.02 - 0.11 | 9% | 0.02 – 0.14 | 16% | 0.02 – 0.08 | 7% | 0.03 – 0.29 | 91% | 200<br>140 | NEPM/EPP<br>Texas AMCV |
| **Ethylbenzene** | 0.01 - 0.06 | 3% | 0.01 - 0.06 | 11% | 0.01 - 0.08 | 4% | 0.01 - 0.07 | 43% | 440 | Texas AMCV |
| **Carbon tetrachloride** | 0.03 - 0.15 | 100% | 0.04 - 0.14 | 100% | 0.01 - 0.13 | 99% | 0.04 - 0.11 | 100% | 2 | Texas AMCV |
| **Trichloromethane** | 0.01 - 0.03 | 10% | 0.01 - 0.05 | 20% | 0.01 - 0.03 | 3% | 0.01 - 0.03 | 9% | 400 | Texas AMCV |
| **Tetrachloroethylene** | 0.01 - 0.02 | 1% | nd | 0% | nd | 0% | nd | 0% | 36<br>2 | EPP<br>Texas ESL |
| **Ethyl acetate** | 0.01 - 0.07 | 20% | 0.01 - 0.07 | 16% | 0.01 - 0.06 | 19% | 0.01 - 0.05 | 17% | 400 | Texas AMCV |
| **Methyl isobutyl ketone** | 0.01 - 0.03 | 1% | nd | 0% | nd | 0% | nd | 0% | 20 | Texas AMCV |
| *N(Aldehyde samples)* | *116* | | *116* | | *58* | | *19* | | | |

| | HF Sites | | Regional sites | | Gas-field sites | | Township site | | Annual/ long-term ambient air quality objective | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Properties A & B | | Tara region & Burncluith | | Wilgas, Miles, Rockwood | | Chinchilla | | ppb | Source |
| | Range (ppb) | DF (%) | Range (ppb) | DF (%) | Range (ppb) | DF (%) | Range (ppb) | DF (%) | | |
| **Formaldehyde** | 0.33 - 2.12 | 100% | 0.46 - 1.55 | 100% | 0.46 - 1.71 | 100% | 0.54 - 1.79 | 100% | 40* | NEPM/EPP (*24h) |
| | | | | | | | | | 9 | Texas AMCV |
| **Acetaldehyde** | 0.08 - 0.94 | 100% | 0.08 - 0.83 | 100% | 0.06 - 1.00 | 100% | 0.11 - 0.83 | 100% | 25 | Texas AMCV |
| **Propanal** | 0.03 - 1.14 | 58% | 0.05 - 0.36 | 68% | 0.04 - 1.14 | 62% | 0.05 - 0.25 | 90% | 55 | Texas AMCV |
| **Butanal** | 0.08 - 0.37 | 34% | 0.12 - 0.39 | 39% | 0.09 - 0.47 | 40% | 0.10 - 0.37 | 50% | 34 | Texas AMCV |
| **Pentanal** | 0.03 - 0.09 | 8% | 0.04 - 0.31 | 12% | 0.03 - 0.09 | 7% | 0.03 - 0.11 | 0% | 50 | Texas AMCV |
| **Hexanal** | 0.05 - 0.14 | 22% | 0.05 - 0.40 | 44% | 0.04 - 0.18 | 28% | 0.04 - 0.15 | 30% | 200 | Texas AMCV |

Table 4 Compounds that were not observed above the detection limit at the HF study site, their maximum detection limits (ppbv), and relevant air quality objective values.

| Compound | Max. DL | Ambient air objective | | |
|---|---|---|---|---|
| | (ppbv) | (ppbv) | Averaging period | Source |
| **2-butoxyethanol** | 0.03 | 780 | annual | Texas ESL |
| **1,1,1-Trichloroethane** | 0.02 | 930 | annual | Texas AMCV |
| **Trichloroethylene** | 0.02 | 10 | annual | Texas AMCV |
| **1,2,4-Trimethylbenzene** | 0.03 | 37 | annual | Texas AMCV |
| **1,2-Dichloroethane** | 0.02 | 170<br>0.72 | 24h<br>annual | EPP<br>Texas AMCV |
| **1,2-dichloropropane** | 0.03 | 10 | annual | Texas AMCV |
| **1,4-Dichlorobenzene** | 0.02 | 27 | annual | Texas AMCV |
| **1-methoxy-2-propanol** | 0.04 | 100 | annual | Texas AMCV |
| **1-methoxy-2-propyl acetate** | 0.02 | 50 | annual | Texas ESL |
| **2-ethylhexanol** | 0.03 | 30 | annual | Texas ESL |
| **Bromochloromethane** | 0.02 | 200 | annual | Texas ESL |
| **Butanol** | 0.04 | 20 | annual | Texas ESL |
| **Butyl acetate** | 0.03 | 990 | annual | Texas AMCV |
| **Chlorobenzene** | 0.03 | 10 | annual | Texas AMCV |
| **Cyclohexanone** | 0.03 | 20 | annual | Texas ESL |
| **Ethyl-tert-butyl-ether** | 0.03 | 5 | annual | Texas ESL |
| **Isobutanol** | 0.03 | 50 | annual | Texas ESL |
| **Isooctane** | 0.03 | 75 | annual | Texas ESL |
| **Isopropylbenzene** | 0.03 | 51 | annual | Texas AMCV |
| **Methylcyclopentane** | 0.03 | 75 | annual | Texas AMCV |

| Compound | Max. DL<br>(ppbv) | Ambient air objective<br>(ppbv) | <br>Averaging period | <br>Source |
|---|---|---|---|---|
| **Methylcyclohexane** | 0.03 | 400 | annual | Texas AMCV |
| **Methyl ethyl ketone** | 0.03 | 3000 | annual | Texas AMCV |
| **Methyl methacrylate** | 0.03 | 50 | annual | Texas AMCV |
| **Methyl-tert-butyl-ether** | 0.03 | 50 | annual | Texas AMCV |
| **Napthalene** | 0.06 | 9.5 | annual | Texas AMCV |
| **n-Heptane** | 0.03 | 175 | annual | Texas AMCV |
| **n-Nonane** | 0.03 | 280 | annual | Texas AMCV |
| **n-Octane** | 0.03 | 380 | annual | Texas AMCV |
| **n-Propylbenzene** | 0.03 | 51 | annual | Texas AMCV |
| **Styrene** | 0.03 | 60<br>110 | 1 week<br>annual | EPP<br>Texas AMCV |
| **Hydrogen Sulphide** | 0.82 | 110<br>14 | 24h<br>90 days | EPP<br>WA DOH |
| **Benzaldehyde** | 0.02 | 2.1 | annual | Texas AMCV |
| **Glutaraldehyde** | 0.02 | 0.05 | annual | Texas AMCV |

## 4.2 Comparison with other sites in the Surat Basin

Table 3 also lists the concentration range and detection frequency (DF %) of the 22 compounds detected at HF study site alongside data from the regional, gas field and township sites in the wider Surat Basin from the same period. The maximum concentrations of all 22 compounds at the other Surat Basin sites were also well below the relevant long-term (annual) air quality guidelines.

Overall, the range of concentrations and detection frequencies observed for each compound at the HF site were similar to those observed at the regional and gas field sites and equal to or less than those observed in the township of Chinchilla. However, there were some exceptions:

- The maximum concentration of toluene observed at the HF site of 0.18 ppb, was 0.14 ppb higher than the maximums observed at the gas field sites but still 0.24 ppb lower than the maximum of 0.42 observed in the township of Chinchilla. The detection frequency of toluene at the HF site was 29%, slightly higher than the DF for the regional and gas field sites of 24% and 22% respectively, but substantially lower than the 100% DF for Chinchilla.

- A maximum of 2.12 ppb of formaldehyde was observed at the HF site which was substantially below the annual NEPM guideline value of 40 ppb, but was still 0.33 – 0.57 ppb higher than the maximum values observed at the gas field, regional and township sites during the study period.
- There were two compounds detected infrequently (1-2%) at the HF study site at very low concentrations (≤ 0.03 ppb) that were not detected at any of the other sites. These were: methyl isobutyl ketone; detected at Property A on one occasion in May 2017 during the non-HF period, and; tetrachloroethylene, detected on two occasions at Property B, once in July 2017 during HF, and the other in August 2017 after the HF period.

## 4.3 Comparison of VOC and aldehyde concentrations during HF and non-HF periods

The range of observed concentrations and detection frequency for each compound detected at the study site for HF and non-HF periods are shown in Table 5. The detection frequencies and concentration ranges for each compound during HF and non-HF periods are presented separately for the Property A and B sites in the Appendices A.2. and A.3. Detection frequencies and concentration ranges for HF and non-HF periods measured at the HF study site, as well as the gas field, regional and township sites are also provided in the Appendices (A.4 and A.5).

For most species measured the concentration range and detection frequency during HF did not differ significantly from non-HF periods. However, there were some exceptions:

- The maximum concentrations of benzene, toluene, m&p xylenes, and ethyl acetate measured during the HF period were 0.04 – 0.09 ppb higher than maximum concentrations measured in the non-HF period. Detection frequencies of these compounds were also 9 – 19% higher during HF periods.
- The maximum concentration of formaldehyde measured during the HF period was 0.49 ppb higher during the HF period than the maximum observed in the non-HF period. The detection frequency for formaldehyde was 100% for both HF and non-HF periods.
- The maximum concentration of propanal measured during the HF period was 0.92 ppb higher during the HF period than the maximum observed in the non-HF period. The detection frequency of propanal was also 41% higher during HF periods.
- The detection frequency of butanal and n-undecane were 17% and 19% higher respectively during HF periods but the observed maximum concentrations did not differ significantly between HF and non-HF periods.

