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Methane and Volatile Organic Compound Emissions in New South Wales

Report for the New South Wales Environment Protection Authority

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Executive Summary

In order to investigate and better understand atmospheric methane (CH_4) emission sources, particularly from the coal seam gas industry, the NSW EPA commissioned CSIRO Energy to undertake a study to develop methods for characterising CH_4 and other gaseous emissions from different area sources in NSW. While there are internationally recognised methods for estimating (rather than measuring) CH_4 and other greenhouse gas emissions from many sectors of the economy for national inventory reporting, some of these methods do not provide sufficient accuracy for baseline monitoring in sensitive areas. Hence, methods for directly measuring emissions at the facility level are necessary for assessing the impacts of certain activities on greenhouse gas emissions, and assessing the effectiveness of mitigation measures.

The specific aims of the project were to firstly develop and trial methods that can be used to locate, identify and quantify CH_4 emissions from the CSG industry in particular but also other industries such as wastewater treatment, municipal solid waste disposal, coal mining, agriculture and natural sources. Secondly, investigations were undertaken to examine the possibility of attributing sources by measuring the chemical composition of the emissions and isotopic ratios of carbon and hydrogen in CH_4 and carbon in carbon dioxide (CO_2). Finally, ambient concentrations of volatile organic compounds were measured at various sites to gain an understanding of source related impacts on ambient air quality and to identify the prevalence of compounds that may specifically characterise a source.

Measurements were made between June 2014 and May 2016 at 16 sites across NSW that included:

- coal seam gas operations,
- landfills,
- wastewater treatment plants,
- agriculture (a rice farm and cattle feedlot),
- coal mining and
- natural sources.

In addition to the on site measurements, ambient CH_4 concentration was measured across NSW throughout the course of the project.

Methane Emissions

A variety of methods for detecting and quantifying CH_4 emissions were examined. Mobile surveys using a cavity ringdown spectrometer mounted in a 4WD vehicle was effective at locating CH_4 sources even while being driven at highway speeds. More than 25,000 km of surveys were driven during the project and a wide variety of CH_4 sources were detected. The surveys indicated that CH_4 concentrations across the state are generally consistent with normal background levels expected in continental locations, with somewhat higher concentrations in urban areas compared to rural regions. There was also often variation in ambient concentrations due to atmospheric mixing conditions – higher concentrations were often observed during the early morning. However, there were many locations in both rural and urban areas where significantly elevated CH_4 concentrations were detected. In some cases, the source of the CH_4 could be identified (e.g. landfills, agriculture, coal mining etc.); however in other instances, the source of the elevated CH_4 concentrations was not apparent. Some of the unidentified sources were located in urban centres where there was no obvious source of CH_4; it is hypothesised that some of these sources may be due natural gas reticulation emissions. Further work is required to confirm this.

Several methods for quantifying CH_4 emission rates were examined. Continuous techniques which include eddy covariance or inverse methods can provide temporal information on emissions over extended periods but they require fixed monitoring installations and because of the number of sites where measurements were required for this project, these techniques were not considered to be feasible. Instead, periodic measurements were made at most sites at least four times (often many more times) using ground level plume traversing and surface flux chamber methods. Later in the project, a tracer gas method was also applied at a number of sites.

The plume traversing method has been used successfully in previous monitoring of CSG wells and elsewhere, and this technique was deployed throughout the current project. The method does, however, require suitable wind conditions and access to the plume so that the CH_4 analyser can transect the plume. Unsuitable topography or the presence of buildings or other obstructions can reduce the effectiveness of the method. Consequently, this approach could only be used successfully at suitable test sites. Despite the limitations of this method, under favourable conditions, it is considered a useful method that has the advantages of simplicity, is rapid and can be applied at a range of scales.

Another approach involved surface flux chambers. These were deployed at a wide range of sites including natural areas, a rice farm, a feedlot, coal mines, a CSG water treatment facility, wastewater treatment plants and landfills. Some sites required the construction of special chambers to suit the particular application – for instance, a floating chamber was used at the wastewater and CSG water treatment facilities.

Overall, flux chambers provide accurate flux results for the area covered by the chamber and the method is simple to use. The main disadvantage is that because the chamber can usually only cover a small area, many measurements are necessary to characterise a given site. Consequently, the technique is relatively slow and labour intensive if used for estimating emissions from large areas. Moreover, for some sites with high levels of emission variation across the surface (e.g. landfills), it can be very difficult to achieve a representative sample hence any site-wide estimate will have a high level of uncertainty. For other sites with less heterogeneity, surface flux chambers can provide good results. The method is well suited to investigate emissions from wastewater treatment plants since it can provide detailed information on emission routes from various parts of the process. However, suitable access to emission sources must be available and this proved to be a limitation at some sites.

During the project, the use of a tracer gas for quantifying emission rates was examined. In this method, a tracer gas (acetylene was used in this project) is released at known rate from the CH_4 source and the concentration of both CH_4 and the tracer is measured downwind. The ratio of the two gases together with the tracer flow rate enable the CH_4 emission to be calculated. A significant advantage of the tracer method over other atmospheric plume dispersion methods is that it is not necessary to have detailed measurements of the plume dispersion characteristics or even the wind speed to calculate emission fluxes. Initial trials of the method using controlled releases of CH_4 at known rates yielded CH_4 flux estimates that were within 10 % of the actual emission rate. The tracer method was used at several locations during the project. Excellent results were obtained at the Narrabri CSG field where other methods could not be readily deployed. There are challenges associated with using the tracer method at large area sources, but encouraging results were obtained at one of the landfill sites. Of all the methods, this technique has considerable promise because of its high level of accuracy, relative simplicity and ability to be deployed at many different sites under widely varying atmospheric conditions.

Methane flux estimates were made at most of the sites examined including selected locations within four CSG fields. No emissions were found from the plugged, abandoned, and suspended wells in the Casino gas field. Emissions from production wells examined in the Camden and Gloucester gas fields were also very low, although in a few instances slightly elevated CH_4 concentrations above background levels were detected in the immediate vicinity of some well pads. The maximum emission rate detected from these wells was 0.03 g CH_4 min^{-1}; most of those examined showed no emissions. However, there were areas within the Camden gas field where significantly elevated CH_4 concentrations compared to background levels were detected on some occasions. In the Narrabri field, two of the six wells examined showed emissions that appeared to be mainly related to the operation of gas-powered pneumatic equipment on the pads. The emission rates measured at these wells ranged between 2.9 and 22.7 g CH_4 min^{-1} (4.2 and 32.7 kg day^{-1}), which are within the range of emissions measured previously on Australian CSG wells. While the uncertainy associated with the individual emission rates determined for these wells is relatively low, extrapolating the few results reported here to the entire industry would introduce a much higher level of uncertainty.

Emissions measured from a produced water treatment facility in the Narrabri field were low and were calculated to be between about 18 and 32 kg CH_4 day^{-1}. However, it is likely that most of the CH_4 contained in the produced water is emitted soon after being pumped to the surface so these estimates are probably an underestimate of the actual emissions associated with water production.

Except for the natural areas and the rice farm, seasonal variation was not detected in the results from these measurements. To some extent, this was because of the relative infrequency of the measurements, which did not provide sufficient temporal resolution. More commonly, however, other factors at each site (e.g. the different operations at landfills, coal mines, etc.) obscured more subtle seasonal variability. Short-term meteorological influences such as changing air pressure is also known to affect emission rates at some sites.

Implications for a NSW Methane Emission Inventory

Estimates of CH_4 emission rates were made at most of the sites visited during the project. However, due to various reasons, we were unable to generate flux estimates that could be considered representative; rather they represent snapshots at that moment in time. All of the estimates made must be considered within the limitations of the measurements made on each site, which often resulted in substantial uncertainty. The uncertainty of the emission flux estimates is derived not only from the measurements but also from the representativeness of the sample. For example, the uncertainty of the flux estimates made for individual CSG well pads is relatively low, especially when the tracer gas method was used. However, we only examined a small number of wells that represent only a few percent of the total number of wells in NSW; the CH_4 emission behaviour of the remaining wells is as yet unknown. In addition, the results obtained here may not be representative of normal average emissions due to diffecences in operation and management practices. Similarly, individual surface fluxes measured using the chamber method have low uncertainty but the heterogeneity of many sites may lead to large uncertainties if the individual measurements are extrapolated to estimate total emissions from large areas.

There was never any intention within the current project to develop an inventory of methane emissions for NSW; however, the results of study suggest that developing an accurate CH_4 emissions inventory for the state will be a major and challenging undertaking. There are numerous CH_4 sources across NSW and while some of these are reported to the federal Clean Energy Regulator under the current National Greenhouse and Energy Reporting legislation, emissions estimates are often subject to significant uncertainties. Moreover, some sources such as agriculture and natural sources are not reported while others may be below the current reporting thresholds. However, when considering the uncertainty of emissions estimates, it is also important to understand the relative contribution of each emission source to the total inventory. Small emission sources, even with very high uncertainty, contribute little to the overall uncertainty of an inventory. Conversely, large sources with high uncertainties (e.g. agriculture) will dominate the uncertainty of the inventory. If attempting to better define a statewide emission inventory, it is therefore worthwhile targeting in the first instance the larger sources.

During this project, several methodologies were examined and tested as to their applicability for directly measuring CH_4 emissions from various sources. The results have also yielded some preliminary flux estimates but these are still a long way from inclusion in a robust inventory for NSW as a whole or even for individual industry sectors. Some of the methods trialled show considerable promise for measuring emissions from some sources on a routine basis; however, other sources may require further development. In yet other cases, current practices or emission factors may yield sufficiently accurate data to develop an inventory, provided the necessary data can be obtained. A summary of the main sources investigated in this project is provided in Table ES.1. The relative size of the emission sources shown in Table ES.1 is a subjective estimate based on current national inventory data and the authors' knowledge of emissions and it is hence acknowleged that these magnitude estimates are at best a rough guide. Also shown in Table ES.1 are some methods for measuring or estimating emissions from these sources. It is noted that other sources of CH_4 exist in NSW (such as biomass burning) but these are not included in Table ES.1.

Table ES.1. Summary of the main sources of CH_4 emissions in NSW. Note that the relative magnitude of the emission sources is a rough guide only.

Source	Relative Emission Source Size	Uncertainty	Notes
Coal Mining	Large	Low to moderate	Fugitive emissions estimated and reported under NGERS. Underground mines measure emissions and have low uncertainty. Open-cut operations use gas content data from coring ahead of mining; moderate uncertainty.
CSG	Currently small in NSW	Moderate to high	Potential emissions from wells, processing plants, water treatment facilities, pipelines etc. Emissions reported under NGERS but some estimates have high uncertainty (although others may have lower uncertainty e.g. some venting and flaring operations). The tracer gas method has application for measuring emissions from well sites and some other infrastructure.
Agriculture	Large	High	Mostly from ruminant animals and liquid manure management. Feasible but difficult to measure; published emission factors for cattle more practical. Rice farming is a small source overall in NSW.
Landfills	Moderate	High	Difficult to measure but methods exist. The tracer gas method shows promise.
Wastewater Treatment	Probably small	High	Feasible to measure with chambers and tracer; most emissions from biosolids storage.
Wetlands	Small	High	Likely to be a small component of NSW inventory. Difficult to measure directly but chambers or methods (e.g. eddy covariance) are feasible.

Volatile Organic Compound Emissions

Volatile organic compounds (VOCs) that are potentially associated with methane emissions sources have been investigated in this project to gain an understanding of source related impacts on ambient air quality and to study the prevalence of compounds which may specifically characterise a land-use activity. As such, it was important to evaluate a large suite of organic compounds and to move to minimum levels of detection beyond that normally required under guidelines for air quality assessment. A suite of compounds that represent VOC emissions from anthropogenic sources was targeted and further, methodologies were implemented to isolate non-standard compounds of both biogenic and anthropogenic origin to provide added insight into source specific emissions that are detectable in ambient air.

The VOC evaluations were based on a substantial site monitoring programme of repeated campaigns to provide indicative information on emissions variability at a particular location as well as those inherent to the activities and processes that dictate source intensity. Ambient monitoring was undertaken for the source categories that were monitored for methane i.e. natural sources, the Camden region of CSG activity, animal feedlot, coal mining, CSG production facilities, landfills and wastewater treatment plants. Rice farming was excluded from VOC monitoring as this source was specifically selected for the purposes of its biogenic methane emissions and as such, ambient VOC determinations were not considered pertinent to this category. Monitoring campaigns for the Camden region encompassed ten sites across suburban and semi-rural areas where CSG operations were active and these sites were also monitored for seasonal variability in their emissions.

This work has reported the ambient concentrations for over 120 volatile organic compounds that are designated as priority pollutants in air quality assessment by Australian and International agencies. The suite of compounds comprised the hydrocarbon VOCs which are prioritised for photochemical assessment but which were targeted in this work as markers for urban transport and off-road vehicle emissions, liquid and gaseous fuels, and other combustion derived emissions. The priority air toxic VOCs were also evaluated as these characterise the emissions from various waste processing and industrial activities and are of importance in air quality assessment for human and environmental health purposes.

Further VOC characterisation studies were undertaken to include non-standard compounds of importance in source recognition. Mass spectral interpretation of the chromatographic output from VOC analyses was used to find and identify new compounds and a sorbent tube collection methodology was also investigated to extend the range of compounds that could be captured and isolated. The classes of compounds that were targeted included sulphur, oxygen and nitrogen containing species that are present as either volatile or semi-volatile compounds in ambient air, and which arise from biogenic as well as anthropogenic processes. These classes of compounds tend to have different chemical and physical characteristics to the priority VOCs and hence are more difficult to capture and isolate. Over 45 compounds, additional to the priority VOCs, were identified in this manner.

The determination of hydrocarbon VOCs in CSG sourced well gases was also undertaken. The focus was on the minor hydrocarbon compounds, i.e. those above C_5 and aromatic compounds, which are not generally measured in these gases. This determination was made on a selection of raw gas samples collected from producing CSG wells, and the analytical methodology was optimised for this specific application. The work was not a requisite of this project however, it was considered that this determination might be informative in the recognition of the CSG methane source impact to ambient air and with respect to human and environmental health.

A portfolio of instrumentation was implemented and methodologies were optimised and validated for priority VOCs, characterisation studies and the well gas hydrocarbons in order to cater for the differences in site sampling techniques and the associated modes of sample introduction, differences in sample matrix, instrumental detection requirements and the various classes of compounds targeted. Instrumental analysis was undertaken using gas chromatography with mass spectrometry and flame ionisation detection (GCMS and GCFID) for determination of priority hydrocarbon and air toxics VOCs, and using GCMS with thermal desorption capability for sorbent tube based characterisation studies; the latter incorporating both electron impact and chemical ionisation modes of mass spectrometry for the elucidation of compound identity.

The results from this work have been evaluated from the perspective of ambient concentration and relevance to source impact on air quality, and compound type and relevance to source characterisation. The reader is referred to Section 7 for a fully referenced discussion of the observations and findings.

General findings from the ambient study are summarised in the following points and findings specific to each source category are summarised subsequently.

- A number of the Freon™ group and other halocarbons (specifically dichlorodifluoromethane, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane and carbon tetrachloride) and certain sulphur containing species (carbonyl sulphide and, tentatively, dimethyl sulphone) were observed at relatively consistent concentration at all sites. They are found at trace concentration (< 0.5ppbv) and are considered compounds which are ubiquitous in the atmosphere.
- The presence, or lack of, a hydrocarbon profile indicative of vehicle exhaust was informative in evaluating contributing sources to the ambient air at a particular site and petrol versus diesel hydrocarbon profiles could also be distinguished. Minor vehicular related impacts were apparent at semi-rural and suburban locations in the Camden region and the impact of on-site vehicles was apparent at a number of operational sites.
- Measurement of VOCs at the Cuba State Forest found minimal impact from anthropogenic activity and as such, this natural source established a baseline for biogenically derived compounds. This enabled land-use source emissions to be effectively allocated for compounds that were common to anthropogenic and biogenic sources (such as ethanol, acetone and other oxygenates).

- From an air quality perspective, ambient concentrations of priority hydrocarbon and air toxic VOCs were generally low (mixing ratios of low ppbv) and, with certain exceptions, in the range expected for the particular source and the location or processes within that environment. Measurements at natural and rural environments, and remote locations associated with mining or CSG activities, were in the trace to low ppbv concentration range and many of the priority VOCs could not be detected in these environments.
- Obvious impacts on ambient VOC concentrations were seen from more intensive sources such as those resulting from animal feeding, municipal solid waste disposal and wastewater treatment, where compounds specific to the activity were apparent, such as biologically derived oxygenates and nitrogenous compounds, solvent residues and chlorinated compounds.
- Source characterisation studies for non-standard VOCs revealed additional compounds and organic classes of compounds to those from the priority VOC suites. The sorbent tube collection methodology was found to extend the range of compounds that could be captured and isolated compared to those from VOC collection by the canister technique. Compounds with strong links to vegetation and biological processes, such as monoterpenes and more complex oxygenated compounds, were apparent at many sites. At higher intensity land-use sites these were overlain with compounds whose attributes were more specific to the source, such as odorous sulphur and nitrogen containing compounds for example.
- Within each source category, site-specific operations and processes also dictated the intensity of the emissions and excursions from more typical measured levels were seen for particular operations at the feedlot, landfill and wastewater treatment sites.
- The effect of the seasons on ambient VOC concentrations was investigated from four monitoring campaigns over a twelve-month period for ten sites across the Camden region. This evaluation showed a link to seasonal variability in the emissions of biogenic compounds and possibly, vehicle related emissions. However, these observations must be tempered by the many other factors, such as source intensity, emissions transport and atmospheric fate, which are well known to affect ambient concentrations of VOCs and other air pollutants.
- The analysis of non-methane hydrocarbon VOCs in CSG sourced well gas was effective in providing quantitative results for minor hydrocarbon compounds which are not commonly measured in these gases, i.e. those above C_5 and aromatic compounds; benzene, toluene and xylenes. Compounds at a concentration down to 0.007ppmv were measurable. The determination was informative in the recognition of a CSG source impact to ambient air and with respect to human and environmental health.

Specific findings for VOC emissions associated with each source category are summarised in the following points:

- *Natural Sources* (Yaegl Nature Reserve, Cuba State Forest)
  Compounds with strong links to vegetation and biological processes (such as isoprene and monoterpenes) and the oxygenated species (such as ethanol, acetone, isopropanol and more complex oxygenates) were observed. The Yaegl site showed a minor traffic related impact from nearby roadways. There was no detectable impact from anthropogenic sources in the ambient air collected from Cuba State Forest. The monitoring of this natural source was used for allocation of biogenic versus anthropogenic activity to the emissions from other land-use sources.
- *Camden Region*
  The overall consistency in the results from ambient monitoring of the Camden sites establishes a database of expected concentrations of priority hydrocarbon and air toxics VOCs for the morning period at rural and semi-rural locations in the Camden region.

  A clear impact from traffic related emissions was seen in the hydrocarbon VOC profile observed in the ambient air for all ten sites monitored in Camden region. However, ambient concentrations of the hydrocarbon VOCs were in the low ppbv range and consistent with levels expected for semi-rural and suburban environments.

Biogenic compounds were apparent in the VOC profile and their emissions are indicative of the semi-rural atmosphere of the Camden regional sites. Compounds associated with biological processes included small oxygenates (ethanol, acetone and isopropanol) which were present at concentrations broadly similar to those observed in the natural environments. 2-butanone and more complex C_4-C_9 aldehydes, ketones and alcohols were also identified in samples from the summer campaign and emissions of isoprene and monoterpenes from vegetation were observed in the VOC profile at many sites.

Hydrocarbon and air toxics VOC profiles were not suggestive of a major industrial source of emissions in the vicinity of the Camden sites.

- *CSG impact on ambient VOCs* – VOC monitoring in the Camden region encompassed a geographical area where CSG production was active. Ethane and propane were present in the ambient air in this region and these compounds are components of CSG sourced well gas. An evaluation was therefore made as to the likely impact of CSG as a source of these emissions to ambient air. Based on measured methane concentrations for the region and ethane and propane concentrations in the CSG sourced well gas, a predicted ambient concentration for these compounds was compared to measured ambient concentrations. This evaluation concluded that ethane and propane emissions from CSG were negligible and their presence in ambient air in the Camden region was derived from other sources. Aromatic compounds were present in the well gas at extremely low concentrations and hence were not a measurable source of aromatic compounds to ambient air in the region (refer later point regarding well gas hydrocarbons).
- *Seasonal variability* – seasonal monitoring of VOCs across the Camden sites showed a general trend towards higher levels of biogenic compounds (such as oxygenated compounds, isoprene and monoterpenes) in the spring and summer campaigns which is consistent with warmer temperatures and a higher intensity of photosynthetically active radiation. Vehicle related hydrocarbon VOCs were generally lower in summer than the levels measured in winter and a reduction in the relative concentration of alkenes compared to alkanes is consistent with the effect of higher rates of photolysis on the more reactive species. Isobutane dominated the hydrocarbon emission profile in the warmer months, which may be indicative of higher evaporative losses from petrol-fuelled vehicles. These results indicate a possible link to seasonal variation particularly in the change in emissions of the biogenic compounds and, tentatively, the vehicle related emissions.

- *Cattle Feedlot* (Jindalee Cattle Feedlot).
  The ambient air at this site was rich in an array of oxygenated, nitrogenous and sulphur-containing compounds commonly associated with animal by-products and odour. Ethanol, acetone and 2-butanone were found at higher concentrations than typically observed in vegetated environments and an excursion in ethanol (253ppbv) was measured on one occasion at the feedlot site. Odorous compounds related to animal by-products such as dimethyl sulphide and dimethyl disulphide, and to other biological processes; C_4 to C_8 aldehydes, ketones and alcohols were apparent in the emissions from this source. There were minimal emissions indicative of a vehicular or other source impacting the site indicating that the compounds found were directly attributable to the feedlot.

  With the exception of an excursion in ethanol, the overall ambient concentration of the priority VOCs associated with this source was lower than other more intensive land-use activities; i.e. landfill and wastewater treatment.

- *Coal mining* (Rix's Creek Coal Mine, Gunnedah Basin mining region).
  Ambient concentrations at the Rix's Creek mine site were generally low in most VOCs compared to semi-rural and the higher intensity land-use sites. Those hydrocarbons that were identified inferred a diesel emissions profile, which is likely to be consistent with the machinery operating at the mine

site. In the case of the Gunnedah Basin mine, it is possible that fugitive emissions of ethane from seam gas contributed to the hydrocarbon profile.

The ambient air in the vicinity of the mine in the Gunnedah Basin showed low levels of compounds associated with vehicle exhaust and vegetation, which may be consistent with on-site mining activities, and the roadside location of the monitoring site.

- *CSG facilities* (Camden, Gloucester, Narrabri).
  The CSG production sites at Camden and Gloucester were characterised by a hydrocarbon profile that was dominated by C_2-C_4 alkane species, an absence in C_2 and larger alkenes and the presence of aromatics. The dominance of alkanes in the hydrocarbon profile is consistent with that measured in CSG sourced well gases, however, these and the aromatics were disproportionately represented in the ambient samples compared to their profile in the well gases. Hydrocarbon concentrations were also not correlated with measured methane in the ambient air at the well pads. Hence, the hydrocarbon profile and concentrations found in the ambient air cannot be interpreted to be linked to CSG production at the Camden and Gloucester sites and an alternative source of VOCs is considered likely. The overall ambient concentration of VOCs measured at the Camden and Gloucester facilities was low compared with semi-rural sites, for example.

  The VOCs present in ambient air samples collected within the Narrabri CSG field and their concentrations were consistent with those found in a natural environment.

- *Landfills* (Summerhill Waste Management Centre, Parkes Waste Facility).
  Compounds associated with household and chemical disposal were elevated in the ambient air at the landfill sites. An excursion in the ambient concentration of acetone (200ppbv), accompanied by 2-butanone (18.0ppbv), were measured on one occasion at the Summerhill Centre. Chlorinated compounds such as trichloroethylene and tetrachloroethylene that are commonly used as markers for landfill emissions were identified at the Parkes Facility albeit at low (< 1ppbv) ambient concentrations. Other chlorinated solvent residues included dichloromethane, chloroform and benzyl chloride. The monoterpenes, limonene and a-pinene, which are used as fragrances in household products, were identified.

  Compounds derived from biological decomposition were also identified. C_4 to C_{12} oxygenates as aldehydes, ketones, alcohols, phenol and esters are associated with biological processes more generally but are likely enhanced due to soil decomposition in landfills. These compounds contribute to the characteristic odour associated with landfills.

  The impact of allied sources such as exhaust emissions from on-site diesel trucks and those from a methane generation system were identified at the Summerhill site.

- *Wastewater treatment* (Singleton Wastewater Treatment Works, Wagga Wagga Wastewater Treatment Plant, Picton Wastewater Treatment Plant).
  In certain aspects of the wastewater treatment process at the Singleton plant, VOCs were measured at ambient levels that were at the high end, or exceeded, those measured at other high intensity land-use sources, such as the landfill and the cattle feedlot. At the sewage inlet to the plant, emissions of acetone (93ppbv) accompanied by 2-butanone, were higher than other land-use sources, with the exception of an excursion in these compounds on one occasion at a landfill site. The Singleton WWTP was significantly higher than other sources in chlorinated compounds at the settling ponds; cis-1,2-dichloroethene (up to 13.5ppbv), trichloroethylene (up to 4.4ppbv) and tetrachloroethylene (up to 58.3ppbv). Compounds associated with odour, such as aldehydes, ketones, alcohols and nitrogenous compounds were apparent in the emissions profile at the Singleton site.

  Source identification and quantification is affected by the proximity of the sampling point, amount and type of emissions, meteorological variables and a range of other factors. However, it is evident that emissions from the Singleton wastewater treatment site were captured at a level that would allow certain oxygenated and halogenated VOCs to be used to characterise the operations at that site at that time. The high levels found at the Singleton site are also of importance when considering and assessing air toxics along with odorous emissions from this source.

In contrast, ambient VOC concentrations at the Wagga and Picton plants were broadly in the range measured at other intensive land-use sources, apart from an excursion in ethanol (40.9ppbv) on one occasion at the inlet location of the Wagga Wagga wastewater treatment plant.

- *CSG sourced well gas* (Camden, Gloucester).
  Hydrocarbon VOCs were characteristically present as the alkane class and straight chain, cyclic and branched alkanes through to C_8 were measured. Alkenes were not present in the hydrocarbon profile of the well gases. Aromatic compounds were detected at low concentration; the highest aromatic content was measured in samples from AGL operations at the Gloucester gas field (around 0.5ppmv benzene, 0.2ppmv toluene, 0.02ppmv xylenes). The detection of the larger alkanes and aromatics correlated with those gases with higher non-methane hydrocarbon concentration. The aromatics are considered consistent with components originating from gas formation processes.

  The ambient air equivalent concentration for the aromatic compounds, based on a worst-case emissions scenario in close proximity to a producing well, was estimated to be low pptv (parts per trillion by volume). This compares favourably with low ppbv (parts per billion by volume) concentrations measured in the ambient air of semi-rural regions that are impacted by low-volume traffic.

In meeting the objectives of the VOC component of the project, this work has brought together a volume of information on the levels of source related organic compounds in the ambient air in the vicinity of land-use activities in regional NSW and provides an ambient VOC database for the Camden region. A basis for future studies into the qualitative and quantitative impacts of various emission sources on air quality has now been established.

Isotopic Analyses

Laboratory analyses of molecular composition and stable isotopes were conducted on source gas samples containing between 0.1 and 100 % CH_4 and/or CO_2. Molecular composition using gas chromatography based natural gas analysers gave very reliable bulk composition results. A GC-IRMS was used to analyse carbon and hydrogen isotopes on CSG and microbial source gases from landfill and wastewater treatment plants. Plots of stable isotope data allowed seemingly similar gas samples to be differentiated into different categories and contributing source characteristics identified. Contributions from thermogenic, CO_2 reduction and acetoclastic/methylotrophic generation were able to be made for samples with mixed origins.

Some gas sampling techniques were found to be unsuited for isotopic analyses because they tended to fractionate the isotopic signature of the gas yielding unreliable results. Extended periods of sample storage may also affect isotopic analyses and consideration must be given to the type of storage containers used for sample collection and storage.

Analyses of ambient CH_4 for carbon and hydrogen isotopes were not possible using the GC-IRMS system directly because of the low concentration of CH_4. A prototype device designed to cryogenically concentrate ambient CH_4 was trialled; however it was adversely affected by significant co-trapping of ambient oxygen and nitrogen from the air. Further development of this system is required. The rationale for developing the prototype system was that it would be able to measure both the carbon and hydrogen isotopes of CH_4; whereas the single commercially available system only measures the carbon isotopes of CH_4 with limitations.

An alternative method using cavity ringdown spectroscopy for measuring isotopic ratios of $^{13}C/^{12}C$ in ambient CH_4 was trialled. Although this technique is now in widespread use, there are some limitations with respect to using these data for source apportionment. With the instruments used in this project, it was apparent that significantly elevated CH_4 concentrations above ambient were required to achieve a satisfactory signal to noise ratio. Best results were achieved when the CH_4 concentration was above about 5 ppm. At this point in time, the cavity ring down spectroscopic technique cannot measure the hydrogen isotopes of CH_4 at atmospheric concentrations, limiting the resolving power for source gas identification using stable isotopes.

1 Introduction

Methane is present in the atmosphere at relatively low concentrations (approximately 1.8 ppmv); however, because of its high global warming potential relative to CO_2, it has a significant effect on the balance of incoming and outgoing energy from the atmosphere (i.e. radiative forcing). Moreover, CH_4 has been increasing in concentration in the atmosphere since pre-industrial times and is the second largest contributor to global warming after CO_2 (IPCC, 2007).

Atmospheric CH_4 is derived from a wide range of natural and anthropogenic sources. Natural sources include wetlands, lakes and rivers, termites, bushfires, oceans, permafrost, and geological sources. Human activities that result in CH_4 emissions are largely associated with agriculture (e.g. ruminant animals, rice production), waste (e.g. landfills, sewage), biomass burning and fossil fuel production and utilisation. On a global scale, it has been estimated that roughly 60 % of CH_4 emissions originate from anthropogenic sources (Kirschke et al., 2013); however, these estimates are subject to very high uncertainty. In addition, there are significant regional variations in emission fluxes of CH_4 (Fraser et al., 2013).

Over the last few years, CH_4 emissions have been the focus of considerable scientific interest, especially in relation to unconventional gas production (shale gas, tight gas, coal seam gas). Although natural gas utilisation may produce lower direct greenhouse gas emissions from combustion compared to other fossil fuels, some recent studies have found high levels of fugitive CH_4 emissions from shale and tight gas production in the United States. The results of these studies, however, have been variable and often have high levels of uncertainties associated with the reported emission estimates (Pétron et al., 2012; Allen et al., 2013; Karion et al., 2013; Caulton et al., 2014a; Schneising et al., 2014; Kort et al., 2014).

At present, almost all unconventional gas production in Australia is derived from coal seam gas (CSG). Most production is currently in Queensland where several export liquefied natural gas plants are in varying stages of production, with the first commencing operation in late 2014. Despite major differences between the U.S. and Australian unconventional gas industries, it has been suggested that Australian CSG production may also result in high levels of fugitive emissions (Grudnoff, 2012). However, a recent study of emissions from a sample of CSG well pads in Queensland and NSW found that CH_4 emissions were generally very low compared to most of the results that have been reported for U.S. shale and tight gas operations (Day et al., 2014). That study, however, only considered well pads – other infrastructure was not examined – and the sample size was small compared to the total number of production wells in Australia. Further investigations into methane emissions in the Surat Basin in Queensland are currently underway (Day et al., 2013; Day et al., 2015).

Coal seam gas production in New South Wales is currently much less than in Queensland but there are several CSG projects in NSW at various stages of development. At present, there is relatively little publicly available information on CH_4 emissions from NSW CSG operations – only six wells included in the Day et al. (2014) study were in NSW. To address this, the New South Wales Environment Protection Authority (NSWEPA) commissioned a study to investigate emissions across NSW. While this study was largely motivated by concern over the NSW CSG industry and to inform future regulatory programmes in relation to air emissions associated with CSG activities in NSW, the study brief also required measurements to be made at other CH_4 sources such as waste management operations (landfills and wastewater treatment plants), agriculture (e.g. intensive cattle feedlots and rice farming), natural sources (e.g. wetlands) and coal mining.

Methods for estimating greenhouse gas emissions from many of these activities already exist, mainly for the purposes of compiling national greenhouse gas inventories. In Australia, for instance, the National Greenhouse and Energy Reporting legislation requires operators of many facilities to estimate and report emissions according to specified methodologies. However, CH_4 emissions are usually estimated rather than actually measured (the notable exception being underground coal mining where fugitive emissions are measured) and consequently may not have sufficient accuracy to be used for baseline monitoring or for assessing the effects of industrial activity within a region on local greenhouse emissions (e.g. increased CSG production), or mitigation measures.

One of the key objectives of the study therefore, was to develop reliable methodologies that can be applied for measuring CH_4 emissions at the facility level from not only CSG operations but also other relevant land-use sectors throughout NSW. The second objective of the study was to investigate the possibility of characterising emissions from various CH_4 sources and using chemical 'fingerprints' to assist in attributing sources. This involved determining isotopic ratios of $^{13}C/^{12}C$ and $^{2}H/^{1}H$ in CH_4 and CO_2 samples collected from various sites, the determination of chemical composition on a wide range of samples, and the determination of ambient concentrations of a suite of volatile organic compounds in the vicinity of each source. Volatile organic compounds were investigated to gain an understanding of source related impacts on ambient air and to study the prevalence of compounds that may specifically characterise a source.

In this report, we present the results of this project, which was conducted between June 2014 and May 2016.

2 Methane Emissions

Atmospheric CH_4 concentrations have increased from about 720 ppb (0.72 ppm) during the mid-18th century to more than 1800 ppb (1.80 ppm) during 2011 (Hartmann et al., 2013). These values represent global averages but there are significant regional and seasonal variations in concentration. Baseline atmospheric monitoring of clean air at the CSIRO Cape Grim station in Tasmania shows that current southern hemisphere clean air concentrations of CH_4 vary between about 1.75 to 1.79 ppm, with the higher concentrations occurring during the winter months (CSIRO, 2015).

According to the most recent IPCC Assessment Report, global CH_4 emissions during 2011 were estimated to be 556 ± 56 Tg CH_4 y^{-1} with 354 ± 45 Tg CH_4 y^{-1} (64 %) attributed to anthropogenic activities and 202 ± 35 Tg CH_4 y^{-1} (36 %) from natural sources (Hartmann et al., 2013). These estimates, however, are subject to considerable uncertainty due in some cases to limited data and also differences in the methodology used to develop the inventories. For instance, Kirschke et al. (2013) estimated the global CH_4 budget for several decades using top-down and bottom-up methods. For the period between 2000 to 2009, top-down methods yielded total emissions of between 526 and 569 Tg CH_4 y^{-1} (mean 548 CH_4 y^{-1}) while the bottom-up approach gave an estimate of 542 to 852 Tg CH_4 y^{-1} (mean 678 Tg CH_4 y^{-1}). Emissions are not evenly spread across the globe and substantial regional variation is apparent (Fraser et al., 2013). While the sources of most of the global CH_4 budget are well understood, improving estimates of emission fluxes is an area of active research.

In Australia, anthropogenic CH_4 emissions from energy use, agriculture, waste management and other sectors are estimated and reported in the annual National Greenhouse Gas Inventory. Table 2.1 summarises the emission estimates reported for Australia during 2013 (AGEIS, 2015). Total emissions were estimated to be 111.8 Mt CO_2-e (~5.3 Tg CH_4) with agriculture (principally from ruminant animals) comprising about 60 % of CH_4 emissions. Fugitive emissions from coal mining and oil and gas production were the next largest source (26 %) followed by waste disposal activities (12 %). Much smaller amounts were emitted through certain land-use activities and industrial processes. Natural sources of CH_4 are not accounted for in the National Inventory. While it has been suggested that up to a third of Australia’s methane emissions are derived from natural sources, there is as yet very little quantitative information on the magnitude of these emissions (Dalal et al., 2008).

Table 2.1. CH_4 emissions in Australia and NSW as estimated in the 2013 National Greenhouse Gas Inventory.

Category	2013 CH_4 Emissions (Gg)	
	Australia	NSW
Energy	**1,483**	**677**
Fuel Combustion	86	27
Fugitive Emissions From Fuels	1,397	650
Industrial Processes	**3.3**	**1.7**
Chemical Industry	0.7	
Metal Industry	2.6	
Agriculture	**3,165**	**709**
Enteric Fermentation	2,685	656
Manure Management	115	20
Rice Cultivation	26	26
Prescribed Burning of Savannas	327	0.1
Field Burning of Agricultural Residues	11	6.2
Land-use, Land-Use Change and Forestry KP	**59**	**19**
Afforestation and reforestation	1.3	0.1
Deforestation	43	15
Forest management	10	1.3
Cropland Management	0.6	0.5
Grazing land management	2.8	1.4
Waste	**615**	**203**
Solid Waste Disposal	495	163
Biological treatment of solid waste	4.9	1.6
Wastewater treatment and discharge	115	38
Total	***5,324***	***1609***

Table 2.1 also shows the CH_4 emission data for NSW during the 2013 reporting year. Here, agriculture is still the dominant emission source but represents only 44 % of total CH_4 emissions compared to about 60 % across the country as a whole. Fugitive emissions from fuels, on the other hand, account for approximately 40 % of NSW's CH_4 emissions, which are due mainly to the state's large coal industry. NSW currently has a very small oil and gas industry so less than 5 % of the state's fugitive emissions are attributed to this sector.

National greenhouse gas inventories are usually compiled according to the general methods described in the 2006 Intergovernmental Panel on Climate Change Guidelines for National Greenhouse Gas Inventories. For the purposes of compiling national inventories, it is usually not practical to measure emissions directly. Consequently, most of the methodologies provided in the 2006 Guidelines rely on using emission factors derived for given processes. In this approach, a measure of the activity of the process is multiplied by the appropriate emission factor to yield the emission rate for that process. While this approach has the advantage of simplicity, significant uncertainty may be introduced if (a) the activity data are incomplete or inaccurate or (b) the emission factor is not well defined.

Although the use of emission factors provides a relatively simple approach for estimating greenhouse gas emissions, the emission factors themselves are based on measurements reported in the open scientific and technical literature. In the following section, we briefly examine methodology that has been applied to measure emissions from some of the main sources of CH_4 in Australia.

2.1 Detection of Methane

There are currently many instrumental methods available to detect and analyse CH_4. In the simplest form, inexpensive handheld gas detection sensors are frequently used in potentially hazardous environments to alert personnel to dangerous levels (i.e. explosive) of CH_4 in certain workplaces such as underground coal mines or gas processing facilities. These instruments generally have limited sensitivity and typically display in units of percentage of lower explosive limit (LEL, i.e. ~5% CH_4 in air v/v).

The next level of complexity includes portable gas detection systems that are usually used for leak detection in industrial applications. Leak detection instruments have higher sensitivity than gas sensors used for general workplace safety applications, often being capable of measuring concentrations of a few ppm above ambient levels. These instruments often have a wand with a sample inlet that can be placed near a potential leak point such as a valve or pipe fitting. Remote sensing instruments are also used for leak detection; these are typically hand held instruments that can be used to quickly scan complex facilities such as gas processing plants for leaks. Remote instruments include open-path laser and infrared imaging cameras.

Mobile open-path laser instruments have often been used to detect leaks in gas infrastructure. One such system, the ALMA G2 instrument which is mounted on a helicopter, was used in Queensland recently to detect CH_4 sources in a CSG production region (Day et al., 2015). Other vehicle mounted laser systems are also now commercially available.

While gas detectors and leak detection systems are critical for safety and routine maintenance at many industrial facilities, these systems are less frequently used in research into CH_4 emissions, particularly at the near ambient levels encountered more distant from the source under investigation. There are many instruments available with sufficient sensitivity to accurately measure low levels of CH_4 in ambient air e.g. FTIR, tuneable lasers, gas chromatography, etc. Some of these systems can be deployed in the field but usually only in fixed installations. Alternatively, samples can be collected and later analysed in a laboratory. However, for detection of CH_4 sources, it is usually more convenient to use a mobile system where a real-time instrument is mounted in a vehicle or aircraft.

The commercial development of cavity ringdown and off-axis integrated cavity output spectroscopy over the last decade has provided instruments with resolution of 1 ppb or less for CH_4. Some of these instruments are also capable of measuring isotopic ratios of ^{12}C and ^{13}C in CH_4, which may provide some information on the source of the CH_4. As a result, these instruments are now commonly in use for measuring CH_4 (and other gasses) in ambient air and there have been numerous studies reported where these instrument were used. In two recent examples, Karion et al. (2013) and Caulton et al. (2014a) used aircraft mounted cavity ringdown instruments to detect and quantify CH_4 emission fluxes from unconventional gas fields in the United States. Vehicle mounted cavity ringdown instruments have also been used successfully for locating CH_4 from a range of sources both in Australia (Maher et al., 2014; Iverach et al., 2015; Day et al., 2015) and overseas (Phillips et al., 2013; Zazzeri et al., 2015).

2.2 Coal Mines

Coal seams usually contain CH_4 and sometimes CO_2 that is stored within the pores of the coal. When the coal is mined, this gas is released to the atmosphere as fugitive emissions. During 2013, fugitive emissions from coal mining in Australia were estimated to be 26.2 Mt CO_2-e, which represents about 5 % of Australia's total greenhouse gas inventory (Department of the Environment, 2015a).

All Australian coal mine operators are required under the National Greenhouse and Energy Reporting (NGER) legislation to report their annual fugitive emissions according to methodology prescribed in the Determination. In the case underground mines, emissions must be determined according to Method 4, i.e. they must be directly measured rather than estimated. Most emissions from underground coal mines are associated with the ventilation air and can be quantified by applying Equation 2.1.

$$Q = V \times (C - C_a) \tag{2.1}$$

Where Q is the emissions rate, V is the volumetric air flow out of the mine and C is the concentration of methane in the air stream and C_a is the methane concentration in ambient air. Any methane that is drained is also measured and included in the total annual emissions. While there may be some uncertainties involved in this approach (Day and McPhee, 2008; Day et al., 2011) in general it yields accurate emission data.

Emissions from open-cut mining, on the other hand, are much more difficult to estimate because gas escapes over the entire mine site, which may be very large in area, so that volumetric flows and concentrations are not readily measured. In an open-cut mine, some of the fugitive emissions are from seam gas released as the coal is excavated. Additional emissions may occur from gas released from strata that are disturbed but not actually excavated, and exposed by the mining process. These emissions are particularly difficult to estimate since they depend on the gas content and composition as well as the nature of the disturbance of the pit floor and highwall and the rate of leakage of the gases. As a result of the technical challenges associated with defining fugitive emissions from open-cut coal mining, research into methodology has been conducted in Australia and elsewhere for more than 20 years (Williams et al., 1993; Kirchgessner et al., 2000; Saghafi et al., 2003; Saghafi, 2005; Saghafi et al., 2008; Saghafi et al., 2012).

Despite the level of research, direct measurement of emissions from individual open-cut is not yet practical for routine reporting, although research is underway to investigate the use of atmospheric methods for this purpose (ACARP Project C24017, http://www.acarp.com.au/Media/ACARPCurrentProjectsReport.pdf). At present, emissions from Australian open-cut coal mines are estimated for the purposes of NGER reporting using either Method 1, which is based on the use of state based emissions factors, or Methods 2 and 3, which use gas content data from strata measured for the reporting mine.

Method 1 was developed from research conducted during the early 1990s where methane concentrations across plumes of methane emanating from a number of mines in NSW and Queensland were measured at ground level (Williams et al., 1993). The concentration data, combined with local wind speed measurements were used in conjunction with a plume model to infer the methane flux from the mines. The results of that study yielded average emission estimates of 3.2 m^3 per tonne of run-of-mine (ROM) for NSW and 1.2 $m^3\ t^{-1}$ for Queensland mines. While these results represented the first quantitative estimates of fugitive emissions from open-cut coal mining in Australia, there are a number of limitations with the methodology that restrict its general applicability, which include:

- Measurements can only be made under suitable atmospheric conditions.
- Ground level plume tracking requires vehicle access to the plume, which is often not possible.
- Separating individual mines can be difficult or impossible if mines are closely spaced.
- The method requires specialised personnel and equipment.
- At the time the Williams study was conducted, limitations in the sensitivity of contemporary instrumentation meant that discriminating low level CH_4 perturbations from background concentrations introduced relatively large errors. However, recent developments in ambient monitoring equipment (e.g. cavity ringdown spectroscopy) have largely overcome this problem and modern commercially available instruments now provide the ability to measure small

concentration differences with much higher precision than older flame ionisation detector instruments.

Because of these issues, and the high uncertainties associated with applying average emission factors to all mines, subsequent research focussed on developing a more manageable alternative method for estimating fugitive emissions.

Initial work in this regard in Australia examined the feasibility of using surface flux chambers for measuring gas emissions (Saghafi et al., 2003). While this work provided important information on the gas release routes within open-cut mines, the methodology required many individual measurements to build up an accurate estimate of emissions. There were also a number of practical and safety limitations involved with personnel operating in some parts of the mining operation. Moreover, because gas release from coal and other strata varies with time, the time of measurement was an important factor in measuring emissions using this method.

Later research investigated using the gas reservoir properties of coal and other strata to determine fugitive emissions of CH_4 and CO_2, which would overcome many of the practical problems of in-pit measurements while potentially providing mine-specific data (Saghafi et al., 2003; Saghafi et al., 2005; Saghafi et al., 2008). The work undertaken by Saghafi et al. (2003, 2005, 2008) now forms the basis for NGER Methods 2 and 3, which both use gas content data measured at the reporting mine to estimate fugitive emissions. Note that Methods 2 and 3 are identical except in the case of Method 3, samples must be obtained in accordance with appropriate Australian standards.