Table 5 The concentration ranges and detection frequencies for the HF study site for the whole study period (All), for the HF-period only, and for the non-HF periods only.

| | All | | HF period | | Non-HF period | |
|---|---|---|---|---|---|---|
| **Compound** | **Range (ppb)** | **DF (%)** | **Range (ppb)** | **DF (%)** | **Range (ppb)** | **DF (%)** |
| *N(VOC Samples)* | *134* | | *48* | | *86* | |
| **2-methylpentane** | 0.01 - 0.11 | 5% | 0.02 – 0.03 | 0% | 0.01 - 0.11 | 8% |
| **3-methylpentane** | 0.01 - 0.03 | 1% | 0.02 – 0.03 | 2% | 0.01 - 0.03 | 1% |
| **n-Hexane** | 0.01 - 0.09 | 13% | 0.02 – 0.06 | 8% | 0.01 – 0.09 | 16% |
| **n-Decane** | 0.01 - 0.08 | 21% | 0.02 – 0.03 | 21% | 0.01 – 0.08 | 21% |
| **n-Undecane** | 0.02 - 0.08 | 15% | 0.03 – 0.08 | 27% | 0.02 – 0.06 | 8% |
| **Cyclohexane** | 0.01 - 0.06 | 1% | 0.02 – 0.06 | 2% | 0.02 – 0.04 | 1% |
| **Benzene** | 0.01 - 0.09 | 21% | 0.02 – 0.09 | 33% | 0.01 – 0.05 | 14% |
| **Toluene** | 0.01 - 0.18 | 29% | 0.01 – 0.18 | 40% | 0.01 – 0.09 | 23% |
| **o-xylene** | 0.01 - 0.03 | 1% | 0.01 - 0.03 | 2% | 0.01 - 0.03 | 0% |
| **m & p-xylenes** | 0.01 - 0.08 | 9% | 0.01 - 0.08 | 15% | 0.01 - 0.04 | 6% |
| **Sum xylenes** | 0.02 - 0.11 | 9% | 0.03 - 0.11 | 15% | 0.02 - 0.05 | 6% |
| **Ethylbenzene** | 0.01 - 0.06 | 3% | 0.01 - 0.06 | 4% | 0.01 - 0.04 | 2% |
| **Carbon tetrachloride** | 0.03 - 0.15 | 100% | 0.06 – 0.10 | 100% | 0.03 – 0.15 | 100% |
| **Trichloromethane** | 0.01 - 0.03 | 10% | 0.01 - 0.02 | 0% | 0.01 - 0.03 | 15% |
| **Tetrachloroethylene** | 0.01 - 0.02 | 1% | 0.01 – 0.02 | 2% | 0.01 – 0.02 | 1% |
| **Ethyl acetate** | 0.01 - 0.07 | 20% | 0.01 – 0.07 | 29% | 0.01 – 0.03 | 15% |
| **Methyl isobutyl ketone** | 0.01 - 0.03 | 1% | 0.01 - 0.03 | 0% | 0.01 - 0.03 | 1% |

| Compound | All | | HF period | | Non-HF period | |
|---|---|---|---|---|---|---|
| | Range (ppb) | DF (%) | Range (ppb) | DF (%) | Range (ppb) | DF (%) |
| | | | | | | |
| *N (Aldehyde samples)* | *116* | | *54* | | *62* | |
| **Formaldehyde** | 0.33 - 2.12 | 100% | 0.42 - 2.12 | 100% | 0.33 – 1.63 | 100% |
| **Acetaldehyde** | 0.08 - 0.94 | 100% | 0.11 – 0.78 | 100% | 0.08 - 0.94 | 100% |
| **Propanal** | 0.03 - 1.14 | 58% | 0.05 - 1.14 | 80% | 0.03 – 0.22 | 39% |
| **Butanal** | 0.08 - 0.37 | 34% | 0.11 – 0.37 | 43% | 0.08 - 0.37 | 26% |
| **Pentanal** | 0.03 - 0.09 | 8% | 0.03 - 0.09 | 6% | 0.03 - 0.08 | 10% |
| **Hexanal** | 0.05 - 0.14 | 22% | 0.05 - 0.14 | 19% | 0.05 - 0.14 | 24% |

Higher detection frequencies and/or higher maximum concentrations during HF periods may have been the result of:

- Emissions from HF or other CSG development activity on site e.g. HF fluids, flowback fluids and CSG.
- Exhaust and evaporative fuel emissions from equipment and vehicles on site and from passing on-road traffic;
- Regional / local emissions not related to HF that coincided with HF activity e.g. smoke from regional/local fires events; emissions from non-CSG industry sources including farming/ agriculture; emissions from natural sources including vegetation;
- Seasonal variability in regional VOC and aldehyde concentrations e.g. enhanced emissions of VOCs and aldehydes in smoke from wood-fired heating during autumn / winter; enhanced photochemical production of aldehydes in the atmosphere during summer;
- Meteorological conditions on diurnal, weekly and seasonal time scales can affect transport and dispersion of chemicals emitted into the air – thus different meteorological conditions between HF and non-HF periods can affect the concentrations

We can use the VOC profiles of known VOC sources that have been characterised in previous studies (see Day et al., 2016 and references within) to investigate their potential contribution to the observed concentrations of VOCs during HF activity. However, it is important to note that given the long sample exposure times of ~ 14 days, the observed concentrations were likely to have been influenced by multiple sources and processes. The following section discusses the sources and processes that may have contributed to the observed concentrations of VOCs during HF at the study site with a particular focus on the air toxics benzene, toluene, xylenes and formaldehyde which are prescribed in the air toxics NEPM.

### 4.3.1 Benzene, Toluene, Xylenes

The maximum concentrations of benzene, toluene, and m&p xylenes measured during the HF period were 0.04 – 0.09 ppb higher than maximum concentrations measured in the non-HF period. Detection frequencies of these compounds were also 9 – 19% higher during HF periods.

Benzene, toluene, ethylbenzene and xylenes, collectively known as the BTEX compounds, share similar sources. It is possible, trace levels of BTEX may be detected in air at HF site, due to (Dunne et al., 2017):

- Vehicle exhaust and evaporative fuel/oil emissions
- Evaporation / leakages from on-site tanks/pipelines holding formation water from the coal seam flowed back from CSG wells
- Fugitive emissions of CSG
- Emissions from prescribed burning, bushfires or woodheaters
- Other industrial/ commercial / domestic emissions

Little publicly available information exists on the levels of VOCs in CSG and groundwater from Australian coal seams and more data is needed to properly characterize these sources (Stearman et al., 2014). The available data suggests BTEX emissions from CSG or from groundwater flowed back from CSG wells are likely to be small. BTEX is either not detected or detected at trace levels (< 1ppb) in CSG (Day et al., 2016, Lawson et al., 2017) and is often below the limit of reporting in data from groundwater samples (Stearman et al., 2014, Schinteie, et al., 2016).

The addition of BTEX compounds to hydraulic fracturing fluids has been strictly regulated in Queensland (SoQ 2010) and fracturing fluids must meet the Australian Drinking Water Guideline for benzene and the Australian and New Zealand Environment Conservation Council guideline for marine and freshwater quality for toluene and xylenes. Consequently HF fluids are not considered a source of BTEX here.

Figure 5 to Figure 7 show time series of BTEX concentrations for Property A and B sampling sites. The concentrations of BTEX compounds were at or below the DL (< 0.04 ppb) for the majority (> 70%) of the measurement period. Most of the time, the observed concentrations of BTEX compounds were similar across all seven sampling sites.

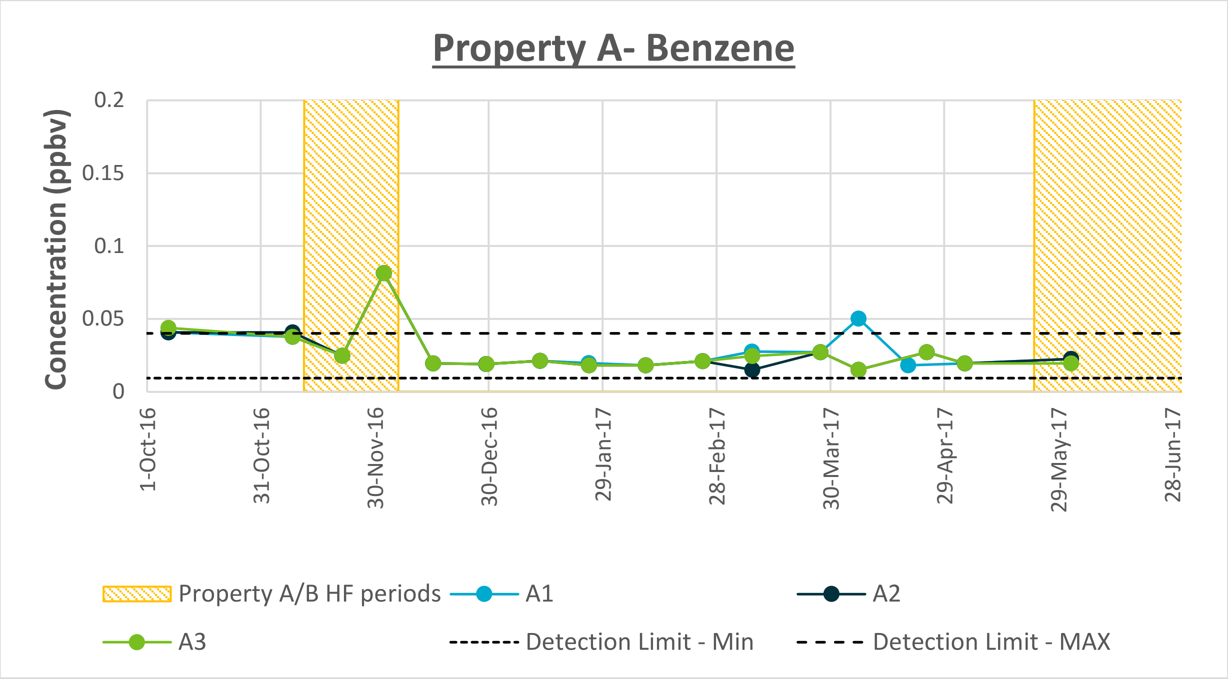
However there were some exceptions to these trends including a peak in benzene concentrations of 0.08 – 0.09 ppb for the sample period 2/12/16 – 15/12/16 detected across all 7 sampling locations (Figure 5). Detection frequencies and concentration ranges for HF and non-HF periods measured at the HF study site, as well as the gas field, regional and township sites are provided in the Appendices A.4 and A.5.

The sample period in which the benzene peak was detected coincided with HF activity at one well on Property A (CNN200) which occurred from 2/12/16 to 6/12/16. If the observed benzene peak was associated with HF at the site it would be reasonable to expect that benzene concentrations at nearby, sites not directly impacted by HF, would be lower. However this was not the case here, and in fact small peaks of similar magnitude were observed across the gas-field sites (range 0.05 – 0.09 ppbv) and regional sites (0.06 – 0.07 ppbv) over the same period indicating a regional source contributed to the increased benzene levels. It is important to note that these concentrations are over 30 times lower than the annual NEPM air quality objective value for benzene of 3 ppb.

The ratio of benzene to toluene differs with source type. Benzene/toluene ratios of 0.2 – 0.6 are typical in urban areas where emissions are dominated by petrol fuelled vehicle emissions whereas diesel exhaust exhibits the opposite relationship with benzene/ toluene ratios >1 (Cope et al., 2014, Day et al., 2016). Benzene / toluene ratios of ~ 0.9 and ~ 3 have been observed in air impacted by emissions from rural fires and from wood smoke respectively (Cope et al., 2014)

For samples from the period 2/12/16 – 15/12/16 the average benzene/toluene ratios observed at the HF study sites were 2.9 (range 2.4 – 3.2), which is similar to those observed across the gas field sites (average = 2.6), and regional sites (average = 2.9) for the same period. Whereas, in the township of Chinchilla, where BTEX emissions were likely to be dominated by traffic emissions with additional contributions from regional smoke, the benzene/toluene ratio for the same period was 0.85.

Data from the Surat Basin Ambient Air Quality Study shows an exceedance of the NEPM ambient air guideline value for fine particulate matter (particle size ≤2.5 µm) at the nearby Miles Airport site, on the 6/ 12/16. This event was investigated using correlations of particle levels with other pollutant data and satellite fire observations in Lawson et al. (2018) who concluded this exceedance was due to a regional smoke event caused by fires 20 - 40 km to the N and NNW of the Miles Airport site. Therefore, it is likely the small peak in benzene concentrations observed across the HF study site as well as the other sites in the Surat Basin was due to this regional smoke event.



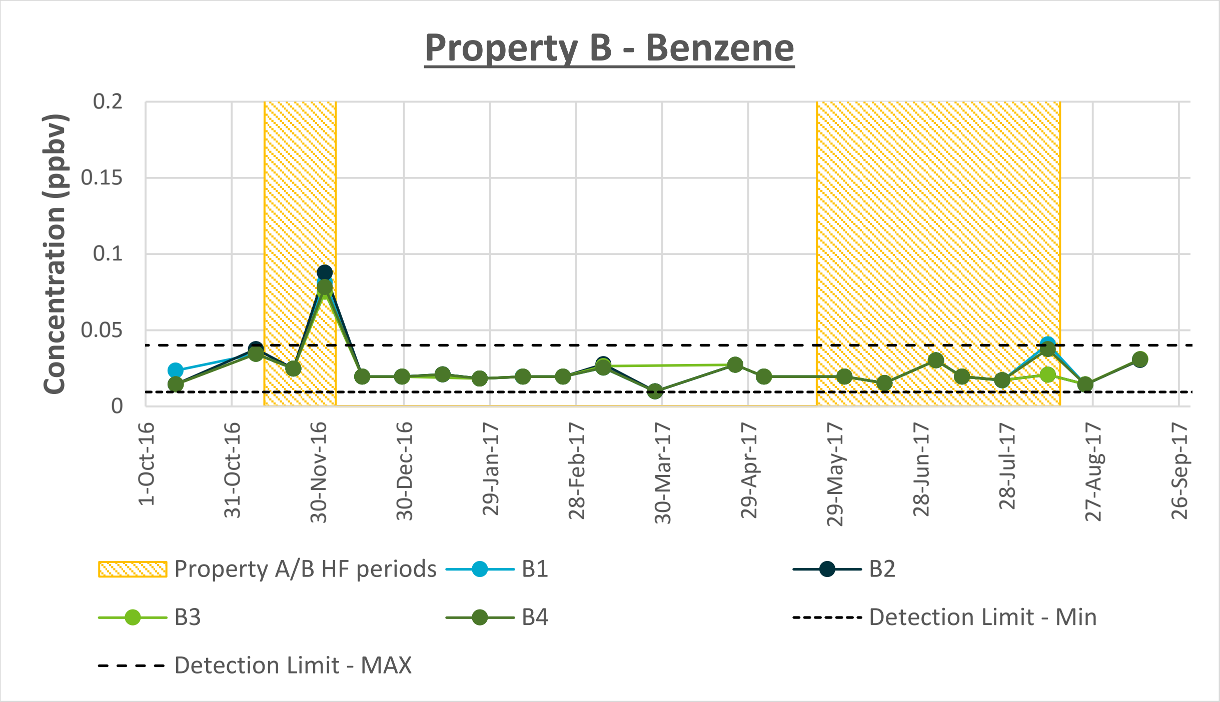


**Figure 5 Time series of benzene data from the Property A (top) and Property B (bottom) sampling sites. The HF period at Property A (12/11/16 – 6/12/16) and Property B (24/5/17 – 16/8/17) are shaded in yellow. Data points represent the start times of the sample exposure periods.**

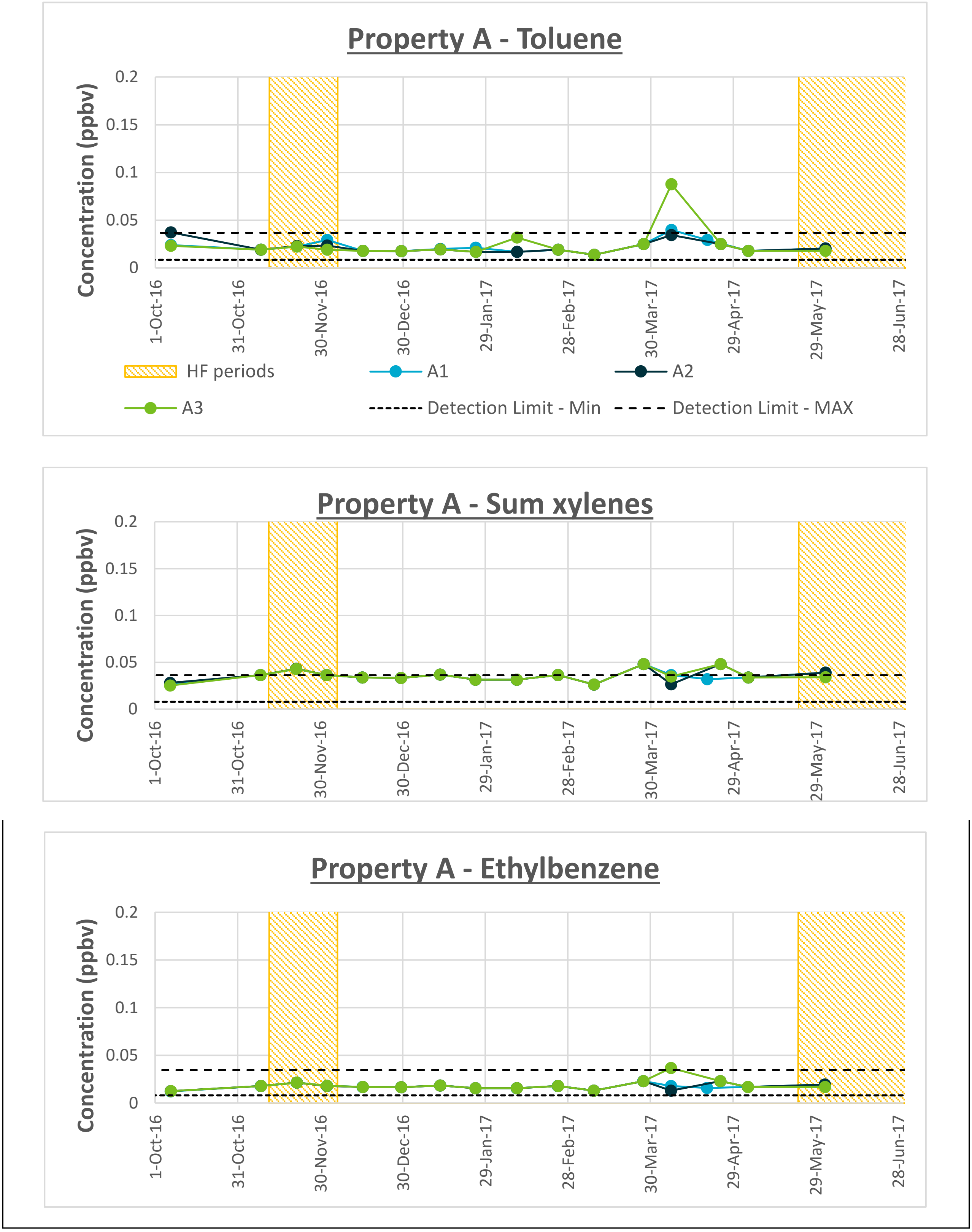


**Figure 6 Time series of toluene, xylene, ethylbenzene data from the Property A sampling sites. The HF period at Property A (12/11/16 – 6/12/16) and Property B (24/5/17 – 16/8/17) are shaded in yellow. Data points represent the start times of the sample exposure periods.**

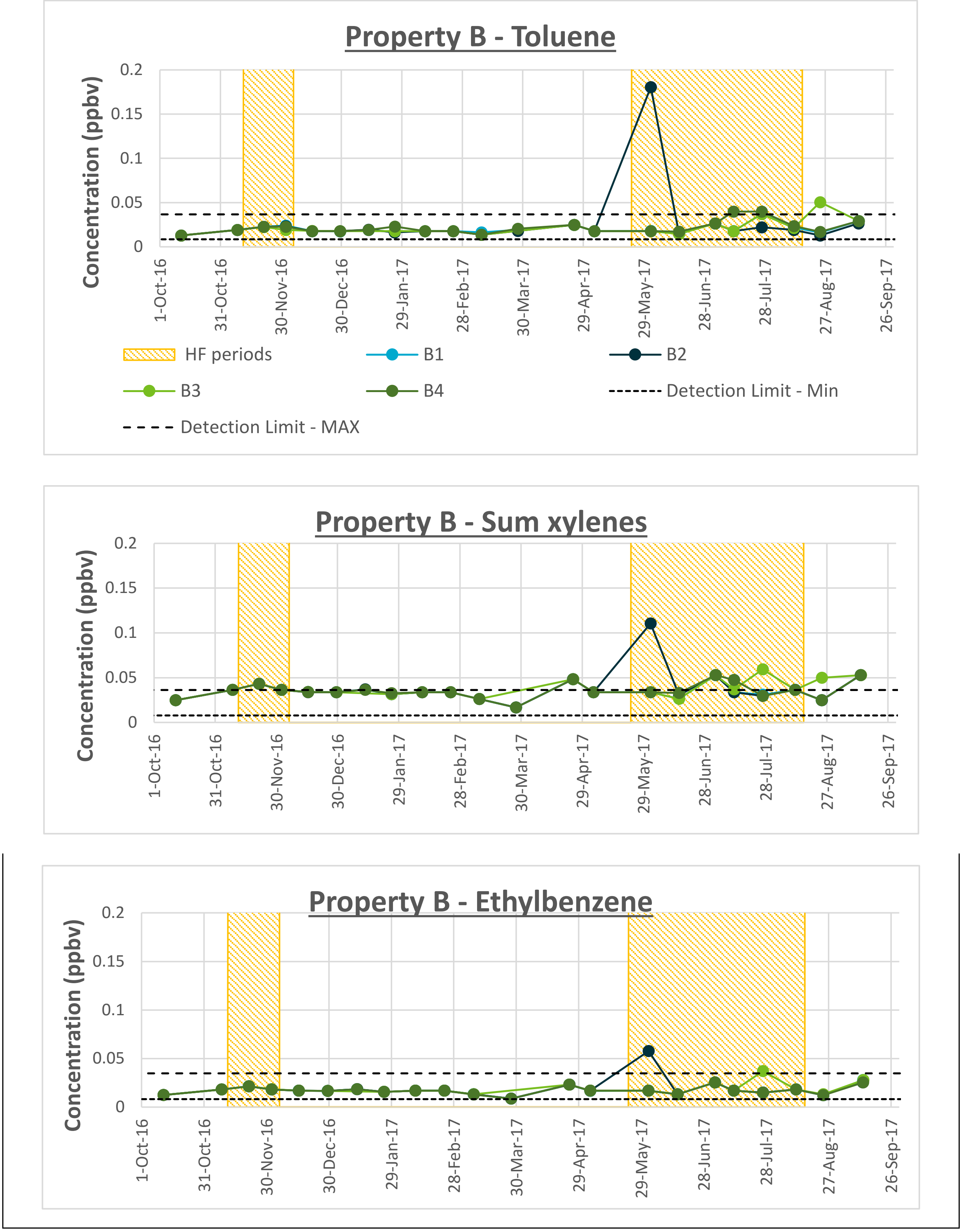


**Figure 7 Time series of toluene, xylene, ethylbenzene data from the Property B sampling sites. The HF period at Property A (12/11/16 – 6/12/16) and Property B(24/5/17 – 16/8/17) are shaded in yellow. Data points represent the start times of the sample exposure periods.**

The concentrations of toluene, xylenes and ethylbenzene were similar across the 7 sampling locations, and they were close to or below the DL for a majority of the measurement period (Figure 5 to Figure 7). There were more occasions during the HF period at Property B where values greater than the DL occurred for toluene, xylenes and, to a lesser extent ethylbenzene, and there was more variability in concentrations between sampling locations which may indicate contributions from local sources.