The general methodology of this reservoir approach involves measuring the in situ gas content of core samples from the target coal seams and other strata collected ahead of mining. A model of a 'gas release zone' is then developed for the mine to estimate annual emissions taking into account the gas released from the coal, other non-coal strata, and that from the highwall and pit floor. Although the methodology is complex and requires a detailed programme of coring and gas content testing (refer to Chapter 3 of the Technical guidelines for the estimation of greenhouse gas emissions by facilities in Australia - July 2014 http://www.environment.gov.au/climate-change/greenhouse-gas-measurement/publications/nger-technical-guidelines-2014), it produces mine-specific emission factors which yield emission estimates with much lower uncertainties than those based on the Method 1 approach. Most Australian open-cut coal mine operators now use Method 2 or 3 for reporting their fugitive emissions to the Regulator.

Emissions generated from extracting coal are the largest component of coal mining fugitive emissions, in some cases accounting for more than 70 % of a mine's total greenhouse gas emissions (Day et al., 2006) but there are several other sources of fugitive emissions associated with mining:

- Post Mining Emissions – Post mining emissions are those that continue during the time the coal leaves the mine and it reaches the end user. These emissions are currently poorly defined and are estimated for NGER reporting by applying an emission factor of 0.014 t CO_2-e per tonne of ROM coal (~0.67 kg CH_4 t^{-1}). At present, only post mining emissions from gassy underground mines are estimated and reported.
- Abandoned Mines – Most mines continue to release fugitive emissions after they have ceased operation. While both underground and open-cut decommissioned mines may emit greenhouse gases, only underground mines are considered for NGER reporting. The method used for estimating these emissions assumes that emissions from abandoned mines reduce over time according to an 'emissions decay curve'. Emissions at a particular point after the mine has closed, E_{dm}, are calculated by the expression:

$$E_{dm} = E_{tdm} \times EF_{dm} \times (1 - F_{dm}) \qquad (2.2)$$

where E_{tdm} is the annual emission rate of the mine at closure, E_{dm} is the emission factor for a mine at a point in time since decommissioning (calculated from the decay formula) and F_{dm} is a factor to account for emissions reduced by the inflow of water into the mine. The term EF_{dm} is given by Equation 2.3:

$$EF_{dm} = (1 + At)^b \qquad (2.3)$$

where *t* is the time elapsed since mine closure and *A* and *b* are mine specific constants.

- Spontaneous Combustion and Low Temperature Oxidation – Waste material from open-cut coal mining often contains some carbonaceous material that may undergo low temperature oxidation. In some cases, spoil piles may undergo self-heating which if unchecked can lead to spontaneous combustion. These processes lead to emissions of greenhouse gases (Carras et al., 2009; Lilley et al., 2012). In some mines, these emissions may be significant but most mines now effectively manage spoil and waste placement to avoid spontaneous combustion (Day et al., 2010). Emissions from spontaneous combustion and low temperature oxidation of coal are not included in national greenhouse gas inventories and are not reported for NGER purposes.

Estimates of fugitive emissions from post mining, abandoned mines and spontaneous combustion are generally subject to very large uncertainties. However, it is likely that the total contribution from these sources represent only a small proportion of greenhouse gas emissions from the coal mining industry.

In NSW, fugitive emissions from coal mining during 2013 were estimated to be 14,381 Gg CO_2-e which is a reduction of about 20 % compared to 2000 levels (Department of the Environment, 2015a). Although coal production has increased by about 70 % over this period (Australian Energy Statistics, 2015), emissions have decreased partially as a result of a shift in production from underground to open-cut mining as well as the implementation of mitigation schemes at many mines, such as flaring and gas capture systems. It is also likely that some of the apparent decrease is due to the implementation of the more accurate Method 2 now used throughout the industry.

2.3 CSG Production

Coal seam gas is one of several types of so-called unconventional gas. Other types of unconventional gas include shale and tight gas. Shale and tight gas occur in source strata with permeability that is much lower than conventional reservoirs and consequently require horizontal drilling and hydraulic fracturing stimulation for economic extraction. Most of the gas in shale and tight gas reservoirs is stored within the pores as compressed gas (i.e. free gas) although some may also be present as adsorbed gas in organic material in shale source rocks. Coal seam gas in contrast, is mainly stored as adsorbed gas within the microporous structure of coal with relatively little free gas. Hydraulic fracturing stimulation may be used on CSG wells but at present is not widely practised in Australian CSG operations, although its application may increase in the future as less permeable seams are developed.

The methods of gas production from the various types of reservoir differ substantially, which may in turn affect CH_4 emissions. Some of the main points of difference between CSG, shale and tight gas are summarised in Table 2.2.

Table 2.2. Key differences between CSG, shale gas and tight gas (from Day et al., 2012)

Property	CSG	Shale Gas	Tight Gas
Source Rock	Coal seams	Low permeability fine grained sedimentary rocks	Various source rocks have generated gas that has migrated into low permeability sandstone and limestone reservoirs.
Depth	300-1000 m	1000-2000+ m	> 1000 m
Gas Occurrence	Physically adsorbed on coal organic matter	Stored within pores and fractures but may also be adsorbed on organic matter.	Within pores and fractures.

Property	CSG	Shale Gas	Tight Gas
Gas Composition	Usually > 95 % methane. Small amounts of CO_2 and other gases may be present.	Mostly methane but may also contain significant quantities of higher hydrocarbons (condensate).	Mostly methane.
Extraction Technology	Vertical and horizontal drilling employed. Hydraulic fracturing is sometimes required. Currently less than 10 % of wells in Australia require this treatment but this may increase as lower permeability seams are targeted.	Hydraulic fracturing and horizontal wells are usually necessary.	Large hydraulic fracturing treatments and/or horizontal drilling are required.
Water Usage	Water must be pumped from seams to reduce reservoir pressure and allow gas to flow. If hydraulic fracturing is necessary, water is required for the fracturing process.	Water is required for hydraulic fracturing	Water is required for hydraulic fracturing.
Extraction Challenges	Removal of seam water and its subsequent disposal.	Overcoming low permeability. Minimising the amount of water required for hydraulic fracturing. Reducing infrastructure footprint.	Reducing infrastructure footprint.

Although CSG production methods are quite different to shale and tight gas, one common feature of all unconventional gas is that many more wells are required for production compared to unconventional gas fields. In unconventional gas fields, wells are drilled progressively over the life of the reservoir; as production declines in old wells and are eventually abandoned, new wells are drilled to maintain the required production rate from the field.

Methane emissions from gas production can occur at all stages of production – exploration, field production, processing, transmission and storage, and distribution. These emissions may be unintentional such as leaking valves and other equipment or accidental events like equipment failures and pipe ruptures that result in gas escaping to the atmosphere. However, some emissions are deliberate and include venting and flaring or the operation of certain types of gas powered pneumatic devices.

In Australia, almost all unconventional gas production is CSG. All gas producers (both unconventional and conventional) are required to estimate their greenhouse gas emissions under the NGER legislation requirements although at present there is no distinction between conventional and unconventional production. Although much of the processing and distribution infrastructure is similar across conventional and unconventional operations, the large number of wells, water extraction and processing facilities, etc. associated with CSG production may provide additional routes for gas loss compared to conventional production methods.

Fugitive emissions from gas operations are estimated by so called 'bottom up' methods which are based on estimating emissions from certain processes or even individual items of equipment then aggregating the results to obtain an estimate for the entire industry. Most of the estimates of fugitive emissions made by the Australian CSG industry for the purposes of NGER reporting are based on the use of emission factors that are provided in either the NGER Determination or the American Petroleum Institute (API) Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Natural Gas Industry (API, 2009). While the API Compendium is extremely comprehensive, much of the data upon which the emission factors were derived are relatively old and often limited. Consequently, some of the methods have very high uncertainties. Moreover, these methods were developed based on North American experience rather than current Australian practices.

Given the rapid growth of unconventional gas production in recent years and the high uncertainties surrounding greenhouse gas emissions, there has been strong interest in fugitive emissions from the sector. Since about 2012, there have been a number of studies, mostly in the U.S. that have attempted to measure fugitive emissions from unconventional gas production, although it should be noted that all of these related to shale or tight gas rather than CSG.

Most of the recent U.S. studies have used 'top-down' methods to estimate emissions for gas producing regions. These methods are based on measuring atmospheric concentrations of CH_4 and other gases and using information on atmospheric transport phenomena to calculate emissions rates for the area under investigation. Some researchers have used ground based methods where measurements were made either from vehicles or fixed monitoring towers (e.g. Pétron et al., 2012). Others have used airborne measurements (e.g. Karion et al., 2013; Caulton et al., 2014a) or satellite data (Kort et al., 2014; Schneising et al., 2014) to estimate emissions from gas production regions.

Top-down methods have the advantage of measuring all emissions over the study area, thus unlike bottom-up approaches, avoid the risk of missing emission sources. However, because all sources are included in the measurements if other unrelated emissions sources are present, complex data analysis and interpreation is required to properly attribute and quantify emission rates. A top-down system using a network of fixed ground stations is currently being developed to provide long term monitoring of CH_4 from CSG and other sources in the Surat Basin in Queensland (Day et al., 2015).

Although top-down methods have certain advantages for measuring emissions, depending on the scale at which they are applied, they usually give little detail on the routes of emissions. Some bottom-up methods, on the other hand, are suitable to measure emissions from individual items of equipment. In a very comprehensive study of fugitive emission from the U.S. gas industry during the 1990s, a number of methods were used to measure emission rates (Kirchgessner et al., 1997). One approach was 'bagging' where the leaking component is enclosed in a flexible enclosure to trap the gas. A carrier gas is then passed through the bag and the emissions rate E, is calculated from the total flow through the bag, f_b, and CH_4 concentration in the gas stream, C, according to Equation 2.4.

$$E = f_b \times C \tag{2.4}$$

Because this method is very time consuming, an alternative method known as the 'Hi-Flow' method was developed. This is similar to the bagging method except that the air around the leaking component is entrained in an airstream generated by a blower and the CH_4 concentration in the entrained airstream is measured with a suitable gas analyser. The emission rate is thus calculated using the same method as given in Equation 2.4. The Hi-Flow system has since been developed into a commercially available portable instrument designed for routine leak rate quantification. However, there been a recent report suggesting that on one type of commercial Hi-Flow instrument, the range switching operation of the gas analyser may cause underestimation of leak rates (Howard et al., 2015).

With properly operating and calibrated instrument, however, the Hi-Flow (and bagging) methods provide accurate emission rates and have been used successfully for measuring emissions rates from unconventional gas infrastructure. In the U.S., Allen et al. (2013) used the Hi-Flow method to measure emissions from leaks, pneumatic devices etc. on well pads while in Australia, Day et al. (2014) used both bagging and a purpose built apparatus similar in principle to the Hi-Flow method to measure emissions from CSG well pads in NSW and Queensland.

Both bagging and Hi-Flow techniques are usually only capable of measuring emissions from single items of equipment so many measurements are required to survey even relatively simple infrastructure like well pads. To reduce the time requirements, preliminary screening of plant is usually conducted using portable leak testing or imaging instruments to locate leaks, which are then quantified using a suitable technique. An alternative method for quantifying emissions from infrastructure is to use atmospheric methods similar to the top-down techniques discussed above. One of the advantages of this approach is that it can also be used at a range of scales. For instance, Hirst et al. (2004) used an atmospheric dispersion method to measure hydrocarbon emissions from an oil and gas field several kilometres downwind. Others have used these methods to measure emissions at distances of less than 50 m from the source (Loh et al., 2009; Tsai et al., 2012). Day et al. (2014) used a ground based traversing method with a vehicle mounted CH_4 analyser to estimate emissions from Australian CSG well pads.

Most atmospheric methods require detailed knowledge of the plume transport characteristics to produce accurate results. In some cases, this information may be difficult to measure or estimate hence the uncertainty of the estimates is increased. Some of these problems are avoided by using a tracer gas that is released at a known rate from the same location as the source under investigation. Provided that the tracer is not reactive and is subject to the same dispersion behaviour as the target CH_4 source, the emission rate can be calculated by multiplying the tracer release rate by the ratio of the methane concentration enhancement (i.e. the measured CH_4 minus the background level) to the tracer enhancement. This method has been used to measure CH_4 emissions from natural gas operations in the U.S. (Lamb et al., 1995; Allen et al., 2013).

2.4 Wetlands

Wetlands have been estimated to account for around 25 % of naturally occurring CH_4 emissions globally (Waletzko and Mitsch, 2014) and hence have been the subject of intensive study over many years. In Australia, however, the contribution of wetlands to the overall CH_4 budget is poorly defined with only a handful of studies reported. In addition, the range of emission rates reported is very wide – Dalal et al. (2008) cite values for emission rates varying over four orders of magnitude between 3 $\mu g\ CH_4\ m^{-2}\ h^{-1}$ and 44 $mg\ CH_4\ m^{-2}\ h^{-1}$.

Australian wetlands are very diverse and include marine and coastal environments, inland wetlands and some man-made regions (Department of the Environment, 2015b). There are many factors that affect CH_4 emissions from wetlands and soil more generally such as temperature, seasonal effects, compaction (i.e. the degree to which air can penetrate the soil), moisture content and vegetation type. Given the diversity of wetland types, the wide range of emission fluxes is unsurprising.

Measuring emission fluxes from wetlands is usually performed using either atmospheric methods or surface flux chambers. A comprehensive review of these methods, including their strengths and weaknesses, is provided in Denmead (2008). Remote sensing methods have also been used to estimate emissions from large areas such as the Amazon Basin (Melack et al., 2004) although because of the coarse spatial resolution of satellite imagery, this is not suitable for smaller areas.

Many of the methods mentioned above are complex requiring specialised instrumentation and sometimes infrastructure such as towers. Flux chambers, on the other hand are relatively simple to use in the field yet provide high sensitivity for measuring low emission fluxes accurately and consequently, this is the most common method used for measuring soil gas emissions.

There are numerous chamber designs available, including a number of commercial systems, but essentially, all operate by enclosing an area of soil by placing a chamber on the ground surface and measuring the concentration of CH_4 (or other gas) within the chamber over time. Typically, the area enclosed by the chamber is less than about 1 m^2. Flux chamber measurements are often made in the ‘static’ mode in which there is no exchange of air between the inside and outside of the chamber and the gas concentration within the chamber is measured over a period of time. The rate of change of CH_4 concentration in the closed chamber is a function of the gas flux. Analyses of the gas within the chamber may be achieved with an analyser connected to the chamber; alternatively, small gas samples may be taken throughout the experiment using a gas syringe for later analyses in a laboratory (by gas chromatography, for example).

Chambers can also be operated in a flow-through mode where a supply of clean air or other carrier gas is passed through the chamber at a constant rate. The flux is a function of the difference in concentration between the incoming and outgoing stream. However, the sensitivity of flow-through systems is less than static chambers so flow through systems are generally only used in areas with higher gas flux.

Despite the relative simplicity of chambers systems there are a number of factors that must be considered when interpreting the results. One of the most obvious is that the chambers only cover a very small area relative to the study region. Hence, many measurements are necessary to achieve a reasonable level of coverage of even small areas. Moreover, the inherent heterogeneity of soils mean that significant differences in flux may occur over small distances.

More subtle factors may also affect the results of flux chamber measurements. Small pressure differences between the inside and outside of the chambers may lead to large errors. Denmead (2008) cites results where a pressure differential of 100 Pa changed the measured flux by a factor of 10. Because of this, static chambers often have a small vent to allow the pressure to equilibrate, especially if an analyser with a flow return system is used to measure the gas concentration.

Because chambers enclose a section of ground, there is the potential to alter the microclimate above the soil, which in turn has the potential to affect gas emissions. Generally, this problem is mainly associated with chambers that are left in place for extended periods – shorter term experiments (of the order of a few minutes) are less likely to cause such changes.

Another point relates to some static chambers where an internal fan is used to ensure that the gas is well mixed within the chamber. It has been demonstrated that high levels of turbulence induced by this mixing may affect the apparent emission flux (Denmead, 2008). It has also been suggested that static chambers may affect the flow of gas when high concentrations are reached in the chamber (Denmead, 2008) and for this reason, flow through chambers may be preferred when flux rates are high. Debate continues as to the optimum design of flux chambers (Pihlatie et al., 2013).

2.5 Cattle Production

Greenhouse gas emissions from livestock in Australia were estimated to be 59.7 Mt CO_2-e during 2013 (Department of the Environment, 2015a), which represents about 70 % of the nation's agricultural emissions. Most of the livestock emissions are due to CH_4 produced by enteric fermentation (56.4 Mt CO_2-e or 2,685 Gg CH_4), with manure management from intensive feedlots contributing a further 3.3 Mt CO_2-e. It has been estimated that about 52 % of enteric fermentation emissions in Australia are derived from cattle (Charmely et al., 2015).

Because agriculture is not included in the NGER legislation, emissions from cattle are estimated for the purposes of compiling the National Greenhouse Gas Inventory using Tier 2 methodology, which essentially relies on a linear relationship between CH_4 production in cattle and their feed intake. However, recent research has shown that some of the factors used for compiling the Australian national inventory may be overestimating emissions by as much as 24 % (Charmley et al., 2015).

Research into greenhouse gas emissions from cattle has been conducted over many years. Much of this work has been conducted using apparatus where individual cattle are enclosed in a flow-through chamber and provided with feed and water for the duration of the test, which may last for up to 24 hours (Tomkins et al., 2011). The temperature and humidity of the chamber are closely controlled while an air stream of perhaps 200-300 L min^{-1} is passed through the chamber. The air flow rate and concentration of CH_4 in the outlet air stream are continuously measured over the duration of the experiment and are used to calculate the daily CH_4 flux for the animal under test. A similar technique uses a hood that surrounds the test subject's head rather than the entire animal (Boadi et al., 2002). While chamber methods are potentially very accurate, they require highly specialised equipment and facilities, emissions are measured under laboratory conditions rather than in the field, and the procedures have a low throughput.

Other methods that allow measurements to be made while cattle forage normally include various atmospheric techniques. One approach uses SF_6 as an inert tracer gas. Here, a permeation tube that releases SF_6 at a known rate is inserted in the animal's rumen. A sampling system attached to the animal collects air from near the animal's nose and mouth, which is later analysed by gas chromatography (Johnson et al., 2007). The emission rate of CH_4 is calculated by multiplying the release rate of SF_6 by the ratio of CH_4 to SF_6 concentrations in the sample. A similar tracer technique has also been used where instead of SF_6, radioactive CH_4 that has been labelled with either ^{14}C or ^{3}H is infused into the rumen (Hegarty et al., 2007).

There have been a number of studies made to validate the tracer method against the chamber method and agreement between the two methods is generally within about 5 % (Grainger et al., 2007; McGinn et al., 2006).

Chamber and tracer methods are designed to measure emissions from individual cattle, however, there have also been numerous studies aimed at measuring emissions from entire herds or intensive feedlot facilities. These studies often used an atmospheric dispersion method where CH_4 concentration is measured downwind of the source and inverted to provide an emission flux using a backward Lagrangian stochastic model (Tomkins et al., 2011; McGinn et al., 2011). This method was used by McGinn et al. (2008) to measure emissions from cattle feedlots in Queensland and Canada.

As well as enteric fermentation, cattle manure may also be a significant source of CH_4 and in some cases N_2O, which is also a potent greenhouse gas. For the purposes of compiling national greenhouse gas inventories, the IPCC CH_4 emission factor for manure management of non-dairy cattle in Oceania is 5 kg CH_4 head^{-1} y^{-1}, which assumes that all manure management is by dispersal on pastures and ranges (IPCC, 1996). However, the amount of CH_4 produced varies substantially depending on the type of management. For most beef cattle in Australia, manure is dispersed throughout the rangelands, which results in mainly aerobic decomposition with low emissions of CH_4. Intensive agricultural facilities like feedlots, on the other hand, tend to use liquid management practices where the manure is held in lagoons. In this situation, decomposition is by anaerobic activity that produces much larger quantities of CH_4. The IPCC emission factor for liquid manure management (such as in a feedlot) in a warm climate with an annual average temperature above 25 °C is 38 kg CH_4 head^{-1} y^{-1}.

Methane emissions from manure lagoons are generally made using some form of floating flux chamber (e.g. Husted, 1993; Kebread et al., 2006) or micrometeorological method (e.g. Kebread et al., 2006; Ro et al., 2013). However, it should be noted that there are obvious health and safety implications associated with direct contact methods such as flux chambers.

2.6 Rice Cultivation

Globally, rice cultivation is one of the main agricultural sources of CH_4 and contributes about 10 % of atmospheric CH_4 emissions (Dalal et al., 2008). In Australia, rice production is only a relatively small component of the local agricultural industry so the proportion of CH_4 emissions from rice cultivation relative to overall agricultural production is much lower than the global average. Current annual CH_4 emissions from Australian rice cultivation are estimated to be 556 Gg CO_2-e (~26.5 Gg CH_4), which represents less than 0.7 % of emissions from the agricultural sector as a whole (Department of the Environment, 2015a). Almost all Australian rice is grown in NSW but even here, the contribution of rice emissions is less than 3 % of all NSW agriculture greenhouse gas emissions (Department of the Environment 2015b).

Specific emission data for Australian rice emissions is very sparse and for the purposes of compiling the National Greenhouse Gas Inventory, emission estimates are made using a Tier 1 method with an IPCC default emission factor of 10 g m^{-2} y^{-1} (Department of the environment, 2015c). Consequently, the uncertainty on these estimates is high (although given the small size of the rice contribution to total greenhouse gas emissions in Australia, this is largely immaterial).

Methane is emitted from rice paddies by several routes: transport through the vascular system within the plants, ebullition and diffusion through water to the atmosphere. It has been estimated that plant transport is the main mechanism (Jain et al., 2004) while ebullition accounts for perhaps 20 % of the flux. Diffusion contributes only a minor component of gas emissions. The rate at which CH_4 is emitted is strongly affected by a wide range of factors. Perhaps the single largest influence on emissions is water management. For instance, mid-season drainage or intermittent flooding, which are practised in some rice growing regions, can significantly reduce CH_4 emissions. The increased aeration of the soil promoted by these management regimes may also lead to increased CH_4 oxidation further reducing emissions (Uprety et al., 2011). Other factors that affect CH_4 emissions are seasonal and diurnal responses, temperature, pH of the water, type of cultivar, fertiliser application and others (Uprety et al., 2011; Dalal, 2008; Jain et al., 2004; Neue, 1997).

Like wetlands, CH_4 emissions from rice fields are most commonly measured using surface flux chambers. Often, these are purpose built for the task and may be deployed manually during field measurement campaigns (e.g. Cicerone et al., 1983; Khalil et al., 1991; Keerthisinghe et al., 1993). Alternatively, automated chambers may be installed in the field for long term monitoring (e.g. Schütz et al., 1989). If permanent fixed chambers are to be used it is important to ensure that they do not affect the growing cycle of the rice. Hence, these chambers have lids that can be automatically opened after each measurement to allow normal airflow to the plants. The chambers are also normally constructed from clear plastic so as not to block sunlight to the plants. Another feature of chambers used for rice emissions is that they must be high enough to accommodate the plants throughout the growing season. Accordingly, chambers are often relatively tall and require internal mixing with a fan to avoid concentration stratification during measurements.

As well as chamber methods, micrometeorological methods such as eddy covariance may also be used for measuring emissions from rice paddies (Uprety et al., 2011).

2.7 Landfills

Emissions from landfills are currently estimated to comprise about 10 % of NSW total greenhouse gas emissions (Table 2.1). Often emissions from landfills that are required to be reported (i.e. those from sites that generate more than 10,000 t CO_2-e per annum) are estimated using Method 1, which is based on estimates of the amount of material within the landfill and that received at the facility during the reporting year, and a first order decay model. Higher order methods are also permitted in which emissions from the site that are not captured are estimated using a series of flux chamber measurements made over a representative area.

Many studies that have examined landfill emissions have used surface flux chambers because of the simplicity and versatility of the method (e.g. Bogner et al., 1995; Mosher et al., 1999; Stern et al., 2007). However, flux chambers only measure a small surface area during each measurement and thus many individual measurements are required to estimate emissions from a large site such as landfills. Moreover, landfills are often particularly inhomogeneous so that large differences in flux may occur over short distances. In one study, emission rates were found to vary over seven orders of magnitude from less than 0.0004 g m^{-2} day^{-1} to more than 4000 g m^{-2} day^{-1}, which introduces potentially very large uncertainties into estimates based on inadequate numbers of flux chamber measurements (Bogner et al., 1997).

As a result of the sampling difficulties posed by chamber methods, other techniques have been investigated to measure emissions from landfills. Most of these methods overcome the sampling problems associated with flux chambers but often require more elaborate equipment and higher levels of data analyses and interpretation. The majority of useful methods are atmospheric techniques and include eddy covariance (Hovde et al., 1995; Tuomas et al., 2007), tracer gases (Czepiel et al., 1996; Mosher et al., 1999; Czepiel et al., 2003; Spokas et al., 2006) and plume mapping (USEPA, 2012; Amini et al., 2013). The latter method may use open path laser instruments to measure the integrated CH_4 concentration between the plume and a series of fixed reflectors (sometimes at elevated locations to measure the vertical component) then combining with local wind speed data to calculate an emission flux from the site. The general methodology of this approach is now the basis of USEPA method OTM 10 – Optical Remote Sensing for Emission Characterisation from Non-Point Sources.

A description of the tracer and flux chamber methods are described in Section 5.2.3 and 5.2.4 of this report, respectively.

2.8 Wastewater Treatment

For the purposes of national greenhouse gas reporting under the current NGER legislation, wastewater treatment plants estimate emissions based on the population of the region they serve. Method 1 use the population and default emission factors to estimate emissions while higher methods (Methods 2 and 3) also use measurements of the chemical oxygen demand (COD) of the effluent. At present, there is no provision for direct measurement of CH_4 emissions from wastewater treatment plants. As a result, estimates for many plants probably have a relatively high degree of uncertainty. However, the contribution of wastewater treatment plants to overall CH_4 emissions is fairly low and based on current estimates (notwithstanding the uncertainty of these estimates), represent less than 3 % of NSW's CH_4 inventory (Table 2.1).

Most wastewater treatment facilities in Australia and elsewhere comprise a number of processes (primary, secondary and sometimes tertiary) with varying levels of CH_4 emissions. A range of techniques has been applied at facilities to measure emissions throughout the treatment process.

Toprak (1995) measured CH_4 and CO_2 emissions rates from an anaerobic waste pond using a fixed system to collect gas evolved from the plant. The apparatus comprised an inverted plastic funnel with a diameter of 365 mm that was fixed below the surface. Gas bubbles were collected in the funnel and the gas flow rate measured directly using a flow meter connected to the funnel. The average gas flow rate measured during the study was approximately 19.6 m^3 day^{-1} (combined CH_4 and CO_2) although there was a significant level of diurnal variation in the rate. Moreover, the volume of gas produced was also found to increase with increasing ambient air temperature.

One of the advantages of such a system is that it can be left in place for an extended period and with a simple logging system can yield continuous emission data, which is not feasible with infrequent periodic measurements. However, this methodology samples over a single, very small area (~ 0.1 m^2) so the representativeness or otherwise introduces a level of uncertainty to the results.

More commonly, flux chambers of some design are used for measuring emission fluxes from wastewater facilities. Czepiel et al. (1993) used a floating metal flux chamber to measure gaseous emissions from the non-aerated parts of the treatment process. For aerated operations, they used a modification of the flux chamber where a collapsible plastic bag supported on a wooden frame was placed in actively aerated ponds.

3 Volatile Organic Compounds

Air quality concerns regarding unconventional gas production has gained momentum in the United States due primarily to the rapid expansion of the onshore gas industry and the associated use of hydraulic fracturing. Methane along with volatile organic compounds (VOCs) and other pollutants have been studied with respect to air quality and health impacts related to the unconventional oil and gas industry (Field et al., 2014). The CSG sector is somewhat different in Australia to that in the United States, as has been discussed in the previous sections, but nevertheless emissions inventories are important in quantifying the contribution of air emissions from a particular source category to ambient air quality.

This study expands the understanding of source emissions with the inclusion of volatile organic compounds for the various methane emissions sources. The VOC emissions have been addressed from an ambient air quality perspective, not as an emissions inventory as such, to provide information on ambient concentrations across a region or close to a particular source and to investigate whether it is possible to ascertain certain characteristics of that source.

The contribution of a source to ambient VOC concentrations at a particular location is dependent on a number of factors, such as the source strength, source proximity, transport mechanisms (dispersion, dilution and mixing), and atmospheric chemical transformation. Meteorology will produce variability in the ambient concentrations observed and photochemistry will reduce the concentration of reactive hydrocarbons in the atmosphere. Emissions may show diurnal variation where the pattern of the measured compounds follows the intensity of the activity. Long term averaging techniques and large data sets are required to allow the seasonal variation of VOC emissions to be detected over shorter term variation arising from the many factors that control emissions flux and fate. While statistical techniques such as positive matrix factorisation are used to identify a source and its relative contribution, this technique requires large sample sizes to generate the data set required for statistical analysis and the identification of factors that may be assigned to specific sources or source groups.

The work conducted for this project focuses on the trace level detection of a large suite of volatile organic compounds in order to gain an understanding of source related impacts on ambient air and to study the prevalence of compounds that may specifically characterise a source. As far as we are aware, a VOC study as comprehensive as this one has not been undertaken in Australian gas fields, nor for the number of source categories examined in regional New South Wales.

4 Isotopic Ratios

The isotopic ratio of carbon in CH_4 ($\delta^{13}C$ CH_4) is a measure of the stable isotopes of carbon ($^{13}C/^{12}C$) within the CH_4 gas molecule being analysed. The units for $\delta^{13}C$ are reported in parts per thousand (‰) against the international standard Vienna Pee Dee Belemnite (VPDB). Similarly the isotopic ratio of hydrogen in methane (δ^2H CH_4) is a measure of the stable isotopes of hydrogen ($^2H/^1H$) within the methane gas molecule. The units for δ^2H are reported in parts per thousand (‰) against the international standard Vienna Mean Standard Ocean Water (VSMOW). The same system of nomenclature can also be used for other hydrocarbons and carbon dioxide.

Often referred to as the isotopic signature or fingerprint of a molecule, this parameter is relevant since different sources and sinks of CH_4 have a different affinity for the ^{12}C and ^{13}C isotopes and similarly for the ^2H and ^1H isotopes. By analysing $\delta^{13}C$ CH_4 and δ^2H CH_4, different sources (of CH_4 in the atmosphere or in the ground) may be distinguished.

4.1 Bulk Gas Composition

The bulk molecular composition of gas is widely used to differentiate the origin of the sample. Biogas derived samples are characterised by high CH_4 and significant carbon dioxide levels (anaerobic methanogenesis) and almost no heavier hydrocarbons. Hydrocarbon derived natural gases are influenced by biogenic versus thermogenic formation (e.g. Strapoc et al., 2011; Scott et al., 1994; Golding et al., 2013), the maturity of their source rocks (e.g. Rezniko, 1969; Stahl, 1974; Connan and Cassou, 1980) and elemental composition of the organic matter in coal or shale source rock, especially hydrogen/carbon ratio (Rice et al., 1989; Boreham et al., 2001). Coal seam gas consists of mainly light hydrocarbons (C_1-C_5) in various proportions and CO_2 (Papendick et al., 2011), and in some cases small amounts of nitrogen (N_2) (Smith et al., 1985; Smith and Pallasser, 1996; Hamilton et al., 2014), hydrogen (H_2), helium (He) (Clayton, 1998) and hydrogen sulphide (H_2S) (Clayton, 1998). The presence of 'wetter' components such as propane, butane, etc. tends to be a reflection of coal or other organic matter rank and pure microbial gases are characterised by exceptionally low concentrations of ethane and heavier hydrocarbons (Li et al., 2008; Faiz and Hendry, 2006). Gas derived from petroleum oil and shale oil/gas accumulations is characterised by a significant greater proportion of heavier hydrocarbons (C_2-C_{5+}) in addition to the CH_4, much more so than in coal seam gas (Golding et al., 2013).

The schematic in Figure 4.1 shows pictoraly some of the most common sources of methane release into the environment from natural and anthropogenic sources (NASA, GISS, 2013). The primary removal mechanism of methane from the atmosphere is through chemical reactions with the hydroxyl radical ($OH^\bullet$) forming CO_2. The $OH^\bullet$ reacts with a number of gases in the atmosphere and is commonly referred to as a chemical species that 'cleans' the atmosphere.

Figure 4.2 is a schematic cross section of the Earth's crust, showing origin, migration and accumulation of CH_4. Origins of CH_4 include conversion of organic material by micro-organisms (biogenesis), thermal decomposition of buried organic matter (thermogenesis) and deep crustal processes (abiogenesis). Buoyant CH_4 migrates upward through rock pores and fractures and either accumulates under impermeable layers or eventually reaches the surface and dissipates into the atmosphere.

Abiogenic CH_4 is the least understood system but its documented discovery at an East Pacific Rise hydrothermal vent and in other crustal fluids supports the occurrence of an abiogenic source of hydrocarbons (Lollar et al., 2006; Horita and Berndt, 1999). This methane is generally formed by the reduction of CO_2, a process which is thought to occur during magma cooling, in hydrothermal systems during rock-water interactions and the serpentinisation of ultramafic rocks. In the context of global hydrocarbon reservoirs, abiogenic contribution is only a minor fraction based on isotopic signatures (Lollar et al., 2002).

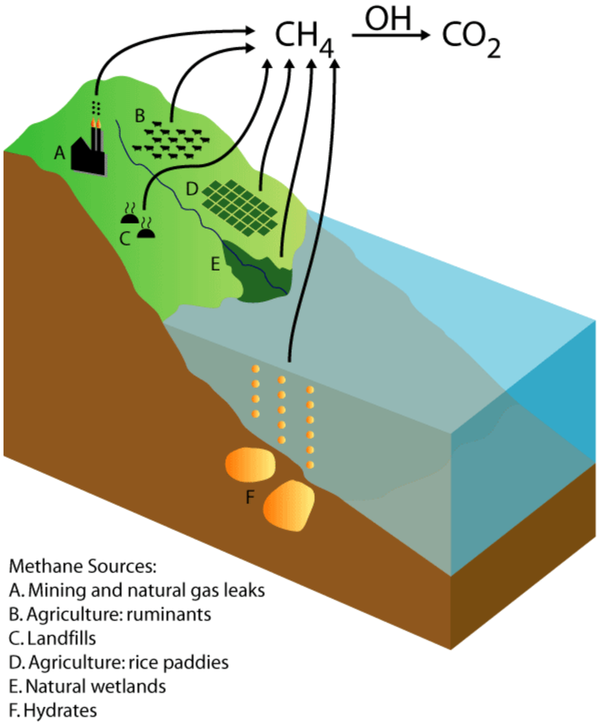

Figure 4.1. Schematic of sources of methane in the environment (NASA, GISS, 2013)

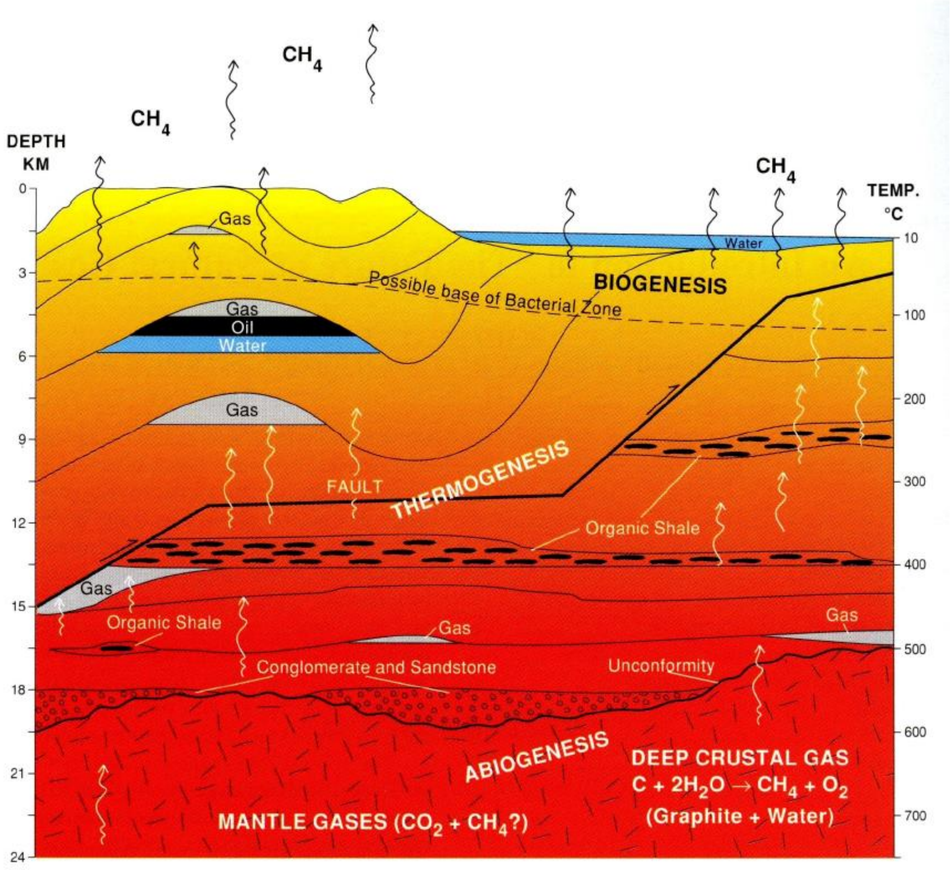

Figure 4.2 Schematic cross section of sub-surface methane generation pathways (Howell et al., 1993)

4.2 Carbon and Hydrogen Isotopes of Gases

The isotopic compositions of natural gases has long been used to help identify its origins (e.g. Golding et al., 2013, Stahl, 1977; Schoell, 1980; Rice et al., 1989; Whiticar, 1994), and the thermal maturities of their source rocks (e.g. Boreham et al., 2001, Stahl and Carey, 1975; Dai and Qi, 1989; Berner and Faber, 1996). Thermogenic gases are generated from organic matter and oil by cracking at high temperature. Methane also forms as a product of anaerobic microbial metabolism. Methane carbon isotope values between -20 to -50 ‰ VPDB typically indicate thermogenic gas and values lower than -50 ‰ are indicative of biogenic influences (Schoell 1980, 1988). Intermediate values (-50 to -60 ‰) may be the result of mixing of thermogenic and secondary biogenic gases. Because variable contributions of the end members can result in a wide variety of carbon isotope values, distinguishing between thermogenic and biogenic contributions can be problematic on the basis of $\delta^{13}C$ signatures alone. Table 4.1 summarises commom natural and anthropogenic methane sources.

Isotopic values for atmospheric CO_2 tend to range from -8 to -12 ‰ depending on air pollution levels (Longinelli et al., 2005, Clark-Thorne and Yapp, 2003) and values for carbon isotopes of CO_2 in coal seams worldwide range between -28 ‰ and +19 ‰ (Smith et al., 1985; Rice, 1993; Kotarba and Rice, 1995; Clayton, 1998). Bacterial reduction of CO_2 leads to isotopically heavier C isotopes in the residual gas, in severe cases positive values (Emery and Robinson, 1993). Carbon isotopic values of CO_2 between -5 to -28 ‰ are indicative of thermogenic sources (Irwin et al., 1977; Chung and Sacket, 1979; Clayton, 1998; Golding et al, 2013). Isotopic values of endogenic CO_2 are close to the main value for elemental C in the upper mantle and vary from -10 to -5‰ (Smith et al., 1985; Javoy et al., 1986; Hoefs, 1987; Jenden et al., 1993).

The hydrogen isotopic composition of CH_4 generated from the biogenic samples utilising anaerobic digestion of organic material generally ranges from -300 ‰ to -350 ‰ VSMOW. Taken together with carbon isotope values of CH_4, these values are generally consistent with bacterial origins and methyl type fermentation. During bacterial CO_2 reduction, the formation water supplies the hydrogen, whereas during fermentation, up to three quarters of the hydrogen comes directly from methyl groups in the coal or other organic precursors, which is already depleted in the heavier deuterium atoms, hence explaining the very depleted hydrogen isotope signature. In contrast, most coal samples (Surat, Bowen, Sydney, Gloucester Basin, etc.) have typical hydrogen isotope values -200 to -260 ‰ VSMOW, depending upon coal thermal maturity and mixing inputs from secondary microbial CH_4 (Golding et al., 2013) which tend to be dominated by bacterial carbonate reduction.

The combination of the $\delta^{13}C$ and $\delta^{2}H$ data for CH_4 in a cross-plot generally provide insights into their origins (see Whiticar, 1999). In Figure 4.3, some differentiation of CH_4 sources is possible but one needs to bear in mind that there are always exceptions to this broad classification due to the intrinsic nature of gases (i.e. multiple sources can rapidly mix, gas samples easily leak and suffer fractionation effects, etc.).

In the present study, analysis of the bulk composition and isotopic compositions of carbon and hydrogen for CO_2 and CH_4 were used to give insights into the origin of gases.

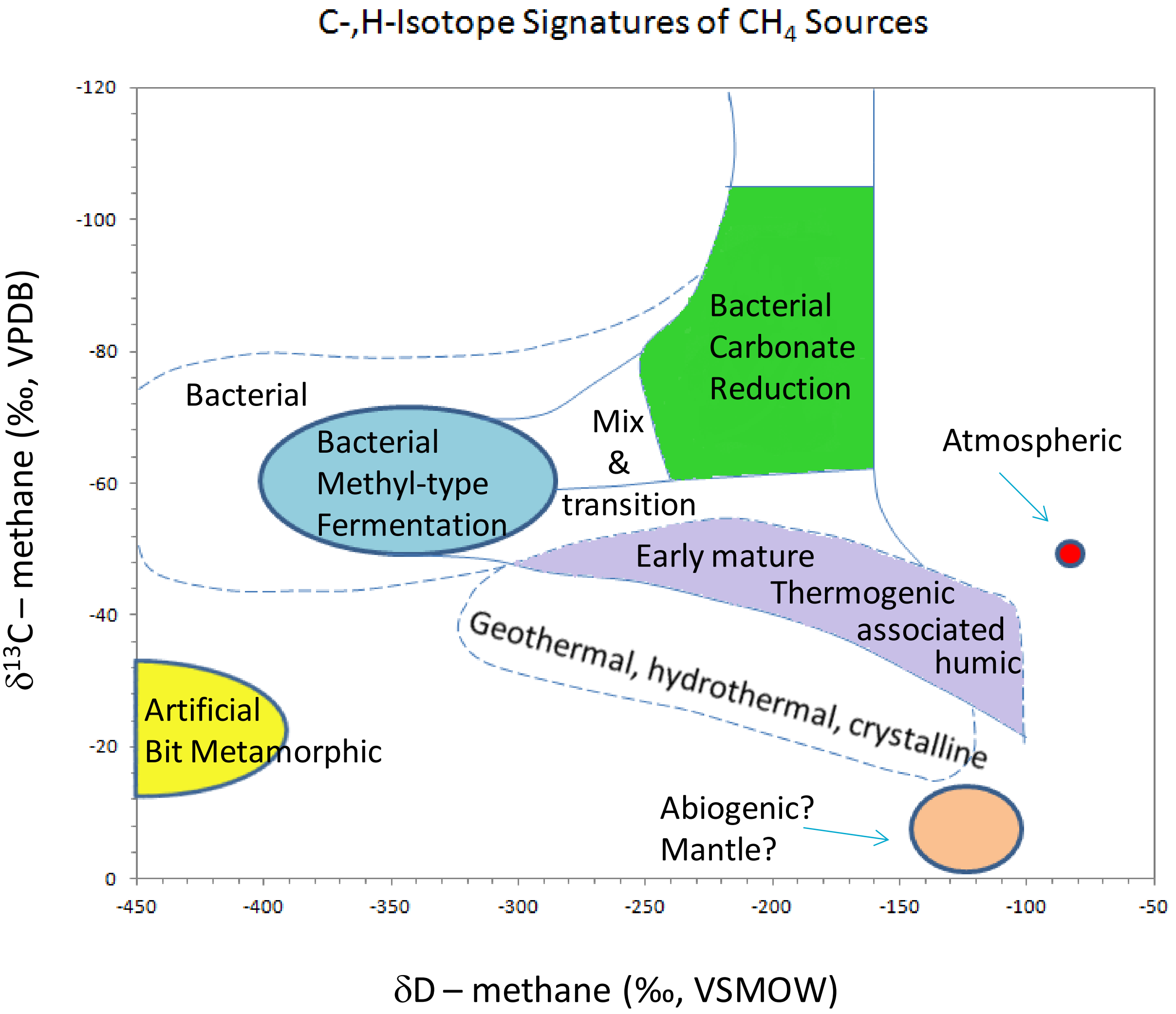

Figure 4.3 Stable isotope cross-plot of carbon and hydrogen isotopes of CH_4 (Whiticar, 1999)

Table 4.1 Carbon and hydrogen isotopes of common natural and anthropogenic CH_4 and CO_2 sources

Methane Source	$\delta^{13}C$ CH_4 (‰ VPDB)	Upper	Lower	$\delta^{2}H$ CH_4 (‰ VSMOW)	Upper	Lower	$\delta^{13}C$ CO_2 (‰ VPDB)	Upper	Lower
Natural Sources									
Wetlands (swamps)	-55	-50	-58	-258	-229	-314	10	18	2
Wetlands (bogs and Tundra)	-65	-52	-70						
Oceans	-59								
Mud Volcanoes	-40								
Termites	-57	-52	-76				-22	-8	-28
Wild Animals	-62								
Atmospheric Methane	-47	-46	-48	-86	-83	-89			
Methane Hydrates	-55	-50	-60						
Permafrost (Siberian Thaw Lakes)	-65	-50	-80	-300	-290	-320			
Anthropogenic Sources									
Biomass burning (C4 vegetation) Savanah Grassland	-17	-14	-20	-200					
Biomass burning (C3 vegetation) Boreal Forest	-26	-23	-30	-200					
Enteric fermentation (C4 vegetation) Ruminants	-50	-45	-55	-340					
Enteric fermentation (C3 vegetation) Ruminants	-63	-60	-76	-350					
Landfill	-56	-51	-62	-254	-230	-310	15	24	5
Food Digester (anaerobic)	-49	-47	-56	-326	-305	-340	10	17	3
Domestic Sewage	-57	-46	-60	-300	-298	-330	8	12	2
Feedlot Manure	-58	-47	-61	-341	-280	-350	4	6	-20
Rice Farms	-62	-59	-67	-323	-305	-365	16	18	-29

Methane Source	$\delta^{13}C$ CH_4 (‰ VPDB)	Upper	Lower	$\delta^{2}H$ CH_4 (‰ VSMOW)	Upper	Lower	$\delta^{13}C$ CO_2 (‰ VPDB)	Upper	Lower
Coal extraction	-35	-14	-77	-223	-219	-230	-17	-12	-25
Coal Seam Gas (Sydney Basin)	-49	-23	-72	-251	-200	-273	15	25	-21
Coal Seam Gas (Surat Basin) production	-56	-50	-60	-212	-205	-217	9	15	-27
Coal Seam Gas (Surat Basin) desorbed	-51	-45	-59	-221	-202	-238	4	8	-3
Coal Seam Gas (Bowen Basin)	-60	-23	-78	-215	-200	-220	19	20	-13
Natural Gas (North Sea)	-35	-25	-37	-180	-178	-213			
Natural Gas (Siberia)	-50	-47	-53	-190	-183	-221			
Natural Gas (Australia)	-38	-27	-50						
Natural Gas (commercial, Eastern Australia)	-39	-35	-41	-214	-200	-220	-2	-1	-9
Traffic Exhaust (California, USA)	-46	-30	-49	-110	-100	-130			

References: (Anthony et al., 2012; Boreham et al., 2001; Burra et al., 2014; Craig et al., 1988; Dlugokencky et al., 2011; Draper and Boreham, 2006; Faiz and Hendry, 2006; Golding et al., 2013; Hamilton et al., 2014; Keeling, C. D., 1960; Kinnon et al., 2010; Li et al., 2008; Lowe et al., 1991; Montiel et al., 2011; Pacific Environment, 2014; Quay et al., 1999; Rust, F. E., 1981; Schaefer et al., 2016; Schoell, M., 1988; Smith et al., 1982; Stevens, C. M., 1988; Stevens and Rust, 1982; Strapoc et al., 2011; Townsend-Small et al., 2012; Umezawa et al, 2012; Zimmerman et al., 1982).