A visible peak in toluene, xylene and ethylbenzene concentrations was observed at the Property B site B2 for the sample period 1/6/17 – 15/6/17 (Figure 7). It is important to note, the maximum concentrations of toluene (0.18 ppb), xylenes (0.11 ppb) and ethylbenzene (0.06) observed during this period were hundreds to thousands of times lower than the annual NEPM air quality objective values.

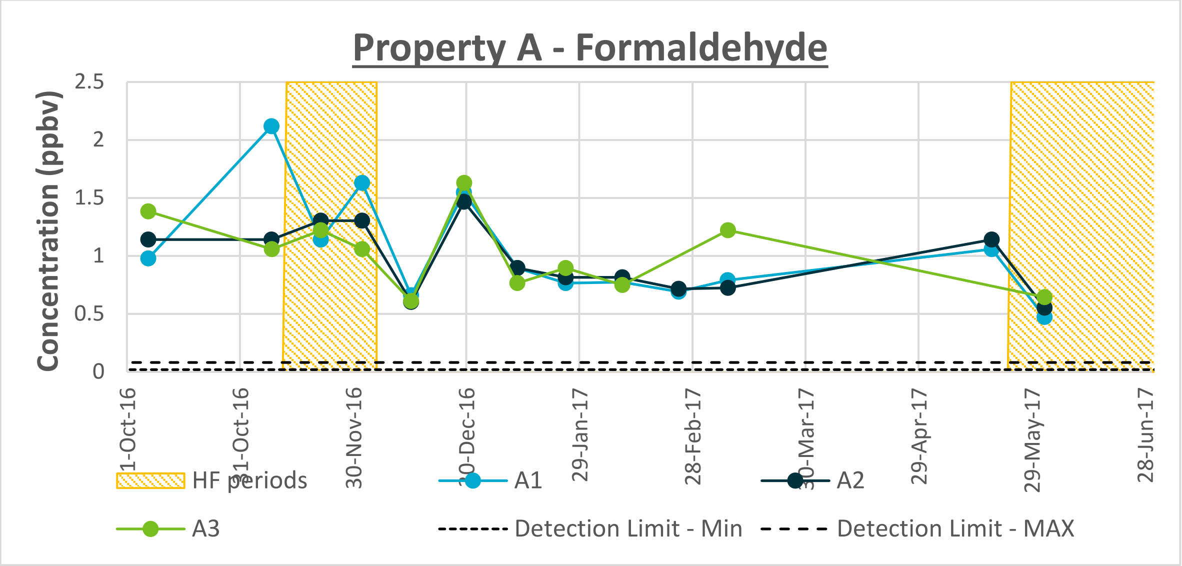
As this peak in toluene, xylene and ethylbenzene concentrations was only observed at one sampling location within the HF study site it was likely the result of a local source of these compounds on the site. There was only 1 day of HF on site within the 15 day sample period (1/6/17 – 15/6/17) which occurred at CON 385. CON 385 is ~ 1.1 km to the WSW of Site B2 and underwent HF from 24/5/17 to 2/6/17. Meteorology data measured at the nearby Miles Airport shows winds were predominantly from the WSW in June 2017 and it is possible activity at CON 385 (site set-up, HF , well completions) impacted the B2 sampling site during the period 1/6/17 – 15/6/17.

Well CON 384 was closest to the B2 sampling location (~ 200 m to the west) where the peak in toluene, xylene and ethylbenzene concentrations were observed. CON 384 underwent HF from 19/6/17 - 23/6/17 outside of the sample period in which the peak event occurred. However, it is possible site set-up activities at CON 384 also contributed to the observed peak in toluene, xylene and ethylbenzene concentrations. The concentration of benzene at Site B2 was less than the DL of 0.02 ppb for this period (19/6/17 - 23/6/17) giving a maximum benzene/ toluene ratio of 0.11. This result is surprising given exhaust from diesel fuelled vehicles and equipment are likely to be the dominant emission sources of BTEX on HF sites and typically exhibit benzene/ toluene ratios > 1 (Nelson et al., 2008). Benzene/ toluene ratios of ~0.5 are typical in petrol fuelled vehicle exhaust (DEWHA 2008) and ratios of 0.2 – 0.6 have been observed in urban areas where emissions are dominated by petrol fuelled vehicle exhaust (Cope et al., 2014). The VOC profile of the peak in toluene, xylene and ethylbenzene is suggestive of vehicle source exhaust however the source/s remain unresolved.

Overall, the concentrations of BTEX compounds were at or close to the DL for a majority of the measurement period including HF periods. Occasional small peaks in the concentration of BTEX compounds were likely to have resulted from both local and regional sources. A regional smoke event was the most likely source of a peak in benzene concentrations observed across the HF study site and other sites in the Surat Basin in December 2016. Analysis of wind direction and VOC profiles indicated, but did not conclusively show, that local emissions from vehicles and activities on site may have contributed to a peak in toluene, xylene and ethylbenzene concentrations observed for a single sample from Site B2 in June 2017.

## 4.4 Formaldehyde

The maximum concentration of formaldehyde of 2.12 ppb was measured at Property A Site A1 during the HF period. This value was 0.49 ppb greater than the maximum concentration measured during non-HF periods and the detection frequency for formaldehyde was 100% for both HF and non-HF periods. Figure 8 shows the time series of formaldehyde concentrations for the Site A and Site B sites.



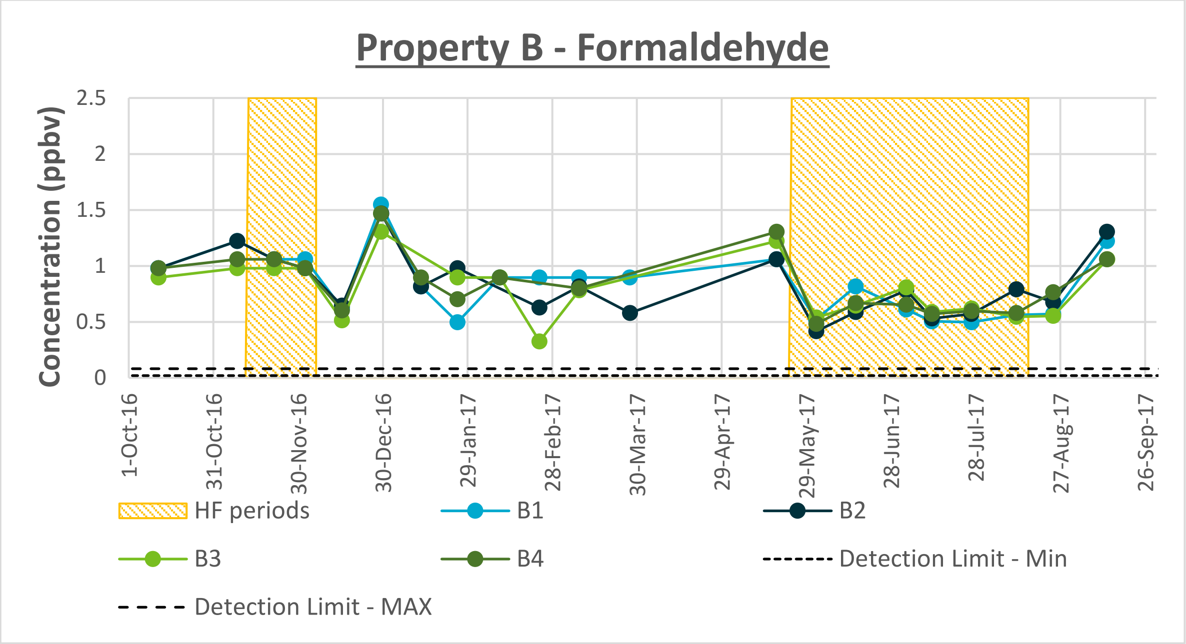


**Figure 8 Time series of formaldehyde from the Property A and B sampling sites. The HF period at Property A (12/11/16 – 6/12/16) and Property B (24/5/17 – 16/8/17) are shaded in yellow. Data points represent the start times of the sample exposure periods.**

Formaldehyde belongs to a class of oxygenated organic compounds known as aldehydes. It is possible, trace levels of these compounds may be detected in air at the HF site, due to (Dunne et al., 2017):

- exhaust emissions from vehicles and diesel powered equipment
- emissions from prescribed burning, bushfires or woodheater emissions
- secondary production from photochemical oxidation of other VOCs and methane in the atmosphere
- other industrial/ commercial/ domestic emissions in the region
- emissions from HF or other CSG development activity on site e.g. HF fluids, flowback fluids and CSG

Formaldehyde was not directly used as a chemical additive in the HF fluids injected into the wells (APLNG, 2016), however its presence in HF fluids as a result of interactions between chemical additives or as a trace contaminant in the chemical additives used is currently not well understood (Kahrilas et al., 2014). No data was found on the occurrence of formaldehyde in CSG or formation water from Australian coal seams. The potential for emissions of formaldehyde to air in CSG or via evaporation from groundwater and HF fluids remains unresolved.

Formaldehyde can be formed in the atmosphere via photochemical oxidation of VOCs and methane. Due to the sunlight dependence of these reactions, formaldehyde concentrations are generally higher in the spring and summer months (September – February) in which HF occurred at Property A; and lower in the autumn- winter months in which HF occurred at Property B. Over the same period as HF activity at Property A (12/11/16 – 6/12/16) the concentrations (average ± standard deviation) of formaldehyde reported for the regional sites (1.11 ± 0.24 ppb), and the gas field sites (1.20 ± 0.26 ppb) were similar to those observed at the HF study sites (1.17 ± 0.23). Over the same period HF activity at Property B (24/5/17 – 16/8/17) the concentrations (average ± standard deviation) of formaldehyde reported for the regional sites (0.79 ± 0.31 ppb) and the gas field sites (0.72 ± 0.24 ppb) were similar to those observed at the HF study sites (0.70 ± 0.24 ppb).

As discussed in the previous section, the concentrations of BTEX measured in samples for the period 2/12/16 – 15/12/16, which coincided with HF activity at Property A, were attributed to a regional smoke event. This smoke event may have also contributed to higher regional background concentrations of formaldehyde for this period (Akagi et al., 2011). The concentrations of formaldehyde for this period reported for the HF sites (range: 0.97 – 1.63 ppb) were similar to those reported for the gas field sites (1.02 – 1.63 ppb) and slightly higher than those reported for the regional sites (0.81 – 1.22 ppb).

The time series of formaldehyde concentrations measured at Properties A and B (Figure 8) show that during HF at Property B, average concentrations of formaldehyde (0.68 ± 0.23 ppb) were broadly similar to those observed during non-HF periods (formaldehyde = 0.87 ± 0.28 ppb) and showed little variability between sampling locations (B1 – B4). However, during HF at Property A (12/11/16 – 6/12/16), concentrations of formaldehyde (average ± standard deviation, 1.33 ± 0.34 ppb) were higher than measurements during non-HF periods (0.94 ± 0.31 ppb) and there was slightly more variability between the three sampling sites (A1 – A3) This may indicate local sources at this site also contributed to the observed formaldehyde concentrations.

It is possible local sources of formaldehyde such as vehicle exhaust contributed to the higher and more variable concentrations observed at Property A sampling sites during HF periods. However, the concentrations of benzene, toluene, xylenes and ethylbenzene measured in samples that coincided with the Site A HF period 8/11/16 – 15/12/16 do not indicate local emissions from diesel and petrol exhaust sufficient to explain the observed formaldehyde concentrations (DEWHA 2008, Nelson et al 2008).

The two highest concentrations of formaldehyde reported for the HF study sites of 2.12 ppb and 1.63 ppb were measured at Site A1 during the sample periods 8/11/16 – 21/11/16 and 2/12/16 – 15/12/16 respectively. In comparison formaldehyde concentrations of 1.14 ppb and 1.30 ppb were reported respectively for Site A2 for the same periods. Formaldehyde concentrations reported for Site A3 for both of these periods were of 1.06 ppb. This suggests Site A1, and to a lesser extent Site A2, may have been impacted by a local source/s of formaldehyde during these periods.

There were 10 days of HF activity on site within the 14 day sample period (8/11/16 – 21/11/16) which occurred at:

- CNN 186 which was ~ 1.6 km to the east of Site A1 and ~ 0.75km ESE of Site A2. HF period: 12 – 16/11/16
- CNN 192 which was ~ 0.9 km ENE of Site A1 and ~ 0.06km E of Site A2. HF period: 16 – 21/11/16

There were 5 days of HF activity on site within the 14 day sample period (2/12/16 – 15/12/16) which occurred at:

- CNN 191 which was ~ 1.3 km NNE of Site A1 and ~ 0.8 km N of Site A2. HF period: 28/11 – 2/12/16.
- CNN 200 which was ~ 2 km NE of Site A1 and ~ 1.6 km N of Site A2. HF period: 2 – 6/12/16.

Meteorology data measured at the nearby Miles Airport for Nov – Dec 2016 indicates winds were predominantly from the ENE during these periods so that Site A 1 and 2 were likely to have been downwind of these wells for some of the period during HF activity.

Conversely, these wells were ~ 0.5 – 2km to the N –NNW of Site A3 which reported the lowest formaldehyde concentrations of the three sampling sites on Property A during the HF period. The well CON 379 is to the south of all three sampling sites on Property A, and underwent HF during the period 21 – 25/11/16 when more similar concentrations were reported across all three sampling sites - 1.14, 1.30, and 1.22 ppb for Sites A 1 - 3 respectively.

Overall, concentrations of formaldehyde observed across the HF site and other sites in the Surat Basin were similar over the study period and showed higher concentrations during summer likely due to contributions from photochemical production of formaldehyde in the atmosphere. On occasion, slightly higher concentrations of formaldehyde were observed at one or two sampling sites which were located predominantly downwind from well pads during HF activity. Further work is required to characterise the potential sources of formaldehyde associated with HF activity which currently remain poorly understood.

# 5 Summary

Here we have presented a study of the ambient concentrations of 54 compounds measured using three different Radiello passive sampling methods capable of measuring a range of 45 VOCs, 7 aldehyde species and $H_2S$. Measurements were undertaken at a site within a region of intense CSG development in the Surat Basin in Queensland from October 2016 to September 2017. Samples were collected at 7 locations within a ~ 5 x 6 km area in which 21 CSG wells underwent HF treatments in late 2016 and mid-2017. A total of 134 VOC samples, 116 aldehyde samples and 138 $H_2S$ samples were successfully collected during the study period.

Sampling occurred during HF periods as well as periods when HF was not occurring. However, there was a range of well development operations occurring at the study site during the measurement period including well integrity testing, perforation, HF site set-up, HF treatment, and well completions. It is not uncommon to observe several different activities each requiring specialised equipment, occurring simultaneously across different well pads.

Samples collected at the site during the study period may have also been impacted by sources of VOCs, aldehydes and $H_2S$ from the surrounding area including:

- Well development, HF and well completions
- Natural sources such as soil and emissions from vegetation
- Local /regional traffic emissions
- Smoke from bushfires, prescribed burning and wood heaters
- Non-HF related CSG industry emissions
- Other industrial, commercial, agricultural and domestic emissions

Given the long sample exposure times of ~14 days, samples collected during activity at the study site were likely to have been impacted by multiple sources and not exclusively by HF.

The study was designed to address three objectives:

**Objective 1**- Provide comparisons of the VOC levels observed at the HF site with Australian federal and state and other relevant air quality objectives.

**Objective 2**- Provide comparisons of the composition of VOCs observed at a HF site with simultaneous measurements from areas within the Surat Basin not directly impacted by HF operations.

**Objective 3**- Provide comparisons of the composition of VOCs observed during HF activity with data from measurements during non- HF periods at the same site.

There were 22 compounds reported above the DL of the Radiello method at the HF study sites on one or more occasions. The maximum concentrations for all 22 compounds detected at the HF study sites during this study were tens to thousands of times below National (NEPM) and State (EPP) long-term (annual) air quality guidelines, and international air quality guidelines (Texas AMCV/ESL) referenced here. The maximum concentrations of the NEPM air toxics benzene, toluene, and xylenes measured at the HF study site were tens to thousands of times lower than their respective NEPM monitoring investigation levels. Only 24-hour goals are specified for formaldehyde in the Air Toxics NEPM (2011) and the Radiello data reported levels of these pollutants cannot be assessed against these short-term guidelines. Instead, the maximum of 2.12 ppb from the radiello data for formaldehyde was compared against the annual Texas AMCV value of 9ppb.

There were 32 compounds including $H_2S$, that were not reported above the DL at the HF sites on any occasion and the maximum DLs for these compounds were tens to thousands of times lower than their relevant air quality guideline values.

A major advantage of the site selected for the present study was its location within the air quality monitoring network operating as part of the current GISERA Surat Basin Ambient Air Quality (SBAAQ) Study (Lawson et al., 2017). The network comprised 10 additional sites at which passive Radiello monitoring was undertaken. Data from 6 of the sampling sites operated as part of the SBAAQ study were compared with data from the HF study site. These SBAAQ sites selected for comparison included 3 sampling sites located within gas fields in proximity to producing CSG wells but not known to be directly impacted by HF activity during the measurement period; 2 regional sites located in areas > 10 km away from CSG infrastructure and 40 – 50 km away from the HF study site; and a single sampling site located within the largest nearby township Chinchilla.

The concentrations and frequency each compound was detected were compared with Radiello monitoring data from regional, gas field and township sites in the wider Surat Basin for the same measurement period. The maximum concentrations of all 22 compounds at the other Surat Basin sites were also well below the relevant long-term (annual) air quality guidelines.

Overall, the range of concentrations and detection frequencies observed for each compound at the HF site were similar to those observed at the regional and gas field sites and equal to or less than those observed in the township of Chinchilla. However, there were some exceptions:

- Maximum concentrations of toluene and formaldehyde observed at the HF site were higher than those observed for the gas field and regional sites not known to be directly impacted by HF. The detection frequency of toluene at the HF site was also slightly higher than the detection frequencies for the regional and gas field sites
- There were two compounds detected infrequently (1-2%) at the HF study site at very low concentrations (≤ 0.03 ppb) that were not detected at any of the other sites. These were: methyl isobutyl ketone; detected at Property A on one occasion in May 2017 during the non-HF period, and; tetrachloroethylene, detected on two occasions at Property B, once in July 2017 during HF, and the other in August 2017 after the HF period.

Data collected during HF and non-HF periods at the study site showed for most species measured, the concentration range and detection frequency during HF did not differ significantly from non-HF periods. However, there were some exceptions:

- The maximum concentrations of the VOCs benzene, toluene, m&p xylenes, and ethyl acetate measured during the HF period were slightly (< 0.1 ppb) higher than maximum concentrations measured in the non-HF periods. Detection frequencies of these compounds were also 9 – 19% higher during HF periods.

- The maximum concentrations of formaldehyde, and propanal measured during the HF period were higher than the maximums observed in the non-HF periods. The detection frequency of propanal was also 41% higher during HF periods.
- The detection frequency of butanal and n-undecane were ~18% higher during HF periods but the observed maximum concentrations did not differ significantly between HF and non-HF periods.

A more detailed analysis of the concentrations of the NEPM air toxics benzene, toluene, xylenes and formaldehyde and the potential factors that may have contributed to their observed concentrations during HF at the study site was undertaken.

In general, the concentrations of BTEX compounds were at or below the DL (< 0.04 ppb) for the majority (> 70%) of the measurement period. Most of the time, the observed concentrations of BTEX compounds were similar across all 7 sampling sites (Sites A 1 – 3, and Sites B 1 – 4).

However there were some exceptions to these trends including:

- A peak in benzene concentrations of ~ 0.1 ppb in December 2016 which coincided with HF at Property A but was attributed to a regional smoke event based on: the widespread nature of this peak benzene event which was observed at other sites across the Surat Basin; information of a smoke event reported as part of the SBAAQ study; and analysis of typical VOC profiles from smoke.
- A peak in toluene, xylene and ethylbenzene concentrations was observed at a single sampling location with the HF site in July 2017. The localised nature of this event and analysis of wind direction indicated, but did not conclusively show, that local emissions from activities on site may have contributed to the peak in toluene, xylene and ethylbenzene concentrations. The VOC profiles of this event are suggestive of petrol fuelled vehicle emissions however the source remains unresolved.
- Concentrations of formaldehyde observed across the HF site and other sites in the Surat Basin were similar over the study period and showed higher concentrations during summer likely due to contributions from photochemical production of formaldehyde in the atmosphere. On occasion, slightly higher concentrations of formaldehyde were observed at one or two sampling sites which were located predominantly downwind from well pads during HF activity. Further work is required to characterise the potential sources of formaldehyde associated with HF activity which currently remain poorly understood.