5 Experimental

5.1 Sampling Sites

The original project brief specified that measurements were to be made at 15 sites across NSW covering a range of CH_4 sources:

- Four main CSG regions i.e. Camden, Narrabri, Gloucester and Casino
- One landfill site at a country location
- One landfill site in major city
- One rice farm
- One coal mine in the Hunter region
- One coal mine in the Narrabri/Gunnedah region
- Four wastewater treatment plant , i.e. sewage treatment plants (STP); three in country NSW; one in the Sydney metropolitan or major regional centre
- One intensive agriculture site such as a feed lot or a pig farm
- One natural source of methane such as natural seep, forest or drainage line.

Sites for field measurements and sampling were selected from each of the categories listed above by the NSWEPA (except the rice farm, which was selected by CSIRO after consultation with CSIRO Agriculture officers). An initial selection was made in consultation with the EPA regional offices, after which facility operators were then invited to participate in the project. A number of the operators of the some of the invited facilities declined to participate, so alternatives were then sought by the EPA. A consequence of this was that none of the coal mines in the Narrabri/Gunnedah region were available to participate in the project so two Hunter Valley mines were included instead.

In the case of CSG operations, the negotiations to gain access to some facilities were somewhat protracted and hence detailed on-pad measurements did not commence at these sites until about the middle of 2015.

In general, sites were selected to be spread across NSW but because in most cases participation in the project was voluntary, the final selection of sites was largely dependent upon the operators agreeing to provide access to their sites. In addition to this, some consideration was given to the proximity of the CSIRO base in Newcastle to some sample sites to assist in the logistics of visits to the sites over the course of the project (for example, the Summerhill Waste Management Centre in Newcastle was selected to represent the city landfill site, and the Singleton Wastewater Treatment Works was chosen as one of the country sewage treatment plants).

A brief description of each site are provided in Table 5.1. Approximate locations of each site are also shown in Figure 6.1 in the Results section.

Table 5.1. Details of the sampling sites investigated during the study

Site	Owner	Category	Approximate Location	Notes
Camden Gas Project	AGL Energy	CSG production	-34.12°, 150.77°	144 wells, with 96 producing. One gas processing plant. The Camden gas project is currently the only CSG producer in NSW selling gas commercially.
Gloucester Gas Project	AGL Energy	CSG production	-32.05°, 151.97°	Four pilot wells producing gas. Produced gas is flared. The project was cancelled in February 2016, and since then all wells have been suspended with no gas production.
Narrabri Gas Project	Santos Limited	CSG production	-30.63°, 149.65°	About 50 pilot wells with gas and water treatment facilities. Some of the gas produced is used in the Wilga Park Power Station; the remainder is flared.
West Casino Gas Project	Metgasco Limited	CSG production	-28.82°, 152.96°	This project is now cancelled. All wells are either suspended or plugged and abandoned.
Parkes Waste Facility	Parkes Shire Council	Country landfill	-33.13°, 148.14°	The largest of a number of landfills operated by Parkes Shire Council. The site has been operating since 1995 and is currently licensed to accept up to 20,000 t of solid waste per annum. Waste is periodically buried – there is no gas capture at this site.
Summerhill Waste Management Centre	Newcastle City Council	Metropolitan landfill	-32.89°, 151.64°	This is the primary waste management facility in Newcastle. It is licensed to accept up to 220,000 t of solid waste per annum. A gas collection system is installed which is used to generate up to 2 MW of electricity on site.
Yanco Agricultural Institute	NSW Department of Primary Industries	Rice farm	-34.62°, 146.42°	The Institute conducts research into sustainable agriculture, especially rice production and horticulture. Measurements were made in an experimental rice crop.
Rix's Creek Coal Mine	The Bloomfield Group	Hunter Valley coal mine (open-cut)	-32.53°, 151.12°	Open-cut operation producing approximately 2.5 Mt run-of-mine (ROM) coal per annum.
Wambo Coal Mine	Peabody Energy	Hunter Valley coal mine (open-cut and underground)	-32.57°, 150.99°	This mine is a combined open-cut and underground operation. Total production is about 7.5 Mt ROM coal per annum.

Site	Owner	Category	Approximate Location	Notes
Camden Gas Project	AGL Energy	CSG production	-34.12°, 150.77°	144 wells, with 96 producing. One gas processing plant. The Camden gas project is currently the only CSG producer in NSW selling gas commercially.
Gloucester Gas Project	AGL Energy	CSG production	-32.05°, 151.97°	Four pilot wells producing gas. Produced gas is flared. The project was cancelled in February 2016, and since then all wells have been suspended with no gas production.
Singleton Wastewater Treatment Plant	Singleton Council	Country STP	-32.60°, 151.18°	The facility located on Army Camp road receives all of the wastewater from Singleton for treatment. The capacity of the facility is about 20,000 equivalent persons (EP).
Dubbo Wastewater Treatment Plant	Dubbo City Council	Country STP	-32.20°, 148.63°	The Boothenba Road plant is the main sewage treatment facility for Dubbo. The plant is currently operating at the limit of its capacity (approx. 38,000 EP) and a new facility adjacent to the existing plant was under construction during this project. The new plant was commissioned during late 2015.
Wagga Wagga Narrung Street Wastewater Treatment Plant	Wagga Wagga City Council	Country STP	-35.09°, 147.36°	The Narrung Street plant is the largest of several wastewater treatment facilities operated by the Wagga Wagga City Council. It treats both domestic and industrial effluent.
Picton Wastewater Treatment Plant	Sydney Water	Metropolitan STP	-34.20°, 150.62°	The Picton plant is one of six treatment facilities in the Hawksbury-Nepean catchment operated by Sydney Water. It has a capacity of approximately 13,000 EP.
Jindalee Feedlot	Teys Australia	Intensive agriculture – cattle feedlot	-34.46°, 147.77°	Cattle are sourced from farms within about a 500 km radius for fattening. The facility has a capacity of around 17,000 head.
Yaegl Nature Reserve	NSW National Parks and Wildlife Service	Natural area	-29.46°, 153.23°	The reserve comprises a floodplain of mainly paperbark forest and some coastal saltmarsh. The total area of the reserve is 312 ha. Because it is a wetland there are no tracks through the reserve so vehicle access is limited.

In addition to these 15 sites, further measurements of ambient concentrations of CH_4 and volatile organic compounds (VOCs) were made within the Camden gas field south of Sydney and at site within the Cuba State Forest, approximately 30 km west of Leeton (approximate location -34.60°, 146.08°). Generally, during field trips, the vehicle-mounted methane analyser was operating for most of the time the vehicle was driven between sites. This provided a large database of ambient methane concentrations across NSW over almost a two-year period.

5.2 Methane Measurements

There are many choices available for measuring CH_4 fluxes as discussed in Section 2. However, this project required measurements to be made at many sites and at multiple times throughout the project period so it was not considered practical to use methods based on fixed installations (e.g. eddy covariance and inverse modelling) for all sites. While such systems have to the potential to yield continuous data, the cost of setting up 16 monitoring systems across NSW would have been prohibitive. Accordingly, we adopted methods that could be applied during periodic visits to each site.

Ambient CH_4 concentrations and in many cases, the emission flux, were measured at the sites listed in Table 5.1 using a range of methods, which are described in the following sections.

5.2.1 MOBILE SURVEYS

Ambient CH_4 concentration was usually measured using a Picarro Model G2301 CH_4, CO_2, H_2O cavity ring-down spectrometer, which was fitted into a four-wheel-drive vehicle. On some other occasions, CH_4 concentrations were measured using other Picarro or Los Gatos Research instruments (see following sections). A Picarro Mobile Kit provided power to the vehicle mounted gas analyser via an inverter that operated off the vehicle's 12 V power supply. An auxiliary battery fitted to the vehicle allowed the instrument to be operated for up to several hours without the engine running. The Mobile Kit also includes a GPS receiver (Hemisphere R330 GNSS receiver) and software so that concentration data can be processed and displayed in GIS software. Wind speed and direction at sampling sites were measured using a 2-dimensional sonic anemometer (Climatronics Sonimometer) mounted on the roof of the vehicle (measurements were made only while the vehicle was stationary).

The nominal operating range of the analyser is 0-20 ppm CH_4 with a resolution of about 1 ppb. However, we have previously found that the analyser can reliably measure concentrations of at least 300 ppm, provided that the instrument is calibrated against suitable standards (Day et al., 2014). The data acquisition rate of the Picarro instrument is typically 0.3 Hz when used to measure CH_4, CO_2 and H_2O concentrations simultaneously, however the acquisition rate decreases when operated above 20 ppm CH_4. Details of the instrument specifications can be found at http://www.picarro.com/products_solutions/trace_gas_analyzers/co_co2_ch4_h2o.

The calibration of the analyser was regularly checked against several standard gas mixtures including a high precision reference air sample containing 1.732 ppm CH_4 and 383 ppm CO_2 prepared by the CSIRO Oceans and Atmosphere, GASLAB (Francey et al., 2003). The CH_4 concentration indicated by the Picarro instrument was always within about 0.2 % of the nominal concentration of the reference air (i.e. <4 ppb CH_4). Other standards were also used from time to time for higher concentrations. These less precise mixtures were commercially purchased calibration standards containing between 10.8 ppm and 103 ppm CH_4.

During mobile surveys, the spectrometer was operated continuously while the vehicle was travelling but also for extended periods when stationary. Air was sampled via a ¼" nylon tube attached to the front of the vehicle about 1 m above ground level. The normal flow rate of sample air to the spectrometer is approximately 100 mL min^{-1}; however, to minimise the lag time between air entering the inlet tube and reaching the analyser, an auxiliary pump in the Mobile Kit was used to increase the flow rate up to about 5 L min^{-1}. The residence time of the sample within the sample line was less than 0.5 s at this flow rate. When used for flux chamber measurements (Section 5.2.4), the auxiliary pump was bypassed using a three-way valve.

Surveys were made by driving the vehicle on public and sometimes private roads at speeds up to about 110 km h^{-1}. The rate of measurement of the instrument was such that relatively small methane anomalies could be detected at highway speed although the response time of the instrument, which was about 14 s, resulted in an offset of several hundred metres at this speed. However, when surveys were made on the selected sites, the vehicle speed was much lower (typically <20 km hr^{-1}) and often little more than walking pace so the offset yielded by the vehicle speed could usually be ignored.

Later in the project, we acquired a Los Gatos Research Ultra-Portable Methane/Acetylene Analyser. This instrument has an operating range of 0-1000 ppm CH_4, 0-1 % C_2H_2 and 0-7 % H_2O (full specifications can be found at http://www.lgrinc.com/documents/LGR_Portable_FAMA_Datasheet.pdf). A GPS receiver could also be connected to the analyser to provide spatial information if required. Calibrations were periodically made using the standard mixtures as for the Picarro; two additional standards containing 4.1 and 20.6 ppm C_2H_2, respectively, were also used.

5.2.2 PLUME TRAVERSES

In some circumstances, it is possible to estimate CH_4 emissions from sources using a plume dispersion method. In this method, the CH_4 concentration profile in a plume originating from the CH_4 emission source is measured at some distance downwind by performing traverses across the plume. This method, among others, was used by Day et al. (2014) to estimate CH_4 emissions from Australian CSG well pads. The technique is illustrated in Figure 5.1.

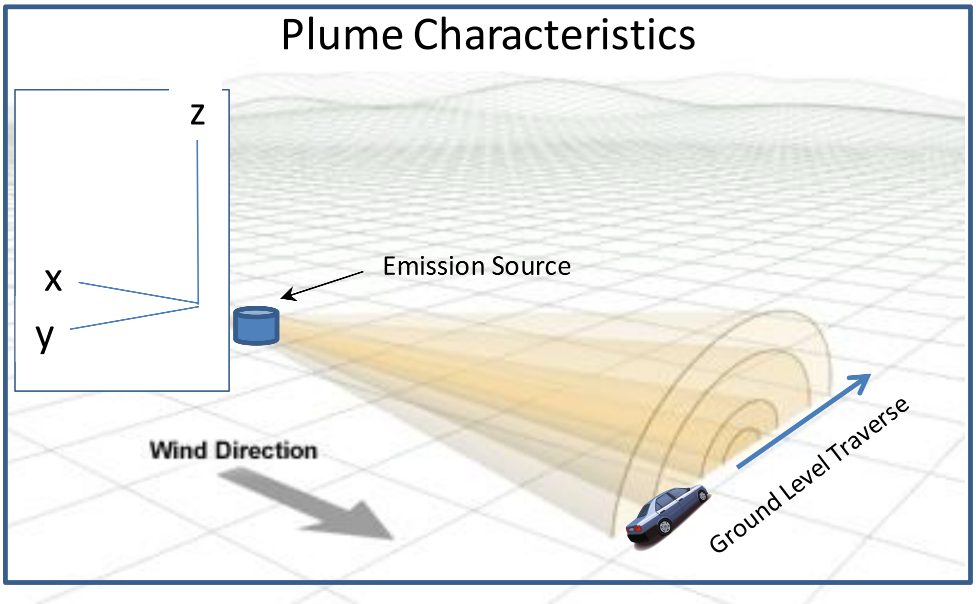

Figure 5.1. Schematic representation of the plume traversing experiments (from Day et al., 2014).

By traversing across a plume downwind of the source, the emission flux, *F*, may be estimated by integrating the CH_4 concentration enhancement, *C*, of the plume in the horizontal, *y*, and vertical, *z*, directions and multiplying by the average wind velocity, *u*.

$$F = u \int_{-y}^{y} \int_{0}^{z} C(y,z)dydz \qquad (5.1)$$

Because concentration measurements are made only at ground level, the vertical dispersion must be estimated by reference to plume dispersion models such as the Pasquill-Gifford curves of σ_z (i.e. the standard deviation of the distribution of CH_4 concentration in the vertical direction) as a function of downwind distance under given atmospheric turbulence conditions (Hanna et al., 1982). In this approach we assume that the maximum CH_4 concentration in the vertical column occurs at ground level; the vertical concentration profile of CH_4 within the plume is then assumed to decrease from the ground level concentration with height according to a Gaussian distribution. Because the maximum concentration must be at ground level, the source must also be at or near ground level. The method is therefore unsuitable for elevated sources, although other plume dispersion methods can often be applied in these cases.

Plumes that undergo significant rise from momentum or buoyancy effects would also be unsuited to these simple ground level traverses because the maximum plume concentration would most likely be well above ground level. While CH_4 is less dense than air and therefore is buoyant, most of the sources examined in this study emit CH_4 over diffuse areas so that any emissions are rapidly entrained in the prevailing air flow, which rapidly dilutes the CH_4. Consequently, the density difference between the plume and surrounding air mass is very small and buoyancy effects are negligible. Previous experiments using ground level traverses have confirmed this (Williams et al, 1993; Day et al., 2014).

Estimating the vertical extent of the plume introduces a significant source of uncertainty because the vertical concentration profile must be estimated from information on the spatial distribution of the source (i.e. an area or point source), downwind distance and prevailing atmospheric stability. Often these data are not well defined. In carefully designed experiments, ground based plume measurements can yield high levels of accuracy (e.g. Loh et al., 2009; Humphries et al., 2012). However, in less favourable conditions, such as short term measurements made during occasional site visits, higher uncertainties are expected. In the case of the CSG well measurements, Day et al. (2014) estimated that the uncertainty of their measurements, which were made within less than 50 m of relatively small point sources, was of the order of 30 % when sufficient traverses could be made to provide a reasonable average. Significantly higher uncertainties of up to 100 % resulted when estimates were based on only one or two traverses. Other researchers using this method have reported uncertainties of a factor of two or three when applied to large diffuse sources such as coal mines (Williams, et al., 1993; Lilley et al., 2012).

Notwithstanding the uncertainties associated with this method, plume traverses were attempted at some sites. Measurements were made using the vehicle-mounted Picarro analyser downwind of the source. Background CH_4 concentrations were measured by performing traverses upwind of the source.

5.2.3 TRACER GAS

Because of the uncertainties associated with ground level traverse methods and other problems associated with site topography, access and variable winds, we investigated an alternative approach to determine emission rates based on the use of a tracer gas. Here, a stable gas unrelated to the source, such as acetylene, is released at a known rate, F_{Tracer}, from the same location as the CH_4 source. Simultaneous downwind measurements of the concentration enhancement (i.e. concentration above background) of both the tracer, C_{Tracer}, and CH_4 C_{CH4}, are made and the emission rate of methane, F_{CH4}, calculated according to Equation 5.2.

$$F_{CH4} = F_{Tracer} \times {}^{C_{CH4}}/{}_{C_{Tracer}} \qquad (5.2)$$

The tracer method avoids the need to estimate the vertical CH_4 profile in the plume. In addition as shown in Equation 5.2, information on wind speed, direction or the width of the plume is not required to calculate the emission rate. The method, however, does require additional analytical capability to measure the tracer gas with sufficient accuracy and precision. It is also essential that the tracer experience the same plume transport phenomena as the target so it is important that the tracer is well mixed in the plume.

A series of experiments were conducted using controlled releases of CH_4 to validate the procedure. Methane was released from a cylinder in an open area at rates that were measured using a flow meter (Fisher and Porter Rotameter) that had been calibrated against a NIST traceable calibrator (Bios DryCal DR2). Acetylene was released from the same location at rates between about 1 and 2 L min^{-1}, which were also measured with the flow meter. Initially samples were collected from within the plume with evacuated stainless steel canisters and later analysed in the CSIRO North Ryde laboratories for CH_4 and C_2H_2 using Fourier transform infrared spectroscopy (FTIR). Although this approach yielded reasonable results, only a small number of plume samples could be analysed and there was a delay of days or even weeks between the time the sample was taken and the analyses.

Later measurements were made using the Los Gatos Research (LGR) Ultra-Portable Methane/Acetylene analyser, which provided real-time analyses of the plume and due to the rapid sampling rate (up to 1 Hz) yielded many data pairs of CH_4 and C_2H_2 concentrations, which improved the precision of the method.

The results of one of the validation experiments are shown in Figure 5.2 where the concentrations of CH_4 and acetylene are plotted as a function of time as the LGR instrument was moved through the plume at between about 20 and 50 m from the source. Unlike the plume traverse methods described in Section 5.2.2, there was no attempt in this experiment to make perpendicular transects across the plume – the instrument was simply moved to ensure that measurements were made within the plume. In this example, the actual CH_4 flow rate (measured by the calibrated flow meter) was 4.32 L min^{-1} and the acetylene flow was 1.95 L min^{-1}, both released from the same point.

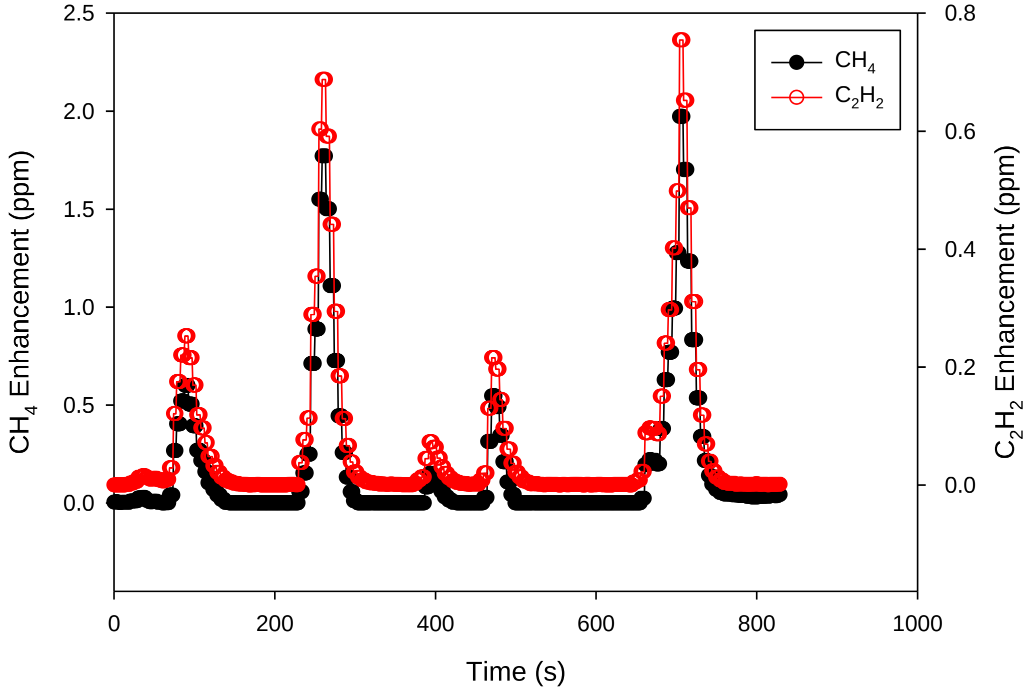

Figure 5.2. Methane and acetylene concentration enhancements measured as a function of time during a controlled release experiment.

There is an excellent correlation between the CH_4 and acetylene traces, which is illustrated even more clearly in Figure 5.3 where the acetylene enhancement is plotted as a function of the CH_4 enhancement.

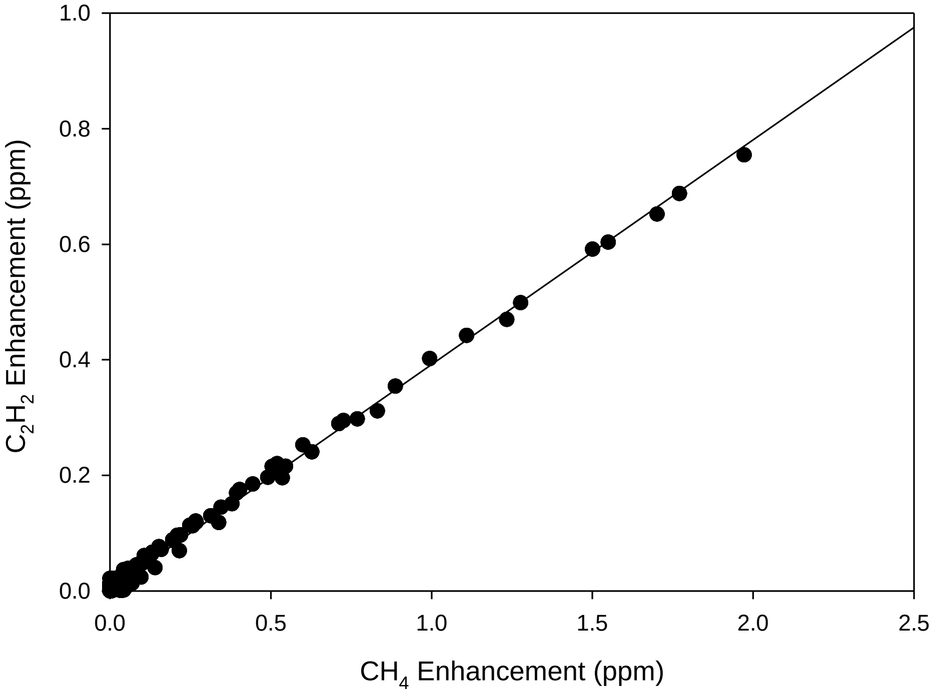

Figure 5.3. Correlation of the methane and acetylene enhancements shown in Figure 5.2.

The CH_4 emission flux calculated from this experiment using Equation 5.2 yielded a mean value of 4.68 L min^{-1}, a difference of about 8 % from the actual emission rate.

A number of other experiments were made using this method and the results of the measurements are summarised in Figure 5.4. These experiments were conducted over two days in light to moderate wind conditions (1-5 m s^{-1}). Measurements were up to about 50 m downwind of the point emission source. It is seen that the CH_4 emission rate determined from the tracer method was in each case well within 10 % of the true CH_4 release rate (indicated by the horizontal lines in Figure 5.4).

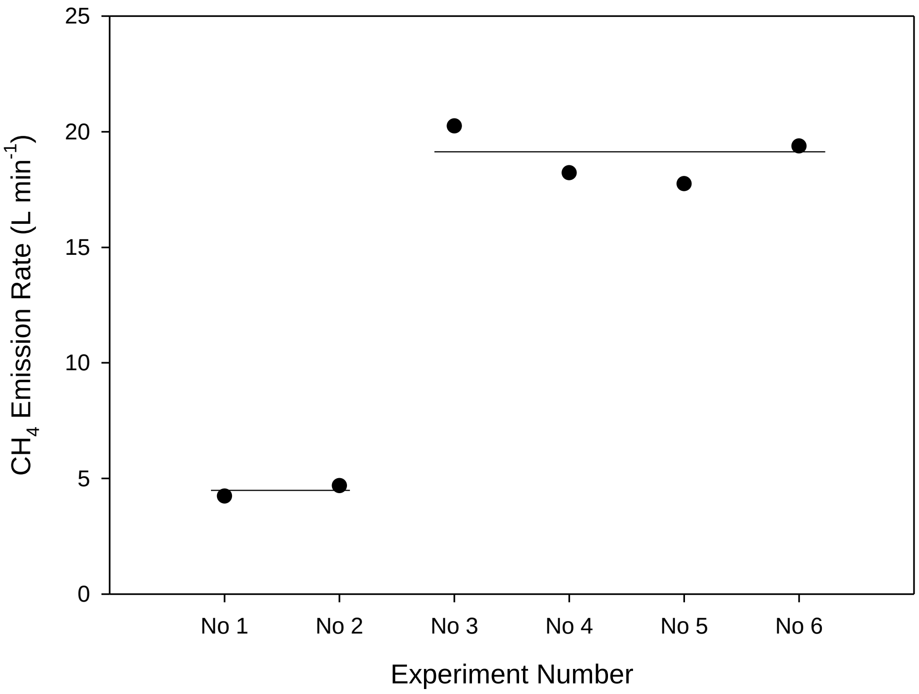

Figure 5.4. Summary of controlled release experiments where the methane emission rate was estimated using the tracer gas method. The horizontal lines show the actual methane release rate (Experiments 1 and 2: 4.32 L min^{-1}; Experiments 3-6: 19.2 L min^{-1}).

Although the use of a tracer is a powerful technique, there are some limitations that must be considered. Firstly, the tracer must be well mixed with the plume for optimum accuracy. This usually means that some level of wind and a reasonable downwind distance are needed to allow adequate mixing to occur. Secondly, the tracer should be released at the same location as the source gases. In some situations such as CSG wells, where CH_4 emissions are released from a relatively small area, it is often simple to release the tracer in approximately the same location as the target. Where the source is released over a larger area, co-release may not be possible. This may be compensated for by sampling further downwind so that the separation from the source and tracer is small relative to the downwind distance. However, for very large sources spread over larger areas (e.g. landfills or coal mines) the downwind distance required may be too large to be practical (e.g. the tracer becomes too dilute to accurately measure). For large sources such as these, alternative methods, perhaps requiring multiple sources of tracer are required. It may also be possible to use a hybrid method of tracer release and plume dispersion methods to estimate emissions from large sources (Lamb et al., 1995).

The tracer technique when available and determined to be suitable was deployed at several sites, including the CSG well sites visited as part of the project.

5.2.4 SURFACE FLUX CHAMBERS

Surface flux chambers were used at many of the selected sites to measure CH_4 and CO_2 emission rates for soil and liquid surfaces. In all cases, the chambers were operated in the static mode where there is no exchange of air with the outside atmosphere so that the CH_4 (and CO_2) concentration within the chamber usually increases with time. Some natural surfaces show a decrease in CH_4 concentration, which is due to microbial activity in the soil. The general principle of the operation of static flux chambers is illustrated in Figure 5.5.

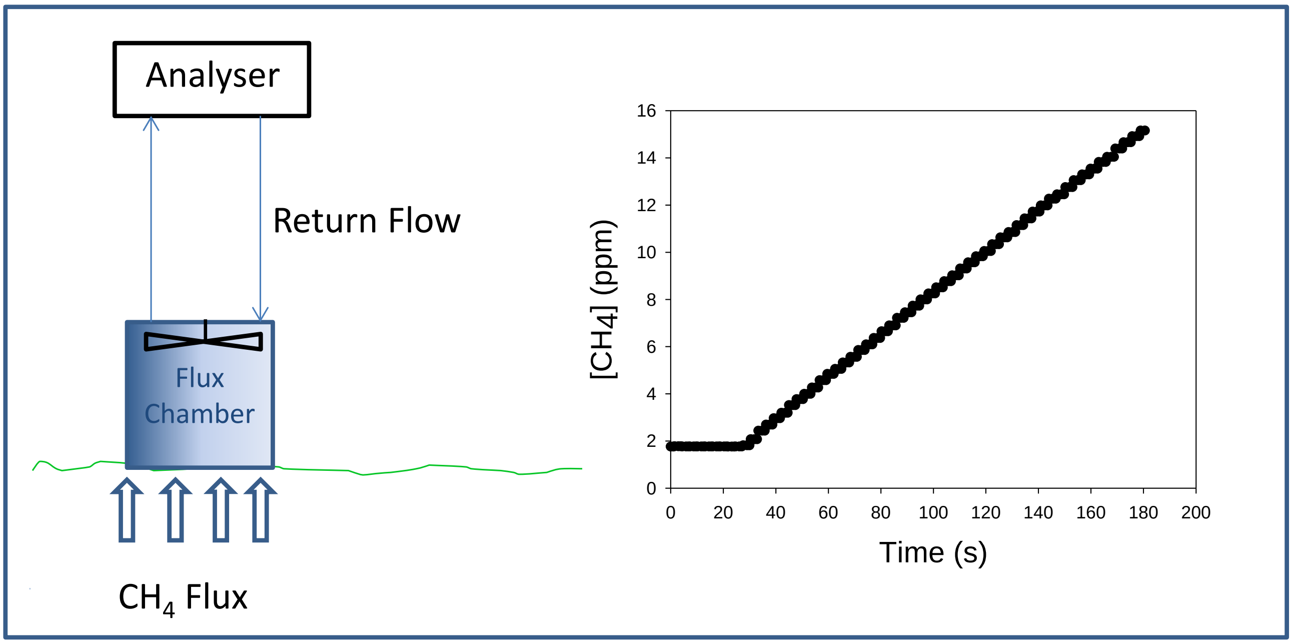

Figure 5.5. Schematic representation of a flux chamber operated in the static mode. The plot to the left shows the methane concentration within the chamber during a controlled release experiment as a function of time.

In this mode of operation the gas flux, *F*, is calculated from the rate of change in concentration inside the chamber, *dC/dt* (i.e. the slope of the plot shown in Figure 5.5) according to Equation 5.3

$$F = \frac{dC}{dt} \times \frac{V}{A} \tag{5.3}$$

where *V* is the volume of the chamber and *A* is the area of surface covered by the chamber.

Chambers can be various sizes and shapes and made from various materials including plastic or metal.

During this project, emissions from ground and liquid surfaces were often measured using a variety of chamber designs. Initially we used a simple chamber comprising a plastic cylindrical chamber 37.5 cm in diameter and 40 cm high with a total volume of about 45 L and an area of coverage of 0.11 m^2. The chamber was connected to the inlet and return ports of Picarro analyser in the vehicle via 6 mm nylon tubing. After placing the chamber on the test surface, the concentration of CH_4 and CO_2 in the chamber was measured over a period of at least several minutes while a small electrically powered fan inside the chamber ensured that the air was well mixed during the experiment.

At some locations, especially where high fluxes were apparent (typically above 10 g CH_4 m^{-2} day^{-1}), a commercially manufactured battery powered portable flux system was used. This system (West Systems, Srl) used an aluminium chamber with a volume of 6 L and surface coverage of 0.03 m^2 (not that the chamber was smaller than other chamber so introduced a slight sampling disadvantage due to is smaller area of coverage). The analytical system was a tuneable laser diode CH_4 analyser and a non-dispersive infrared CO_2 analyser housed in a portable case.

While these two systems were suitable for most of the sites where surface flux measurements were made (e.g. natural surfaces, landfills, coal mines), there were some occasions when more specialised chambers were required. In particular, wastewater treatment plants and the rice farm required purpose built chambers to adequately measure emissions.

At one wastewater treatment plant, we fitted fixed chambers in two of the ponds and made measurements of flux during periodic visits to the site. One of the chambers is shown in Figure 5.6.

Figure 5.6. Fixed flux chamber in operation at the Singleton wastewater treatment plant

Each chamber was constructed from a 60 L polyethylene drum with the base removed and fixed to a walkway so that the open base of the chamber was submerged in the liquid. A length of 6 mm tubing allowed the chamber to be connected to the vehicle mounted analyser. A recirculating fan provided mixing within the chamber during each measurement. Because CH_4 and CO_2 accumulated in the chambers during intervening site visits, prior to flux measurements, each chamber was flushed with clean air for several minutes until the CH_4 and CO_2 concentrations within the chamber were close to ambient levels. The fixed chambers were only deployed at the Singleton wastewater treatment plant.

In addition to the fixed chambers, floating systems were built to enable the spatial distribution of emissions to be determined on water surfaces. The chambers were made from 60 L polyethylene drums cut in two and fitted with a circular float (Figure 5.7). Tubing was fitted so the unit could be attached to the Picarro analyser while a battery powered fan provided internal mixing. These chambers could be used up to about 20 m from the vehicle and were used at all four wastewater treatment sites. The floating chambers were also used to measure CH_4 flux from a CSG water treatment facility and occasionally on the wetland.

Figure 5.7. Floating flux chamber in use at a sewage treatment plant

Flux measurements at the rice farm also required specially designed and built chambers. Since measurements were made during the growing season, the chambers had to have sufficient height to accommodate the rice plants, which reached a maximum height of about 1.2 m before harvesting (Figure 5.8).

Figure 5.8. Purpose-built flux chamber used for measuring CH_4 emissions from rice

The photograph on the left of Figure 5.8 shows the chamber in position immediately after the rice crop was sown while the right hand image shows the chamber in use about two months into the growing cycle. During each measurement, the chamber was placed over the rice to seal onto a fixed polyethylene base, which was permanently set into the soil. The CH_4 concentration in the chamber was measured as for the other chambers by connecting a nylon tube (visible in left hand photo) to the Picarro instrument in the vehicle, which is parked at the side of the paddock. The chamber was also mixed continuously during each measurement using a small electrically powered fan visible on the top of the chamber. Six bases were installed in the rice field and left in position for the duration of the growing season. This allowed measurements to be made at various locations to assess the spatial variability of the emission profile. As well as measurements made on the fixed bases, other locations throughout the paddock were selected from time to time.

5.3 Volatile Organic Compound Determinations

5.3.1 PRIORITY VOCS

The volatile organic compounds (VOCs) targeted in this study are prioritised under Australian and International guidelines for air quality assessment. They comprise a comprehensive range of compounds that also allow the evaluation of source contribution and source recognition, of importance in this project. These compounds are incorporated into two VOC suites termed the 'PAMS hydrocarbon suite' and the 'TO-15 air toxics suite'.

The PAMS (Photochemical Assessment Monitoring Stations) suite is prioritised under United States Environmental Protection Agency (USEPA) and California Air Resources Board (CARB) protocols as the major organic precursors to the formation of ozone in the atmosphere. The suite comprises 57 aliphatic and cyclic hydrocarbons, including aromatic compounds, in the C_2 – C_{12} hydrocarbon range which, by their nature, provide information on urban transport emissions, liquid and gaseous fuels and combustion derived emissions. Of importance to this project, these components assisted in attributing compounds to the primary source emissions as well as identifying possible contributing sources for each source category.

The TO-15 (Toxic Organics - Method 15) air toxics suite is prioritised under USEPA ambient air quality guidelines for human and environmental health. The TO-15 suite comprises 65 organic compounds that include halogenated and oxygenated species, along with certain hydrocarbons. These compounds characterise the emissions from various waste processing and industrial activities and aspects of emissions from natural processes.

Included in these suites are the aromatic compounds prioritised under the Australian National Environmental Protection (Air Toxics) Measure (Air Toxics NEPM), i.e. the BTX group; benzene, toluene and xylenes (NEPC, 2011). Note that formaldehyde and benzo[a]pyrene are also NEPM priority air toxics but these were not included in this study for a number of reasons. Formaldehyde is prioritised due to its toxicity as a primary emission (particularly from furnishings to indoor air and as a component in exhaust emissions to ambient air) and its role as a secondary pollutant of importance in the formation of atmospheric aerosol. These aspects were of lesser importance to the major aims of this work; the characterisation of VOCs from methane sources. Formaldehyde is also reactive and therefore requires a specific method of sampling and analysis that involves *in-situ* derivatisation as the mode of collection and liquid chromatography as the method of analysis. Benzo*[a]*pyrene is a particle-bound, semi-volatile compound that is primarily generated from combustion sources. This compound requires a filter-based method of collection and specific analytical and instrumental modes of analysis. Particles and semi-volatile organics were not the prime focus of this study.

The VOC suites are listed in Tables 5.2 and 5.3 for PAMS hydrocarbon and TO-15 air toxics VOCs respectively. The compounds are named according to IUPAC convention except where the alternative name is in common usage (such as toluene rather than methylbenzene) and in this case, both names are provided. The VOC tables of site results, presented in Appendix B, use the primary name as listed in Tables 5.2 and 5.3 and compounds common to both suites are reported in the PAMS listing only. The compounds are ordered by chromatographic retention time (down each column) as this provides a level of guidance as to their relative boiling point and volatility.

These compounds were determined using dedicated instrumentation that incorporated gas chromatography and detection using mass spectrometry and flame ionisation (GCMS and GCFID). These methodologies provided analysis at trace levels, below 0.1 part per billion by volume (ppbv) mixing ratios (also loosely termed concentration) in ambient air, for each of the priority air pollutants. The low detection limits enhanced the number of compounds identified in the VOC profile, which then assisted in emissions allocation to a particular source.

The sampling, analytical and instrumental methodologies implemented for the determination of priority VOCs are detailed in Section 5.3.4 together with the results of method validation and reporting protocols.

Table 5.2 USEPA/CARB PAMS Hydrocarbon VOC Suite

USEPA PAMS Hydrocarbon VOCs		
Ethene	2-Methylpentane	Ethylbenzene
Ethane	3-Methylpentane	*m*-Xylene (1,3-dimethylebnzene)
Acetylene (ethyne)	1-Hexene	*p*-Xylene (1,4-dimethylbenzene)
Propene	n-Hexane	Styrene (phenylethene)
Propane	Methylcyclopentane	*o*-Xylene (1,2-dimethylbenzene)
Isobutane (2-methylpropane)	2,4-Dimethylpentane	n-Nonane
1-Butene	Benzene	Isopropylbenzene
n-Butane	Cyclohexane	n-Propylbenzene
trans-2-Butene	2-Methylhexane	*m*-Ethyltoluene (1-ethyl-3-methylbenzene)
cis-2-Butene	2,3-Dimethylpentane	*p*-Ethyltoluene (1-ethyl-4-methylbenzene)
Isopentane (2-methylbutane)	3-Methylhexane	1,3,5-Trimethylbenzene
1-Pentene	Isooctane (2,2,4-trimethylpentane)	*o*-Ethyltoluene (1-ethyl-2-methylbenzene)
n-Pentane	n-Heptane	1,2,4-Trimethlybenzene
Isoprene (2-methyl-1,3-butadiene)	Methylcyclohexane	n-Decane
trans-2-Pentene	2,3,4-Trimethylpentane	1,2,3-Trimethylbenzene
cis-2-Pentene	Toluene (methylbenzene)	1,3-Diethylbenzene
2,2-Dimethylbutane	2-Methylheptane	1,4-Diethylbenzene
Cyclopentane	3-Methylheptane	n-Undecane
2,3-Dimethylbutane	n-Octane	n-Dodecane

Table 5.3 USEPA TO-15 Air Toxics VOC Suite

USEPA TO-15 Air Toxics VOCs		
Propene	*cis*-1,2-Dichloroethene	Dibromochloromethane
Dichlorodifluoromethane	n-Hexane	1,2-Dibromoethane
Chloromethane	Ethyl acetate	Tetrachloroethylene (tetrachloroethene)
1,1-Dichloro-1,1,2,2-tetrafluoroethane	Chloroform (trichloromethane)	Chlorobenzene
Chloroethene (vinyl chloride)	Tetrahydrofuran (oxolane)	Ethylbenzene
1,3-Butadiene	1,2-Dichloroethane	*m*-Xylene (1,3-dimethylebnzene)
Bromomethane (methyl bromide)	1,1,1-Trichloroethane	*p*-Xylene (1,4-dimethylbenzene)
Chloroethane (ethyl chloride)	Benzene	Bromoform (tribromomethane)
Ethanol	Carbon tetrachloride (tetrachloromethane)	Styrene (phenylethene)
Acrolein (prop-2-enal)	Cyclohexane	*o*-Xylene (1,2-dimethylbenzene)
Acetone (propanone)	1,2-Dichloropropane	1,1,2,2-Tetrachloroethane
Trichlorofluoromethane	Bromodichloromethane	*p*-Ethyltoluene (1-ethyl-4-methylbenzene)
Isopropanol (2-propanol)	Trichloroethylene (trichloroethene)	1,3,5-Trimethylbenzene
1,1-Dichloroethene	1,4-Dioxane (1,4-dioxacyclohexane)	1,2,4-Trimethylbenzene
Dichloromethane (methylene chloride)	Methyl methacrolate (methyl-2-methylpropenoate)	Benzyl chloride (chlorophenylmethane)
Carbon disulphide (methanedithione)	n-Heptane	1,3-Dichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	*cis*-1,3-Dichloropropene	1,4-Dichlorobenzene
trans-1,2-Dichloroethene	Methyl isobutyl ketone (4-methyl-2-pentanone)	1,2-Dichlorobenzene
1,1-Dichloroethane	*trans*-1,3-Dichloropropene	1,2,4-Trichlorobenzene
Methyl *tert*-butyl ether (2-methoxy-2-methylpropane)	1,1,2-Trichloroethane	Napthalene (bicyclo[4.4.0]deca-1,3,5,7,9-pentene)
Ethenyl acetate (vinyl acetate)	Toluene (methylbenzene)	Hexachloro-1,3-butadiene
2-Butanone	Methyl n-butyl ketone (2-hexanone)	

5.3.2 DETERMINATION OF NON-STANDARD COMPOUNDS

Further characterisation of VOCs present in the ambient samples from each source category was undertaken for the determination of non-standard compounds. Non-standard compounds are additional to those measured as priority VOCs and their identification provides further information for source recognition purposes. This determination was achieved by re-examination of the chromatographic output from the VOC analysis for additional peaks that were not included in the priority compound suites. These signals were interpreted using their mass spectral output and, where signal intensity and clarity allowed, the compounds were identified. The results from the most informative VOC analysis for each source (those of higher concentration and tendency to compound diversity) were processed in this manner. Over 30 additional compounds were identified from examination of the VOC output, as listed in Table 5.4.

A sorbent collection and instrumental technique was also investigated to evaluate its power in organic characterisation of emissions from the various land-use sources. This technique has the potential to isolate more reactive species (such as nitrogen and sulphur containing compounds), more complex polar species (such as large oxygenated compounds) and those classed as semi-volatile organic compounds (SVOCs). These classes of compounds can be less amenable to canister collection due to these physical and chemical characteristics. The sorbent technique requires dedicated instrumentation comprising thermal desorption and GCMS (TD-GCMS) and both electron ionisation and chemical ionisation modes of mass spectrometry were utilised to extend capability in mass spectral elucidation and compound identification. Fourteen compounds additional to those identified by evaluation of the VOC output were identified using the sorbent technique. The sorbent methodology tended to preference compounds of greater polarity (e.g. esters) and lower volatility (e.g. C_{10} to C_{12} oxygenates) compared with those from the VOC output, as can be seen in Table 5.4.

The methodologies used for determination of non-standard compounds using the chromatographic output from VOC analysis and by sorbent tube techniques are detailed in Section 5.3.5.

Table 5.4 Non-standard compounds identified from characterisation studies of selected sources using evaluation of VOC output and by sorbent techniques

Non-standard Compounds	
Characterisation using VOC Output	Sorbent Technique
Carbonyl sulphide	Carbonyl sulphide
Sulphur containing; likely dimethyl sulfone	Sulphur containing; likely dimethyl sulfone
Dimethylsuphide	Alcohol; likely 2-butanol
Nitromethane	Butylester
Butanal	Ketone; likely 4-methyl-4-penten-2-one
Bromopropane	C_7 oxygenate; possibly alkylester
Nitrogenous	C_7 oxygenate; possibly alcohol
Oxygenated; likely alcohol	Benzaldehyde
C_4 aldehyde; likely 2-methylpropanal	a-Pinene
2-Pentanone	Phenol
Pentanal	C_8 ketone; possibly 6-methylheptanone
C_5 aldehyde; likely 3-methylbutanal	C_8 oxygenate
C_5 aldehyde; likely 2-methylbutanal	Monoterpene; possibly 3-carene
Nitroethane	C_8 aldehyde; likely octanal

Non-standard Compounds	
Characterisation using VOC Output	Sorbent Technique
Nitrogenous	Monoterpene; likely p-cymene
Dimethyldisulphide	Limonene (monoterpene)
Hexanal	Acetophenone
Furfural	C_9 oxygenate; likely nonanal or nonenol
3-Heptanone	C_{10} oxygenate; likely decanal or decenol
Heptanal	C_{11} oxygenate; likely undecanal
Oxygenate; possibly 2-ethylhexanal	C_{12} aldehyde
a-Pinene (monoterpene)	C_{12} ketone
Benzaldehyde	
a-Methylstyrene	
C_7 oxygenate; likely alcohol	
C_8 alcohol; possibly 2-ethyl-1-hexanol	
Monoterpene; likely p-cymene	
Limonene (monoterpene)	
Eucalyptol (1,8-cineole) (monoterpenoid)	
Chloroacetophenone	
Phenyl alcohol or like	
C_9 oxygenate; possibly nonenol or nonanal	
C_{10} oxygenate	

5.3.3 HYDROCARBON VOCS IN CSG SOURCED WELL GASES

The determination of minor hydrocarbon VOCs, that is those above C_5, in CSG sourced well gases was undertaken. This analysis was not a requisite of this project; however, it was considered that the determination might be informative in the recognition of a CSG source impact to ambient air and with respect to human and environmental health. The minor hydrocarbons are not commonly measured in well gases, as the focus is usually on determining the composition of the gas as its bulk components (i.e. methane and C_2 to C_5 hydrocarbons), and instrumental techniques are optimised for this purpose. The use of high sensitivity instruments, such as those implemented for VOC analysis in this project, enabled the analysis of minor constituents in the C_5-C_8 hydrocarbon range as well as aromatic compounds, including the air toxics; benzene, toluene and xylenes.

All hydrocarbons from the PAMS hydrocarbon VOC suite were targeted and non-methane hydrocarbons (NMHCs) in the range C_2 to C_5 were also determined to provide a measure of relative concentration to the C_5-C_8 compounds. For C_2 to C_5 compounds with concentration > 100ppmv the analysis was considered to be semi-quantitative and data from molecular composition analysis is referenced for these bulk constituents (refer Section 5.4.1).

The methodology for VOC analysis in ambient air samples was re-designed for well gas analysis to accommodate the methane sample matrix and an investigation for the determination of minor hydrocarbon VOCs in a selection of well gas samples was undertaken. The methodology adopted for this aspect of the work is detailed in Section 5.3.6.

5.3.4 ANALYTICAL METHODOLOGY FOR PRIORITY VOCS

The methodology for determination of ambient VOCs used passivated stainless steel canisters as the means of sample collection and instrumental analysis was undertaken using gas chromatography with flame ionisation detection (GCFID) and mass spectrometry (GCMS). Using these techniques, a whole air sample is obtained in a clean and relatively inert sampling medium and GCMS analysis provides high-level sensitivity and accuracy in species quantification and in the confirmation of compound identity. GCFID supports the determination of C_2 hydrocarbon isomers that cannot be determined under the GCMS instrumental conditions required to analyse for compounds in the range C_3-C_{12}, due mainly to the specific modes of pre-concentration required. This methodology is proven for ambient, trace level analysis of the species listed. A description of the methodology and its optimisation and validation follows.

Sampling and analytical procedures are based on USEPA TO-14A (USEPA (1), 1999) and TO-15 (USEPA (2), 1999) standard methodologies for determination of VOCs in ambient air using canister collection and gas chromatography with flame ionisation detection (GCFID) and mass spectrometry (GCMS), respectively. The species prioritised under the USEPA TO-14A methodology include primarily simple aromatics and halogenated compounds and hence a subset of compounds from the USEPA TO-15 priority air toxics listing were also determined to include a more comprehensive range of halogenated species and certain oxygenated species. The VOC assessment of C_2 to C_{12} compounds from the PAMS hydrocarbon suite was undertaken based on similar principles to that of USEPA TO-14A and TO-15 methodologies, incorporating in-house methods that are specific to the instrumental analysis of the PAMS suite of compounds.

Ambient sample collection involved the use of Silco® treated passivated stainless steel canisters. These undergo a rigorous cleaning procedure prior to sampling involving repeated evacuation and pressurisation under humidified nitrogen. The evacuated canisters are deployed to the sampling site, the canister is opened and the air is drawn into the canister, under vacuum, until it reaches atmospheric pressure. This mode of sampling is termed instantaneous or 'grab' sampling and provides a snapshot of ambient concentrations. At the laboratory, the canisters containing the sample are pressurised with zero air and the pressure difference is measured using a pressure transducer to determine sample dilution. A clean canister is filled with zero air with each batch of samples to check for the presence of zero air or system related artefacts.

The instrumental analysis involves the transfer of optimised volumes of the canister sample, under mass flow control, to dual cryogenic traps (a multicomponent adsorbent trap and a glass-bead trap) used to concentrate the VOC analytes, and their subsequent thermal desorption to a combined GC/FID/MS instrument (Varian CP-3800 GC/FID/4000 Ion-trap MS). A sample volume of 300mL and a pre-column split ratio of 10:1 were used to introduce the ambient samples to the instrument. A set of time-programmed valves regulates the flow path from the canister manifold to purge sample lines and traps, transfer sample to the cold-traps, and direct the sample path from the traps to a system of columns for pre-focussing and gas chromatographic separation of the organic compounds. This is accomplished using four GC columns; a CP-Sil 5CB methyl siloxane pre-column (15m x 0.32mm ID, 1µm DF), an Al_2O_3/KCl PLOT column (50m x 0.32mm ID) for separation of C_2-C_5 compounds, and a VF-1MS methyl siloxane column (60m x 0.32mm ID, 1µm DF) for separation of C_6-C_{12} compounds, prior to dual-FID detection. Another VF-1MS column of the same dimensions is used for simultaneous analysis of C_3-C_{12} compounds using MS detection.

The compounds detected in the samples were speciated against standard gas mixtures using GCMS analysis operated in the mode of electron impact ionisation (GCMS-EI) and using an ion-trap design of mass spectrometer. Software that compares both the retention time and the mass spectra of each of the sample components against the standard compounds is used to ensure that false positives are minimised. Integration of the component peak is based on selected ions that are specific to the compound. These operations are especially important in the analysis of trace level and complex samples such as those encountered in this study. The external standard method is used for quantification of sample components. GCFID analysis is used for C_2 isomers (ethane, ethene and acetylene) due to the required specificity of instrumental cold-trapping for these analytes. Higher hydrocarbons were also measured by FID analysis and were used as a check on GCMS derived results.

Of importance in the method validation is the observance and minimisation of method and system related artefacts, some of which may present as target compounds. Artefacts may also present as degradation products of collected analytes or from interactions with co-collected species. Equally, loss of target compounds can occur due to each of these parameters. Artefacts can be generated from, or on, canister surfaces, from gases used for canister pressurisation, from transfer lines and components of the instrument introduction paths, from the adsorbent materials used for cold-trapping and from compound reactions with adsorbent materials. The quality assurance process included batch monitoring of instrumental background and method blank samples and, where necessary, account was made for any artefacts found.

The method has been optimised, validated and calibrated based on a 57 component certified PAMS hydrocarbon standard gas mixture (Scott Speciality Gases Inc.) and a 65 component certified TO-15 standard gas mixture (Scott Speciality Gases Inc./Air Liquide Ltd/Restek Corporation). PAMS hydrocarbon VOCs are listed in Table 5.2 and TO-15 air toxics VOCs are listed in Table 5.3. The GCFID chromatogram of C_2 to C_4 hydrocarbon subset from the PAMS gas mixture is shown in Figure 5.9, and the GCMS chromatograms obtained from analysis of the PAMS and TO-15 standard gas mixtures are shown in Figures 5.10 and 5.11, respectively.

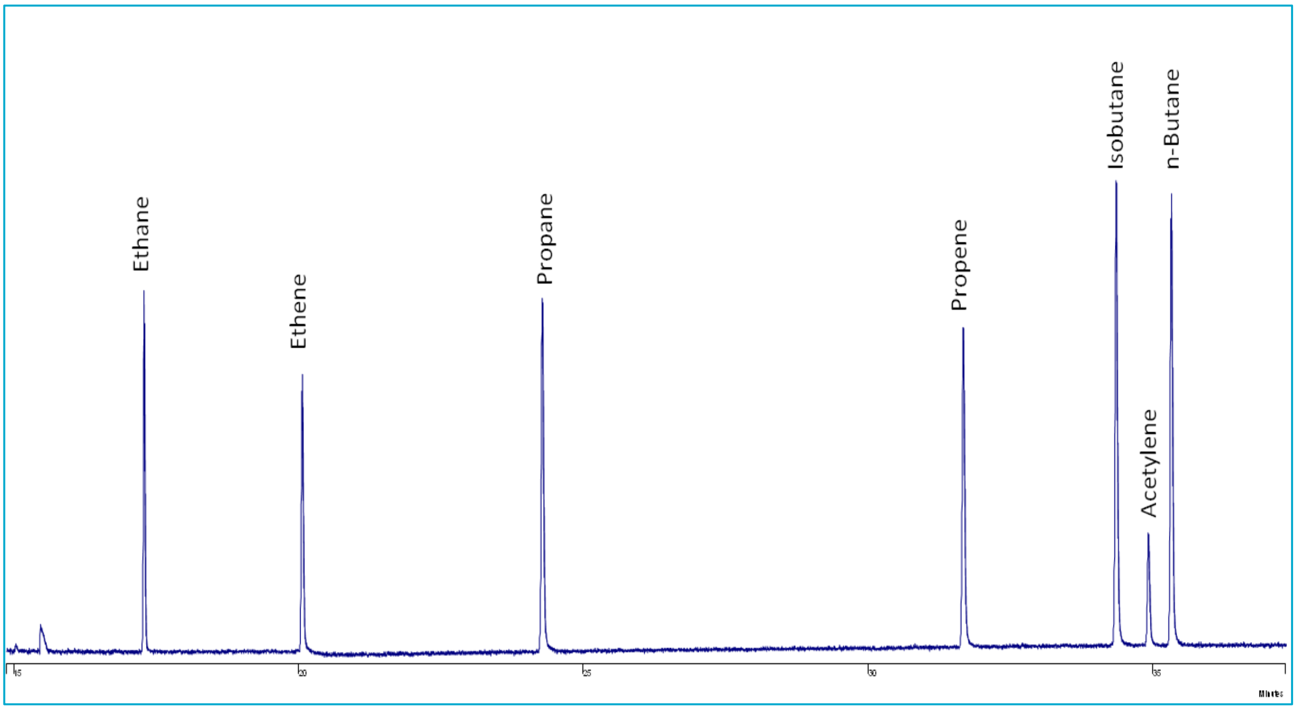

Figure 5.9 Portion of the GCFID chromatogram showing C_2 to C_4 hydrocarbons from the PAMS hydrocarbon standard gas mixture

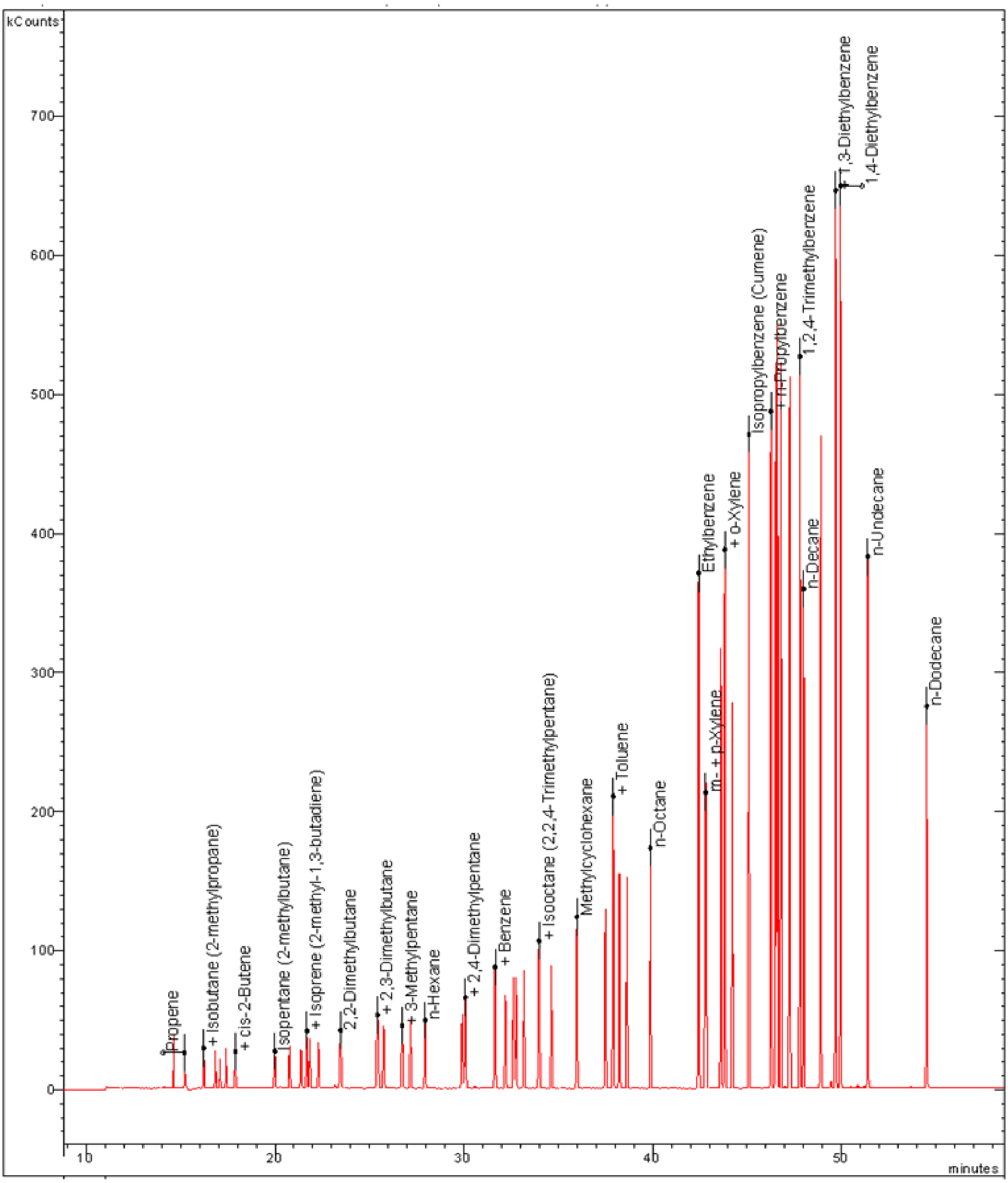

Figure 5.10 GCMS chromatogram of C_3 to C_{12} compounds from USEPA PAMS hydrocarbon standard gas mixture.
Note that all peaks from the 57-component standard are present (as listed in retention time order in Table 5.2). The peaks are labelled in this Figure to a readable size; some peaks are not labelled for the sake of clarity.

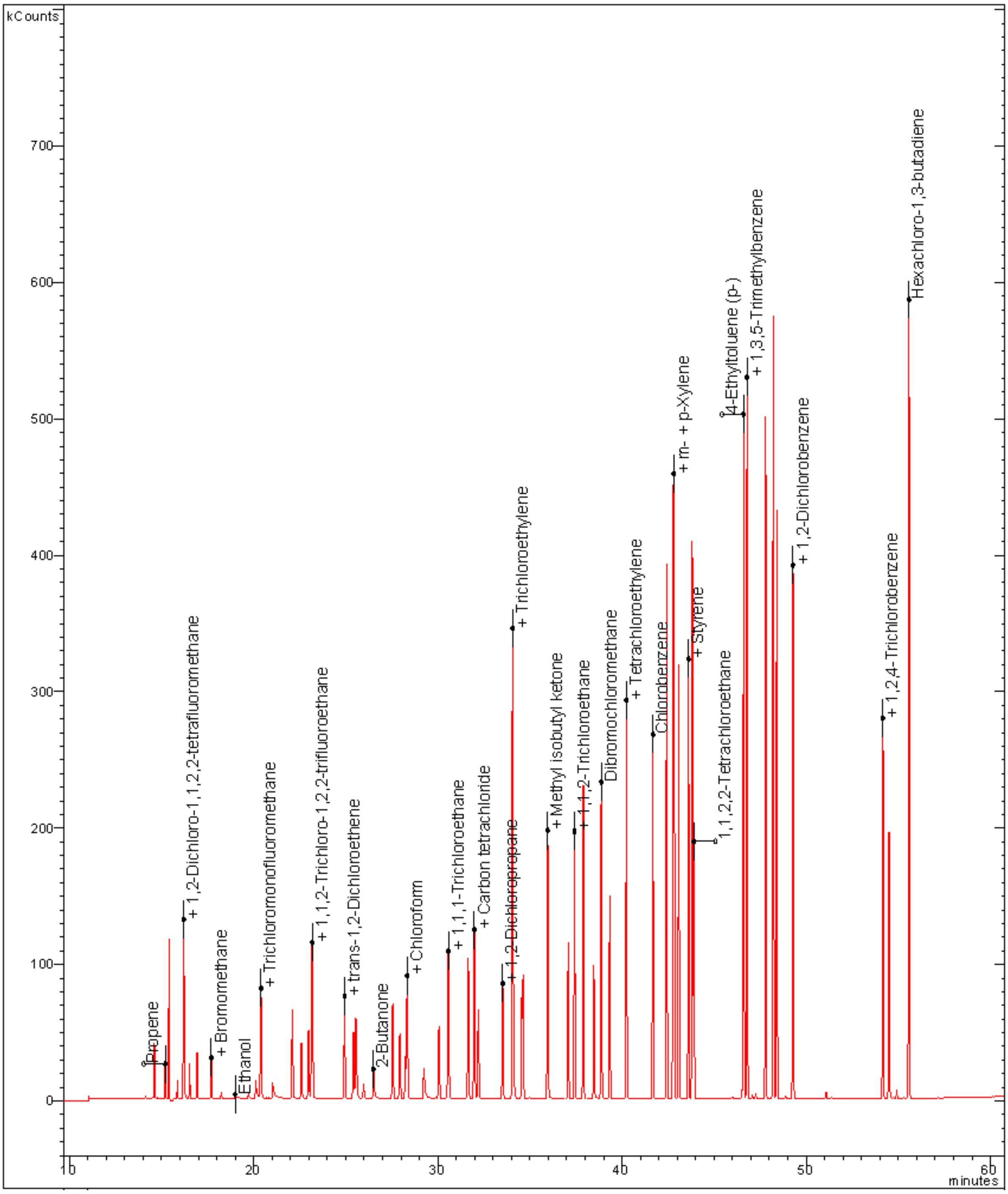

Figure 5.11 GCMS chromatogram from analysis of USEPA TO-15 air toxics VOC standard gas mixture.
Note that all peaks from the 65-component standard are present (as listed in retention time order in Table 5.3) but only some have been labelled for the sake of clarity.

Method Proficiency

The assessment of method proficiency complied with the requirements of the standard methods, and the results of method validation and on-going batch-to-batch quality assurance testing are summarised in the following paragraphs. For ease of reading, the results of method proficiency are reported as an average of all quality control data from GCMS and GCFID analyses of compounds from the PAMS and TO-15 suites. GCFID analysis of C_2 isomers generally returned similar levels of proficiency as GCMS. The exception is the lower sensitivity of the GCFID and hence method detection limits for GCFID are reported separately to GCMS, as described below.

The linearity of concentration was established from a multipoint calibration over the concentration range 1 to 100ppbv with a resultant r^2 value of > 0.99 obtained from the least-squares regression line (average for all compounds). The precision associated with the slope of the regression line (equivalent to the signal response factor) was 5-15% dependent on compound. Polar compounds inherently obtain lower precision due to their reactivity, surface interactions and water solubility (Kelly and Callahan, 1993).

The analytical precision obtained from replicate analysis of the gas standards at nominal concentration (0.98, 3.3, 8.3, 25.0ppbv, dependent on concentration range of individual compounds in the samples) averaged ± 4% RSD. Precision from duplicate analysis of samples at minimal concentration (0.05-0.5ppbv), averaged ± 10% RPD for the target compounds.

Accuracy, as the result from analysis of an independent standard at nominal concentration against the calibration, averaged 90-110% recovery. The compounds that were common to the PAMS and TO-15 standard gas mixtures were routinely compared using the results from calibration and from samples. Acceptable recovery, in the range averaging 85-100%, was found between the two suites. This also tested, to some extent, the validity of the certified mixtures.

The sensitivity of GCMS analysis using ion-trap and extracted ion manipulations allowed detection at concentrations down to parts per trillion by volume (pptv) levels. The minimum concentration achievable is specific for each compound and is primarily dependent on the ions selected for quantitation, ion intensity, presence of co-eluting species and the physical and chemical characteristics of each compound. Many compounds were identifiable at an ambient concentration of 5pptv (0.005ppbv) and, although not statistically relevant at this level, this provided valuable information for the source characterisation aspect of this work. The process of determining detection limits is quite complex and is described for the various aspects of the determination below. Appendix A lists the results of these determinations.

The *instrumental (or instrument) detection limit (IDL)* is the minimum detectable concentration in the sample as it is presented to the instrument's detector. This incorporates the volume of sample taken to the adsorbent trap and any instrumental variables prior to detection, in this case the outlet split ratio at the cold trap. The IDL was determined using both statistical analysis and by examination of chromatographic and mass spectral output, and these methods are described in the following paragraphs.

Statistical determination of the IDL was calculated from 5-replicate analyses of the standard gas mixture prepared at a concentration of 10-fold the expected detection limit (i.e. at a concentration of 1ppbv), as per the criteria for this evaluation. The t-value for 4-degrees of freedom at the 99% confidence interval was applied to the resultant standard deviation to calculate the detection limit for each compound. The statistically derived IDL for the PAMS hydrocarbon compounds ranged from 0.04 to 0.2ppbv and averaged 0.1ppbv across the suite. The IDL for the TO-15 air toxics suite ranged from 0.06 to 0.4ppbv and averaged 0.1ppbv. Results for individual compounds are listed in Appendix A.

An IDL determined from inspection of the chromatographic output is a method in common practice. Here the response of the analyte peak at minimal concentration is compared to the background noise and a detection limit is calculated based on a standard value of signal to noise of 2.5. The GCMS method adopted for this work achieves an analyte response using selected ions for each analyte. This not only provides superior selectivity in a complex ambient air matrix but also effectively minimises contribution of background ions to the analyte signal and hence increases the signal to noise ratio for each compound (i.e. improves the detection limit). Together with the advantage of the ion-trap MS system in also allowing simultaneous full-scan acquisition and mass spectral confirmation of each analyte at the time of peak integration, a higher level of confidence in qualitative compound detection is achieved. It must be understood however, that this does not necessarily mean a higher level of quantitative confidence as the error associated with the integration is the same. The chromatographically derived IDL for the PAMS suite ranged from 0.001 to 0.2ppbv and averaged 0.02ppbv. The IDL for the TO-15 suite ranged from 0.001 to 0.3ppbv and averaged 0.03ppbv.

In the case of the analytes measured by GCFID, the statistical and chromatographically based detection limits are very similar as, with no other means of assessment, the standard deviation of the response equates to the level of background noise. The FID detection limits are therefore higher than those from MS analysis. An average IDL of 0.4ppbv was determined for C_2 compounds measured by GCFID.

The *method detection limit (MDL)* is the value directly applicable to the minimum detectable concentration in the sampled air. In this work, the MDL accounts for pressurisation of the canister sample prior to analysis and therefore applies the appropriate dilution multiplier to the IDL. Additionally, a factor accounting for the effect of background artefacts on the sample detection limit is applied for affected compounds. For this study these factors resulted in a MDL which was generally a 2-fold multiple of the IDL, or somewhat higher for a minimum number of compounds. As a general guide, the MDL for PAMS compounds averaged 0.2ppbv and 0.05ppbv (by statistical and chromatographic derivation, respectively) and 0.3ppbv and 0.07ppbv for TO-15 compounds. Refer Appendix A for MDLs applicable to individual compounds.

The *limit of reporting (LOR)* is a convention that applies a multiplier to the MDL to account for sampling and analytical variables and therefore provides a more conservative and rigorous limit to the reported result. In this work, a 3-fold multiplier is applied to the MDL to determine the LOR.

The results for IDL, MDL and LOR under statistically derived confidence limits and under MS and FID chromatographic evaluation are listed for each compound in Appendix A. Reporting to the detection limit is described in the following sub-section.

Examination of the stability of individual compounds under the conditions of sampling and analysis found a somewhat inconsistent result for carbon disulphide, which is an analyte in the USEPA TO-15 suite. Carbon disulphide appeared somewhat unstable in the sample analysis and it was found in method blanks at somewhat variable concentration. Sulphur compounds are known to be reactive and many species tend to be unstable under canister collection and storage and under cold-trapping and thermal desorption. Variations in sample humidity can also affect the result obtained. As accuracy within the acceptable limits was therefore in doubt, this compound was not included in the reported VOC suite. All other compounds from the PAMS and TO-15 suites met with stability criteria.

VOC Reporting

Where PAMS and TO-15 compounds are common to both standard mixtures, the result from the PAMS suite is reported. As previously discussed, carbon disulphide was the only compound from the TO-15 which was not reported in this study.

The concentrations of target species measured in ambient samples are reported as a mixing ratio in units of parts per billion by volume (ppbv). For ease of reading and uniformity in the text, the term ‘concentration’ will be used as a substitute for the more correct term ‘mixing ratio’.

For emissions characterisation purposes, which is of importance to this project, is it considered acceptable to use the method detection limit obtained from chromatographic inspection as this provides a greater number of compounds on which comparison may be made or on which trends may be shown. It must be emphasised that this requires appreciation of the fact that a higher level of error must necessarily be associated with concentrations at these trace levels and hence a higher level of understanding of the significance of the data is required.

Where no chromatographic or mass spectral signal is observed at the retention time for a compound, or where this signal is less than the chromatographic IDL, the compound is reported as “not detected” (ND).

Note that if the results were to be used for air quality assessment purposes by OEH/EPA, only the data at and above the LOR provide sufficient statistical rigour for this type of assessment. Hence if the results are to be on-reported for air quality assessment or other purposes, only those data which are greater than the LOR can be used, and minimum data must be reported as < LOR.

5.3.5 ANALYTICAL METHODOLOGIES FOR NON-STANDARD COMPOUNDS

Non-standard compounds are those additional to compounds measured as priority VOCs. They may be observed to be present in the sample from canister based VOC analysis or those collected and analysed by sorbent techniques, using methodology described in the following sub-sections. Over 45 non-standard compounds were identified using these techniques, as listed in Table 5.4, and these are tabulated for each source category in the discussion of site results in Section 7.

Non-Standard Compounds by Canister VOC Analysis

The sample chromatograms obtained from the priority VOC analyses were re-examined for non-standard compounds. If a non-standard compound was found its organic characteristics were elucidated using mass spectra and structural library search. Where signal intensity and mass spectral purity allowed, the compounds were identified, else an organic class was determined and assigned to the component. For quantitative measurements, a thorough validation process would be required using authentic reference standards for each compound. Stability of certain species such as sulphur and oxygenated compounds would also require assessment. Whilst samples contained in Silco® treated canisters provided improved stability compared to nickel passivated canisters (Summa® canisters) this aspect would need to be validated for each new compound in order to ensure accuracy in quantitative measurements. As such, the results from these determinations were purely qualitative.

Non-Standard Compounds by Sorbent Tube Analysis

Some trace level compounds, especially sulphur, oxygen and nitrogen containing organics are not amenable to sampling with canisters due to their reactivity and instability on canister surfaces and in the presence of moisture. However, it is possible to collect certain classes of these species using sorbent tubes packed with suitable adsorbent materials (Hunter Daughtrey et al., 2001; Rodriguez-Navas et al*.,* 2012). This technique has the potential to provide additional information to identify compounds specific to particular sources of importance in this study, for example wastewater treatment plants and animal feedlots, which are not necessarily known to emit significant emissions of air toxics. Due to the specificity and complexity associated with both the sampling and instrumental aspects of this technique, this component of the project was designed to be investigative in nature. The sorbent tube methodology was therefore applied to the sampling of ambient air at sites that were found, by the canister analysis, to contain significant levels of non-standard compounds.

The sorbent methodology is based on USEPA TO-17 (USEPA (3), 1999) and uses pumped sorbent tube collection of ambient air, thermal desorption of collected analytes, cryogenic secondary trapping and GCMS analysis. UK Environment Directive LFTGN 04 was also used as guidance for monitoring of trace components in landfill gas (Environment Agency, 2004). The sorbent tubes that were selected for this project contained a combination of sorbent materials, namely; Tenax® and Sulficarb® (previously Unicarb®), from Markes Corporation. A schematic of the sorbent tube is shown in Figure 5.12. The sorbent combination was selected for its inert qualities in the presence of relatively reactive compounds, and for its amenability to collection and desorption of low to mid volatility hydrocarbon, oxygenated, and sulphur containing species which are likely to be relevant to this study. A secondary cold-trap adsorbent was selected to optimise for these compounds of interest and here a proprietary air toxics packing (Markes Corporation) was used.

Where canister results were suggestive of the relevance of the sorbent tube technique, tubes were deployed to those sites at a subsequent visit. Sample collection with a sorbent tube uses a portable sampling unit designed for mass flow controlled pumped sampling. Ambient air is drawn through the sorbent tubes at a calibrated flow rate for a specific time period. Flow rate is optimised for the tube parameters, within the limits of manufacturers specifications, and sampling time is optimised dependent on the physical and chemical nature of the compounds targeted (such as volatility and associated break-through volume) and the likely ambient concentrations of these compounds at the site under test. The sample collection volume must generate the required analyte mass for instrumental analysis. Flow rates of 100-150 mL min^{-1} for 10-20 mins were generally used. Using the sample volume and mass of analyte determined from the analysis the ambient concentration (ppbv) can be determined.

Analysis of sorbent tubes incorporates a thermal desorption stage and for this a Markes Ultra 2™ tube autosampler and Unity 2™ thermal desorption unit (Markes International Ltd) was used. This system is interfaced to the GCMS instrument that comprised a Varian 450-GC gas chromatograph and Varian 240-MS ion trap mass spectrometer (Varian Corporation, now Agilent Technologies Ltd). This instrument differs from the system used for VOCs by canister collection in that it is capable of collecting electron impact ionisation mass spectra as well as chemical ionisation mass spectra, giving it extra advantages in the characterisation of unknowns, as discussed further below. Later in the project the thermal desorption system was interfaced to an Agilent 7890A GC and 7000 series Triple Quad MS (Agilent Technologies Ltd). This instrument operates by different principles in its generation of electron impact mass spectra and provided further insight into the identification of non-standard compounds.

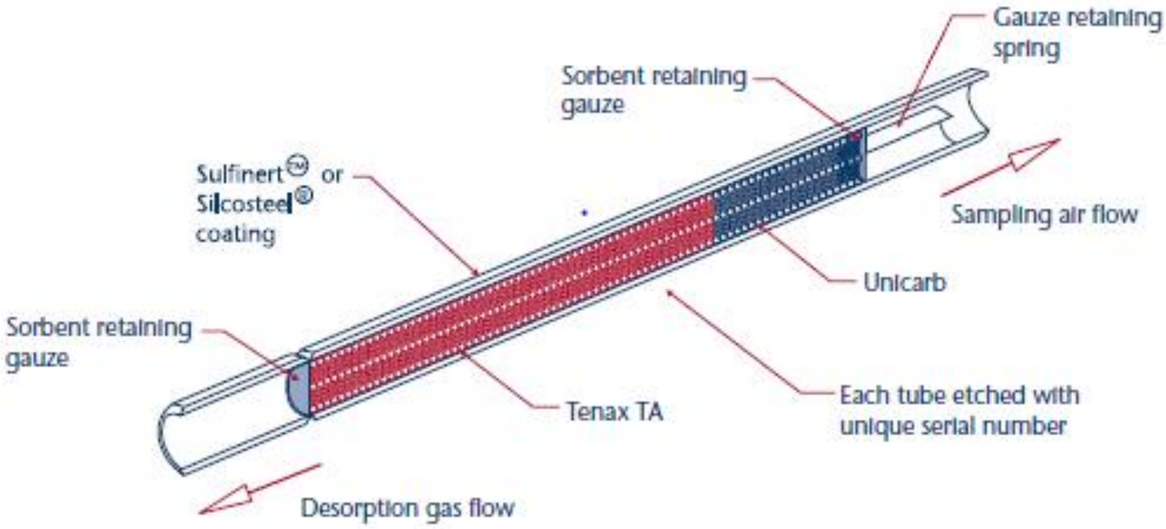

Figure 5.12 Sorbent tube schematic (reference UK Directive, LFTGN 04, EA 2004)

The thermal desorption protocol requires attention to various parameters effecting the efficiency of transfer of analytes through various stages of the process. Variables of temperature, flow and time were tested and optimised for initial purging of air and moisture from the primary collection tube, for desorption of the primary tube, for secondary cold-trapping, for purging residual oxygen from the cold trap, for thermal desorption of the cold-trap, for optimisation of the outlet split and analyte recollection, for control of analyte mass to the GC column and for the focussing of analytes at the head of the column. Chromatographic parameters affecting component separation and mass spectral detection parameters were also optimised. The PAMS and TO-15 standard gas mixtures were used for method optimisation and a system for transfer of aliquots of the gas standards onto the sorbent tubes was developed.

Of importance in the method validation is the observance and minimisation of method and system related artefacts, some of which may present as target species. They may also present as degradation products of collected analytes or from interactions with co-collected species. Equally, loss of target species can occur due to each of these parameters. Artefacts are particularly problematic with sorbent methodologies both in the tube collection phase and the cold-trapping and desorption phases of the methodology (Dewulf et al., 1999). This can be dependent on the type and grade of the material and other factors associated with the methodology such as co-collected species, and temperature and moisture control. Co-collected species, such as ozone, NO_2 and limonene can enhance certain degradation products (Clausen and Wolkoff, 1997) and benzaldehyde, phenol and acetophenone are candidates as Tenax® artefacts (along with others). These are also likely to be found as analytes from certain sources monitored in this project. In this work, sorbent tubes were monitored for sorbent artefacts as both field exposed and laboratory (unexposed) blanks. For example, artefacts in a field blank can be seen in Figure 5.13. These compounds were reported as identified in the sample only when present at greater than 20-times the blank levels. Consideration was also made for their formation in association with co-collected species.

The chromatographic output from desorption of the sorbent tube samples was examined for standard compounds and any additional peaks were then examined using their mass spectra obtained from electron impact ionisation (EI-MS). NIST software was used for mass spectral structure searching and compound matching to gain the identity of the compound. Using the Varian ion-trap mass spectrometer it was also possible to determine the molecular weight of a compound using chemical ionisation as the mode of analysis (CI-MS). The ion-trap uses methanol vapour as the reagent gas and positive ion CI-MS produces a clear mass spectrum containing the $[MH]^+$ ion (the protonated molecular ion) for certain compounds. This provides enhanced sensitivity and specificity particularly for oxygenated and nitrated compounds.

The knowledge of a compound's molecular weight, obtained from CI-MS, together with its EI mass spectra allowed structural elucidation and characterisation of a specific identity, or an organic class, for minor compounds in the source emissions. Using CI-MS it was also possible to search the chromatogram for the $[MH]^+$ ion of particular compounds of interest. Where a hit was found the EI-MS chromatogram was then examined for a peak at the exact retention time and its mass spectra evaluated for purity to the compound of interest. This technique was used to search for characteristic compounds such as odour compounds, for example thiols (mercaptans), various oxygenates, acids and nitrated compounds. This information was drawn from various sources of literature, such as Fang et al. (2012), Rodrigues-Navas et al. (2012) and the UK landfill directive (Environment Agency, 2004). Experience from previous projects undertaken in the assessment of biogenic emissions from eucalypt species also assisted in the identification of monoterpenes and related biogenic compounds (Nelson et al., 2000, Nelson et al. 2004).

In order to attain accurate quantitative results, sorbent tube analysis requires comprehensive validation of such variables as stability, artefact generation, sorbent collection and desorption efficiency, and the optimisation of instrumental parameters. The use of authentic standards for each new compound isolated is also required. However, on the basis that the sorbent is an improved medium for stabilisation of some targeted compounds when compared with canisters, it was considered useful to allow a semi-quantitative estimate of concentration to assist with source characterisation. The response of a similar class of compound, at known concentration, from the TO-15 suite was used for this determination. As the exact response of the compound is not known, the error associated with this approach will be necessarily high. As such, the data reported for the characterisation studies is reported as a range.

Characterisation of ambient samples using the sorbent tube methodology was successful in isolating many of the non-standard compounds identified from the canister characterisation studies as well as a number of additional compounds. The sorbent tube collection showed greater specificity towards monoterpenes and greater selectivity towards the more complex oxygenated compounds and nitrogen and sulphur containing compounds than the canister collected sample.

An example of the successful isolation of non-standard compounds by sorbent tube analysis is shown in Figure 5.13. This figure shows a portion of the chromatogram from the TO-15 air toxics standard gas mixture (plot 1) and the same portion of the chromatogram for samples from Singleton wastewater treatment plant (plot 2), from Summerhill landfill (plot 3) and the field blank (plot 4). A number of additional compounds to that of the TO-15 standard can be seen in the sample chromatograms and some differences in the type of compounds can be seen in those isolated from wastewater treatment compared to the landfill. Figure 5.13 also shows the importance of the field blank and the identification of components associated with the sorbent material itself in order that false positives are not reported as sample components.

Reporting of Non-Standard Compounds

Qualitative compound identification is reported for the characterisation studies undertaken using the canister samples for VOC analysis, as previously discussed.

Semi-quantitative data are reported as a concentration range, in units of ppbv, for the characterisation studies undertaken using sorbent technology. It must be stressed that this result can only be used to provide indicative information of the relative concentration of compounds found at a particular site, or for source comparison.

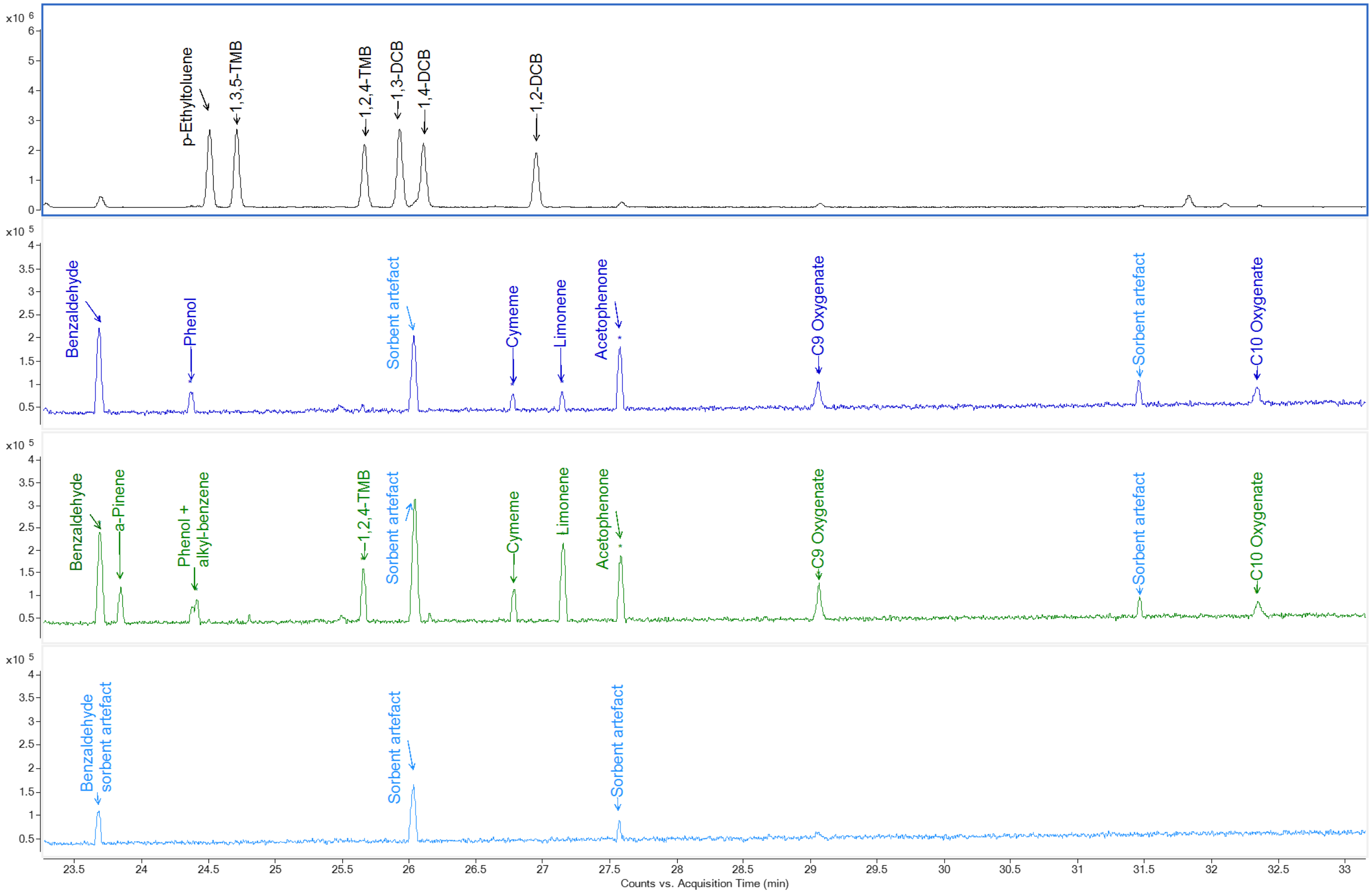

Figure 5.13 Section of EI-MS chromatogram from sorbent tube analysis. Plot 1 (top): TO-15 air toxics standard compounds. Plot 2: Mass spectral identification of non-standard compounds in an ambient sample from Singleton wastewater treatment plant. Plot 3: Summerhill landfill. Plot 4 (bottom): Sorbent artefacts isolated from field blank.

5.3.6 ANALYTICAL METHODOLOGY FOR HYDROCARBON VOCS IN CSG SOURCED WELL GAS

The minor hydrocarbons, that is those above C_5, are not generally measured in well gases, as the focus is usually on determining the composition of the gas as its bulk components (i.e. methane and C_2 to C_5 hydrocarbons), and instrumental techniques are optimised for this purpose. The use of high sensitivity instruments, such as those implemented for VOC analysis in this project, enabled the analysis of minor constituents in the C_5-C_8 hydrocarbon range as well as aromatic compounds, including the air toxics; benzene, toluene and xylenes. All hydrocarbons from the PAMS hydrocarbon VOC suite were targeted and non-methane hydrocarbons (NMHCs) in the range C_2 to C_5 were determined to provide a measure of relative concentration to the C_5-C_8 compounds.

The methodology for VOC analysis in ambient air samples was re-designed for well gas analysis to accommodate the methane sample matrix. The sample presented to the instrument must be substantially composed of nitrogen for operation of mass flow controllers in determining accurate flow and hence the volume of sample delivered for analysis. High levels of methane are also unsuitable in the cold-trapping process and will affect analyte trapping efficiency. Hence well gas samples require dilution to reduce methane concentration. In order to bring the concentration of other bulk hydrocarbons within the linear range of the instrument, large dilutions would be required. However, this would mean that the minor hydrocarbons would be at a concentration well below detectable limits. A compromise was therefore established which focused on the minor hydrocarbons at the expense of accuracy for C_2 to C_5 hydrocarbons. The flame ionisation detector (FID) was used for quantitation of C_2-C_5 hydrocarbons as this detector has a significantly wider linear range than the MS detector and effectively minimises the error due to non-linearity at high concentration. The GCMS was used for the target species due to its higher sensitivity.

The well gas samples collected into IsoTube® canisters for methane and isotope measurements were used for the NMHC determinations. Dilutions of the well gas sample were prepared between 1:1000 and 1:10,000 to assess instrumental requirements as well as determine the sensitivity to trace species in the well gas. A plot comparing the level of dilution to signal strength determined that quenching of the FID was evident where the smaller hydrocarbons were at very high concentration, as was expected. However, the deviation amounted to an error of up to 15% relative standard deviation (RSD) for the C_2-C_5 compounds across the dilutions tested, which was considered acceptable for initial investigation purposes. The 1:1000 dilution was therefore selected to maximise sensitivity to the aliphatic and aromatic hydrocarbons > C_5. The detection limit for this analysis under the parameters used is 7ppbv (0.007ppmv).

It must be emphasised that this method is optimised for the minor hydrocarbon components of the well gas. Hence, at concentrations > 100ppmv, the reported concentrations for C_2-C_5 hydrocarbons are considered semi-quantitative and the results are reported as a guide to the relative concentration of the C_5-C_8 hydrocarbon compounds. The concentrations of bulk constituents in the well gas are determined using the molecular composition analysis (refer Section 5.4.1).

5.4 Isotopic Analyses

A range of methane sources and varying methane concentrations were measured for their molecular and isotopic compositions at the sites listed in Table 5.1 using a range of methods, which are described in the following sections.

5.4.1 GAS SAMPLES

In the scope of the NSW EPA Methane Emissions project, there was a large diversity of gas samples that were scheduled to be taken, ranging from 'clean' air samples containing trace constituents (methane ~1.8 ppm) all the way to more concentrated samples such as landfill biogas (methane ~50-60 %) to commercial reticulated natural gas or coal seam gas taken at the wellhead (methane ~90-99 %). These large concentration ranges necessitated a varied number of sample collection strategies and the associated sample analyses.

The large dynamic range of methane concentrations (6 orders of magnitude) presented quite a challenge to have multiple analysis methods that could handle the concentration range. Prior experience with natural gas, coal seam gas and shale gas analyses for the fossil fuel energy sector meant that samples in the low to 100 % range had well established methodologies where gas was available at positive pressure. Locations and facilities that produced diffuse venting of methane at elevated concentrations would prove to be a challenge, particularly where no gas collection system was available. The biggest problem arose at having to analyse ambient methane concentrations. Although atmospheric scientists regularly measure global atmospheric methane levels at several sites around the globe, the instruments and sampling equipment are custom built and kept ultra-clean to minimise contamination issues (Umezawa et al., 2012). Access to clean air monitoring analytical facilities in Australia was not available. The problem was that no easily accessed facilities exist to measure high precision isotopes of methane at ambient air levels within an 'industrial landscape' full of heavier hydrocarbons, non-target volatile organic compounds and elevated levels of other permanent gases such as carbon dioxide, carbon monoxide, hydrogen sulphide, etc. To this end, an experimental program was enacted to investigate whether a prototype instrument could be built to achieve the stated aims; tailored for gas samples taken from rural/urban/industrialised environments.