In summary, measurements of VOCs and aldehydes by passive Radiello monitoring at a HF site reported levels that were well below national, state and relevant international annual ambient air quality guidelines which are designed to protect human health, wellbeing and the environment, and were similar to those measured at other regional and gas field locations in the Surat Basin not known to be directly impacted by HF during the measurement period. While a regional smoke event was most likely responsible for a small peak in benzene concentrations, there was some indication that local sources including well development activities on site may have been associated with occasional peaks in the 14-day average concentrations of toluene, xylenes, ethylbenzene and formaldehyde, as well as higher concentrations and/or detection frequencies of propanal, butanal, n-undecane, and ethyl acetate. However the specific sources of these compounds remain unresolved.

A better understanding the factors that influence the concentration of VOCs and aldehydes in the atmosphere during well development activities including HF requires:

- Techniques capable of higher time resolution measurements that are on the same scale as the well development activities occurring on site (typically occur over 1 -2 days). The 14-day sample time employed in this study is not useful for capturing short term events. Many compounds measured were at or close to the DL for a majority of the time and reducing the sampling period would result in higher DL and therefore a greater number of non-detects.
- More information on the composition of VOCs and aldehydes in HF fluids, flowback water and CSG, in order to better understand their potential to act as sources of air pollutants on HF sites.
- More detail of conditions and activity on site including equipment and vehicle traffic, and local meteorology.
- A better understanding of the long –term regional influences on VOC and aldehyde levels e.g. seasonal variability, smoke events, and regional scale emissions (natural, industrial, agricultural).

Further work is also required to better understand the impact of HF on air quality more broadly. VOCs and aldehydes are only one group of compounds that are relevant to air quality. The National Environment (ambient air quality) Protection Measure, like the air toxics NEPM, prescribes air quality objectives for several other air pollutants including carbon monoxide (CO), oxides of nitrogen ($NO_x$), ozone ($O_3$), sulphur dioxide ($SO_2$), airborne particles (PM) and lead (NEPM 2016). Additional measurement systems capable of capturing a range of important air pollutants are required to better assess the impact of HF on air quality. To this end, a brief description of a more comprehensive study of air quality at another HF site undertaken as part of Phase 2 of this project is provided in the subsequent section.

# 6 Further work

This report was produced as part of Phase 1 of the GISERA Air, Water and Soil Impacts of Hydraulic Fracturing: Phase 2 (W.11). Phase 2 (W.12) of the project involves a more comprehensive investigation of air, water and soil quality during HF at a site in the Darling Downs based on detailed peer-reviewed study designs developed for air quality (Dunne et al., 2017) and water and soil quality (Apte et al., 2017) studies as part of Phase 1.

The study location was a farmland property of approximately 600 ha containing 10 CSG wells which underwent HF between September and October 2017. The measurement program ran from July – December 2017 covering periods prior to HF, during HF activity, and after HF had concluded. Measurements were conducted at 6 different sampling locations within the field, five of which were located adjacent to wells (within ~130 m).

Across the 6 sites, 16 different air quality variables were measured utilising a mixture of continuous measurement systems for CO, $NO_x$, $O_3$, and airborne particles and integrated sampling of VOCs, aldehydes and particulates onto specialised sample cartridges or filters. Particular highlights of the measurement program undertaken by CSIRO and project partners for this study include:

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

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

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

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

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

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

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

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

As described in the preface, CSIRO Land and Water undertaking a parallel study of the impact of HF on surface water, groundwater and soil. The proposed measurements of surface water, groundwater and soil occurred at the same time as some of the air quality measurements described in this report and also during the Phase 2 air quality study. The measurements of surface water groundwater and soil 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 + water + proppant)
- Flow-back fluids at multiple time intervals from selected well site operations
- Soil samples taken in the vicinity of selected HF well sites

The data from this study will provide important information on the composition of HF fluids and flowback water, which will improve our understanding of their potential to act as sources of air pollutants on HF sites. The final report for the Phase 2 study is expected to be released in early 2018. More information and project updates can be found at: https://gisera.csiro.au/project/air-water-and-soil-impacts-of-hydraulic-fracturing-phase-2/

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# Appendices

## A 1 Data capture for each sampling site

| | | | Property A | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Report ID | Sample Start | Sample end | 1 | | | 2 | | | 3 | | | Notes |
| | | | VOC | Aldehyde | $H_2S$ | VOC | Aldehyde | $H_2S$ | VOC | Aldehyde | $H_2S$ | |
| M161892 | 6-Oct-16 | 25-Oct-16 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M162114 | 8-Nov-16 | 21-Nov-16 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M162259 | 21-Nov-16 | 2-Dec-16 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M162260 | 2-Dec-16 | 15-Dec-16 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M162261 | 15-Dec-16 | 29-Dec-16 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M162262 | 29-Dec-16 | 12-Jan-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M170108 | 12-Jan-17 | 25-Jan-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M170122 | 25-Jan-17 | 9-Feb-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M170180 | 9-Feb-17 | 24-Feb-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | VOC Sample contami<br>Site B 1-4 n-hexane d<br>excluded. |
| M170226 | 24-Feb-17 | 9-Mar-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | Site A 3- aldehyde sa<br>damaged |
| M170292 | 9-Mar-17 | 27-Mar-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M170330 | 27-Mar-17 | 6-Apr-17 | 1 | 0 | 1 | 0 | 0 | 1 | 1 | 0 | 0 | Radiello sampler sho<br>Site A 1 - 3- no aldehy<br>samples<br>Site A 3- H2S sampler<br>damaged |
| M170382 | 6-Apr-17 | 24-Apr-17 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | Radiello sampler sho<br>Site B 4- no aldehyde<br>samples<br>Site B 1- H2S sample<br>damaged<br>Site B 3- all samples<br>damaged |
| M170430 | 24-Apr-17 | 4-May-17 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | Radiello sampler sho<br>Site A 1 - 3- no aldehy<br>samples |
| M170495 | 4-May-17 | 18-May-17 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | Radiello sampler sho |

| | | | Property A | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Report ID | Sample Start | Sample end | 1 | | | 2 | | | 3 | | | Notes |
| | | | VOC | Aldehyde | $H_2S$ | VOC | Aldehyde | $H_2S$ | VOC | Aldehyde | $H_2S$ | |
| | | | | | | | | | | | | Site A 1 - 3- no aldehy samples<br>VOC Sample contami Site B 1-4 2methylpe data excluded. |
| M170535 | 18-May-17 | 1-Jun-17 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | Site A 3- all samplers damaged<br>Sample contaminatio<br>Site A 1&2 all VOC da removed |
| M170612 | 1-Jun-17 | 13-Jun-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| **TOTAL** | All | | **16** | **13** | **17** | **16** | **13** | **17** | **16** | **11** | **15** | |
| | HF periods | | **4** | **5** | **5** | **4** | **5** | **5** | **4** | **4** | **4** | |
| | Non-HF periods | | **12** | **8** | **12** | **12** | **8** | **12** | **12** | **7** | **11** | |
| | Site A HF period | | **3** | **3** | **3** | **3** | **3** | **3** | **3** | **3** | **3** | |
| | Site A non-HF periods | | **13** | **10** | **14** | **13** | **10** | **14** | **13** | **8** | **12** | |

| | Property B | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Report ID | Sample Start | Sample end | 1 | | | 2 | | | 3 | | | 4 | | | Notes |
| | | | VOC | Aldehyde | $H_2S$ | VOC | Aldehyde | $H_2S$ | VOC | Aldehyde | $H_2S$ | VOC | Aldehyde | $H_2S$ | |
| M161892 | 11-Oct-16 | 25-Oct-16 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M162114 | 8-Nov-16 | 21-Nov-16 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M162259 | 21-Nov-16 | 2-Dec-16 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M162260 | 2-Dec-16 | 15-Dec-16 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M162261 | 15-Dec-16 | 29-Dec-16 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M162262 | 29-Dec-16 | 12-Jan-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M170108 | 12-Jan-17 | 25-Jan-17 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 1 | Site B 3- sampl damaged |
| M170122 | 25-Jan-17 | 9-Feb-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M170180 | 9-Feb-17 | 23-Feb-17 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | Site B 2- aldeh data missing fr report<br>VOC Sample contamination Site B 1-4 n-he data excluded. |
| M170226 | 23-Feb-17 | 9-Mar-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | Site B 4 – aldel sampler dama |
| M170292 | 9-Mar-17 | 27-Mar-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| M170382 | 27-Mar-17 | 24-Apr-17 | 1 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 0 | 1 | 0 | 1 | Radiello sampl shortage:<br>Site B 3 & 4- no aldehyde samp<br>Site B 1- no H2 sample |
| M170430 | 24-Apr-17 | 4-May-17 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | Radiello sampl shortage:<br>Site B 1 - 4- no aldehyde samp |
| M170495 | 4-May-17 | 18-May-17 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | Radiello sampl shortage: Site - no data.<br>VOC Sample contamination<br>Site B 1-4 2methylpentar excluded. |
| M170535 | 18-May-17 | 1-Jun-17 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | VOC Sample contamination |

|  | Property B |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Report ID** | **Sample Start** | **Sample end** | **1** |  |  | **2** |  |  |  | **3** |  | **4** |  |  | **Notes** |
|  |  |  | VOC | Aldehyde | $H_2S$ | VOC | Aldehyde | $H_2S$ | VOC | Aldehyde | $H_2S$ | VOC | Aldehyde | $H_2S$ |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | Site B 1-4 all V data excluded. |
| M170612 | 1-Jun-17 | 15-Jun-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  |
| M170663 | 15-Jun-17 | 3-Jul-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  |
| M170708 | 3-Jul-17 | 12-Jul-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  |
| M170754 | 12-Jul-17 | 26-Jul-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  |
| M170804 | 26-Jul-17 | 11-Aug-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  |
| M170868 | 11-Aug-17 | 24-Aug-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  |
| M170925 | 24-Aug-17 | 12-Sep-17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  |
| **TOTAL** | All |  | **22** | **21** | **22** | **22** | **20** | **23** | **20** | **19** | **21** | **22** | **19** | **23** |  |
|  | HF periods |  | **9** | **11** | **10** | **9** | **10** | **10** | **9** | **10** | **10** | **9** | **10** | **10** |  |
|  | Non-HF periods |  | **13** | **10** | **12** | **13** | **10** | **13** | **11** | **9** | **11** | **13** | **9** | **13** |  |
|  | Site B HF period |  | **6** | **7** | **7** | **6** | **7** | **7** | **6** | **7** | **7** | **6** | **7** | **7** |  |
|  | Site B non-HF periods |  | **16** | **14** | **15** | **16** | **13** | **16** | **14** | **12** | **14** | **16** | **12** | **16** |  |