For low level methane concentrations in ambient air, samples were collected for isotopic analyses using the same type of passive stainless steel canisters used for sampling of VOCs, which are described in Section 5.3.4. At the sampling site, grab samples or time averaged samples were then taken by varying the rate of atmospheric in-rush into the canister from the initial vacuum pressure in the canister. At the laboratory, samples were pressurised with helium to provide a positive pressure above atmospheric levels thus allowing several sample aliquots to be taken without isotopic fractionation (which progressively occurs as a gas sample in a rigid container is withdrawn causing the pressure to drop below atmospheric pressure, (Eby et al., 2015). The other alternative is to use an oil free piston compressor with stainless steel tanks fitted with stainless steel dip tubes and a double valve configuration to enable thorough flushing prior to sampling (Lowe et al., 1991). The later technique has the added advantage of being able to produce pressurised samples (typically 3 to 7 Atmospheres), thus ensuring sufficient volumes of sample to allow multiple aliquots to be taken.

With the more concentrated samples, multilayer composite material foil lined gas sampling bags (SKC Inc.), single use disposable aluminium canisters (Isotech Laboratories Inc.) and stainless steel sample cylinders (Swagelok Company) were utilised. Careful selection of sample containers was necessary as not all containers had sufficient integrity to limit diffusion and micro-leakage of the contents out or atmospheric contamination in; parameters critically important for stable isotope analyses. A prior CSIRO internal study on gas stability for carbon isotopes on a CH_4/CO_2 mixture found that from several different gas sample containers routinely encountered, 50 % fractionated the gas such that the results were erroneous and would have distorted the stable isotope interpretation. The main sources of fractionation were due to adsorption on wall material (CO_2 in Tedlar™ type gas bags), micro-leakage through glass vials with rubber septa (puncturing of septa by syringe needles never fully reseals) or micro-leakage with aluminised plastic bladders (originally designed for liquids, not gas samples).

Gas samples associated with water columns such as swamps and flooded rice paddocks required the use of bubble traps or custom liquid/headspace sampling jars from Isotech known as Isojars™. The bubble traps consisted of an inverted container from which the air could be displaced by water and then allow the accumulation of individual bubbles until a sufficient volume of sample gas was present. A small manifold at the top of the trap then allowed the gas to be moved to a gas sample container using hydrostatic pressure of the water column to produce a sufficient differential gas pressure, easily achieved by lowering the bubble-trap into the water column. The advantage of this sampling strategy allowed for gas to be collected with no water phase which would contain bacteria and organisms that would otherwise alter the gas mixture upon transport/storage. The disadvantage was that for very slow bubble formation (i.e. swamps, rice paddies and sewage settling ponds), days to weeks of accumulation could be required to achieve an isotopically equilibrated headspace gas. At industrial facilities, leaving long term bubble traps and a subsequent second trip to retrieve gas is not always feasible due to logistics and resourcing.

The use of Isojars allowed a grab sample of the water/sediment/gas bubbles to be taken quickly. Where sufficient gas bubbles can be sampled into the Isojar, the sealed system can then be injected with a bactericide to halt any further microbial re-work of the sample and kept refrigerated prior to laboratory gas analysis. For other Isojar samples where the sampling conditions prevent capture of any significant amounts of venting gas, water/sediment/mud could also be collected as a sealed microcosm container and a headspace created by injecting helium gas and withdrawing the same volume of water. Incubation at site temperature conditions allows methane to be generated insitu within 4-8 weeks, allowing sufficient methane to be generated for analysis; although not exactly the same as trapping methane gas in the field, the sealed microcosm can be used to produce analogous gas samples representative of the sampling location.

5.4.2 ANALYTICAL METHOD FOR GC-IRMS ANALYSIS OF GASES FOR C-ISOTOPES

The carbon isotopic composition of gases was measured by GC-C-IRMS (gas chromatography/combustion/isotope-ratio mass spectrometry). The GC-C-IRMS system consisted of a GC unit (6890N, Agilent Technologies, USA) connected to a GC-C/TC III combustion device coupled via open split to a Delta V Plus mass spectrometer (ThermoFisher Scientific, Germany). The analytes of the GC effluent stream were oxidised to CO_2 and H_2O in the combustion furnace held at 1000 °C on a CuO/Ni/Pt catalyst. Water was removed on-line by a Nafion membrane and the CO_2 was transferred to the mass spectrometer to determine carbon isotope ratios. 20-100 µL of sample gas was injected to the split/splitless inlet system (Agilent Technologies, USA), working in split mode (20:1 ratio). The inlet was held at a temperature of 200 °C. The gas components were separated on a fused silica capillary column (PoraPlot Q, 25 m x 0.32 mm ID, Varian). The GC was held isothermally at 40 °C. Helium was the carrier gas, set to a constant pressure of 14.3 psi. All gas samples were measured in duplicate with a standard deviation of ≤0.5 ‰ for the standards and samples. The quality of the carbon isotope measurements was checked regularly by measuring secondary standards of pure CH_4 and CH_4/CO_2 mixtures with known isotopic composition as determined by inter-comparison on dual bellows inlet mode on a Finnigan MAT 252 against international primary carbonate standards prepared by the phosphoric acid method.

In addition to the IRMS analyses, some samples were analysed for C isotopes using Picarro CRDS instruments. These instruments and the methods used are described in Section 8.3 of this report.

5.4.3 ANALYTICAL METHOD FOR GC-IRMS ANALYSIS OF GASES FOR H-ISOTOPES

The hydrogen isotopic composition of gases was measured by GC-TC-IRMS (gas chromatography/temperature conversion /isotope-ratio mass spectrometry). The GC-TC-IRMS system consisted of a GC unit (6890N, Agilent Technologies, USA) connected to a GC-C/TC III interface device coupled via open split to a Delta V Plus mass spectrometer (ThermoFisher Scientific, Germany). After passing through the GC, hydrocarbons were reduced to H_2 and elemental carbon in the temperature conversion reactor held at 1450 °C. H_2 was transferred on-line to the mass spectrometer to determine hydrogen isotope ratios. 20-200 µL of sample gas was injected to the split/splitless inlet system (Agilent Technologies, USA), working in split mode (20:1 ratio). The inlet was held at a temperature of 200°C. The gas components were separated on a fused silica capillary column (PoraPlot Q, 25 m x 0.32 mm ID, Varian). For CH_4 analysis, the GC was held isothermally at 40°C. Helium was the carrier gas, set to a constant pressure of 14.3 psi. All gas samples were measured in duplicate with a standard deviation of ≤3 ‰ for most of the compounds and samples. The H_3^+ factor was determined daily by measuring 10 reference gas peaks with increasing amplitude. This factor had an average value of 2.487 ± 0.056 ppm/nA. The quality of the hydrogen isotope measurements was checked regularly by measuring secondary standards of pure H_2 and pure CH_4 with known isotopic composition as determined by inter-comparison on a TC-EA against international primary solid hydrogen isotope standards.

5.4.4 ANALYTICAL METHOD FOR GC-IRMS ANALYSIS OF GASES BY A CRYOGENIC CONCENTRATOR

The analysis of atmospheric CO_2 at ~400 ppm was measured by conventional GC-IRMS and involved a 2 mL injection on the GC with a low split (5:1 ratio); this represented the lower concentration range that was achievable by direct injection. Analysing methane at typical atmospheric concentrations (~1.8 ppm) was not possible due to the IRMS detection limits for quantitative and linear results. In order to achieve suitable signal to noise ratios for methane and other hydrocarbons at such trace levels, a cryogenic concentrator was designed as a module to the front end of the GC-IRMS. The concentrator consists of three Valco valves and a cryogenic micro-trap utilising Poraplot Q packing material (100-120 mesh size) in a continuous flow of helium carrier gas. A splitless injection of sample (~20-50 mL air) is then passed through the trap at liquid nitrogen temperature while the carrier gas is vented. Following sufficient trapping time to flush the entire sample through, the microtrap is then put in-flow into the GC-IRMS. Ballistic heating of the micro-trap to 200°C then releases the components in a rapid manner, ensuring high signal to noise ratio peaks are available for GC-IRMS analysis. The analysis of the components by carbon and hydrogen isotopes using separate injection/analysis runs then follows the established isotope methods described previously.

5.5 Molecular Composition Gas Analyses

Certain samples collected during the course of the project had relatively high concentrations of methane present and hence were amenable to analysis using a dedicated natural gas analyser, which is based on an Agilent Technologies 6890N gas chromatograph. The gas sample container (i.e. FlexFoil bag, Isotube or stainless steel cylinder) was connected to the vacuum manifold on the Agilent GC to evacuate the air dead-volume. Then the gas sample was introduced through the vacuum manifold into a sample loop (0.25 mL) at atmospheric pressure for GC analysis on an Agilent 6890N Natural Gas Analyser, with a thermal conductivity detector (TCD). Four packed columns with Valco valve column switching are used to separate the gases, a 2 foot 12 % UCW982 on PAW 80/100 mesh (pre-column), a 15 foot 25 % DC200 on Paw 80/100 mesh, a 10 foot HaysepQ 80/100 mesh and a 10 foot Molecular Sieve 13X 45/60 mesh column. The oven was isothermally maintained at 90 °C throughout the 20 minute run. The amount of separated gas components was determined against an external standard calibration. At 90 °C, oxygen and argon co-elute on the 13X molecular sieve column to form one combined peak.

6 Results and Observations – Methane Emissions

Fifteen generic test sites covering a range of activities and locations were identified in the project brief for monitoring (refer to Section 5.1 for details on the selected sites). Specific sites were selected where possible to cover the range of activities required but also to provide a geographic distribution across NSW. As a result, many of the sites were hundreds of kilometres apart, which required careful planning to address logistical issues. Moreover, during the initial stages of the project it became apparent that measuring CH_4 emission rates from many of these sites would be challenging, with certain site-specific factors requiring consideration. Factors such as the local topography, presence of buildings and other infrastructure at and around the test sites, local weather conditions, land access, operations at test sites, all had the potential to affect measurement. Consequently, emission measurements generally required specific methods tailored for each site. To assist in method development, two sites that were close to the CSIRO Newcastle laboratories were selected to trial different approaches to measuring emissions (Summerhill Waste Management Centre and the Singleton Wastewater Treatment Plant). Accordingly, these sites were visited more frequently than most of the others selected for investigation.

Because of the number of sites and their geographic distribution along with the time constraints of the project, it was not possible to make CH_4 flux measurements at all sites (such as coal mines) as originally intended. Where we were unable to measure emissions directly, other techniques were used to estimate emissions based on accepted methodology. A summary of the site visits is shown in Table 6.1. The location of each site is also shown in Figure 6.1.

Table 6.1. Dates of field measurements made at each site.

Site	Autumn	Winter	Spring	Summer	Total Site Visits
Camden Gas Project	16/3/2016	19/8/2015	20/11/2015	12/1/2016	4
Gloucester Gas Project	21/3/2016	16/7/2015	23/9/2015	19/1/2016	4
Narrabri Gas Project	5/5/2015, 6/5/2015	21/7/2014, 28/7/2015, 29/7/2015	15/9/2015, 16/9/2015	9/2/2016, 10/2/2016	9
West Casino Gas Project	11/5/2015	25/7/2014	7/11/2014	25/2/2015	4
Parkes Waste Facility	23/4/2014	28/8/2014	No spring visit	3/12/2014, 19/2/2015	4
Summerhill Waste Management Centre	9/4/2015	1/7/2014, 16/7/2014, 7/8/2014, 9/7/2015	8/10/2014,	26/2/2015, 27/2/2015, 4/2/2016, 23/2/2016	10
Yanco Agricultural Institute	21/4/2015	4/8/2015	14/10/2014, 15/10/2014	1/12/2014, 2/12/2014, 22/12/2014, 23/12/2014, 18/2/2015	9
Rix’s Creek Coal Mine	14/4/2015	22/7/2015	10/10/2014	18/2/2016	4

Site	Autumn	Winter	Spring	Summer	Total Site Visits
Wambo Coal Mine	No autumn visit	15/7/2015	29/9/2014, 21/10/2015	18/2/2015, 17/2/2016	5
Singleton Wastewater Treatment Works	26/3/2015	2/7/2014, 20/8/2014, 8/7/2015	9/9/2014, 2/10/2014, 31/10/2014	11/12/2014, 28/1/2015	9
Dubbo Wastewater Treatment Plant	4/5/2015	28/8/2014	11/11/2015, 12/11/2015	23/2/2015, 24/2/2015	6
Wagga Wagga Narrung Street Wastewater Treatment Plant	21/4/2015	26/8/2014	19/11/2015	17/2/2015	4
Picton Wastewater Treatment Plant	29/4/2015	6/8/2014	25/11/2015	13/1/2015	4
Jindalee Feedlot	22/4/2015	28/8/2014	18/11/2015	16/2/2015	4
Yaegl Nature Reserve	7/5/2015	12/7/2014	6/11/2014	25/2/2015, 26/2/2015	5
Camden Surveys[1]	29/4/2015	6/8/2014	20/11/2014	25/2/2015	4
Cuba State Forest	21/4/2015	4/8/2014	14/10/2014	2/12/2014, 18/2/2015	5

Note 1 – The Camden surveys did not include well pad measurements.

The results of the CH_4 field measurements are presented in the following sections.

6.1 Regional Surveys of Ambient CH_4 Concentration

During the project, mobile surveys were made using the Picarro analyser. While the vehicle was driven to and from test sites, the Picarro gas analyser was often operated to measure ambient CH_4 concentrations across NSW over about an 18-month period between July 2014 and November 2015. Measurements were mostly made during daylight hours from early morning to late afternoon, although some night time data were also collected. More than 25,000 km of such surveys were undertaken during the project (Figure 6.1). Most of these surveys were made while driving on public roads but measurements were sometimes made on private land near the selected facilities.

Figure 6.1. Map showing the routes of the mobile surveys. The selected sampling locations are also shown.

The results of the surveys are summarised in Figure 6.2 where the hourly average of CH_4 concentration are plotted for the period between June 2014 and December 2015. A large amount of data was also collected when the vehicle was engaged in measurements at the selected sampling sites but these are not included in the surveys because the CH_4 levels during these operations were generally much higher (often tens or hundreds of ppm) than background and were not representative of regional ambient CH_4 concentrations. The data in Figure 6.2 are presented on a dry basis (i.e. corrected for atmospheric moisture) to allow comparison of data measured under different humidity conditions. For comparison, data from the CSIRO atmospheric baseline monitoring stations at Cape Grim in Tasmania and Cape Ferguson in Queensland are also plotted.

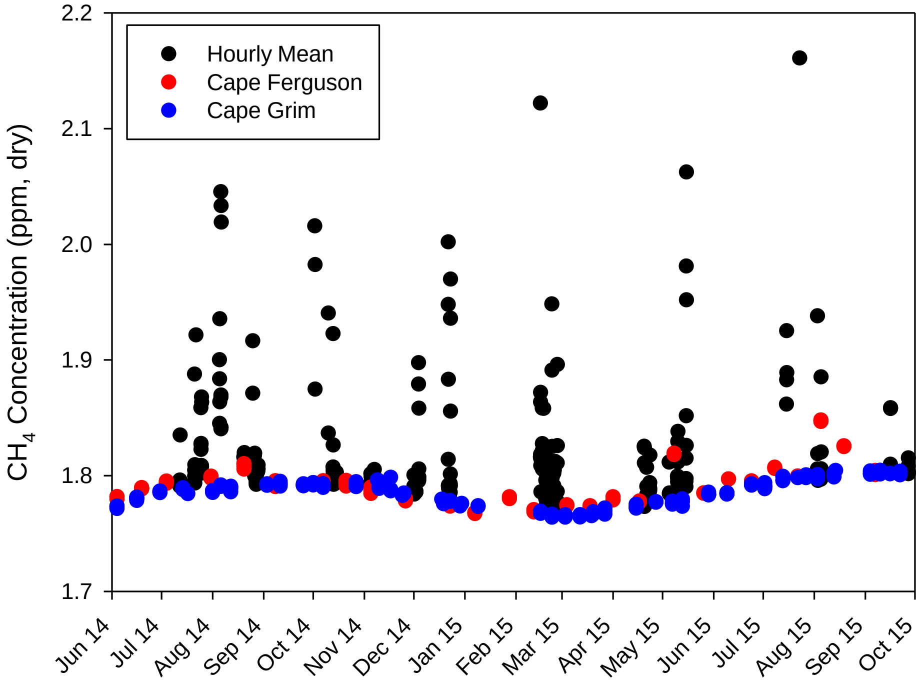

Figure 6.2. Hourly averaged CH_4 concentration data from mobile surveys for all monitored hours (black markers). Data from the baseline monitoring stations at Cape Grim (blue markers) and Cape Ferguson (red markers) are also shown.

In general, the hourly averages tend to cluster close to the baseline data measured at Cape Grim and Cape Ferguson; however it is obvious that there are many occasions when the ambient CH_4 concentrations measured during the survey were significantly higher. In many cases, this can be attributed to atmospheric conditions where CH_4 was more concentrated in the near surface layer during still early morning or night time conditions. To remove this effect, we filtered the data to include only those measured during the hours of 11 am to 4 pm local time when atmospheric mixing was highest. The scatter in the results was significantly reduced but nevertheless there were many occasions when the ambient levels were somewhat higher than baseline.

Almost all of the mobile surveys originated from Newcastle (the location of the CSIRO Energy Centre) and often passed through the Hunter Valley, which is one of Australia,'s main coal producing regions. Hence, it is not unexpected that ambient CH_4 levels along the main roads through the Hunter region are elevated compared to normal background levels in NSW, especially since many mines are adjacent to the roads. This high level of ambient CH_4 is not representative of NSW in general so the hourly data were further filtered to remove those surveys made through the coal producing region of the Hunter Valley. These data are shown in Figure 6.3, along with the Hunter Valley only data (green markers).

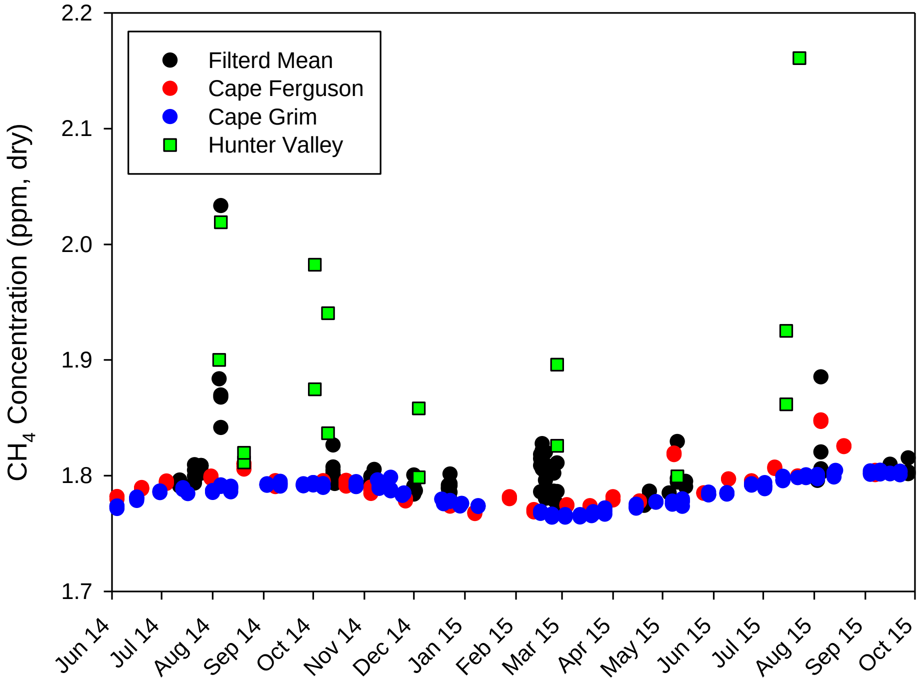

Figure 6.3. Hourly averaged CH_4 concentration data from mobile surveys collected between the hours of 11 am and 4 pm local time (black markers). Data from the Hunter Valley are shown separately (green markers).

In this case, the ambient levels are much closer to the baseline monitoring stations although there are still a number of occasions when substantially elevated levels of CH_4 were observed. These mostly corresponded to surveys through the metropolitan area of Sydney. Urban areas typically have higher CH_4 concentrations than non-urban areas (Blake, et al., 1984; Lowry et al., 2011; Phillips et al., 2013) although many of the peaks observed were clearly associated with nearby local sources. The Hunter Valley-only data in Figure 6.3 (green markers), clearly showing the generally higher levels compared to elsewhere in the state.

While the hourly mean CH_4 concentrations were generally well below 2 ppm, there were often short periods when much higher concentrations were measured. The highest ambient CH_4 recorded during the mobile surveys was 28.0 ppm or more than 26 ppm above ambient levels. Usually, these CH_4 concentration excursions lasted only a few seconds, although there were other occasions when elevated levels were measured over prolonged periods (e.g. through the Hunter Valley). Of the mobile data, which were collected over more than 300 hours, there were 102 instances where the peak CH_4 concentration exceeded 2 ppm, 31 above 3 ppm, 20 above 4 ppm, 16 above 5 ppm and 6 above 10 ppm. The top 20 source locations detected during this project (where the peak 3-second average CH_4 concentration was above 3.2 ppm) are listed in Table 6.2 where the maximum CH_4 concentration, location and description of the likely source are shown.

Table 6.2. Details of the top 20 peak CH_4 concentrations detected during the mobile surveys. The likely source is also indicated (note that site visits to these locations were not made). The CH_4 concentrations were averaged over 3-seconds and are reported on a dry basis.

Date	Maximum CH_4 (ppm, dry)	Location	Notes
26/02/2015	27.987	-32.9578, 151.5428	The source was the underground coal mine vent shaft next to M1 near Wakefield
6/08/2014	21.533	-33.1107, 151.4615	The source was the underground coal mine vent shaft and gas drainage facility adjacent to M1 near Morisset
19/11/2015	19.192	-34.1803, 150.7245	The source was the underground coal mine vent next to Hume Motorway at Douglas Park.
23/04/2015	18.220	-32.5447, 150.997	The source was immediately obvious but was likely to have been due to coal mining operations next to Golden Highway, west of Singleton
20/07/2014	15.291	-32.4281, 151.0517	The source was the underground coal mine vent shaft next to New England Hwy near Ravensworth
22/02/2015	14.796	-32.8239, 151.5938	The source was the underground coal mine vent shaft next to John Renshaw Drive near Beresfield
17/11/2015	14.675	-34.4451, 147.533	Sharp peak in Hoskins Street, Temora. Source unknown.
23/12/2014	14.075	-33.8224, 150.8529	The source was the Eastern Creek Waste Management Centre adjacent to M7.
23/04/2015	8.629	-32.9701, 151.6887	Large peak in suburban Charlestown (Newcastle) against a generally high background during early evening. Source unknown.
23/12/2014	8.235	-35.1201, 147.3779	Very narrow peak over railway at Wagga Wagga. Unknown source.
14/04/2015	6.841	-32.5992, 151.1992	Broad peak on New England Hwy near Singleton against a generally high background. Possibly from coal mining operations elsewhere in the Hunter Valley.
14/07/2015	6.109	-32.583, 151.0111	Emissions from coal mining operations near Wambo coal mine
19/02/2015	5.130	-33.419, 149.61	Sharp peak in Kelso on Great Western Hwy. Source unknown.

Date	Maximum CH_4 (ppm, dry)	Location	Notes
19/02/2015	4.819	-33.6349, 150.78	Hawksbury Waste Management Centre adjacent to Blacktown Rd, South Windsor.
20/07/2014	4.486	-32.6477, 151.2492	Broad peak off high early morning background on New England Hwy. Source not clear but possibly from coal mining elsewhere in the Hunter Valley.
5/08/2014	3.726	-34.0471, 150.7605	Broad peak in Narellan off high early morning background. Source unknown.
28/08/2014	3.721	-32.2166, 148.6331	Abattoir along Yarrandale Rd Dubbo
13/10/2014	3.617	-34.2442, 150.659	Hume Motorway near Pheasants Nest Bridge. Source unknown.
6/08/2014	3.311	-34.1828, 150.6074	Argyle Street, Picton. Source unknown.
23/12/2014	3.249	-33.7904, 151.1356	M2 adjacent to Macquarie Park Cemetery. Source unknown.

It is important to note that these sites represent only those where the highest CH_4 instantaneous (i.e. 3-s average) ambient concentrations were detected. However, high CH_4 levels alone do not necessarily correspond to large emission sources. The peak concentrations measured here are as much a function of the proximity to the source and prevailing atmospheric conditions as they are to the relative size of the source.

One of the most common CH_4 sources encountered during mobile surveys conducted within this project was coal mining activities, in particular emissions from underground mine ventilation shafts in the Hunter region but also in the Illawarra. These facilities typically have outlet flow rates of 200 m^3 s^{-1} or more with up to about 1 % (10,000 ppm) CH_4 in the vented airstream. Because they are frequently within 200 m of roads, they were often readily detected by the surveys. As discussed previously, coal mining operations, including open-cut mining, resulted in elevated CH_4 levels in the Hunter Valley, with broad CH_4 peaks often detected during still, early morning conditions along the New England and Golden Highways.

Many of the sites listed in Table 6.2 were surveyed a number of times throughout the project period and while in most cases the emissions were detected during each survey (except when wind conditions were unfavourable), the maximum concentrations measured on each occasion differed markedly. For instance, CH_4 concentrations near the vent located near Wakefield, varied between 28 ppm and 3.5 ppm. This is a clear demonstration that caution must be exercised when interpreting concentration data in relation to emission sources.

Apart from coal mining, waste management facilities also often resulted in locally high CH_4 concentrations. In Table 6.2 above, the Eastern Creek and Hawksbury facilities both in the outer Sydney metropolitan area yielded amongst the highest CH_4 levels detected (excluding underground mine vents). Although not shown in Table 6.2, other landfills, wastewater treatment plants and intensive agriculture facilities located close to the survey routes also yielded elevated CH_4 levels when the wind conditions were suitable.

In addition to numerous CH_4 concentration maxima that could be attributed to particular sources, there were also many CH_4 peaks encountered throughout the surveys where the emission source was not obvious and could not be identified. Some of these were significant such as those shown in Table 6.2. In Temora, for instance, a large peak of 14.7 ppm CH_4 was detected whilst driving on the main street through the town. A similar narrow CH_4 peak was found in Wagga Wagga with a maximum of more than 8.2 ppm on the Sturt Highway near the railway overpass. Both the Temora main street and Wagga Wagga railway bridge peaks were found on several repeat visits to each site but at different concentrations. A significant unexplained CH_4 peak of 5.1 ppm was also found in Kelso (near Bathurst) but only one visit was made to this location.

Previous measurements made by this laboratory during 2013 have also found high levels of CH_4 in urban areas in Stockton (near Newcastle) that could not be explained by other local sources such as coal handling operations. Figure 6.4 shows a survey of the Stockton area where measurements conducted over several days revealed local CH_4 concentrations of up to 22 ppm. The peaks were generally very sharp suggesting localised, and numerous, sources within a relatively small area. Although CH_4 emissions were detected near the Kooragang Island coal loading facility, the low levels detected could not account for the high concentrations measured throughout Stockton.

Figure 6.4. Mobile survey of CH_4 concentration in the Newcastle region near Stockton. The maximum CH_4 3-s average peak measured in Stockton was approximately 22.0 ppm.

One possible explanation for the unattributed urban peaks encountered during this project is leakage of gas from natural gas distribution infrastructure. This could include high pressure mains but also domestic connections or even appliances. Methane emissions from leaking gas distribution systems is well known; Carras et al. (1991) reported significant gas loss from the Sydney reticulation system during the early 1990s. More recently, Phillips et al. (2013) found urban pipeline leakage throughout Boston in the United States, using ground based surveys similar to those used in the present study. A team from the University of NSW and Royal Holloway University of London also using mobile surveys recently reported elevated CH_4

concentrations throughout Sydney and various country towns, which they attributed to leaking gas distribution pipe networks (Kelly et al., 2015).

At this stage, the sources of the high urban CH_4 concentration peaks found during this project and elsewhere remain speculative but is an area that warrants further investigation to locate and quantify these sources.

6.2 Natural Sources

Initial measurements were made at Yaegl Nature Reserve which was a site selected by the EPA to represent a natural wetland. Additional measurements were also made throughout the project within Cuba State Forest, on the banks of the Murrumbidgee River (approximate sampling site location 34.60°S, 146.08°E). This site was selected by CSIRO staff primarily to provide a background site for comparison with the VOC surveys conducted around Camden (see Section 7.4) but also as a natural site largely unaffected by industrial or vehicle emissions. Limited measurements were also made in Bongil Bongil National Park, south of Coffs Harbour (approximate sampling site location 30.420°S, 153.033°E) during February 2015.

Yaegl Nature Reserve is a small protected area of melaleuca forest on the floodplain of the Clarence River, approximately 2 km west of the town of MacLean. It is mostly wetland with an area of 313 ha which is bounded by the Pacific Highway to the northwest and urban development and agricultural land on the other borders. There are no tracks within the reserve and consequently vehicle access is very limited. For this project, best access was via Fallows Lane that ran along the western edge of the reserve (Figure 6.5); however, this road was impassable during wet weather. Some limited vehicle access for flux chamber measurements was also available at one point on the southern edge of the reserve.

Because of the limited access to the reserve, mobile surveys were only conducted on public roads. The routes taken are shown in Figure 6.5. In general, the ambient CH_4 levels near the wetland were indistinguishable from concentrations measured away from the reserve. A summary of the average CH_4 concentrations measured during each survey is shown in Table 6.3. Because of the proximity to roads and urban areas, it is important to note that this site may not be indicative of more remote natural areas, especially in relation to VOC emissions (which are discussed in Section 7.1.1).

Table 6.3. Summary of the ambient CH_4 concentrations measured in and around Yaegl Nature Reserve.

Survey Date	Time	CH_4 Concentration (ppm, dry basis)			Notes
		Mean	Minimum	Maximum	
12 July 2014	9:14 am to 12:14 pm	1.8257	1.8059	1.9309	Ground was quite dry; little free water
6 November 2014	6:15 am to 2:52 pm	1.8000	1.7926	1.8895	Heavy rain the previous night; ground was very wet
25 February 2015	10:38 am to 3:22 pm	1.7802	1.7631	1.9193	Heavy rain had occurred during the previous week. The ground was saturated with large amount of free water.
26 February 2015	6:52 am to 8:22 am	1.9411	1.8794	1.9929	Conditions as described above. Survey made only in early morning.
7 May 2015	7:24 am to 10:19 am	1.8086	1.7944	2.3150	Very wet conditions due to recent rain.

Except for the result found on 26th February 2015, the mean CH_4 concentrations exhibited slight seasonal variation similar to that observed in the regional survey results where higher CH_4 levels occurred during the cooler months. However, the results from the 26th February (red trace in Figure 6.5) yielded a mean concentration over the survey of about 160 ppb or about 9 % higher than that measured on the previous day (25th February). This apparent anomaly is due to the time of the survey. Most of the other surveys were conducted over the entire course of a day when atmospheric mixing was highest. The survey made on the 26th February, on the other hand, was made during the early morning between about 7:00 and 8:20 am local time, under cool still conditions. Note that similar elevated CH_4 levels were also usually encountered on other surveys made at various other locations under these conditions, especially during the cooler months of the year.

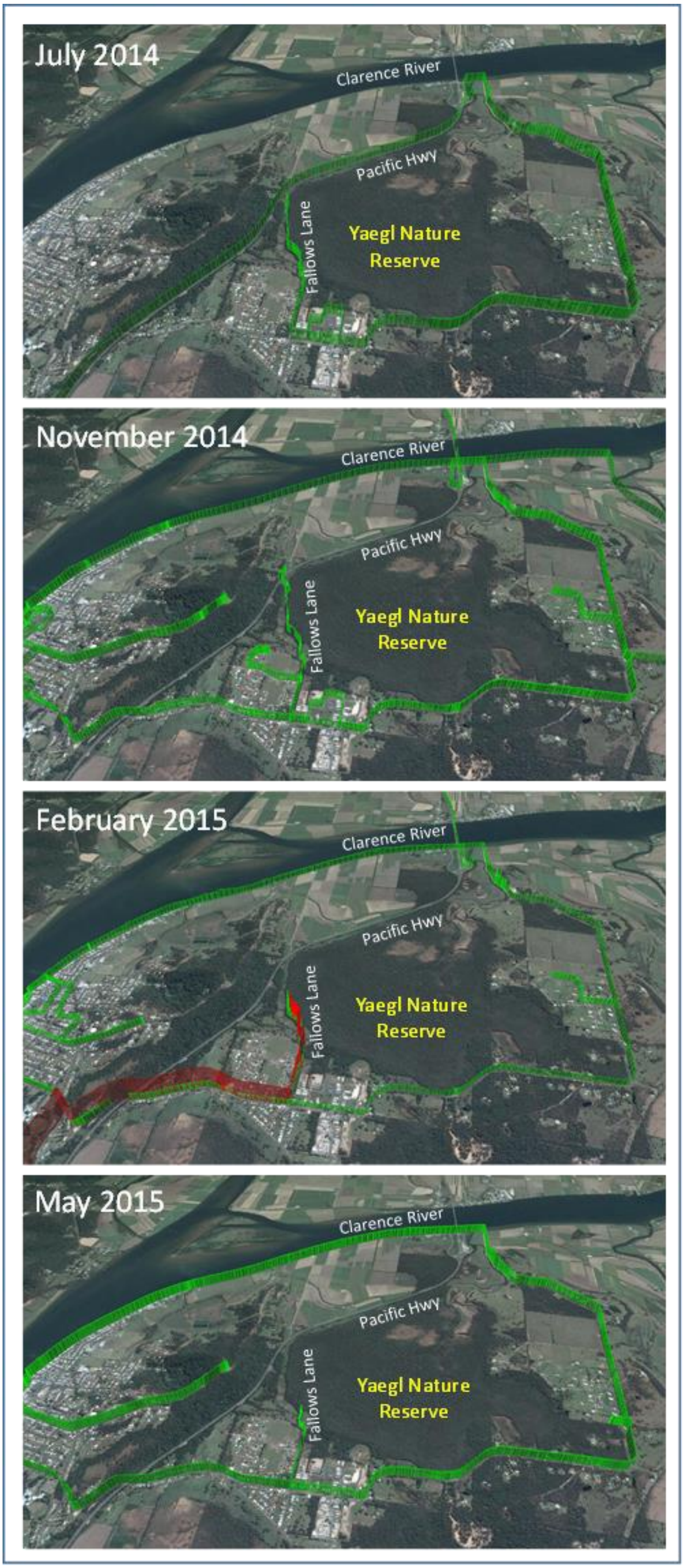

Figure 6.5 Mobile surveys of Yaegl Nature Reserve. The red trace represents data collected in the early morning, which were significantly higher than later in the day.

As well as the mobile surveys, surface flux chambers were used during each visit to Yaegl Nature Reserve to attempt to determine the CH_4 emission rates from various surfaces. CO_2 emission rates were also measured since CO_2 is usually associated with gas emissions from natural surfaces. However, as discussed, access to the site was very limited and consequently chamber measurements were restricted to the edges of the reserve. Nevertheless, we were able to conduct flux measurements on a range of surfaces from grassland to flooded wetland within the forest. A summary of the surface emission fluxes measured using the chambers is provided in Table 6.4 (units are in g m^{-2} day^{-1}).

Table 6.4. Summary of the surface flux chamber emission rates in g m^{-2} day^{-1} measured at Yaegl Nature Reserve.

	July 2014		Nov 2014		Feb 2015		May 2015	
	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
Mean	0.0102	5.35	0.0078	25.02	0.0056	24.37	0.0087	13.68
Min	-0.0010	3.20	-0.0085	3.36	-0.0021	4.99	-0.0022	2.01
Max	0.0628	7.88	0.1095	65.47	0.0330	65.47	0.0390	24.18
Std Dev	0.0258	1.69	0.0262	13.62	0.0085	13.74	0.0142	6.84
n	6	6	19	33	40	40	16	16

The data are also shown in Figure 6.6 where the mean CH_4 emission flux are plotted as a function of the time of year. Average CH_4 fluxes were generally below 0.01 g m^{-2} day^{-1} although as shown in the errors bars in Figure 6.6 (which represent the maximum and minimum values measured during each site visit) there was a significant amount of variation within each data set. High variability is often a feature of chamber measurements on natural surfaces due to the inherent heterogeneity of natural soils (Denmead, 2008). Highest emission rates were usually associated with wet surfaces that had stagnant water present. Figure 6.6 shows that there was generally little variation in the average emission flux over the sampling period, although the high variability in this dataset would tend to obscure any seasonal effects.

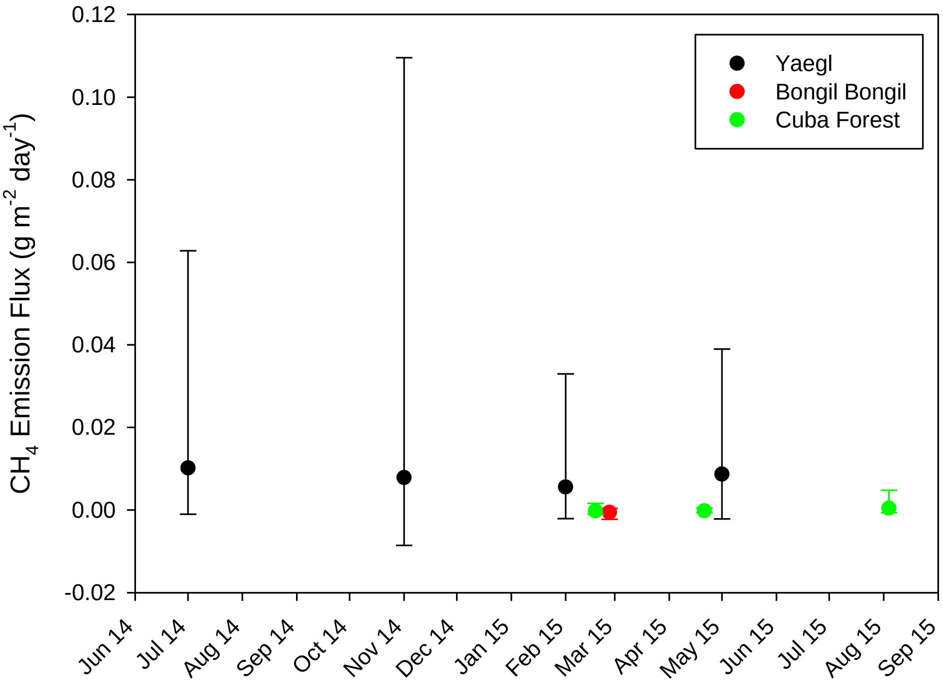

Figure 6.6. Mean CH_4 emission flux measured during each sampling campaign. The error bars represent ±1 standard deviation from each data set.

The CH_4 emission rates measured at the Yaegl site are consistent with other Australian wetland emissions. Dalal et al. (2008) cited results from several studies made between 1995 and 2007 ranging from 3 μg CH_4 m^{-2} h^{-1} (0.072 mg CH_4 m^{-2} day^{-1}) to 44 mg CH_4 m^{-2} h^{-1} (1.06 g CH_4 m^{-2} day^{-1}). In our study, the mean CH_4 emission rates were between about 5 and 10 mg CH_4 m^{-2} day^{-1} with the maximum value of 110 mg CH_4 m^{-2} day^{-1}. The results are also very similar to those measured at an artificial wetland in Ohio in the U.S. where emission rates within the wetland varied between 74 and 192 mg CH_4 m^{-2} day^{-1} (Waletzko and Mitsch, 2014). Assuming that the average rate of all site visits (i.e. 0.007 g m^{-2} day^{-1}), the total CH_4 emission from the 313 ha site 22 kg day^{-1}, or approximately 8,000 kg $year^{-1}$. However, it should be noted that only a very small fraction of the total area was surveyed and only for a limited time during each 24-h period so the uncertainty on these estimates is high.

For comparison with the Yaegl results, surface flux measurements were made in rainforest at Bongil Bongil National Park during February 2015 and at Cuba State Forest between February and August 2015. Like all of the flux chamber measurements presented in this report, measurements were made during daylight hours.

Parts of Cuba Forest are also designated wetlands (Department of the Environment, 2015b), although the surface flux measurements were made in the drier parts of the forest (i.e. there was no flooding at the time of the measurement). The results of the measurements made at other sites are also plotted in Figure 6.6. These sites yielded lower CH_4 emissions that were close to zero or slightly negative largely due to the absence of free water at these sites. At Yaegl, highest surface emissions were associated with stagnant water, presumably due to the activity of anaerobic microbial activity. In contrast, negative emissions fluxes indicate that atmospheric CH_4 is being consumed by the soil. Methane uptake by soils is well known and indeed is an important sink – it has been estimated that globally, as much as 6 % of atmospheric CH_4 is consumed by aerobic soils (Dalal et al., 2008).

The range of CH_4 emission rates measured at Cuba State Forest was much less than seen at Yaegl. This is likely due to the similarity of ground surfaces across the Cuba SF during the measurement campaigns (i.e. dry open forest floor, whereas at Yaegl, the ground surface was more variable in respect of the vegetation coverage and especially the amount of water present.

Given the very low CH_4 emission rates, the ranges of values was also correspondingly less than observed at the Yaegl site.

In contrast to the CH_4 emissions, CO_2 emission fluxes appeared to show seasonal variation with highest emissions occurring during the November and February Yaegl sampling campaigns (Figure 6.7). The results from the Cuba Forest site also show a similar cyclical pattern. Although only one set of measurements was made at Bongil Bongil National Park and so in isolation does not provide temporal information, it nevertheless yielded the highest average CO_2 emission flux, which was during summer.

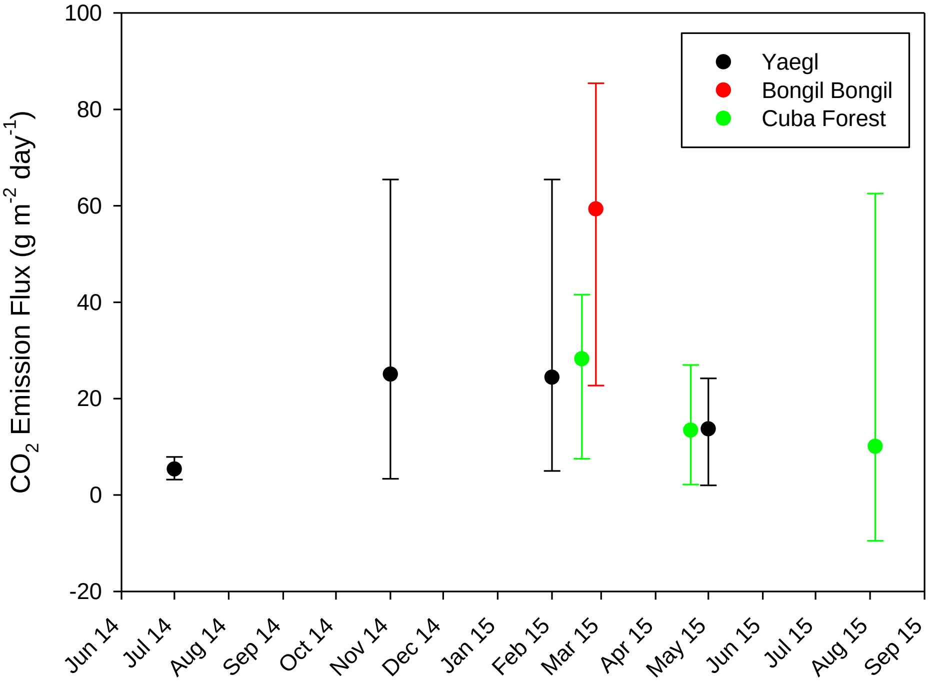

Figure 6.7. Mean CO_2 emission flux measured during each sampling campaign. The error bars represent ±1 standard deviation from each data set.

While the CO_2 emission rates appeared to exhibit some degree of seasonal variation, it is also possible that local weather events may affect emissions. In the week or so preceding the February and May visits to the Yaegl site, for instance, there had been very heavy rain in the area so that emissions may not have been representative of the season. To properly discern seasonal variations in flux, more frequent measurements over a longer period would be required, which were beyond the scope of this project.

6.3 Rice Farm

Measurements were made during six site visits on an experimental rice crop (Reiziq variety) at the NSW Department of Primary Industry Yanco Research Station. The area of the paddock where the measurements were performed was about 7,400 m^2. The flux chamber bases were installed in the paddock on 14th October 2014 about one week after the crop had been sown. At that time, the paddock had not been flooded and was essentially freshly tilled bare earth. The results of the flux chamber measurements are presented in Figure 6.8 and show the average emission flux measured during each site visit (note that all of the measurements made during this project were made during daylight hours).

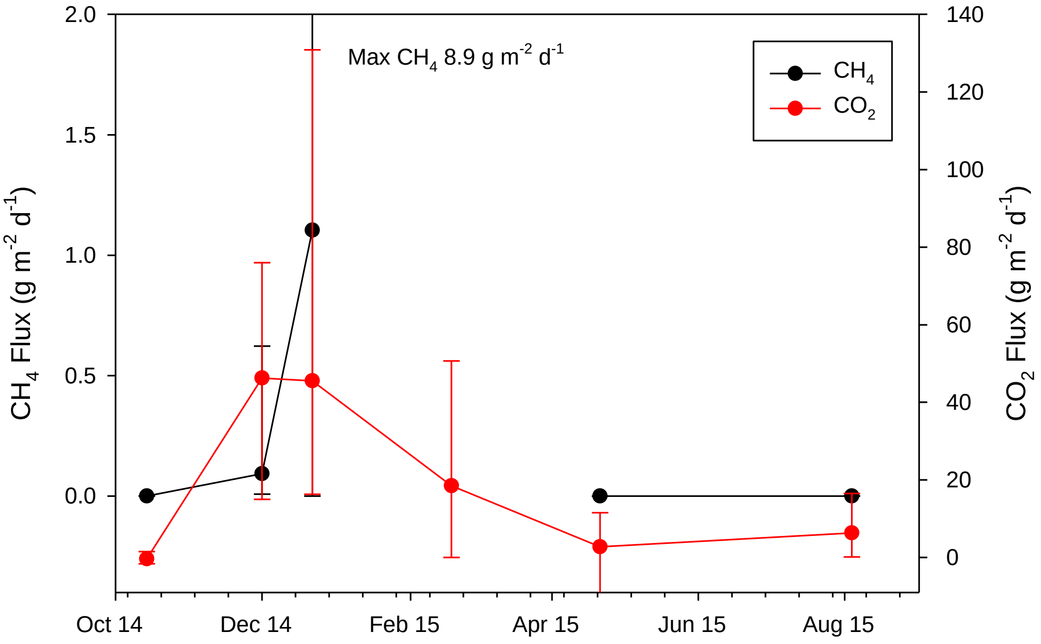

Figure 6.8. CH_4 (black markers) and CO_2 (red markers) fluxes measured at the rice farm.

During the initial visit in October 2014 prior to flooding the paddock and before significant growth had occurred, emissions of both CH_4 and CO_2 were very low, even compared to natural surfaces, with the CO_2 showing a slightly negative rate (Figure 6.8). Surveys around the site at the time of this first visit also showed that ambient CH_4 concentrations were indistinguishable from background levels.

Subsequent visits were made in December 2014, February 2015, April 2015 and August 2015. Highest CH_4 emissions were measured on 22nd December 2014, with an average emission rate of about 1.1 g CH_4 m^{-2} day^{-1} (Figure 6.8). However, it is likely that relatively high emissions were occurring at the time of the February visit, given that the highest ambient CH_4 concentrations in the vicinity of the paddock were measured at the time (Figure 6.9). The average ambient CH_4 concentration measured during these surveys around the paddock, which were made between about 11 am and noon local time, was about 1.84 ppm with a maximum of 2.07 ppm, approximately 270 ppb above prevailing background level of 1.78 ppm. Unfortunately, flux chamber measurements could not be made during this visit because gas bubbles dislodged from the mud by staff placing the chambers tended to saturate the CH_4 analyser thus making flux measurements impractical. This problem was not encountered during other site visits. Carbon dioxide fluxes were less affected due to the much higher dynamic range of the analyser for CO_2.

At the maximum CH_4 emission flux measured (1.1 g CH_4 m^{-2} day^{-1}), the daily emission from the paddock would have been about 8.1 kg CH_4. It is difficult to estimate the total emission of CH_4 from the crop during the growing season due to the changing emission rate and the relatively few measurements made across the season. Despite this, the flux chamber method appears to be well suited to measuring rice emissions and provided sufficient measurements were made during the season, should yield a robust estimate.

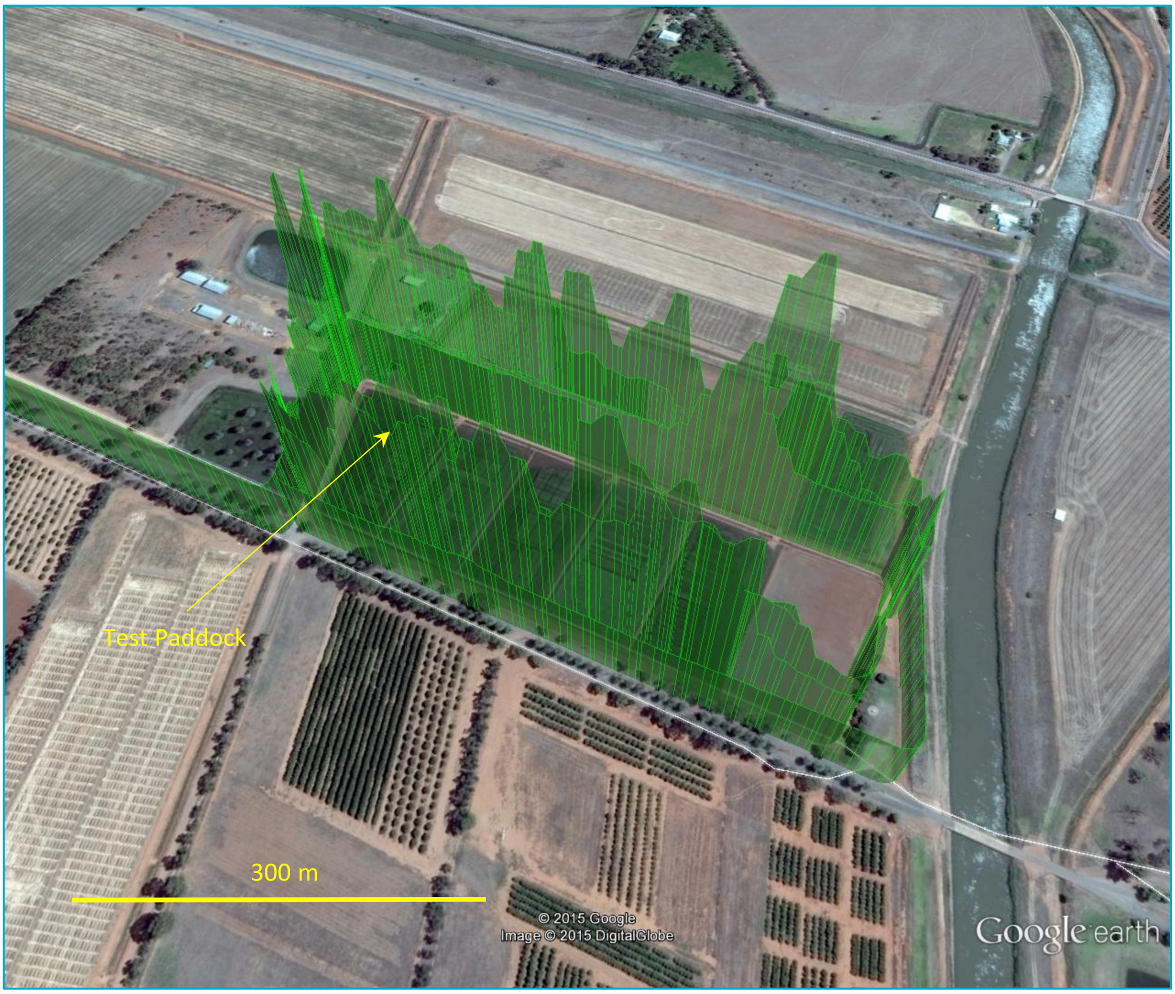

Figure 6.9. Mobile survey of the rice paddocks at the Yanco rice farm made during February 2015 showing elevated CH_4 concentrations near the test site. The maximum CH_4 concentration was approximately 2.1 ppm compared to the background of 1.78 ppm level away from the rice paddock.

While CH_4 was a dominant emission during the growing season, CO_2 was also present in significant amounts. Highest CO_2 emissions were observed during the two December visits (about 46 g CO_2 m^{-2} day^{-1}) with slightly less at around 34 g CO_2 m^{-2} day^{-1} during February.

After the crop was harvested in late March and the water drained from the paddock, both CH_4 and CO_2 emission rates decreased to about the initial levels, although the CO_2 rates were positive (about 3 and 6 g CO_2 m^{-2} day^{-1} in April and August, respectively).

There are only three measurement periods included here so it is difficult to discern seasonal variation in emission rates with a high degree of confidence. However, it is well established that CH_4 emissions from rice crops show an increase soon after the start of the growing season with a steady increase until the crop is harvested (Cicerone et al., 1983; Schütz et al., 1989; Khalil et al., 1991; Neue, 1997; Neue et al., 1997; Chen et al., 2013).

The average CH_4 emission fluxes measured here of between 0 and 1.1 g CH_4 m^{-2} d^{-1} are generally consistent with previous studies of rice paddy emissions. Emission rates are often reported as seasonal averages, which are generally below about 1.5 g m^{-2} d^{-1}. For example, Chen et al. (2013) cite a range of emissions from Chinese rice paddies of between about 0.06 and 1.1 g m^{-2} d^{-1} while Khalil and Rasmussen (1991) measured a seasonal average emission rate in a Chinese paddy of 1.4 g m^{-2} d^{-1}. Emissions from Italian rice production have been estimated to be between 0.14 and 0.38 g m^{-2} d^{-1} (Schütz et al., 1989) and in California the seasonal emission rate was measured at 0.28 g m^{-2} d^{-1} (Cicerone et al., 1983). However, emission rates show strong diurnal variations with daily minimum and maximum values differing by as much as a factor of five in some cases (Schütz et al., 1989). While our results are generally consistent with other studies it is worth noting that the variability across studies can be extremely high. The Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC, 1996) lists a comprehensive summary of experimental studies that have reported CH_4 emissions from rice cultivation around the world. The reported emission rates range from 0.02 to 99 mg m^{-2} h^{-1} (0.0005 to 2.38 g m^{-2} d^{-1}). The default IPCC emission factor for Australian rice cultivation is based on an estimate of emissions from the Griffith region of 2.8 mg m^{-2} h^{-1}, which is equivalent to 0.067 g m^{-2} d^{-1}. This is at the low end of the results measured during this project; however, the IPCC figure represents the average for the growing season (approximately 150 days).

The results presented in Figure 6.8 represent the average measurements made during daylight hours on each site visit. However, we also examined the spatial distribution of emissions along the line of chambers sites within the test paddock. The CH_4 and CO_2 fluxes measured at each location during the 22nd December 2014 are shown in Figures 6.10. Also shown is the emission flux from the water channel adjacent to the crop.

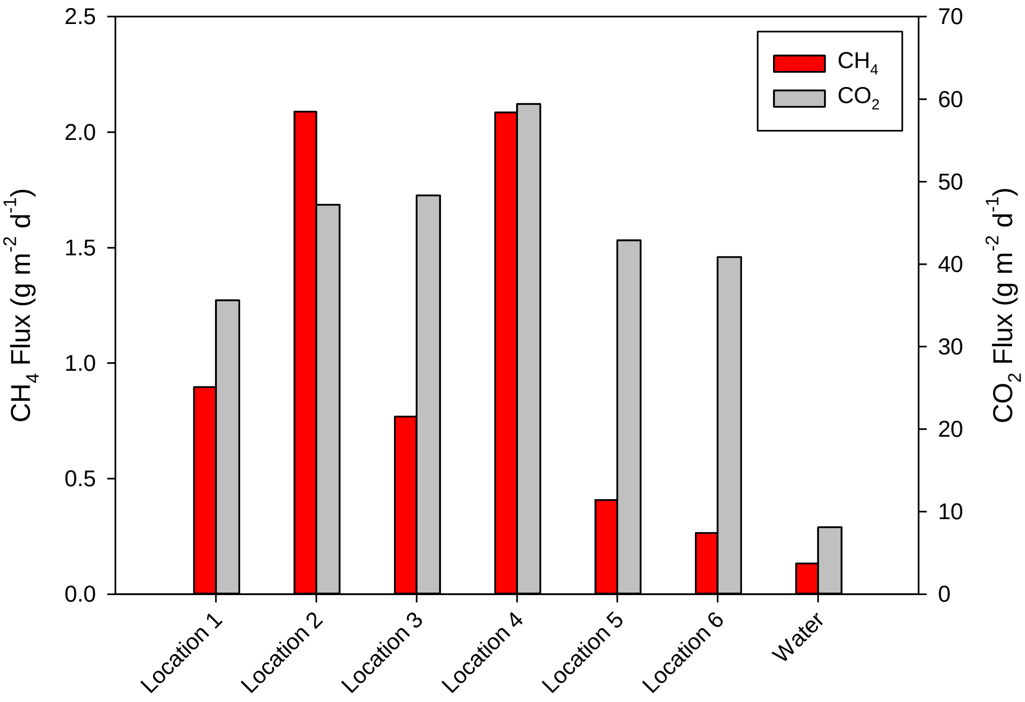

Figure 6.10. CH_4 and CO_2 fluxes measured in the rice crop at various locations on 22 December 2014. Emission from a water channel adjacent to the crop are also shown.

The results of this example show that the measured CH_4 flux varied by a factor of five across the six sampling sites. Carbon dioxide flux also varied although the extent of variation was less than CH_4. Note that both CH_4 and CO_2 flux from the free water (i.e. no rice plants present) were significantly lower than the sites amongst the rice. For CH_4, the emission rate in this case was approximately 0.13 g CH_4 m^{-2} day^{-1} – similar emission rates were measured for free water during the other site visits while the paddock was underwater. Presumably this 'water only' emission represents the contribution of anaerobic bacteria while the higher emissions measured in the area under crop are also include CH_4 generated by the plants themselves. Alternatively, the presence of plants provides a substrate suitable for anaerobic bacteria to produce CH_4.

6.4 Cattle Feedlot

Not surprisingly, the cattle feedlot was found to be a significant source of CH_4 with consistently elevated concentrations compared to local background levels measured during mobile surveys throughout the facility on each of the four site visits (Figure 6.11). A summary of the CH_4 concentrations measured at the site is provided in Table 6.5.

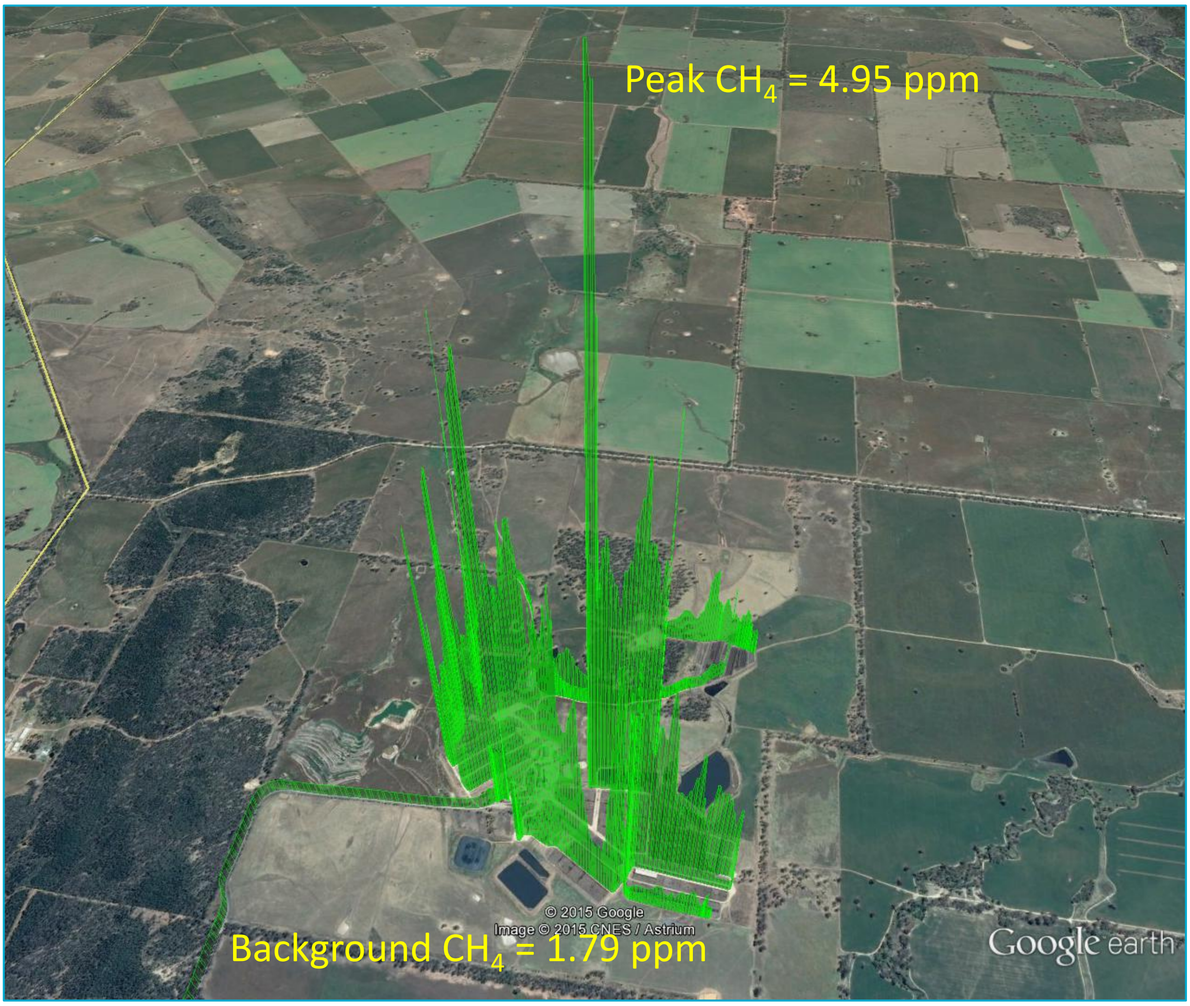

Figure 6.11. Jindalee feedlot showing the elevated CH_4 concentrations throughout the facility. In this example from August 2014, the peak CH_4 concentration was approximately 4.95 ppm (dry basis) compared to the background of about 1.79 ppm (measured upwind).

Table 6.5. Summary of ambient CH_4 concentrations measured within the feedlot. Local background concentrations were measured upwind of the feedlot in each case.

	28 August 2014	16 February 2015	22 April 2015	18 November 2015
Local Time	7:55 am to 11:18 am	7:13 am to 12:37 pm	8:41 am to 1:34 pm	8:02 am to 12:03 pm
Temperature (°C)	10-15	24-29	16	23
Wind speed (m s^{-1})	2.5-6	1.5-3.5	3	4
Wind Direction	SE	NW	SW	NW

	28 August 2014	16 February 2015	22 April 2015	18 November 2015
Mean (ppm, dry basis)	2.1210	2.3806	2.1642	2.2624
Maximum (ppm, dry basis)	4.9540	11.0497	7.8730	14.8724
Background (ppm, dry basis)	1.7948	1.7933	1.7792	1.7924

A large proportion of the CH_4 produced in feedlots is due to enteric fermentation from the cattle themselves but manure management, from both lagoons and piles, also produces large amounts of CH_4.

Methane emissions from cattle were estimated from the stocking rate of the feedlot and published data on cattle emissions. We were advised that the feedlot has a capacity of approximately 17,000 head, which remains generally constant throughout the year. There have been many studies of emissions from cattle in both Australia and elsewhere, with a correspondingly wide range of emission rates reported. Cottle et al. (2011) reviewed a number of studies from between 1997 and 2008 that ranged in CH_4 emissions from about 95 to 270 g CH_4 day^{-1} head^{-1}, with a mean of 177 g CH_4 day^{-1} head^{-1}. Using the mean value, emission from enteric fermentation at this feedlot are estimated to approximately 3,000 kg CH_4 day^{-1} or 1,100 t CH_4 year^{-1}.

We did not measure emissions from the manure ponds because of difficulty of access. Instead, we used an emission factor of 38 kg CH_4 head^{-1} y^{-1} (i.e. the default IPCC emission factor for liquid manure management in a warm climate). This yielded an estimate of approximately 650 t CH_4 per annum.

About 30 flux chamber measurements were made at various times elsewhere throughout the feedlot, including on areas where dried manure was stored and also on a carcase burial area. However, as with all of the flux chamber measurements, the total area surveyed with flux chambers was only a very small proportion of the total facility area. Consequently, any overall emission estimate based on a relatively small sample is subject to uncertainty.

Emissions from the carcase piles were generally quite low compared to other feedlot sources; most were well below 1 g m^{-2} day^{-1} (the maximum was 2.5 g m^{-2} day^{-1}; mean 0.3 g m^{-2} day^{-1}). The manure piles yielded higher emissions of up to 27.5 g m^{-2} day^{-1} but with an overall average for these sites of 6.9 g m^{-2} day^{-1}.

Both the carcase and manure piles also produced CO_2 emissions. For the carcase piles, maximum CO_2 emissions were less than 50 g m^{-2} day^{-1}, which is similar to the CO_2 fluxes measured on natural sites (Section 6.2). The manure heaps, however, were very much higher. In one case, an emission flux of more than 5,500 g m^{-2} day^{-1} was measured; overall the average manure pile CO_2 flux was 2,350 g m^{-2} day^{-1}. The high CO_2 fluxes are indicative of strong aerobic microbial activity.

The approximate area of the manure piles was about 13,000 m^{2}. Thus using the average emission rates for CH_4, the total CH_4 emission from the piles is about 89 kg CH_4 day^{-1}, or 32.5 t CH_4 year^{-1} (~685 t CO_2-e year^{-1}) Although significant, this represents only a minor component of the feedlot's overall CH_4 emissions. The annual emission of CO_2, on the other hand, is around 11,000 t CO_2, assuming an average CO_2 flux across the pile of 2,350 g m^{-2} day^{-1}. However, as mentioned above, these estimates are based on a small coverage so must be considered in this context.

6.5 Coal Mines

Measurements were made at two open-cut coal mines in the Hunter Valley – Rix's Creek and Wambo. As discussed in Section 2.2, measurement of fugitive emissions from open-cut coal mines is a technically challenging undertaking – the current state of the art for estimating emissions for reporting purposes requires boreholes be drilled ahead of mining to measure the gas content in the strata. Measurements of this nature were beyond the scope of this project. Instead, flux chamber methods and mobile surveys were used, although these were not suitable to yield accurate flux measurements from the mines. Rather they provide an indication of the level of CH_4 produced around each mine site.

We had originally proposed to use ground level traverses to attempt to estimate flux in the manner of Williams et al. (1993). However, the selection of the mines meant that this was generally not feasible. In the case of Wambo, the open-cut operation is collocated with an underground operation so it is not possible to separate the open-cut and underground contributions. This, along with the presence of a number of other large open-cut mines nearby makes separating the contribution to the plume from other sources difficult. Moreover, access to suitable roads for traversing is limited.

The Rix's Creek mine was also unsuited to ground level traversing due to the fact that this mine is a very low gas mine, i.e. it does not produce a CH_4 plume.

6.5.1 WAMBO

The Wambo mine is a large open-cut operation that is co-located with an underground mine. Total run-of-mine production is currently around 7.5 Mt of coal per annum. Site visits were made to this site on the 15th July, 21st October 2015 and 17th February 2016. During each visit, mobile surveys of ambient CH_4 concentrations within the pit and elsewhere were made as well as surface flux chamber measurements in various parts of the mine.

Mobile surveys within the pit showed that there was a significant amount of CH_4 present, which is to be expected from a mine of this size. Figure 6.12 shows the CH_4 concentration profile within the pit as measured during the July 2015 visit.

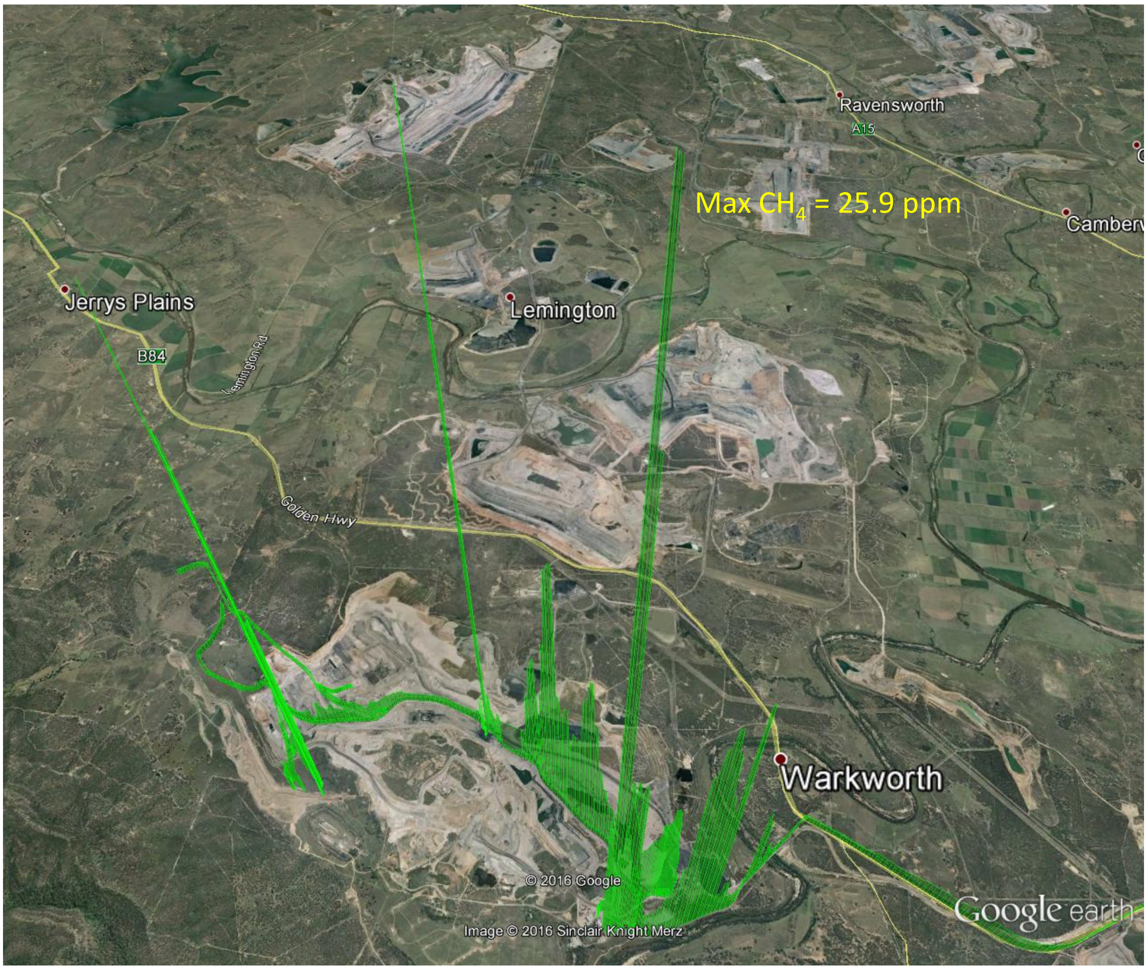

Figure 6.12. Mobile survey of in-pit CH_4 concentrations at the Wambo mine.

Within the pit, CH_4 concentrations were typically well above 2 ppm with numerous areas of much higher concentrations. In the example shown in Figure 6.12, the maximum concentration measured during the mobile survey was 25 .9 ppm CH_4.

The relatively high concentrations encountered at Wambo are unsurprising given the large amount of coal produced at this mine; even a low in situ gas content would result in a significant release of CH_4 during normal operations. However, in addition to CH_4 released through the open-cut mining operations, the main ventilation shaft of the underground mine is located within the pit so that a large proportion of the gas released from the underground mine is also released within the open-cut pit.

Total CH_4 emission rates were not estimated at Wambo for this project because as discussed above, the topography and access restriction rendered plume traversing methods impractical. Flux chamber methods were also unsuited due to the very large size of the area of the mine as well as the temporal nature of emissions from some parts of the operation (i.e. gas is lost rapidly from freshly extracted coal). Although estimates of emissions can be made using Method 1 of the NGERS methodology, this approach is known to have a very high level of uncertainty. Moreover, Wambo contains an underground operation that would not be accounted for using the Method 1 approach.

As discussed in Section 2.2, Wambo, like all other Australian coal mines, estimates and reports emissions to the Clean Energy Regulator. For the open-cut operation, emissions are estimated using Method 2 or 3, both of which are based on gas content data derived from cores taken ahead of mining. This method yields emission estimates with substantially less uncertainty than Method 1 but overall there are still significant areas of uncertainty related to the frequency of measurement (usually very infrequent) and the representativeness of the coring data upon which the estimates are based.

Emissions from the underground mine, on the other hand, are measured directly. The technique used for measuring underground emissions involves measuring the CH_4 concentration within the ventilation airstream and volumetric flow rate (see Equation 2.1). Often measurements are based on monthly ventilation surveys within the mine but in some cases, continuous measurements are made that yield emission rates with uncertainties less than 10 % (Day et al., 2011; Day et al., 2015).

Individual mine data are reported to the Clean Energy Regulator directly and publicly accessible data on the fugitive emissions from Wambo are not available. However, flux chamber measurements were made at various locations throughout the mine. Although these results cannot be used to estimate an overall emission rate from the mine, they nevertheless provide an indication of the range of emissions that occur across the mining operation. These measurements were made on rehabilitated spoil, coal storage areas and on recently exposed coal seams. A summary of the flux chamber results is shown in Table 6.6. The results shown in Table 6.6 are a compilation of 26 measurements made within the mine.

Table 6.6. Average CH_4 and CO_2 emission fluxes measured at different locations within the Wambo mine.

	Mean CH_4 Flux ($g\ m^{-2}\ day^{-1}$)	Mean CO_2 Flux ($g\ m^{-2}\ day^{-1}$)
Rehabilitated Spoil	-0.006	19.5
Coal Stockpile	5.34	6.96
Spoil Pile	-0.001	-0.077
Coal Bench	0.000	0.003
Ripped Coal	16.7	16.5
Pit Floor	0.082	4.88

The CH_4 and CO_2 emission fluxes measured on the rehabilitated spoil are consistent with those found on natural vegetated surfaces (Section 6.2). Low surface emissions were also found on spoil material, a coal bench and the pit floor, from which coal had been removed.

The emissions from spoil material are similar to other measurements of spoil material unaffected by spontaneous combustion (Carras et al., 2009). Similarly, the pit floor also showed low emissions although there was a slight CO_2 flux. This may have been due to low temperature oxidation of the carbonaceous dust that largely covered the floor.

It was somewhat surprising that the coal bench showed virtually no emissions of either CH_4 or CO_2. This bench had been exposed approximately one week prior to the measurements being made, but during this time, it seems that any gas initially present had had sufficient time to desorb from the surface coal. It is likely however, that breaking up the coal would release more gas. Indeed, the ripped coal (which had been broken up less than an hour before the measurements) showed a relatively large flux of CH_4. A CO_2 flux was also apparent which may have been due to a small amount of CO_2 in the seam gas or possibly produced as a result of low temperature oxidation that occurs when coal is exposed to ambient oxygen.

In the case of the product coal stockpile, most of the measurements yielded relatively low CH_4 fluxes, typically below about 2 $g\ m^{-2}\ day^{-1}$. Presumably the low emissions were due to the coal having been stored for some time; however, CH_4 emissions from fresh coal from the underground mine (measured during July 2015) were much higher with a maximum of 19.7 $g\ m^{-2}\ day^{-1}$.

6.5.2 RIX'S CREEK

Rix's Creek is a very low gas mine and mobile surveys made within the pit showed little if any elevated CH_4 concentrations relative to the surrounding region. Figure 6.13 shows one of the surveys (made on 10th October 2014) where the maximum CH_4 concentration measured during the early morning was approximately 2.7 ppm. Although this is significantly above normal background levels, the concentration was no different to areas outside the pit. Over a period of several hours, the CH_4 concentration in the Rix's Creek pit reduced to about 1.8 ppm CH_4 as atmospheric mixing occurred.

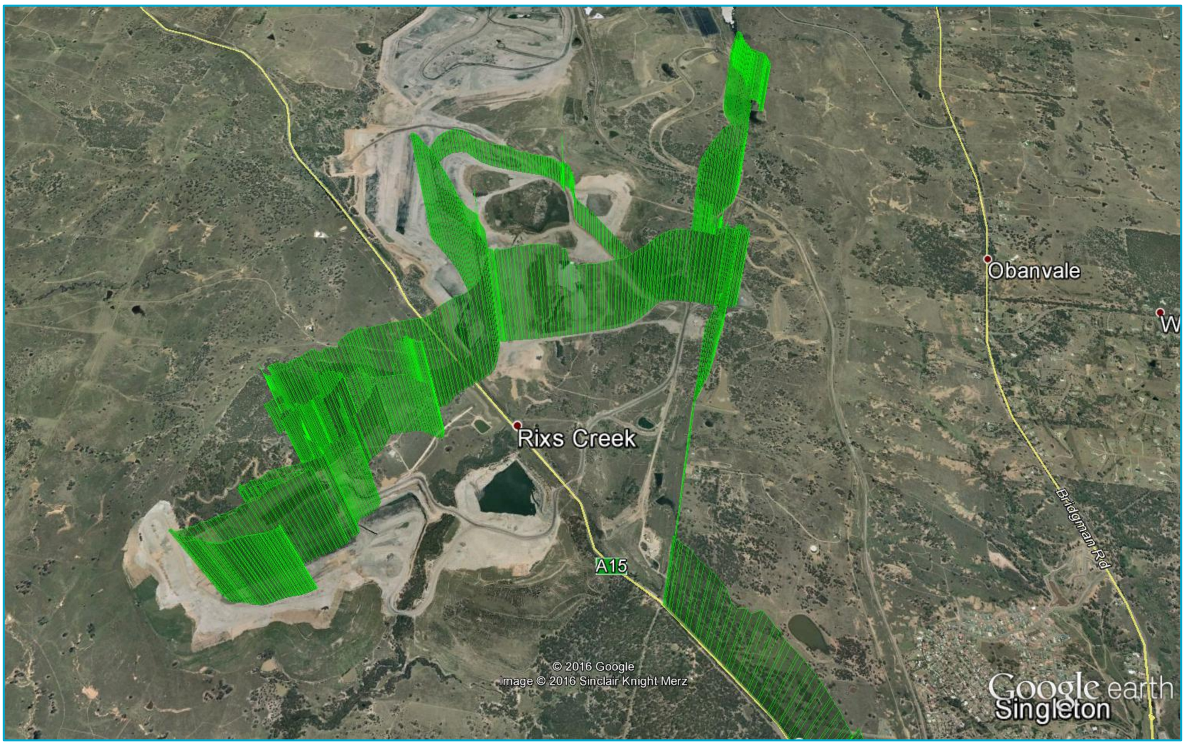

Figure 6.13. In-pit mobile survey of CH_4 concentrations made on 10th October 2014. The maximum CH_4 concentration during this survey was approximately 2.7 ppm.

This was typical of other site visits made during 14th April 2015, 23rd July 2015 and 18th February 2016 where the in-pit CH_4 concentrations were essentially the same as the surrounding region. Even during early mornings within active mining areas when CH_4 would be expected to be at its highest levels, ambient concentrations within the mine were less than about 3 ppm. This contrasts with the much higher concentrations measured in the Wambo mine.

Flux chamber measurements made during each of the four visits on surfaces within the pit confirmed that the coal extracted from the mine has an extremely low gas content, which accounts for the lack of CH_4 detected during the mobile surveys within the mine. Even on coal that had been freshly excavated the CH_4 emission flux was essentially zero in most cases. The maximum CH_4 emission flux recorded was 0.05 g CH_4 m^{-2} day^{-1}, which was made on coal that had been excavated less than one hour previously. Most of the small amount of gas present in Rix's Creek coal is CO_2 and this was reflected in higher CO_2 surface fluxes; CO_2 fluxes up to about 500 g m^{-2} day^{-1} were found on fresh coal. Coal and other carbonaceous material can undergo oxidation in ambient air so it is possible that a small proportion of the CO_2 observed in these emissions is due to low temperature oxidation of coal.

Much lower CH_4 and CO_2 fluxes were observed in other parts of the mine. Surface flux chamber measurements made on rehabilitated ground showed emission fluxes very similar to natural surfaces, with negative CH_4 fluxes and CO_2 levels indicative of vegetation respiration. This is very similar to the emissions from rehabilitated ground at the Wambo mine. A summary of the surface flux emissions determined at the Rix's Creek mine is shown in Table 6.7.

Table 6.7. Summary of the CH_4 and CO_2 surface flux chamber emission rates in g m^{-2} day^{-1} measured at the Rix's Creek Mine.

	10th October 2014		14th April 2015		23rd July 2015		18th February 2016	
	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
In-pit Emissions								
Mean	0.002	9.3	0.007	107.6	0.007	30.0	0.011	48.8
Min	0.000	-0.9	-0.012	1.1	0.002	-1.9	0.000	3.9
Max	0.017	71.7	0.032	558.5	0.012	66.8	0.051	163.8
Rehabilitated and Natural Ground Emissions								
Mean	0.003	4.1	0.001	18.4	-0.012	12.5	-0.001	10.3
Min	-0.001	-0.24	-0.003	1.7	-0.066	-6.2	-0.002	5.4
Max	0.020	23.1	0.004	65.8	0.051	54.4	0.000	15.6

Assuming that the surface fluxes measured at the Rix's Creek are representative of the entire mine, the total annual CH_4 flux from the mine (the active pits cover a combined area of approximately 600 ha) would be about 5.5 t CH_4 $year^{-1}$. Even assuming that the maximum emission rate measured (0.051 g m^{-2} day^{-1}) is representative the total flux is about 110 t CH_4 $year^{-1}$.

It is interesting to note that although the results of the surface flux chamber measurements at Rix's Creek suggest that it is essentially a zero-gas mine, based on its annual production of around 2.5 Mt, using the NGER Method 1 emission factor of 3.2 m^3 t^{-1} would yield an estimate of annual fugitive emissions of more than 5,000 t CH_4 (>110,000 CO_2-e), which is likely to be a substantial overestimate of the actual emission flux. Consequently, like most other Australian open-cut coal mines, Rix's Creek now uses Method 2 for estimating fugitive emissions, which uses actual in situ gas content data (refer to Section 2.2 for a description of Method 1 and Method 2). However, the data are not publicly available at the mine level.

6.6 CSG Facilities

One of the main objectives of the study was to estimate CH_4 emissions from CSG operations across NSW. At the time the study commenced, there were four CSG projects at various stages of development in NSW:

- Camden Gas Project operated by AGL Energy,
- Gloucester Gas Project operated by AGL Energy,
- Narrabri Gas Project operated by Santos Limited and
- West Casino Gas Project operated by Metgasco Limited.

Since then however, the Metgasco operation has had its exploration licences cancelled as part of a NSW government buy-back and AGL Energy have decided not to proceed with the Gloucester project.

Site visits were made to each gas project at least four times during the project to cover all four seasons. These visits required the cooperation and collaboration with site staff who facilitated access to the CSG test sites and ensured that safety protocols were observed during periods when measurements were made on or near well pads or other infrastructure. CSIRO personnel were also required to undertake safety inductions prior to working on the AGL Camden and Gloucester and Santos Narrabri sites.

During visits to the AGL Camden and Gloucester and Santos Narrabri sites, NSW EPA staff were also present during most of the measurement periods. In some cases, the EPA conducted independent leak detection surveys of the well pads concurrently with the CSIRO measurements. These leak detection measurements were undertaken as part of the EPA's normal compliance monitoring programmes conducted at each of these sites. It should also be noted that each CSG operator conducts regular leak detection and repair monitoring on their facilities in accordance with their Environmental Proection Licence.

The results of the measurements made at the four CSG sites during project are discussed in the following sections.

6.6.1 WEST CASINO GAS PROJECT

An initial visit was made to the Metgasco operations during July 2014 where mobile surveys of the ambient CH_4 concentrations were made throughout the gas field. Subsequent visits (made during November 2014, February 2015 and May 2015) included both mobile surveys of ambient CH_4 concentrations as well as surface flux chamber measurements around well heads.

The results of the mobile surveys through the gas field are summarised in the five-number plots shown in Figure 6.14.

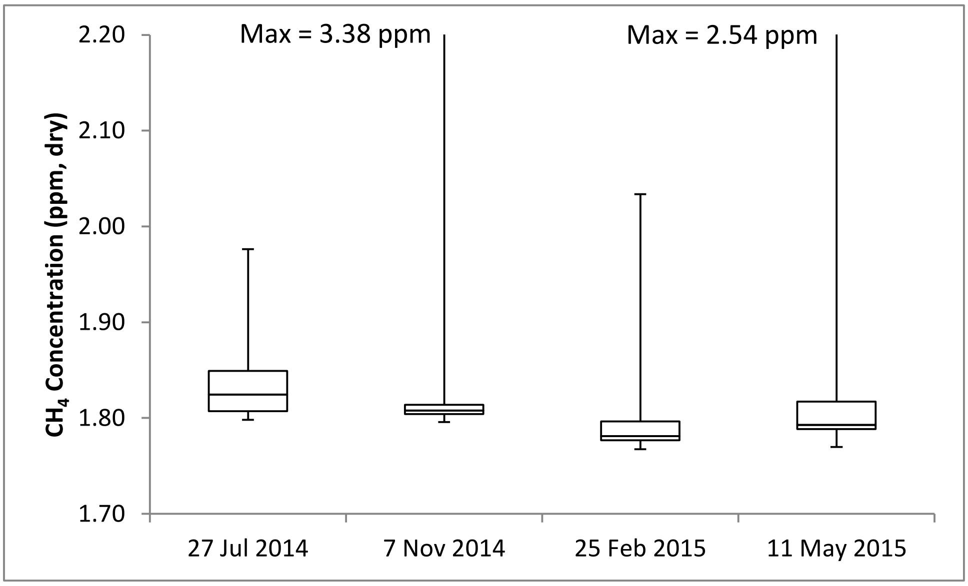

Figure 6.14. Box and whisker plot of the ambient methane concentrations measured throughout the Casio gas field. The maximum concentration measured during November 2014 was 3.38 ppm and during May 2015, the maximum was 2.54 ppm.

The median 3-s average ambient concentrations showed the characteristic seasonal pattern of slightly lower values during the warmer months (cf. Figures 6.2 and 6.3, which show seasonal variation of CH_4 concentrations measured during all of the regional surveys and also at the Cape Grim and Cape Ferguson baseline monitoring stations) but there were occasions when much higher ambient CH_4 concentrations were encountered. For example, during the November 2014 survey the maximum CH_4 concentration measured was 3.38 ppm (dry basis) while in May 2015, a maximum of 2.54 ppm was observed.

None of the five wells visited showed any sign of elevated levels of CH_4 in the vicinity except for Well 3. In this case, the CH_4 was identified as being due to cattle grazing at the well site. Other elevated levels of CH_4 measured during the mobile surveys were attributed to nearby cattle, swampy ground or the generally higher early morning concentrations due to low mixing conditions. Overall, the ambient CH_4 concentrations were consistent with other rural areas.

Because the wells in this field are no longer producing gas, the main aim of the site measurements was to determine if CH_4 was leaking from the wells into the surrounding soil. Accordingly, surface flux measurements were made at selected well sites during November 2014, February 2015 and May 2015. During the first site visit where well access was available (i.e. November 2014), five well pads were examined. However, on subsequent visits, heavy rain during the preceding weeks meant that access to some of the wells was not practical and hence only two were examined during the February and May 2015 site visits. All of the wells examined were either decommissioned where only the well head remained in place (all other surface equipment had been removed) or plugged and abandoned.

The results of the CH_4 and CO_2 surface flux measurements are summarised in Figure 6.15 and 6.16, respectively.

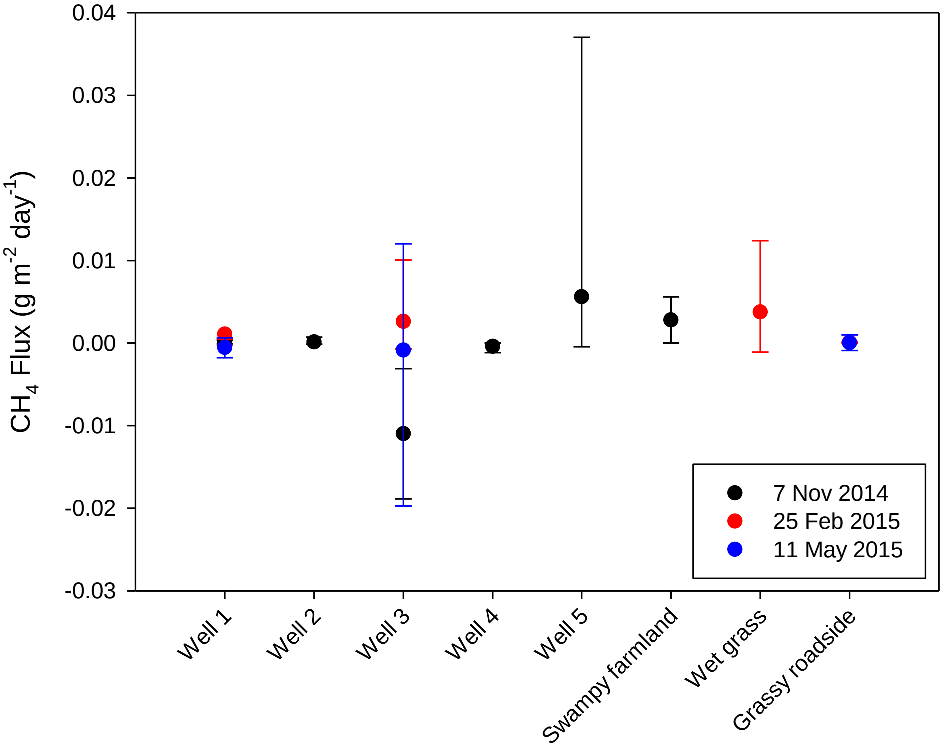

Figure 6.15. Average CH_4 flux measured with surface flux chambers on the ground on well sites in the Casino gas field. Also shown are fluxes measured on other surfaces within the region. The error bars represent the maximum and minimum fluxes measured at each site.

The average CH_4 fluxes on the well sites were all below 0.006 g CH_4 m^{-2} day^{-1} (6 mg CH_4 m^{-2} day^{-1}), which is indistinguishable from other surfaces within the Casino region that were not associated with gas production. These other sites included saturated pasture with free water present (identified as swampy farmland), and grassed areas near roads. While the average CH_4 emissions from well sites were similar non-CSG sites, Well 5 had a single emission measurement of about 0.037 g CH_4 m^{-2} day^{-1} (37 mg CH_4 m^{-2} day^{-1}), which was significantly higher than other measurements measured at this site and elsewhere in the region. However, this was the highest of 13 individual measurements made within about a 10 m × 10 m square at this location; the other results were considerably lower and similar to the other sites. The reason for this single high value is not known but was consistent or less that many of the flux measurements made on the natural wetland in Yaegl Nature Reserve (the maximum CH_4 flux in Yaegl NR was approximately 110 mg CH_4 m^{-2} day^{-1}, Section 6.2).

Well 3 showed a slightly unusual negative flux (Figure 6.15) during the November 2014 site visit. However, the result was skewed by a single result of 0.019 g CH_4 m^{-2} day^{-1}; other replicates were closer the average measured at the other sites. A similar single negative flux was also measured during May 2015 but the mean flux was less affected due to the larger number of replicates and was accordingly closer the results measured on the other sites.