## A 2 Detection Frequencies for HF and non-HF periods measured at Property A and B

| | Property A | | | Property B | | |
|---|---|---|---|---|---|---|
| **Compound** | **All** | **HF period** | **Non-HF period** | **All** | **HF period** | **Non-HF periods** |
| *N (VOC samples)* | *48* | *12* | *36* | *86* | *36* | *50* |
| **2-methylpentane** | 7% | 0% | 9% | 4% | 0% | 7% |
| **3-methylpentane** | 2% | 0% | 3% | 1% | 3% | 0% |
| **n-Hexane** | 11% | 0% | 15% | 14% | 11% | 17% |
| **n-Decane** | 23% | 33% | 19% | 20% | 17% | 22% |
| **n-Undecane** | 13% | 25% | 8% | 16% | 28% | 8% |
| **Cyclohexane** | 1% | 0% | 3% | 1% | 3% | 0% |
| **Benzene** | 27% | 50% | 19% | 17% | 28% | 12% |
| **Toluene** | 25% | 17% | 28% | 31% | 47% | 20% |
| **o-xylene** | 0% | 0% | 0% | 1% | 3% | 0% |
| **Ethylbenzene** | 2% | 0% | 3% | 3% | 8% | 2% |
| **m & p-xylenes** | 6% | 0% | 8% | 10% | 19% | 4% |
| **Carbon tetrachloride** | 100% | 100% | 100% | 100% | 100% | 100% |
| **Ethyl acetate** | 27% | 50% | 19% | 16% | 22% | 12% |
| **Trichloromethane** | 15% | 0% | 19% | 7% | 0% | 12% |
| **Tetrachloroethylene** | 0% | 0% | 0% | 2% | 3% | 2% |
| **Methyl isobutyl ketone** | 2% | 0% | 3% | 0% | 0% | 0% |
| *N (Aldehyde samples)* | *37* | *14* | *23* | *79* | *40* | *39* |
| **Formaldehyde** | 100% | 100% | 100% | 100% | 100% | 100% |
| **Acetaldehyde** | 100% | 100% | 100% | 100% | 100% | 100% |
| **Propanal** | 54% | 100% | 26% | 59% | 73% | 46% |
| **Butanal** | 41% | 71% | 22% | 30% | 33% | 28% |
| **Pentanal** | 16% | 21% | 13% | 4% | 0% | 8% |

| | Property A | | | Property B | | |
|---|---|---|---|---|---|---|
| Compound | All | HF period | Non-HF period | All | HF period | Non-HF periods |
| **Hexanal** | 35% | 50% | 26% | 15% | 8% | 23% |

## A 3 Concentration ranges for HF and non-HF periods measured at Property A and Property B

| | Property A - Concentration range (ppb) | | | Property B - Concentration range (ppb) | | |
|---|---|---|---|---|---|---|
| **Compound** | **All** | **HF period** | **Non-HF period** | **All** | **HF period** | **Non-HF periods** |
| *N(VOC Samples)* | *48* | *12* | *36* | *86* | *36* | *50* |
| **2-methylpentane** | 0.02 – 0.11 | 0.02 – 0.03 | 0.02 – 0.11 | 0.01 – 0.05 | 0.02 – 0.03 | 0.01 – 0.05 |
| **3-methylpentane** | 0.02 – 0.03 | 0.02 – 0.03 | 0.02 – 0.03 | 0.01 – 0.03 | 0.02 – 0.03 | 0.01 – 0.03 |
| **n-Hexane** | 0.02 – 0.04 | 0.02 – 0.03 | 0.02 – 0.04 | 0.01 – 0.21 | 0.02 – 0.09 | 0.01 – 0.09 |
| **n-Decane** | 0.02 – 0.05 | 0.02 – 0.03 | 0.02 – 0.05 | 0.01 – 0.08 | 0.02 – 0.03 | 0.01 – 0.08 |
| **n-Undecane** | 0.03 – 0.08 | 0.03 – 0.08 | 0.03 – 0.06 | 0.02 – 0.07 | 0.03 – 0.07 | 0.02 – 0.05 |
| **Cyclohexane** | 0.02 – 0.04 | 0.03 – 0.03 | 0.02 – 0.04 | 0.01 – 0.06 | 0.02 – 0.06 | 0.01 – 0.04 |
| **Benzene** | 0.02 – 0.08 | 0.02 – 0.08 | 0.02 – 0.05 | 0.01 – 0.09 | 0.02 – 0.09 | 0.01 – 0.03 |
| **Toluene** | 0.01 – 0.09 | 0.02 – 0.03 | 0.01 – 0.09 | 0.01 – 0.18 | 0.01 – 0.18 | 0.01 – 0.05 |
| **o-xylene** | 0.01 – 0.03 | 0.02 – 0.02 | 0.01 – 0.03 | 0.01 – 0.03 | 0.01 – 0.03 | 0.01 – 0.03 |
| **m & p-xylenes** | 0.01 – 0.02 | 0.02 – 0.02 | 0.01 – 0.02 | 0.01 – 0.08 | 0.01 – 0.08 | 0.01 – 0.04 |
| **Sum xylenes** | 0.03 – 0.05 | 0.03 – 0.04 | 0.03 – 0.05 | 0.02 – 0.11 | 0.03 – 0.11 | 0.02 – 0.05 |
| **Ethylbenzene** | 0.01 – 0.04 | 0.02 – 0.02 | 0.01 – 0.04 | 0.01 – 0.06 | 0.01 – 0.06 | 0.01 – 0.03 |
| **Carbon tetrachloride** | 0.03 – 0.15 | 0.07 – 0.10 | 0.03 – 0.15 | 0.05 – 0.14 | 0.07 – 0.10 | 0.05 – 0.14 |
| **Ethyl acetate** | 0.01 – 0.04 | 0.02 – 0.04 | 0.01 – 0.03 | 0.01 – 0.07 | 0.01 – 0.07 | 0.01 – 0.03 |
| **Trichloromethane** | 0.01 – 0.03 | 0.01 – 0.02 | 0.01 – 0.03 | 0.01 – 0.02 | 0.01 – 0.02 | 0.01 – 0.02 |
| **Tetrachloroethylene** | 0.01 – 0.02 | 0.01 – 0.02 | 0.01 – 0.02 | 0.01 – 0.02 | 0.01 – 0.02 | 0.01 – 0.02 |
| **Methyl isobutyl ketone** | 0.01 – 0.03 | 0.02 – 0.02 | 0.01 – 0.03 | 0.01 – 0.03 | 0.01 – 0.03 | 0.01 – 0.03 |
| *N (Aldehyde samples)* | *37* | *14* | *23* | *79* | *40* | *39* |

|  | Property A - Concentration range (ppb) |  |  | Property B - Concentration range (ppb) |  |  |
|---|---|---|---|---|---|---|
| Compound | All | HF period | Non-HF period | All | HF period | Non-HF periods |
| **Formaldehyde** | 0.47 – 2.12 | 0.47 – **2.12** | 0.60 – 1.63 | 0.33 – 1.55 | 0.42 – 1.30 | 0.33 – 1.55 |
| **Acetaldehyde** | 0.12 – 0.78 | 0.22 – **0.78** | 0.12 – 0.61 | 0.08 – 0.94 | 0.11 – 0.53 | 0.08 – 0.94 |
| **Propanal** | 0.05 – 1.14 | 0.09 – **1.14** | 0.05 – 0.22 | 0.03 – 0.76 | 0.05 – 0.76 | 0.03 – 0.22 |
| **Butanal** | 0.12 – 0.37 | 0.15 – 0.37 | 0.12 – 0.37 | 0.08 – 0.37 | 0.11 – 0.26 | 0.08 – 0.37 |
| **Pentanal** | 0.04 – 0.09 | 0.05 – 0.09 | 0.04 – 0.07 | 0.03 – 0.08 | 0.04 – 0.08 | 0.03 – 0.08 |
| **Hexanal** | 0.05 – 0.14 | 0.07 – 0.14 | 0.05 – 0.14 | 0.05 – 0.11 | 0.05 – 0.11 | 0.05 – 0.11 |

# A 4 Detection Frequencies for HF and non-HF periods measured at the HF study site, as well as the gas field, regional and township sites

| | HF Sites | | | Regional sites | | | Gas-field sites | | | Township site | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Property A & B | | | Tara region & Burncluith | | | Wilgas, Condabri Nth, Rockwood | | | Chinchilla | | |
| **Compound** | **All** | **HF period** | **Non-HF period** | **All** | **HF period** | **Non-HF periods** | **All** | **HF period** | **Non-HF period** | **All** | **HF period** | **Non-HF period** |
| *N (VOC samples)* | *134* | *48* | *86* | *45* | *18* | *27* | *67* | *25* | *42* | *24* | *10* | *14* |
| **2-methylpentane** | 5% | 0% | 8% | 9% | 0% | 16% | 3% | 0% | 5% | 27% | 11% | 38% |
| **3-methylpentane** | 1% | 2% | 1% | 7% | 6% | 7% | 1% | 0% | 2% | 48% | 56% | 43% |
| **n-Hexane** | 13% | 8% | 16% | 15% | 11% | 17% | 18% | 16% | 19% | 43% | 44% | 42% |
| **n-Decane** | 21% | 21% | 21% | 16% | 22% | 11% | 21% | 24% | 19% | 39% | 22% | 50% |
| **n-Undecane** | 15% | 27% | 8% | 18% | 28% | 11% | 15% | 32% | 5% | 39% | 67% | 21% |
| **Cyclohexane** | 1% | 2% | 1% | 0% | 0% | 0% | 0% | 0% | 0% | 17% | 22% | 14% |
| **Benzene** | 21% | 33% | 14% | 22% | 33% | 15% | 24% | 36% | 17% | 61% | 100% | 36% |
| **Toluene** | 29% | 40% | 23% | 24% | 28% | 22% | 22% | 36% | 14% | 100% | 100% | 100% |
| **o-xylene** | 1% | 2% | 0% | 4% | 11% | 0% | 0% | 0% | 0% | 48% | 78% | 29% |
| **m & p-xylenes** | 9% | 15% | 6% | 16% | 22% | 11% | 7% | 20% | 0% | 91% | 89% | 93% |
| **Ethylbenzene** | 3% | 4% | 2% | 11% | 17% | 7% | 4% | 8% | 2% | 43% | 67% | 29% |
| **Carbon tetrachloride** | 100% | 100% | 100% | 100% | 100% | 100% | 99% | 100% | 98% | 100% | 100% | 100% |
| **Trichloromethane** | 10% | 0% | 15% | 20% | 28% | 15% | 3% | 0% | 5% | 9% | 0% | 14% |
| **Tetrachloroethylene** | 1% | 2% | 1% | 0% | 0% | 0% | 0% | 0% | 0% | 0% | 0% | 0% |
| **Ethyl acetate** | 20% | 29% | 15% | 16% | 22% | 11% | 19% | 24% | 17% | 17% | 22% | 14% |
| **Methyl isobutyl ketone** | 1% | 0% | 1% | 0% | 0% | 0% | 0% | 0% | 0% | 0% | 0% | 0% |
| *N(Aldehyde samples)* | *116* | *54* | *62* | *41* | *22* | *19* | *58* | *30* | *28* | *19* | *10* | *9* |
| **Formaldehyde** | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% |
| **Acetaldehyde** | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% |

|  | HF Sites |  |  | Regional sites |  |  | Gas-field sites |  |  | Township site |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Property A & B |  |  | Tara region & Burncluith |  |  | Wilgas, Condabri Nth, Rockwood |  |  | Chinchilla |  |  |
| Compound | All | HF period | Non-HF period | All | HF period | Non-HF periods | All | HF period | Non-HF period | All | HF period | Non-HF period |
| **Propanal** | 58% | 80% | 39% | 68% | 68% | 68% | 62% | 67% | 57% | 74% | 90% | 56% |
| **Butanal** | 34% | 43% | 26% | 39% | 41% | 37% | 40% | 50% | 29% | 42% | 50% | 33% |
| **Pentanal** | 8% | 6% | 10% | 12% | 9% | 16% | 7% | 0% | 4% | 5% | 0% | 11% |
| **Hexanal** | 22% | 19% | 24% | 44% | 50% | 37% | 28% | 28% | 25% | 32% | 30% | 33% |