Since the surface CH_4 fluxes are apparently natural rather than leakage from CSG wells, it is possible that there is seasonal variation. However, it is not possible to discern any seasonal variation in these data because of the small number of data points. Moreover, as was the case with the natural wetland (Section

6.2) local weather events such as heavy rain at the time of the measurements are likely to obscure any seasonal effects. Given the inherent variability of surface flux measurements due to inhomogeneity of the soil, vegetation, periodic weather events etc., it would be necessary to conduct measurements more frequently over a long period of time to detect any seasonal effect. Alternatively, other methods (e.g. eddy covariance) may be preferable for detecting seasonal variation since they can provide continuous measurements.

Like the CH_4 fluxes measured within the Casino gas field, the CO_2 fluxes measured across the well sites were consistent with fluxes measured on natural surfaces (Figure 6.16). The average CO2 fluxes were mostly below 30 g CO_2 m^{-2} day^{-1} although at Well 4 measured during November 2014, the mean flux was approximately 64 g CO_2 m^{-2} day^{-1}. However, this was still within the range of CO2 emission fluxes measured at the three natural sites discussed in Section 6.2. No seasonal effects were observed in the CO2 flux data due to the variability within the results.

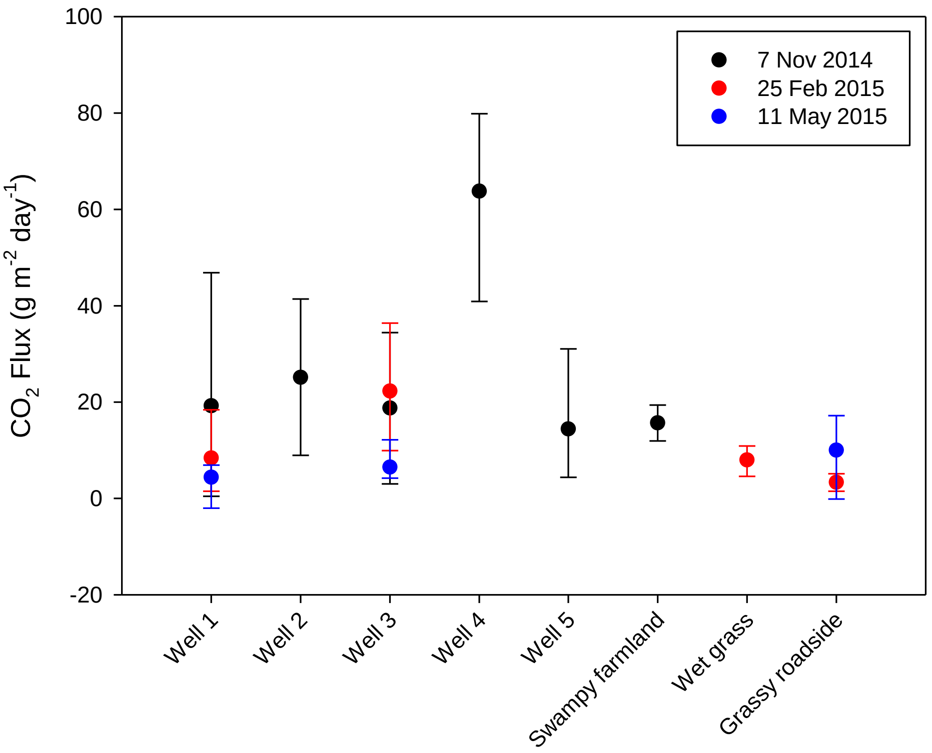

Figure 6.16. Average CO_2 flux measured on the ground on well sites in the Casino gas field. Also shown are fluxes measured on other surfaces.

6.6.2 GLOUCESTER GAS PROJECT

At the commencement of surveys, only four wells were operating within the Gloucester project. In January 2016, however, AGL announced that the project would not proceed and hence during the January and March site visits all of the wells had been shut-in (i.e. closed down) and were no longer producing gas.

A summary of the ambient CH_4 concentrations measured through the gas field during the four site visits is shown in Figure 6.17. Most of the time, CH_4 concentrations were around expected background levels except in the immediate vicinity of two of the wells; G1 and G2. The highest ambient concentration of 5.82 ppm CH_4, which appeared as a brief spike, was found during the July 2015 visit. Elevated CH_4 concentrations were also found during the September 2015 (maximum about 3.25 ppm CH_4) but no elevated concentrations were observed during the January and March 2016 visits after the wells had been shut in. The maximum concentrations observed during the January and March 2016 visits were not associated with gas wells; in both cases, the CH_4 peaks appeared to be due to nearby cattle or water bodies.

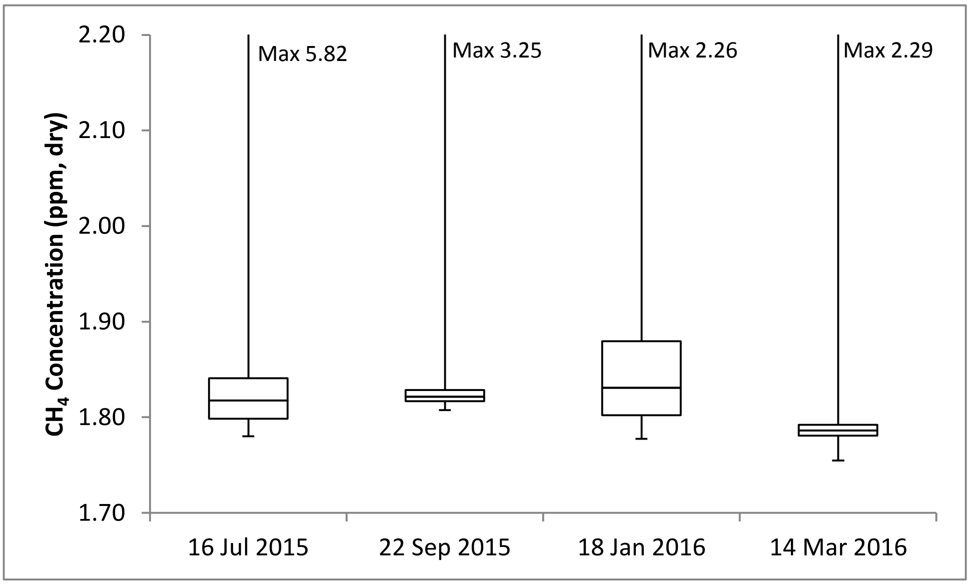

Figure 6.17. Box and whisker plot of the ambient methane concentrations measured throughout the Gloucester gas field.

Well G1 is located adjacent to a large water tank and it is likely that some of the elevated levels were due to degassing of water held in the tank; several measurements made within the tank confirmed the presence of slightly elevated concentrations. It is also possible that some CH_4 was released from the well itself, although we were unable to find the source by leak detection methods.

The other well that yielded higher CH_4 concentrations, Well G2, was within 50 m of a flare where gas produced from the field was combusted. Although gas flares typically have combustion efficiencies of more than 98 % (Caulton et al., 2014b) a small amount of unburned CH_4 is likely to be emitted in the exhaust. Given that we were unable to locate a CH_4 source on the well pad, it is possible that the observed elevated concentrations were from the flare exhaust.

6.6.3 CAMDEN GAS PROJECT

The AGL Camden site is the only commercial CSG project operating in NSW, supplying about 5 % of the state's natural gas. Field measurements were made throughout the gas field in August 2015, November 2015, January 2016 and March 2016. These site visits included mobile surveys through the general area and at six well pads within the field. Some of the pads housed two well heads and hence a total of nine wells were examined in detail during the project.

In addition to these four trips, we also made four other separate visits to the gas field (but not to individual wells) during August 2014, November 2014, February 2015 and April 2015 as part of the Camden VOC surveys discussed in Section 7.4 of this report. During these surveys, early morning ambient CH_4 concentration were collected using mobile surveys through the same general area as the well pad measurements.

The mobile survey data for the eight field visits are shown in Figure 6.18. One of the characteristics of these surveys was that the CH_4 concentrations were often well above normal background levels, especially during the early morning. In the August 2014 survey, the median concentration was above 2.7 ppm or almost 1 ppm above background. Similarly, the April 2015 median was significantly above background at approximately 2.2 ppm while the January 2016 survey gave a median value of around 3.2 ppm.

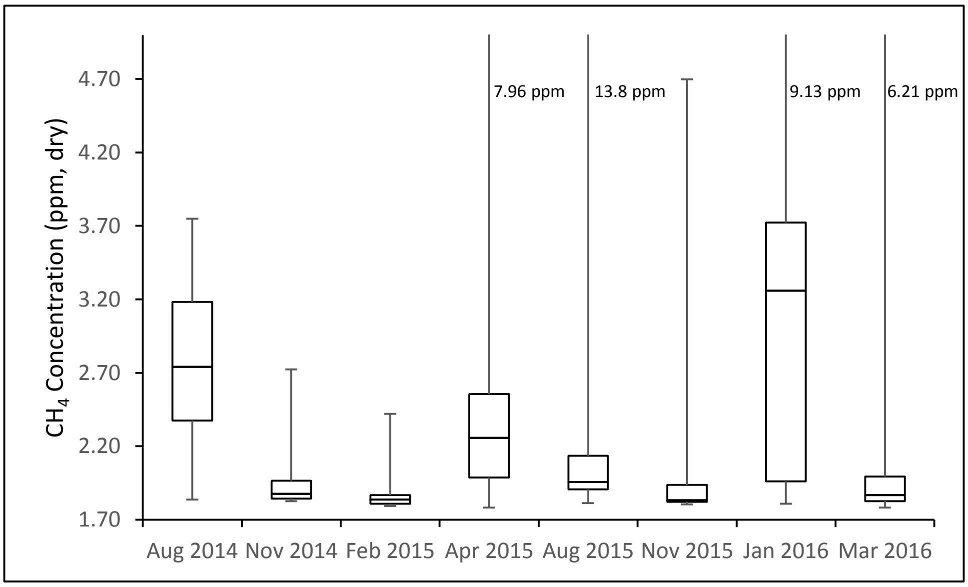

Figure 6.18. Box and whisker plot of the ambient CH_4 concentrations measured throughout the Camden gas field. The maximum concentrations measured during April 2015, August 2015, January 2016 and March 2016 are indicated (they are off scale in this plot).

The ambient concentrations measured through the Camden region are relatively high compared to normal background ambient levels, which is in contrast to the Casino, Gloucester and Narrabri fields where the concentrations were generally close to natural background levels. Most of the elevated CH_4 concentrations were measured during the early morning under stable atmospheric conditions, which tend to concentrate CH_4 near the ground surface. This effect was observed at most other sites when surveys were made in the early morning; as atmospheric mixing increased later in the day CH_4 concentrations tended to decrease and approach background levels. The effect of mixing is illustrated in Figure 6.19 where the CH_4 profile measure at around 7:00 am local time during the January 2016 Camden survey is compared to the concentration measured along the same route about 5 hours later.

In the initial run (green trace), which was made under calm conditions, it is clear that the CH_4 concentration is substantially elevated for most of the route; the maximum concentration was approximately 5.6 ppm with an average of 3.7 ppm. The minimum value was 1.86 ppm. The later run (red trace), however, shows much lower concentrations of most of the route with an average of 1.88 ppm, although still slightly above natural background levels. Although the second, later run was much lower, there were some locations where elevated CH_4 were observed, particularly a large, narrow spike with a maximum concentration of 9.1 ppm about 1.5 km west of Menangle on Woodbridge Road. A repeat pass confirmed the presence of the peak. During these later traverses, a light wind of less than 2 m s^{-2} was blowing from the SE.

The source of this CH_4 peak is not known although it was within 50 m of a CSG well (but not one of those examined during this study) so it is possible that CH_4 was being emitted from the well during these two surveys. Surveys were made past this site on each of the other site visits at different times of the year but the source was not detected on any of these passes.

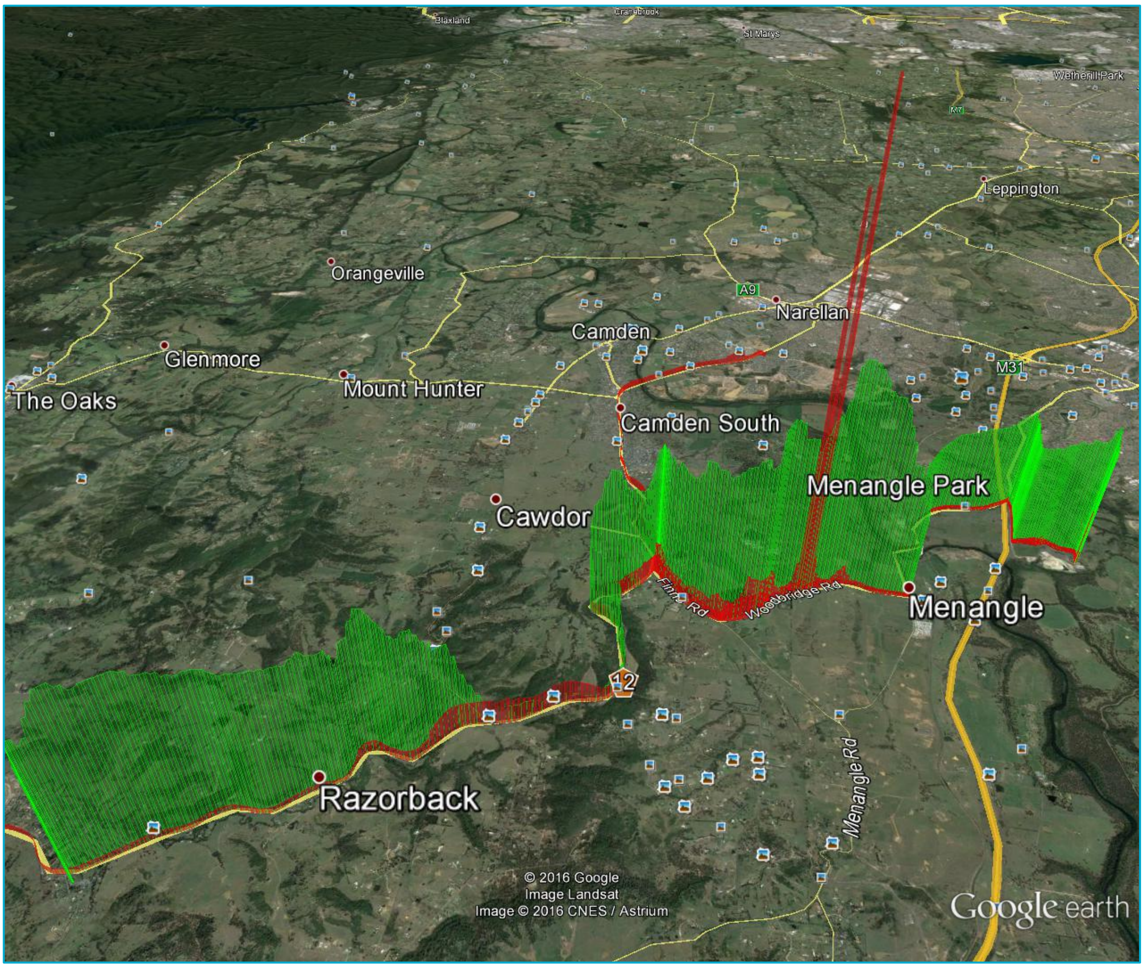

Figure 6.19. Methane concentration profiles through part of the Camden gas field made on 12th January 2016. The green trace represents measurements made at approximately 7 am; the red trace is from a similar run made about 5 hours later. The maximum concentration is the morning run was 5.6 ppm; the later maximum was 9.1 ppm (due to small intense source west of Menangle).

The reason for the generally elevated CH_4 concentrations observed during some of the Camden surveys is not clear, although urban CH_4 levels are usually higher than non-urban regions such as the other gas producing regions examined in this study (Blake, et al., 1984; Lowry et al., 2011; Phillips et al., 2013). CSG is possibly a contributor to the higher levels given the presence of the transient peak west of Menangle, and higher concentrations were found within the immediate vicinity of the Rosalind Park gas plant. Elevated CH_4 concentrations have been also measured by others in the vicinity of the gas plant (AGL, 2014). However, most of the highest concentrations measured during these field campaigns were observed well outside the gas field. For instance, at about 7:30 am on 6th August 2014 under almost calm conditions, the maximum CH_4 concentration of approximately 3.8 ppm (dry basis) was measured at Mt Annan to the north of the CSG field while on 29th April 2015, the ambient concentration in a motel carpark in Campbelltown was almost 8 ppm at 7:15 am under calm conditions.

The waste management facility at Spring Farm is also a significant source of CH_4 and substantially elevated levels were routinely encountered in the vicinity. During the August 2015 survey, the peak CH_4 concentration measured adjacent to the facility was 13.8 ppm. A previous study also found strongly elevated CH_4 concentration of more than 16 ppm near the landfill (AGL, 2014).

Well Emissions

At each well pad, an initial survey of at least six circuits of the pad was made using the vehicle mounted CH_4 analyser. All of the sites had good vehicle access so it was possible in each case to conduct these surveys within about 10 m of the actual well and the surface infrastructure (Figure 6.20).

Figure 6.20. One of the well pads examined at the AGL Camden site. In this example, there are two wells on the pad. Vehicle tracks from the circuits are visible in the foreground.

The results of these surveys almost exclusively did not detect any elevated CH_4 levels near the wells, which suggests that they were not emitting CH_4. A previous study of Australian CSG wells found that of the 43 examined, most had some level of emission, although often very low (Day et al., 2014). Of the six well sites examined during the present study at the AGL site in Camden, emissions were only detected at two; the first during the August 2015 campaign and the second during the March 2016 trip.

Figure 6.21 shows CH_4 concentrations measured around the well during the 19th August 2015 site visit over approximately a 15-minute period between 10:40 am and 10:55 am local time; this is the result of 10 circuits around the well, less than 10 m from the well head. During the survey, the wind was from the NE with an average speed of 2.5 m^{-2}.

On each circuit, a CH_4 peak is apparent downwind of the source although the concentration varied considerably. For example, the peak made on the second pass (numbered 2 in Figure 6.21) was barely present, whereas the next pass (3) yielded the largest CH_4 perturbation. This illustrates the meandering nature of the plumes, especially under light wind conditions and shows why it is necessary to make sufficient traverses to develop a reasonable average.

The average emission rate from the well calculated using Equation 5.1 from the 10 traverses was very low, at approximately 0.03 g CH_4 min^{-1}. No further emissions were detected from the well during subsequent site visits between August 2015 and March 2016.

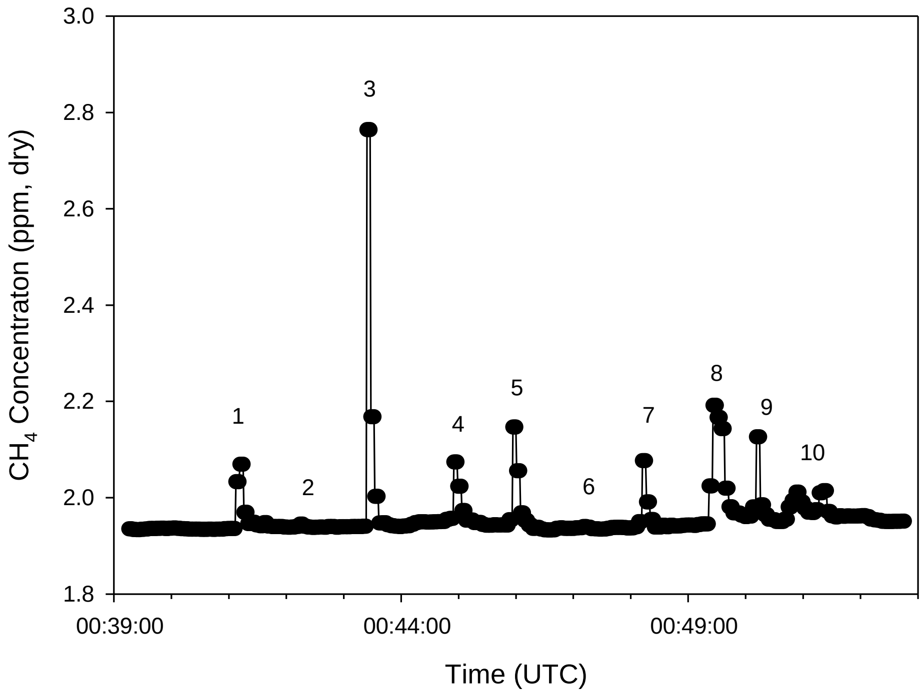

Figure 6.21. CH_4 concentration profile measured at a CSG well during circuits of a CSG well in the Camden field on 19th August 2015. The numbers on the figure denote the number of each circuit made around the well pad.

A second well with very slight emissions was also detected during the March 2016 field visit. Previous inspections of this well did not reveal any other emissions during the project period. In this case, the concentration perturbations produced by the CH_4 source were only about 20 ppb above background; this compares with the peaks in Figure 6.21 where the maximum perturbation was about 800 ppb. Since the downwind distance from the well was also about 10 m, the emission rate at this second source was very low indeed. On pad measurements made by AGL field staff and a NSWEPA inspector using handheld gas detectors located the leak on a non-return valve on the gas line that had been subject to maintenance the week prior to the CSIRO visit. Once the leak had been located, the AGL personnel isolated the valve and vented the gas in the line and repaired the leak on site. Measurements made with both the leak detectors and the Picarro instrument after the repair confirmed that no further emissions were occurring.

During the venting of the gas for the repair, CH_4 concentrations up to about 20 ppm was measured within about 20 m of the well. This provided an opportunity to measure isotopic ratios of the gas product gas using the Picarro G2132-i analyser. Note that the elevated CH_4 concentrations persisted for only a few minutes after the gas had been vented before declining to background levels once the released gas had been dissipated. The results of these measurements are discussed in Section 8.3 of this report.

6.6.4 NARRABRI GAS PROJECT

Measurements were made in the Santos gas project area southwest of Narrabri. The measurements were made to quantify fugitive emissions from gas production facilities at a range of locations within the gas field, including:

- six CSG well pads in the Bibblewindi, Dewhurst and Tintsfield regions,
- a section of the pipeline easement that connects the gas field to the Wilga Park Power Station and
- the water treatment facility at the Leewood facility.

In addition, mobile surveys were made throughout the field on public roads. Site visits were made during July 2014, May 2015, July 2015, September 2015 and February 2015.

The results of the mobile surveys through the gas field are summarised in Figure 6.22 where the ambient CH_4 concentration statistics for each visit are presented as five number plots. The median concentrations clearly show the seasonal variation observed in surveys made elsewhere (see Figures 6.2 and 6.3). In general, there was very little variation in concentration during each survey with the 25 % and 75 % quartiles barely differing from the median. In other words, there was no sign of unusually elevated CH_4 concentration over most of the gas field. However, localised CH_4 peaks were occasionally detected. During the September 2015 survey, a peak of more than 10 ppm was detected. Most of the highest peak CH_4 concentrations were measured in close proximity to several CSG wells within the Bibblewindi region of the Pilliga State Forest and the Tintsfield area to the north (the emissions rates from the two Bibblewindi wells were measured separately, as discussed below). Another large spike of about 6.8 ppm CH_4 was detected further south in the Dewhurst region during May 2015, which was most likely also due to emissions from a well about 100 m away, but we were unable to positively confirm the source with on-pad measurements at the time. Subsequent surveys did not reveal elevated CH_4 concentrations at this location.

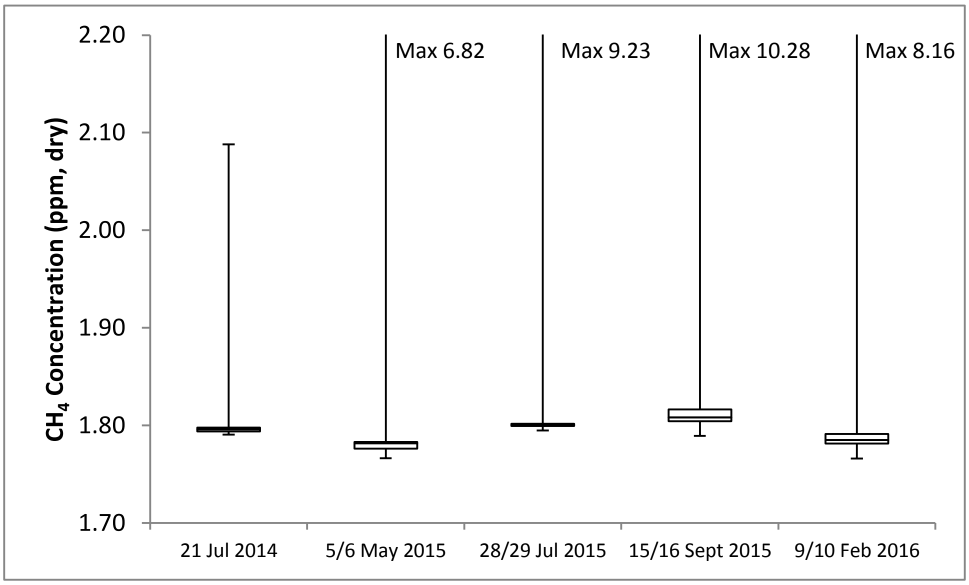

Figure 6.22. Box and whisker plot of the ambient CH_4 concentrations measured throughout the Narrabri gas field.

Most of the peak CH_4 concentrations observed during the mobile surveys were attributed to gas wells within about 50 m of the survey vehicle but there were also numerous other wells within similar distances of the survey routes that showed no sign of elevated CH_4. However, it should be noted that source detection using the mobile survey method is influenced by factors such as local wind conditions, size of the source and whether or not it is intermittent or continuous. Hence infrequent surveys that show 'negative' results do not necessarily confirm that the absence of a CH_4 source. This was illustrated in the case of the Camden surveys discussed in Section 6.6.3 where what was probably a CSG well source was detected during two passes during one survey but not in any of several others made in the same area at different times of the year.

The mobile surveys through the Narrabri Gas Project area included driving along a 17 km section of the gas pipeline easement. During these surveys, the gas pipeline was within a few metres of the CH_4 analyser inlet. Because of the high sensitivity of the Picarro instrument, even a small leak in the pipe would have been detectable under the conditions of the surveys (cf. very small emission sources on Camden well pads were readily detected approximately 10 m from the source). Although source detection is dependent upon suitable wind conditions, during the pipeline surveys the wind was very light and in any case, the survey route was sheltered from wind to a large extent by the forest on either side of the easement. No elevated CH_4 levels detected near the pipeline on any of the surveys thus confirming the integrity of this section of the pipeline.

The project area contains about 45 producing wells with numerous suspended or plugged and abandoned wells throughout the area. Six wells were selected for close examination to detect and quantify CH_4 emissions rates. For each of the selected wells, surveys were made within about 20 m or less from the well head using the vehicle mounted CH_4 analyser in the same manner as the other CSG sites. Usually, at least six complete circuits of the well were made over a period of 10 to 15 minutes on each occasion. Some examples of the well surveys are shown in Figure 6.23.

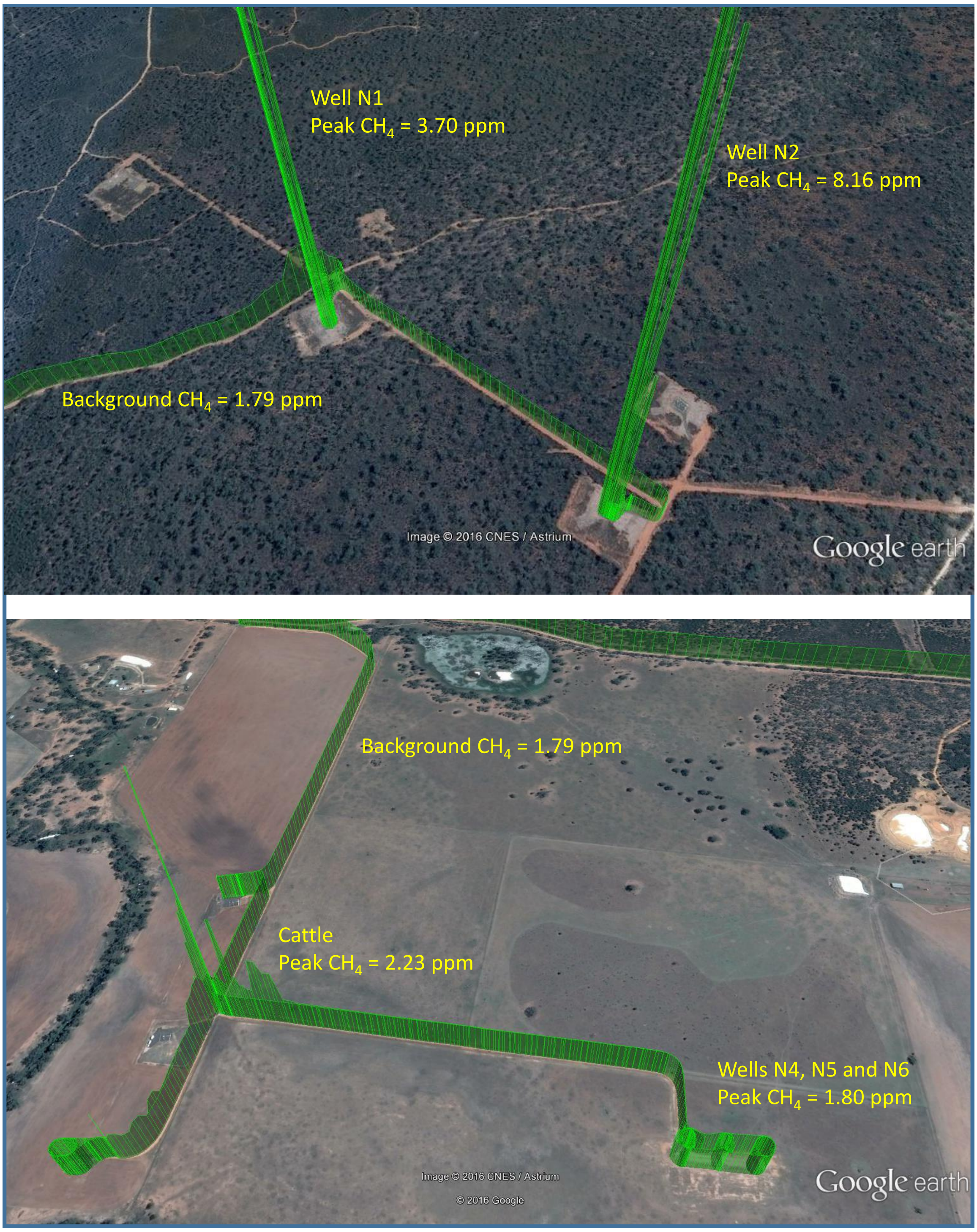

Figure 6.23. Mobile surveys of CH_4 concentration in the vicinity of Wells N1, N2, N4, N5 and N6 made during February 2016. The maximum CH_4 concentration (dry basis) of peaks and background are indicated. Note the magnitude of the peaks associated with cattle grazing near Wells N4, N5 and N6.

Figure 6.23 shows the elevated CH_4 concentrations in close proximity to Wells N1 and N2; however it is also apparent that the concentration decreased to normal background levels within a relatively short distance from each well. In contrast CH_4 levels were barely distinguishable above ambient near Wells N4, N5 and N6. Although not shown, CH_4 concentrations near Well N3, which was a suspended well, were also identical to background.

For some of these wells, we measured the emission rate of CH_4 from the well pad. Initial measurements were made using the ground level plume traversing technique (see Section 5.2.2). For later measurements, we used the more accurate tracer method (with the LGR analyser) after the safety aspects of the method had been cleared by the Santos production team. A summary of the results of the CH_4 emission rates measured at each well is provided in Table 6.8. Also shown is the maximum CH_4 concentration enhancement (i.e. maximum CH_4 concentration minus the local background CH_4 concentration) measured in the immediate vicinity of each well.

Table 6.8. Summary of results from CSG well emissions in the Narrabri gas field. The peak CH_4 enhancement measured during each mobile survey is shown for each well; these were measured with about 20 m of the well head (except in July 2014 where measurements were made 50-100 m from the well head). Also shown is the measured emission flux for each well. Dashes indicate that measurements were not made. Results marked with (t) were obtained using the tracer method.

	July 2014		May 2015		July 2015		September 2015		February 2016	
	CH_4 Enhancement (ppm)	CH_4 Flux ($g\ min^{-1}$)	CH_4 Enhancement (ppm)	CH_4 Flux ($g\ min^{-1}$)	CH_4 Enhancement (ppm)	CH_4 Flux ($g\ min^{-1}$)	CH_4 Enhancement (ppm)	CH_4 Flux ($g\ min^{-1}$)	CH_4 Enhancement (ppm)	CH_4 Flux ($g\ min^{-1}$)
Well N1	0.02	-	-	-	7.74	2.9	8.48	14.9 (t)	1.92	4.2 (t)
Well N2	0.30	-	-	-	9.66	3.6 (t)	5.80	8.1 (t)	6.38	22.7 (t)
Well N3	-	-	-	-	0.00	0.0	0.01	0.0	0.00	0.0
Well N4	-	-	0.036	0.02	0.01	0.0	0.02	0.0	0.00	0.0
Well N5	-	-	0.280	0.18	0.03	0.0	0.01	0.0	0.02	0.0
Well N6	-	-	0.006	0.00	0.00	0.0	0.10	0.1 (t)	0.00	0.0

Emissions from four of the wells (N3, N4, N5 and N6) were in all cases very low with CH_4 enhancements usually close to zero. On one occasion (6th May 2015), Well N5 showed somewhat elevated CH_4 concentrations at 0.28 ppm above background, which since there were no obvious sources such as cattle nearby, was probably due to a piece of equipment operating on the pad. The estimated emission rate for this source however, was very low at less than 0.2 CH_4 min^{-1}. On all subsequent visits to these wells, emissions were negligible.

Two wells (N1 and N2), however, consistently showed much higher emissions rates. At these wells, CH_4 enhancements of between about 2 and 10 ppm were observed within 20 m of the well pad. During July 2014, when access to the well pads was not available because negotiations to access well pads had not been concluded, surveys conducted outside the well enclosures (within approximately 50-100 m of the well head) also showed elevated CH_4 concentrations, although because of the greater distance, the concentrations were much lower than on subsequent visits. At the time of these surveys, the wind conditions were light and variable and this combined with significant vegetation between the vehicle and emission source meant that the plume was ill defined. Consequently, we were unable to estimate the emission flux on this occasion.

On other occasions, emission rates varied between 2.9 and 14.9 g CH_4 min^{-1} for Well N1 and 3.6 and 22.7 g CH_4 min^{-1} for Well N2. The main source of CH_4 on these wells seemed to be a flow control valve on each well (Figure 6.24); a handheld leak testing instrument indicated high levels of CH_4 (> 1000 ppm) next to the valves on both wells. An additional source was located on Well N4 during the July 2015 visit were CH_4 was found to be leaking around the seal on the water pump shaft.

Figure 6.24. Flow control valve and actuator on Well N1 (the green device in the centre of the photgraph)

Flow control valves of the type illustrated in Figure 6.24 (and other devices) are often actuated using pneumatic systems that operate from gas pressure from the well. Many of these devices release CH_4 as part of their normal operation; emissions may be via intermittent releases or continuous bleeding of gas (USEPA, 2006). Recent work in the United States found that intermittent and 'low bleed' pneumatic devices used on unconventional gas wells released CH_4 at 5.9 ± 2.4 g CH_4 min^{-1} and 1.7 ± 2.4 g CH_4 min^{-1}, respectively (Allen et al., 2013). Note that pneumatic devices were also used on some of the wells in the

Camden and Gloucester gas fields; however, in some of those cases the systems operated off compressed air rather than gas and therefore did not emit CH_4.

Overall, the emission rates measured on the Narrabri wells are comparable to measurements made previously at CSG wells throughout NSW and Queensland, where the mean emission rate was 3.2 g CH_4 min^{-1}, but with a range of zero to about 44 g CH_4 min^{-1} (Day et al., 2014).

Since most of the gas wells within the Narrabri Gas Project require dewatering, water treatment facilities have been established to accommodate water produced from the wells throughout the field. At present, treatment is limited to storage in purpose built ponds but approval has been granted to construct a reverse osmosis plant at Leewood that would treat all produced water onsite.

Produced water is a potential emission route for CH_4 so during two of the site visits, we measured emissions from the ponds at the Leewood facility, which currently accepts all of the produced water from the field. The facility comprises four ponds, covering a total area of roughly 12 ha. Each pond is lined with an impervious waterproof liner; the water level in the ponds varies according to the amount of water received and water management practices.

Methane emissions from the ponds were measured using floating flux chambers, except where the water level was too low to allow access of our equipment. Because access to the water was somewhat restricted by the steep slope into the pond, measurements were confined to a few designated access points on each pond (Figure 6.25).

Figure 6.25. Water retention pond at the Leewood facility in the Narrabri Gas Project. Note the rope ladders for accessing the water.

Emissions from the Leewood ponds were measured during the 16th September 2015 and 10th February 2016 visits. Summaries of the CH_4 and CO_2 results are shown in Figures 6. 26 and 6.27, respectively.

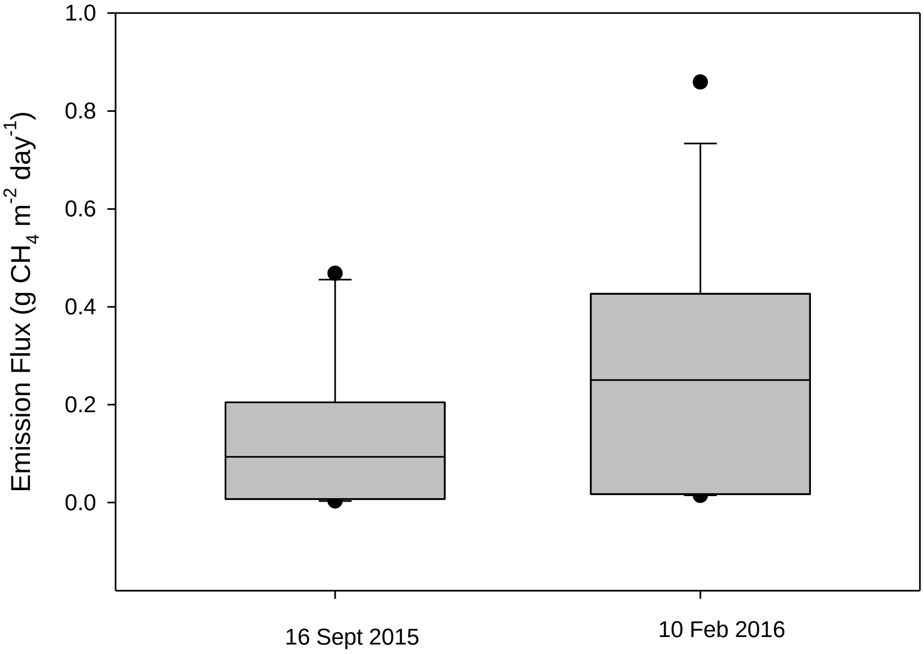

Figure 6.26. Summary of CH_4 emission fluxes measured in the water treatment facility in the Narrabri gas field. Middle line represents the median, the upper and lower bounds of the shaded boxes are the 75 and 25 % quartiles, and the dots show the minimum and maximum values, respectively.

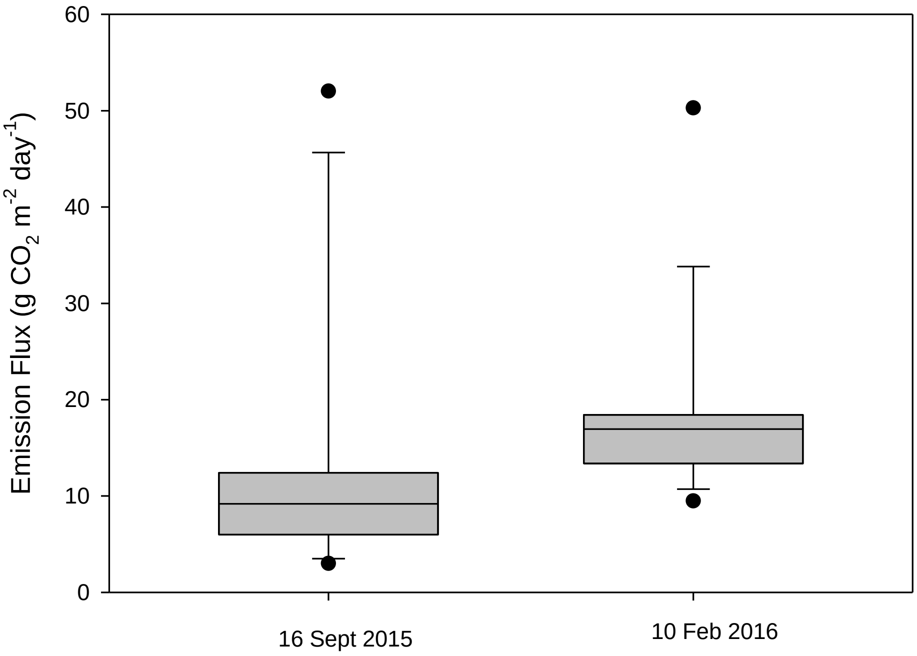

Figure 6.27. Summary of CO_2 emission fluxes measured in the water treatment facility in the Narrabri gas field. Middle line represents the median, the upper and lower bounds of the shaded boxes are the 75 and 25 % quartiles, and the dots show the minimum and maximum, respectively.

The plots represent the median (centre line in the box) while the 25 % and 75 % percentiles are represented by the lower and upper bounds of the box, respectively. The minimum and maximum values measured are shown as the round markers and the error bars represent the 10 % and 90 % percentiles.

The CH_4 fluxes were quite low, with a mean emission rate of about 0.15 g m^{-2} day^{-1} during September 2016 and a little higher at 0.26 g m^{-2} day^{-1} during February 2016, although the range of fluxes measured at different locations was similar on both occasions. In both cases, the mean CO_2 flux was much higher than that of CH_4 by about two orders of magnitude (September CO_2 flux = 13.1 g m^{-2} day^{-1}; February CO_2 flux = 18.4 g m^{-2} day^{-1}). Because there is relatively little CO_2 present in CSG, it seems likely that the higher rates of CO_2 flux were the result of microbial activity within the ponds rather than degassing of dissolved CO_2.

Based on a total pond area of 12 ha, the CH_4 emission flux from the water holding facility was 12.6 g min^{-1} (18.1 kg day^{-1}) during September and 22.3 g min^{-1} (32.1 kg day^{-1}) during February. Given the size of the facility, these emission rates are very low.

Although the maximum CH_4 emission from the water storage ponds estimated during these sites visits were low at about 32 kg day^{-1}, the water had been held in the ponds for some time (possibly weeks) during which much of the dissolved CH_4 originally present in the produced water would have outgassed to the atmosphere. It is therefore probable that the actual emissions from the facility are higher than indicated by these single measurements. The actual amount of CH_4 released will be determined by the concentration of CH_4 dissolved in the water under seam conditions, which is dependent upon the temperature, pressure and salinity of the water. While the solubility of CH_4 in saline water at the surface is low, significantly higher amounts of CH_4 are dissolved under the pressures encountered in CSG reservoirs. For instance, published solubility data show that at 100 kPa and 30°C, the solubility of CH_4 is about 0.001 g CH_4 kg^{-1} of water, whereas at 5 MPa (i.e. equivalent to approximately a 500 m deep seam) more than 0.18 g CH_4 kg^{-1} is dissolved (Duan et al., 1992). It would be expected therefore that the bulk of the CH_4 contained in the produced water at seam pressure would be released very soon after the water was pumped to the surface (e.g. at the separator at the well head, high point vents in the gathering lines, and soon after entering the holding ponds), with the remainder slowly degassing in the holding ponds. It is the latter component that was measured during the site visits to the Leewood facility. Accurately determining emissions from CSG water treatment would therefore require detailed measurements to be made over the entire water handling process.

6.7 Landfills

6.7.1 PARKES WASTE FACILITY

The Parkes Waste Facility is located about 2 km west of Parkes and covers a total area of approximately 80 ha. More detail on the facility is shown in Table 5.1. Mobile surveys were made over four site visits on 28th August 2014, 3rd December 2014, 19th February 2015 and 23rd April 2015 in and around the facility to measure ambient CH_4 levels, with highest concentrations localised near the active tipping site of the landfill. Elevated CH_4 concentrations were also measured in the vicinity of the batters of a capped cell. The maximum CH_4 concentration measured during mobile surveys around the landfill (1 m above the ground surface) was 16.6 ppm (dry) measured during the 23rd April 2015 visit.

Attempts to estimate CH_4 flux using ground level traverses were generally unsuccessful due to wind conditions that were unfavourable for the available access at the time of each visit. Instead, we used flux chambers throughout the site to measure emissions.

Surface flux measurements confirmed that the bulk of the CH_4 from the site was from a localised region centred on the active tipping area (Figure 6.28). Waste material was dumped at this location by trucks and private vehicles then periodically levelled and compacted by a bulldozer. Because of the uneven surface, flux chamber measurements were sometimes difficult to perform. In addition, the extremely heterogeneous nature of the material meant that the emission rates within the tipping area were extremely variable. For example, emission rates from sites within only a few metres were sometimes found to vary by almost a factor of 20. The maximum emission rate measured within the active waste dumping area was 35 g m^{-2} day^{-1}.