## A 5 Concentration ranges for HF and non-HF periods measured at the HF study site, as well as the gas field, regional and township sites

| | HF Sites | | | Regional sites | | | Gas-field sites | | | Township site | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Property A & B | | | Tara region & Burncluith | | | Wilgas, Miles, Rockwood | | | Chinchilla | | |
| **Compound** | **All** | **HF period** | **Non-HF period** | **All** | **HF period** | **Non-HF periods** | **All** | **HF period** | **Non-HF period** | **All** | **HF period** | **Non-HF period** |
| *N (VOC samples)* | *134* | *48* | *86* | *45* | *18* | *27* | *67* | *25* | *42* | *24* | *10* | *14* |
| **2-methylpentane** | 0.01 - 0.11 | 0.02 - 0.03 | 0.01 - 0.11 | 0.01 - 0.07 | 0.01 - 0.03 | 0.02 - 0.07 | 0.01 - 0.08 | 0.01 - 0.03 | 0.02 - 0.08 | 0.01 - 0.21 | 0.01 - 0.04 | 0.01 - 0.21 |
| **3-methylpentane** | 0.01 - 0.03 | 0.02 - 0.03 | 0.01 - 0.03 | 0.01 - 0.04 | 0.01 - 0.03 | 0.01 - 0.04 | 0.01 - 0.04 | 0.01 - 0.03 | 0.01 - 0.04 | 0.01 - 0.10 | 0.02 - 0.10 | 0.01 - 0.08 |
| **n-Hexane** | 0.01 - 0.09 | 0.02 - 0.06 | 0.01 - 0.09 | 0.01 - 0.04 | 0.02 - 0.04 | 0.01 - 0.04 | 0.02 - 0.06 | 0.02 - 0.06 | 0.02 - 0.04 | 0.02 - 0.15 | 0.02 - 0.15 | 0.02 - 0.11 |
| **n-Decane** | 0.01 - 0.08 | 0.02 - 0.03 | 0.01 - 0.08 | 0.01 - 0.06 | 0.01 - 0.03 | 0.01 - 0.06 | 0.01 - 0.04 | 0.02 - 0.04 | 0.01 - 0.04 | 0.01 - 0.08 | 0.01 - 0.04 | 0.01 - 0.08 |
| **n-Undecane** | 0.02 - 0.08 | 0.03 - 0.08 | 0.02 - 0.06 | 0.02 - 0.10 | 0.02 - 0.10 | 0.02 - 0.06 | 0.02 - 0.07 | 0.03 - 0.06 | 0.02 - 0.07 | 0.02 - 0.10 | 0.02 - 0.08 | 0.02 - 0.10 |
| **Cyclohexane** | 0.01 - 0.06 | 0.02 - 0.06 | 0.02 - 0.04 | 0.01 - 0.05 | 0.02 - 0.05 | 0.01 - 0.04 | 0.02 - 0.06 | 0.02 - 0.05 | 0.02 - 0.06 | 0.02 - 0.07 | 0.02 - 0.05 | 0.02 - 0.07 |
| **Benzene** | 0.01 - 0.09 | 0.02 - 0.09 | 0.01 - 0.05 | 0.02 - 0.07 | 0.02 - 0.07 | 0.02 - 0.04 | 0.01 - 0.09 | 0.02 - 0.09 | 0.01 - 0.04 | 0.02 - 0.28 | 0.02 - 0.28 | 0.05 - 0.14 |
| **Toluene** | 0.01 - 0.18 | 0.01 - 0.18 | 0.01 - 0.09 | 0.01 - 0.13 | 0.01 - 0.05 | 0.01 - 0.13 | 0.01 - 0.04 | 0.01 - 0.03 | 0.01 - 0.04 | 0.03 - 0.42 | 0.07 - 0.42 | 0.03 - 0.29 |
| **o-xylene** | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.04 | 0.01 - 0.03 | 0.01 - 0.04 | 0.01 - 0.07 | 0.01 - 0.07 | 0.01 - 0.06 |
| **m & p-xylenes** | 0.01 - 0.08 | 0.01 - 0.08 | 0.01 - 0.04 | 0.01 - 0.11 | 0.01 - 0.11 | 0.01 - 0.03 | 0.01 - 0.06 | 0.01 - 0.06 | 0.01 - 0.03 | 0.02 - 0.22 | 0.03 - 0.22 | 0.02 - 0.15 |
| **Sum xylenes** | 0.02 - 0.11 | 0.03 - 0.11 | 0.02 - 0.05 | 0.02 - 0.14 | 0.02 - 0.14 | 0.02 - 0.05 | 0.02 - 0.08 | 0.02 - 0.08 | 0.02 - 0.07 | 0.03 - 0.29 | 0.05 - 0.29 | 0.03 - 0.21 |
| **Ethylbenzene** | 0.01 - 0.06 | 0.01 - 0.06 | 0.01 - 0.04 | 0.01 - 0.06 | 0.01 - 0.06 | 0.01 - 0.05 | 0.01 - 0.08 | 0.01 - 0.08 | 0.01 - 0.03 | 0.01 - 0.07 | 0.01 - 0.07 | 0.01 - 0.05 |
| **Carbon tetrachloride** | 0.03 - 0.15 | 0.06 - 0.10 | 0.03 - 0.15 | 0.04 - 0.14 | 0.06 - 0.09 | 0.04 - 0.14 | 0.01 - 0.13 | 0.06 - 0.09 | 0.01 - 0.13 | 0.04 - 0.11 | 0.06 - 0.09 | 0.04 - 0.11 |

| | HF Sites | | | Regional sites | | | Gas-field sites | | | Township site | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Property A & B | | | Tara region & Burncluith | | | Wilgas, Miles, Rockwood | | | Chinchilla | | |
| Compound | All | HF period | Non-HF period | All | HF period | Non-HF periods | All | HF period | Non-HF period | All | HF period | Non-HF period |
| **Trichloromethane** | 0.01 - 0.03 | 0.01 - 0.02 | 0.01 - 0.03 | 0.01 - 0.05 | 0.01 - 0.05 | 0.01 - 0.05 | 0.01 - 0.03 | 0.01 - 0.02 | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.03 |
| **Tetrachloroethylene** | 0.01 - 0.02 | 0.01 - 0.02 | 0.01 - 0.03 | 0.01 - 0.02 | 0.01 - 0.02 | 0.01 - 0.02 | 0.01 - 0.03 | 0.01 - 0.02 | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.03 |
| **Ethyl acetate** | 0.01 - 0.07 | 0.01 - 0.07 | 0.01 - 0.02 | 0.01 - 0.07 | 0.01 - 0.05 | 0.01 - 0.07 | 0.01 - 0.06 | 0.02 - 0.04 | 0.01 - 0.06 | 0.01 - 0.05 | 0.01 - 0.05 | 0.01 - 0.04 |
| **Methyl isobutyl ketone** | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.03 | 0.01 - 0.04 | 0.01 - 0.03 | 0.01 - 0.04 | 0.01 - 0.04 | 0.01 - 0.04 | 0.01 - 0.04 |
| *N(Aldehyde samples)* | *116* | *54* | *62* | *41* | *22* | *19* | *58* | *30* | *28* | *19* | *10* | *9* |
| **Formaldehyde** | 0.33 - 2.12 | 0.42 - 2.12 | 0.33 - 1.63 | 0.46 - 1.55 | 0.46 - 1.39 | 0.54 - 1.55 | 0.46 - 1.71 | 0.46 - 1.63 | 0.46 - 1.71 | 0.54 - 1.79 | 0.64 - 1.79 | 0.54 - 1.22 |
| **Acetaldehyde** | 0.08 - 0.94 | 0.11 - 0.78 | 0.08 - 0.94 | 0.08 - 0.83 | 0.08 - 0.81 | 0.10 - 0.83 | 0.06 - 1.00 | 0.06 - 0.60 | 0.13 - 1.00 | 0.11 - 0.83 | 0.14 - 0.83 | 0.11 - 0.67 |
| **Propanal** | 0.03 - 1.14 | 0.05 - 1.14 | 0.03 - 0.22 | 0.05 - 0.36 | 0.05 - 0.36 | 0.06 - 0.25 | 0.04 - 1.14 | 0.04 - 1.14 | 0.05 - 0.31 | 0.05 - 0.25 | 0.06 - 0.25 | 0.05 - 0.22 |
| **Butanal** | 0.08 - 0.37 | 0.11 - 0.37 | 0.08 - 0.37 | 0.12 - 0.39 | 0.12 - 0.36 | 0.13 - 0.39 | 0.09 - 0.47 | 0.09 - 0.39 | 0.11 - 0.47 | 0.10 - 0.37 | 0.10 - 0.37 | 0.11 - 0.34 |
| **Pentanal** | 0.03 - 0.09 | 0.03 - 0.09 | 0.03 - 0.08 | 0.04 - 0.31 | 0.04 - 0.09 | 0.04 - 0.31 | 0.03 - 0.09 | 0.03 - 0.09 | 0.04 - 0.09 | 0.03 - 0.11 | 0.03 - 0.11 | 0.04 - 0.08 |
| **Hexanal** | 0.05 - 0.14 | 0.05 - 0.14 | 0.05 - 0.14 | 0.05 - 0.40 | 0.05 - 0.40 | 0.06 - 0.13 | 0.04 - 0.18 | 0.04 - 0.12 | 0.05 - 0.18 | 0.04 - 0.15 | 0.04 - 0.13 | 0.05 - 0.15 |

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