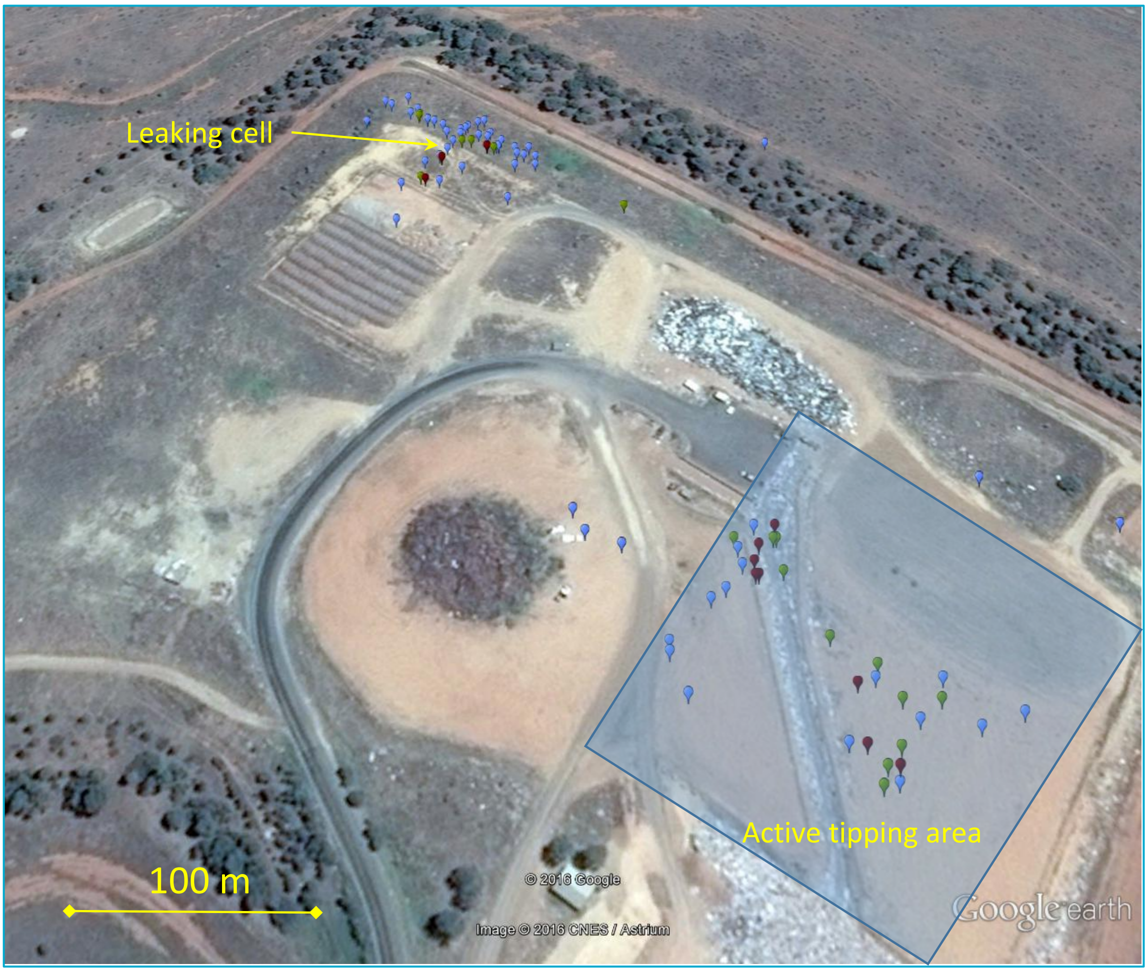

Figure 6.28. Parkes Waste Facility showing the locations where flux chamber measurements were made within the active area of the facility. This is a compilation of measurements made during four separate site visit. The blue markers represent low emissions (< 1 g CH_4 m^{-2} day^{-1}), Green markers intermediate (1 to 10 g CH_4 m^{-2} day^{-1}) and red are high emissions (>10 g CH_4 m^{-2} day^{-1}).

The other location where high emission rates were found was on the batters of a covered cell. Mobile surveys indicated the presence of CH_4 in this location and detailed chamber measurements on the batters located the emission source. This was found to be a relatively small area of only a few metres square but with emission rates of up to approximately 66 g CH_4 m^{-2} day^{-1}. Most of the other locations in this area yielded significantly lower emission rates although there were the occasional ‘hot spots’ on top of the cell within about 25 m of the main source on the batters. This suggests that although the capping of the cell was generally effective at containing CH_4 generated by the buried waste, there were some pathways available for gas egress.

Figure 6.28 shows the location of flux measurements made within the active area of the facility. However, a significant area of the tip contains covered waste in cells that have been revegetated (Figure 6.29) and mobile surveys and surface flux measurements were also made within these areas. The mobile surveys showed no sign of elevated CH_4 emissions at these revegetated sites and the flux chamber measurements returned very low results consistent with natural background levels, thus confirming the integrity of the surface cover.

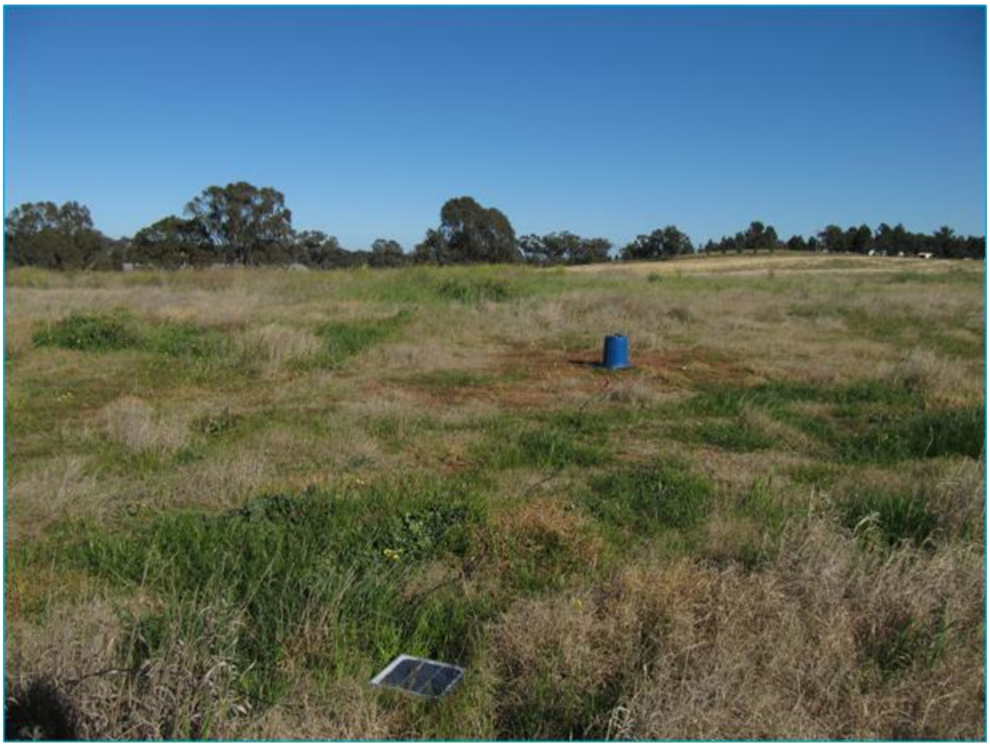

Figure 6.29. Revegetated covered cell at Parkes Waste Facility

At most of the locations where surface flux measurements were made, CO_2 emissions were occurring concurrently with CH_4 (Figure 6.30). The CO_2 flux was always greater than the CH_4 flux, in some cases by several orders of magnitude (in some locations with low CH_4 flux). However, when appreciable CH_4 was present, the CO_2 flux was roughly about a factor of seven higher than the CH_4 flux.

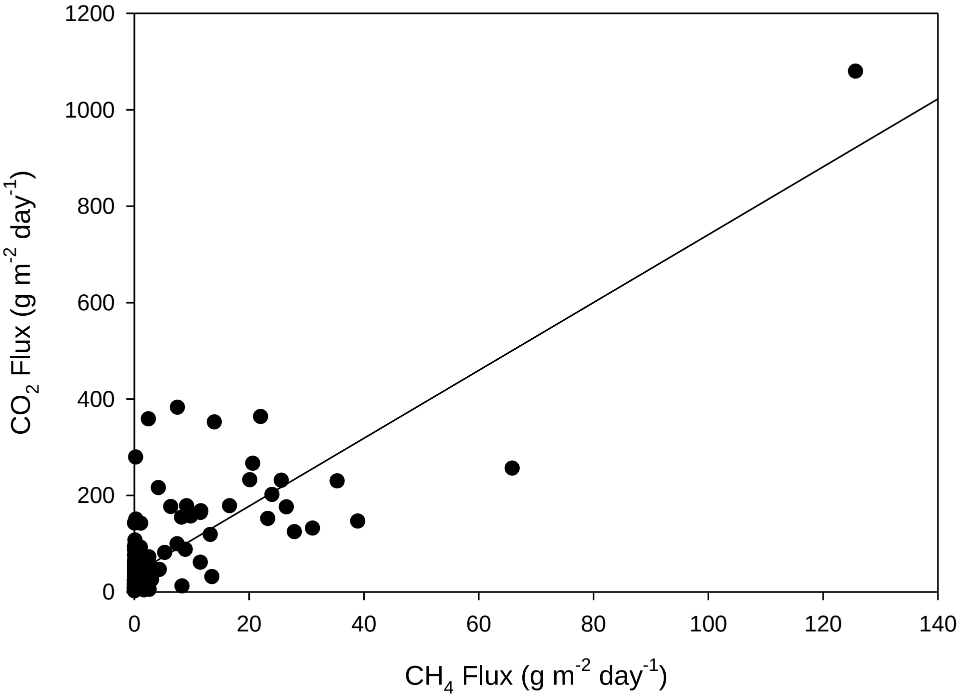

Figure 6.30. CO_2 surface flux as a function of CH_4 flux measured at the Parkes Waste Facility. Although the correlation is poor, the slope of the line is approximately seven.

Most of the flux chamber measurements were made on the ground surface, but a number of measurements were also made in the active waste tipping area at different depths. The purpose of these measurements was to determine if surface disturbances were likely to affect flux measurements, given that to surface of the area is frequently modified by operations on the site. For these measurements, the flux of the surface was first measured as usual, then remeasured on the same location immediately after 20 mm and 100 mm of soil had been removed. In all cases, the emission rate of both CH_4 and CO_2 increased as a linear function of depth as illustrated in Figure 6.31.

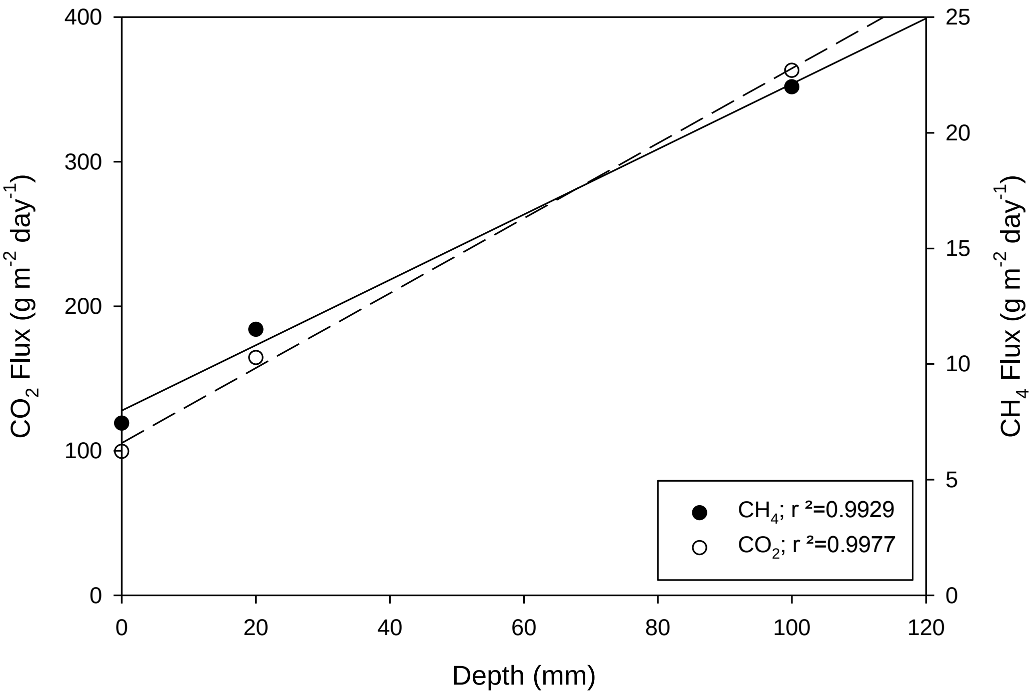

Figure 6.31. CH_4 and CO_2 flux as a function of depth below surface in the active tipping area

The results of these experiments show that the emission flux of both CH_4 and CO_2 are likely to be strongly affected by even quite small disturbances to the material within the active area of the landfill. This is important when considering how to representatively sample and measure landfill sites. The use of flux chambers themselves may affect the results obtained at some locations within the landfill if any surface clearing or preparation is required to make individual measurements. Hence, in these areas alternative methods of flux measurement may be more accurate.

It is instructive to compare the images in Figures 6.32 and 6.33. Although these were taken in approximately the same location five months apart, it is evident that the surface of the site changes due to normal operations at the facility. In Figure 6.33, the waste has been covered with soil, which given that small changes in surface covering result in large changes in emission rate, is likely to affect emissions from this section of the facility. The other point to note is that the covered section is very wet due to a storm that passed through the area during the site visit. It is highly likely that such weather events, as well as the normal day-to-day operations at the landfill, will affect emission rates. Infrequent periodic visits to the site such as those made for this project, therefore, are unlikely to be able to detect seasonal variability, if it exists.

Figure 6.32. Active tipping area of Parkes Waste Facility during the 28th August 2014 visit.

Figure 6.33. Section of freshly covered waste close to the area shown in Figure 6.32 above. This photograph was taken on 3rd December 2014.

The total CH_4 emission flux from the waste facility was estimated from the results of the flux chamber measurements made over the four site visits. Since only two sites with significant CH_4 emissions were identified during the visits (the active tipping area and cell batters, see Figure 6.28), the average emission rate from each area was calculated from the flux chamber measurements made in each region multiplied by an estimate of the area of each location. Using this approach, we estimate that the emissions from the main CH_4 producing areas are about 117 kg CH_4 day^{-1} or 43 t CH_4 y^{-1}, assuming a constant emission rate over the entire year. However, as discussed above there is a very high uncertainty associated with this estimate.

6.7.2 SUMMERHILL WASTE MANAGEMENT CENTRE

Site visits were made to the Summerhill Waste Management Centre 10 times between July 2014 and February 2016 (see Table 6.1 for site visit dates). A relatively large number of visits were made to this site because it was close to the CSIRO Newcastle Energy Centre so provided an opportunity to develop and trial methodology.

The total area of the waste management facility is of the order of 200 ha; however, we conducted measurements on the mixed solid waste site, where the largest proportion of CH_4 is produced, with an area of about 25 ha (Figure 6.34).

Figure 6.34. Summerhill Waste Management Centre. The green shaded area represents the approximate total area of the facility. The red and yellow areas indicate the mixed waste and inert waste landfills, respectively.

The facility has an inert waste site located at the western end of the site (yellow area in Figure 6.34) but the bulk of waste material is currently dumped in the mixed waste landfill (red area in Figure 6.34), which is the void of an abandoned open-cut coal mine. Initial surveys using the vehicle mounted analyser around the site confirmed that the mixed waste landfill was the main source of CH_4 within the Centre and measurements were therefore concentrated in this region. Previous studies undertaken by environmental consultants on behalf of Newcastle City Council have also shown that most of the CH_4 generated is from this area (confidential report, 2009).

Like most landfills, the mixed waste site has been divided into a number of cells into which waste is placed and sealed with a cover layer when full. There are several cells at the site which have been sealed in this way and subsequently remediated.

Most of the initial work at the Summerhill Waste Management Centre was focussed on mobile surveys to locate high flux regions and surface flux chamber measurements to determine CH_4 and CO_2 emission rates. During later visits, we also trialled the trace gas method to determine the total flux from the site. The plume traversing method was also employed simultaneously during these trials which afforded an opportunity to compare the results.

More than 120 flux chamber measurements were made across the site. Measurements made on the covered cells showed that CH_4 emission rates from the surface were very low – i.e. generally indistinguishable from natural surfaces which is consistent with the measurements made on remediated cell at the Parkes Waste Facility. The low emission rates on these sites at Summerhill may indicate that the cover layers are effective barriers against gas release but the gas reticulation system in place at this site may also likely to have removed much of the CH_4 produced in these cells.

Most of the high emissions were located near the active tipping region and especially on the batters of a partially covered waste pile (shaded area in Figure 6.35).

Figure 6.35. Summerhill Waste Management Centre showing the locations where flux chamber measurements were made. This is a compilation of measurements made during four separate site visit. The blue markers represent low emissions (< 1 g CH_4 m^{-2} day^{-1}), Green markers intermediate (1 to 10 g CH_4 m^{-2} day^{-1}) and red are high emissions (>10 g CH_4 m^{-2} day^{-1}). The shaded area near the centre of the image shows the most intense CH_4 emissions area within the landfill.

The emission fluxes within this area varied significantly. As can be seen in Figure 6.35, there are numerous locations within the shaded high flux area that yielded low emission rates of less than 1 g CH_4 m^{-2} day^{-1} (blue markers) but there are frequently other high emission points (red and green markers) within close proximity with rates several orders of magnitude higher. This is consistent with the results observed at the Parkes Waste Facility, although, the highest emission rate measured at Summerhill (493 g CH_4 m^{-2} day^{-1}) was about 15 times higher than at Parkes. Like the Parkes Waste Facility, day-to-day operations occurring at Summerhill are likely to strongly affect emissions across the site and these will mask more subtle variations due to seasonal changes.

Despite the large number of individual measurements made across the landfill, it is obvious from Figure 6.35 that the total coverage of the measurements represents only a very small proportion of the total area. Moreover, there were some locations where restricted access, difficult terrain or operating machinery prevented measurements from being made. Hence, it is possible that some high flux locations were not identified during the chamber surveys. This is also true of the vehicle mounted surveys since the terrain of the site often precluded vehicle access.

Most of the high CH_4 flux sites were also accompanied by high CO_2 flux (Figure 6.36). On average, the CO_2 flux was about 2.5 times that of CH_4 (slope of the line in Figure 6.36) although as shown in Figure 6.36, there was a significant amount of variability across measurements.

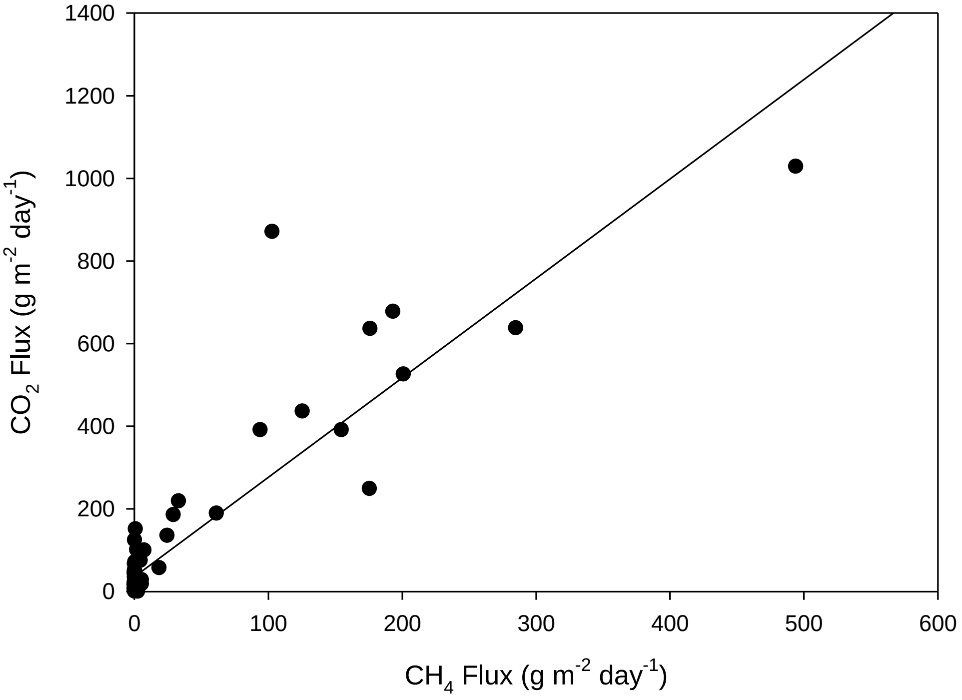

Figure 6.36. CO_2 surface flux as a function of CH_4 flux measured at Summerhill Waste Management Centre

Summerhill has a gas collection system in place where gas from covered cells is collected in a reticulation system and used to produce electricity on site. The average composition of the gas collected via the pipe network at the point just before entering the engines was about 51 % CH_4 and 35 % CO_2 (see Table D.6.1 in Appendix D), i.e. a ratio of approximately 0.7 compared to the CO_2:CH_4 ratio of 2.5 observed in the flux chamber results. This means that the bulk gas was rich in CH_4 whereas the gas emitted from the landfill surface was CH_4 lean and suggests that there is a significant amount of oxidation of CH_4 occurring in the surface layers before the CH_4 is emitted from the surface. The gas collection system operates under slight negative pressure so it is conceivable that air is drawn into the landfill, which may contribute, to this oxidation.

Although surface flux chambers are frequently used to measure emissions from landfills (e.g. NGER Method 2), one problem with the method is that many measurements are necessary to properly characterise the site. Moreover, landfills in particular are extremely heterogeneous with large variations in flux occurring over very small area (an effect that was frequently observed during this study). It is also often impractical to reach some areas of a working landfill (due to access or safety issues) so these areas cannot be measured.

With these limitations in mind, we trialled some atmospheric methods using crosswind traverses and tracer gas releases. These experiments were conducted during the site visits made on 4th February and 23rd February 2016.

On the day of the first set of experiments (4th February), conditions were overcast with a strong SSW breeze (> 10 m s^{-1}) and a temperature of 22 °C. The tracer gas experiment was conducted according to the method described in Section 5.2.3, using acetylene as the tracer and the LGR analyser. Acetylene was released in the landfill at the location shown in Figure 6.37 at a rate of about 66 g min^{-1}. The release point was selected to be close to the main CH_4 release region of the landfill (shown as the orange shaded area in Figure 6.37), which had been previously identified by flux chamber measurements made across the site. However, the acetylene release was a point source whereas the CH_4 was an area source. Because the accuracy of the tracer method depends on the tracer undergoing the same plume dispersion properties as the target gas, we attempted to minimise the effect of the differing source areas by measuring the CH_4 and acetylene concentrations a reasonable distance downwind so that the tracer had sufficient time to mix in the plume. The sensitivity of the analytical system to CH_4 and the tracer gas, however, places a practical limit on the maximum distance that measurements can be made with this technique.

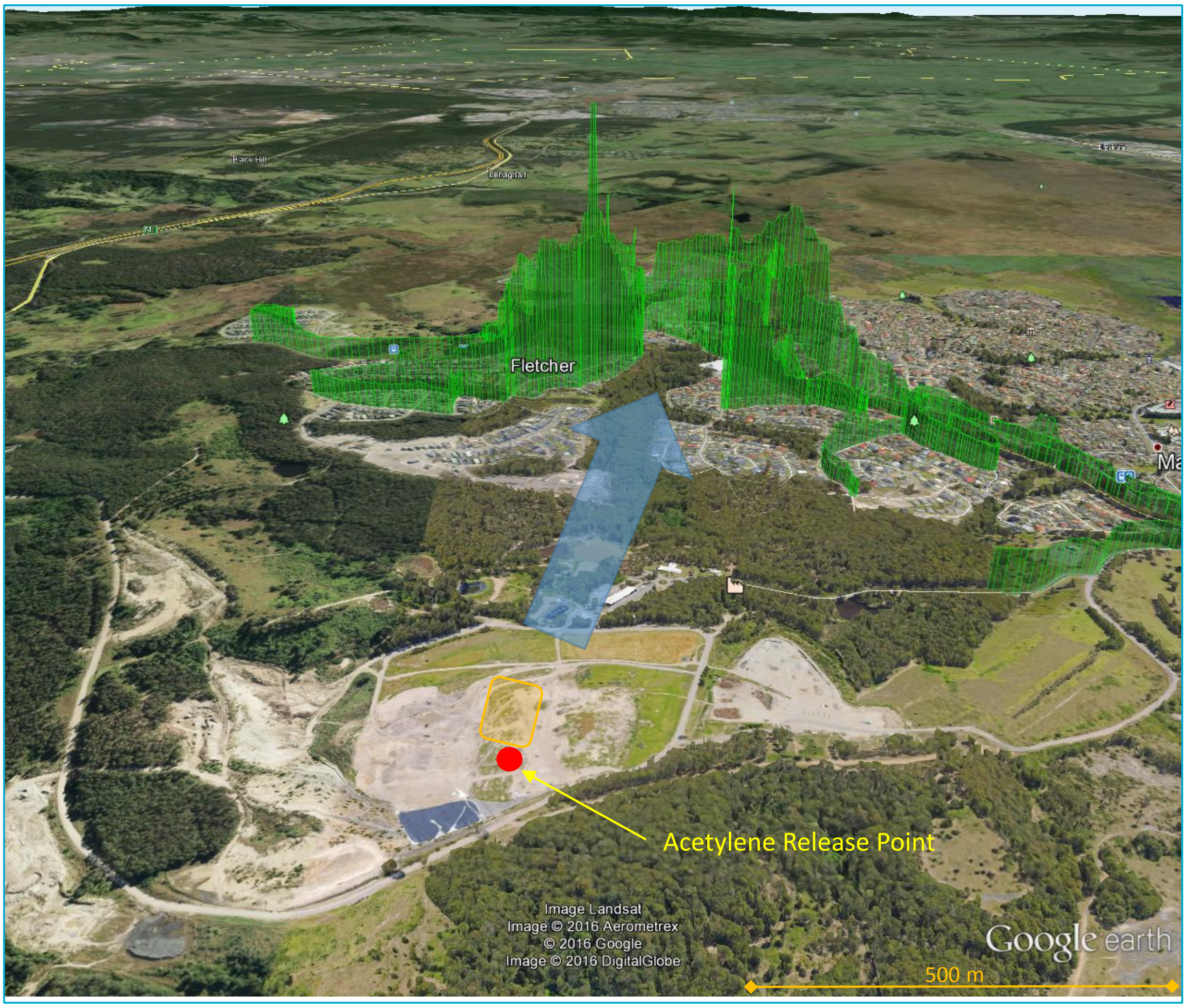

Figure 6.37. Methane plume (green trace) detected during the first tracer experiment conducted at Summerhill Waste Management Centre on 4th February 2016. The large blue arrow shows the direction of the wind at the time and the orange shaded area represents the main CH_4 emission area of the landfill. The location of the acetylene release is also shown.

Downwind CH_4 and acetylene concentrations were measured to the north of the site along Minmi Road, approximately 2 km from the release point as indicated by the green trace in Figure 6.37, which represents the CH_4 concentrations measured along the route. Elevated acetylene concentrations were detected coincident with the CH_4 plume suggesting that the tracer had been reasonably well mixed into the plume over the fetch. While CH_4 concentrations were readily detected with maxima between 0.4 and 0.5 ppm above ambient levels, acetylene concentrations were only slightly above the detection limit of the analyser (1 ppb resolution), with maxima up to about 5 ppb. Hence, the signal to noise ratio on the acetylene measurements was relatively poor which increased the uncertainty of flux estimates yielded by this experiment. Nevertheless, acetylene peaks were clearly discernible above the noise in the signal and the average CH_4 emission rate from the landfill over about one hour was estimated to be approximately 4,600 g min^{-1} (6,600 kg day^{-1}).

For comparison, flux estimates were also made according to the plume traversing method detailed in Section 5.2.2. The SSW wind produced a plume that could be traversed along Minmi Road shown as the green trace in Figure 6.37. Several traverses made over about one hour and showed that the plume was well defined with a crosswind width along the traverse route of about 1.2 km.

Under these conditions, we estimated using the plume dispersion method that the CH_4 emission rate from the site was about 5,000 g min^{-1} or about 7,200 kg day^{-1}. A similar estimate of the acetylene flux was also made using this technique. Although the acetylene concentrations were low and subject to a significant amount of uncertainty, the flux was estimated to be 61 g min^{-1}, which compares to the actual release rate of 66.5 g min^{-1}. This suggests that the estimate for the CH_4 emission rate was reasonable.

A second experiment was conducted several weeks after the first but under different atmospheric conditions. On this occasion, the weather was fine and sunny (temperature about 28 °C) with a moderate easterly breeze (~ 6 m s^{-1}). These conditions allowed traverses to be made along the private road to the west of the landfill (Figure 6.37), about 700 m from the tracer source. The closer proximity meant that the acetylene and CH_4 enhancements observed (Figure 6.38) during the traverses were about a factor of three higher than the first experiment where the acetylene levels were only just above the detection limit. Hence, the results of the second experiment are considered to be the more accurate.

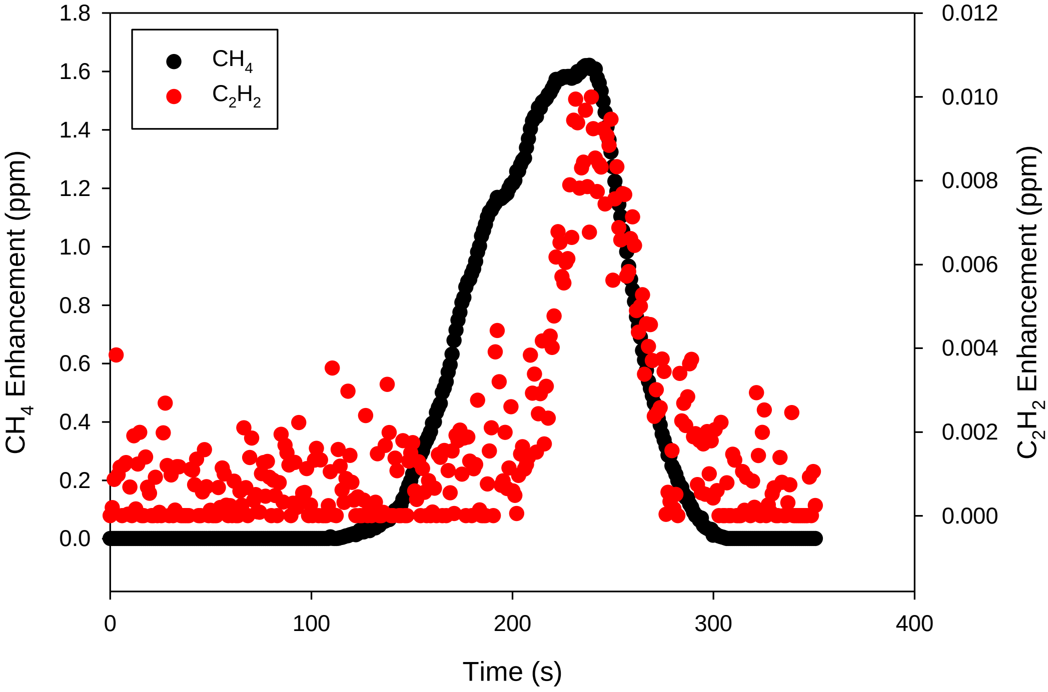

Figure 6.38. Methane (black markers) and acetylene (red markers) concentrations measured during the second tracer experiment conducted at Summerhill Waste Management Centre on 23rd February 2016.

The tracer method on this occasion yielded a total emission flux from the site of about 10,400 kg CH_4 day^{-1}. An estimate based on ground level traverses of the plume indicated a similar flux of 9,400 kg CH_4 day^{-1}. The acetylene release rate calculated from the ground level plume traverse yielded 56 g C_2H_2 min^{-1}, which compared reasonably well to the actual rate of 66.5 g min^{-1}.

A summary of the daily CH_4 emission rates estimated using the atmospheric methods and the chamber methods is provided in Table 6.9. Annual CH_4 emission rates expressed as CO_2 equivalent (CO_2-e) are also shown in Table 6.9, assuming that the emission rate was constant over the entire year for the sake of comparison since facility emissions are often reported on an annual basis. These were calculated using a 100-year global warming potential factor for CH_4 of 21, which is still used for the purposes of compiling national greenhouse gas inventories in Australia. However, it must be remembered that the annual rates shown in Table 6.9 were extrapolated from point measurements, which is likely to introduce a high level of uncertainty in addition to that associated with the measurements themselves.

Table 6.9. Summary of the CH_4 flux estimates for the Summerhill Waste Management Centre.

Method	Measurement Date	CH_4 Flux	
		kg day^{-1}	t CO_2-e y^{-1}
Flux Chamber	Various	1,722	13,197
Tracer (Expt 1)	4th Feb 2016	6,586	46,788
Tracer (Expt 2)	23rd Feb 2016	10,369	79,477
Plume Traverse (Expt 1)	4th Feb 2016	7,194	55,144
Plume Traverse (Expt 2)	23rd Feb 2016	9,400	72,053

Although the second set of experiments conducted during February 2016 indicated a higher CH_4 emission rate from the site than the first experiment, it must be noted that on both occasions there was a significant level of uncertainty in the datasets. For instance, the estimates of the acetylene flux made on both occasions using the ground level plume traverses differed from the true emission rate by more than 15 %. This is of the same order of the differences observed in the two CH_4 estimates and consequently, it is not possible to conclude that the actual emission rates were significantly different. However, it has been shown previously that landfill emissions can vary substantially with atmospheric pressure. Researchers in the U.S. found that emissions from a landfill site varied linearly by almost a factor of five over a pressure interval between about 1007 and 1023 mbar (Czepiel et al., 2003). It is therefore possible that some of the variability between the two experiments made here is a result of differing ambient conditions prevailing at the time of each measurement.

Despite the level of uncertainty, there is a general convergence of the emission estimates within the range of approximately 6,500 to 10,000 kg CH_4 day^{-1}, which is much higher than the estimates derived from surface flux chamber measurements. Our estimate of CH_4 flux based on the surface flux chambers (averaged over all site visits) was 1,722 kg CH_4 day^{-1}, almost a factor of five lower than the estimates yielded by the atmospheric methods. While these estimates were made at different times, and operational activities may have affected the emission rate, it seems unlikely that the observed differences between methods can be accounted for by operations alone.

One explanation is that the flux chamber measurements are not properly characterising the entire landfill. As noted above, flux chambers only measure emissions from a very small fraction of the total surface since it is impractical to completely cover the entire area. Consequently, the uncertainty associated with extrapolating from a relatively small area to the entire site is large. This is especially so given the variability in surface emission rates over even a few metres.

6.8 Wastewater Treatment

Four wastewater treatment facilities were selected by the NSWEPA for examination details of which are provided in Table 5.1. Although some wastewater treatment plants now incorporate CH_4 capture systems, which apart from mitigating greenhouse gas emissions greatly simplifies emission measurement, none of the plants included in the study set were so equipped.

We made a number of preliminary measurements at the Singleton Waste Water Facility to determine the most appropriate methodology for subsequent field visits to the other sites. Like all of the other sites in this project, mobile surveys were used at each wastewater treatment facility for locating emission sources. We also attempted to measure CH_4 emission rates at each plant using initially ground level plume traverses where this was feasible. However, this was mostly not practical due to the layout of the plant or unfavourable wind conditions. Most of the flux measurements were therefore made using surface flux chambers that were developed for the purpose.

6.8.1 SINGLETON

At the Singleton wastewater treatment plant, primary treatment is in two Intermittently Decant Extended Aeration (IDEA) activated sludge tanks. The tanks are intermittently stirred to aerate the raw sewage then decanted to allow solids to settle. The decanted liquid flows into the secondary treatment ponds where the total detention time is approximately 27 days, after which the effluent is discharged to wetlands before eventually entering the Hunter River.

Mobile surveys around the facility showed that most CH_4 was produced in the primary treatment tanks with negligible amounts emitted from the other ponds and facilities on the site. On several occasions, plume traverses were made to estimate the emission rate from the two treatment ponds. Figure 6.39 shows an example of the technique made during July 2014.

On this occasion, the wind was ideal for performing traverses because it was blowing directly across the two treatment ponds visible in the foreground. The resultant methane plume is clearly evident in Figure 6.39, shown as the green trace immediately downwind of the source. Upwind traverses were identical to local background CH_4 concentrations, confirming that there were no other sources of CH_4 contributing to the plumes measured at this site during this visit.

The average wind speed during these traverses was around 3 m s^{-1}, which yielded an average CH_4 emission rate of about 7.7 kg day^{-1}, derived from 10 individual traverses across the ponds. Notice in Figure 6.39 there are a number of other ponds visible in the foreground. Traverses made across these ponds, however, showed that they were not sources of CH_4.

Figure 6.39. Methane plume (shown as the green trace) detected during a downwind traverse of the effluent ponds at the Singleton wastewater treatment plant.

The traverses indicated that the CH_4 flux varied with the operation of the plant. During the decanting phase, gas bubbles could be seen breaking the surface of the liquid in the tank and CH_4 concentration in the plume appeared to be reasonably steady. However, when the stirrers were started the downwind CH_4 concentration increased significantly for a short period (less than one minute), presumably as the CH_4 trapped in the sludge was released due to the physical agitation. The CH_4 level then reduced to a low level during the remainder of the aeration phase of the operation.

During the early stages of the project we made a number of traverses at the edge of the IDEA tanks along the path shown in Figure 6.39 and found generally similar emission rates. However, as expected using the ground traversing method, there was a substantial amount of variability between individual traverses due to the meandering nature of the plume. The results of these flux measurements are shown in Figure 6.40.

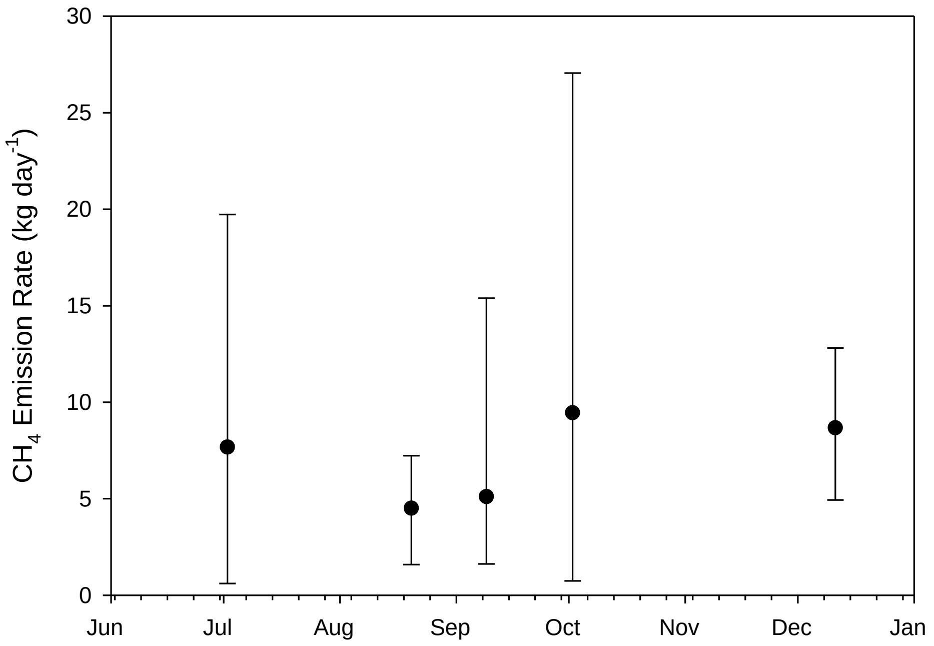

Figure 6.40. CH$_4$ emission rates estimated using plume traverses for the IDEA tanks at Singleton wastewater treatment pland during 2014.

The average emission rates, derived of from six traverses made during each visit, are shown as the solid markers in Figure 6.40; the error bars represent the minimum and maximum value from each data set. Each set of traverses was conducted over a period of approximately 15 minutes and were made during the day between about 10:00 am and 1:00 pm local time.

The overall average from all five sets of measurements is 7.1 kg CH$_4$ day^{-1}. Given the inherent uncertainty of this estimation technique, the results show reasonable agreement but because of the variability within the measurements (indicated by the wide range of minimum and maximum values), it is not possible to discern any seasonal variation that may be associated with the emissions.

Because most of the CH$_4$ was released from the IDEA tanks, we constructed flux chambers that could be fixed into position within the tanks (see Figure 5.6 in Section 5) for measuring emission flux from the tanks. One chamber was installed in each tank and left in position, the intention being to visit the site every two to three weeks over the course of the project to determine temporal variation. However, initial measurements made using the chambers yielded unexpectedly low CH$_4$ emission rates. Average emission rates measured by these chamber were around 0.04 g CH$_4$ m^{-2} day^{-1}, although the CO$_2$ flux was much higher averaging about 138 g CO$_2$ m^{-2} day^{-1}. Based on the emission rates measured with the flux chamber, the overall CH$_4$ emission from the IDEA tanks was estimated to be less than 0.5 kg CH$_4$ day^{-1}, which is very much lower than the rates estimated by the traversing.

The reason for the discrepancy was that the fixed chambers were located in about the centre of the tanks; however, we later found using the floating flux chamber (Figure 5.7 in Section 5) that there was a large spatial distribution of CH$_4$ emission rate along the length of each tank. The majority of CH$_4$ was released within about 8 m of the inlet end of each tank. The maximum CH$_4$ flux measured within this region was 38.6 g CH$_4$ m^{-2} day^{-1}, which was measured about 7 m from the inlet. This is almost 1000 times higher than the flux measured on the fixed chamber located near the centre of the tanks. The average CH$_4$ flux in this high flux region was 28.9 g CH$_4$ m^{-2} day^{-1}.

Flux chamber measurements made along the length of the tank showed a general trend of an exponential decay in emission rate as a function of downstream distance (Figure 6.41).

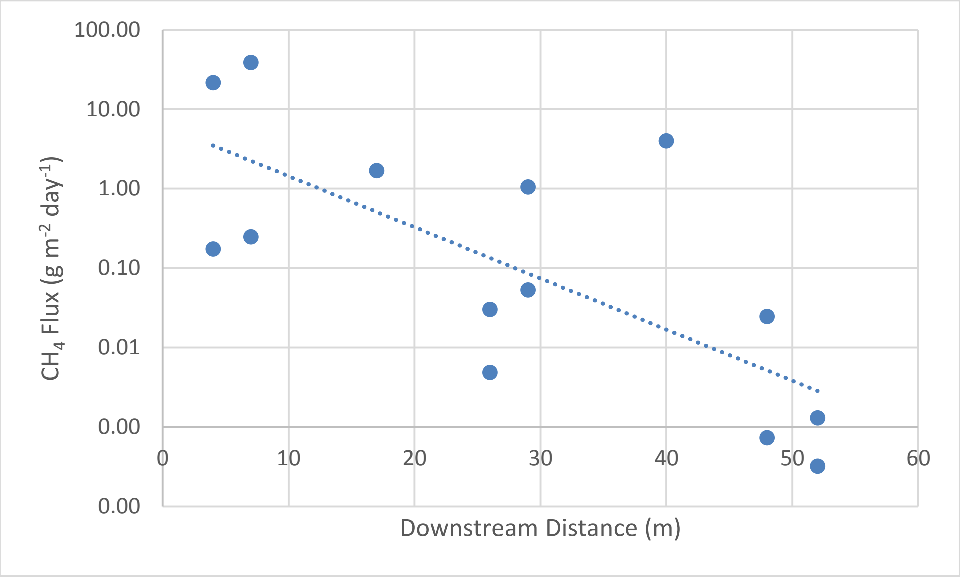

Figure 6.41. CH_4 emission flux measurements as a function of downstream distance from the inlet of an IDEA tank at the Singleton wastewater treatment plant.

Figure 6.41 also shows that there is by a large amount of variation in the CH_4 emission rate along the length of the tanks. One of the main reasons for this was that the surface emissions appeared to be very uneven, with a large proportion of the CH_4 appearing to be released by ebullition (i.e. bubbling). During flux chamber measurements, high fluxes would be encountered if large bubbles were released into the chamber. Even cursory observation of the tanks showed that the distribution of bubbles was very uneven although as mentioned already, most of the emissions originated toward the inlet end of the IDEA tanks.

6.8.2 WAGGA WAGGA

Measurements were made at the Narrung Street sewage treatment plant, which is the largest of a number of wastewater treatment facilities operated by Wagga Wagga Shire Council. Domestic and industrial waste are treated via primary, secondary and tertiary process before being discharged in the adjacent Murrumbidgee River or recycled for irrigation purposes.

Initial measurements were made at the site on 26th August 2014. These measurements were limited to mobile surveys and ambient air sampling for VOC analyses. Subsequent visits made on 17th February, 21st April and 19th November 2015 also included measurements using the floating flux chamber developed for the Singleton facility. The flux chamber measurements were limited to the newer section of the plant where good access to the tanks was provided via purpose built walkways. An older section was still in operation but access to the tanks was difficult and consequently surface flux measurements were not made within the tanks.

Ground level traverses were not feasible at the site due partly to limited vehicle access for suitable transects. In addition, the newer treatment plant is elevated above ground level (Figure 6.42) and consequently the CH_4 plume from the tanks was above the level of the vehicle mounted analyser.

Figure 6.42. Inlet of the newer treatment system at the Wagga Wagga facility. Note that the tanks are elevated above ground level.

Although traverses for the purposes of estimating emission flux were not possible, the mobile surveys nevertheless showed that like the Singleton plant, most of the CH_4 is produced in the anaerobic digestion part of the process, with relatively little CH_4 produced in the later stages. Elevated concentrations of CH_4 were always found near the inlet of the facility pictured in Figure 6.42.

Flux chamber measurements were made within the new section of the plant, which comprises a number of tanks arranged in series. Within the inlet tank, emission fluxes were comparable to the levels seen within high flux region near the inlet of the Singleton IDEA tanks. The average emission flux within the inlet tanks was 28.1 g CH_4 m^{-2} day^{-1}, with a maximum of 34.1 g CH_4 m^{-2} day^{-1}.

Within the rest of the system, emissions, like at Singleton were very low by comparison. The average emission in the aeration/decanting and outlet sections were 0.18 and 0.03 g CH_4 m^{-2} day^{-1}, respectively. Based on these average fluxes and the area of the tanks (estimated from Google Earth), the overall emissions from the new section of the Wagga Wagga plant are estimated to be 6.5 kg CH_4 day^{-1}, which is similar to the estimate made for the Singleton facility.

6.8.3 DUBBO

The Boothenba Road wastewater treatment plant is currently the main sewage treatment facility for the City of Dubbo. At the time the project was commenced a significant upgrade and expansion for the facility was underway. The new treatment plant was commissioned during late 2015 and was in operation at the time of the final site visit in November 2015.

The older plant, which is still in use, uses primary screening and grit removal followed by secondary treatment in an oxidation tank and two settling tanks. The site also has five biosolids lagoons. Treated effluent is held in two large retention ponds for recycling.

Measurements were made on 28th August 2014, 23rd and 24th February 2015, 4th May 2015 and 11th and 12th November 2015. The first set of measurements made during August 2014 comprised mobile surveys around the site using the vehicle mounted Picarro to identify the main CH_4 emission sources. One of the surveys is shown in Figure 6.43.

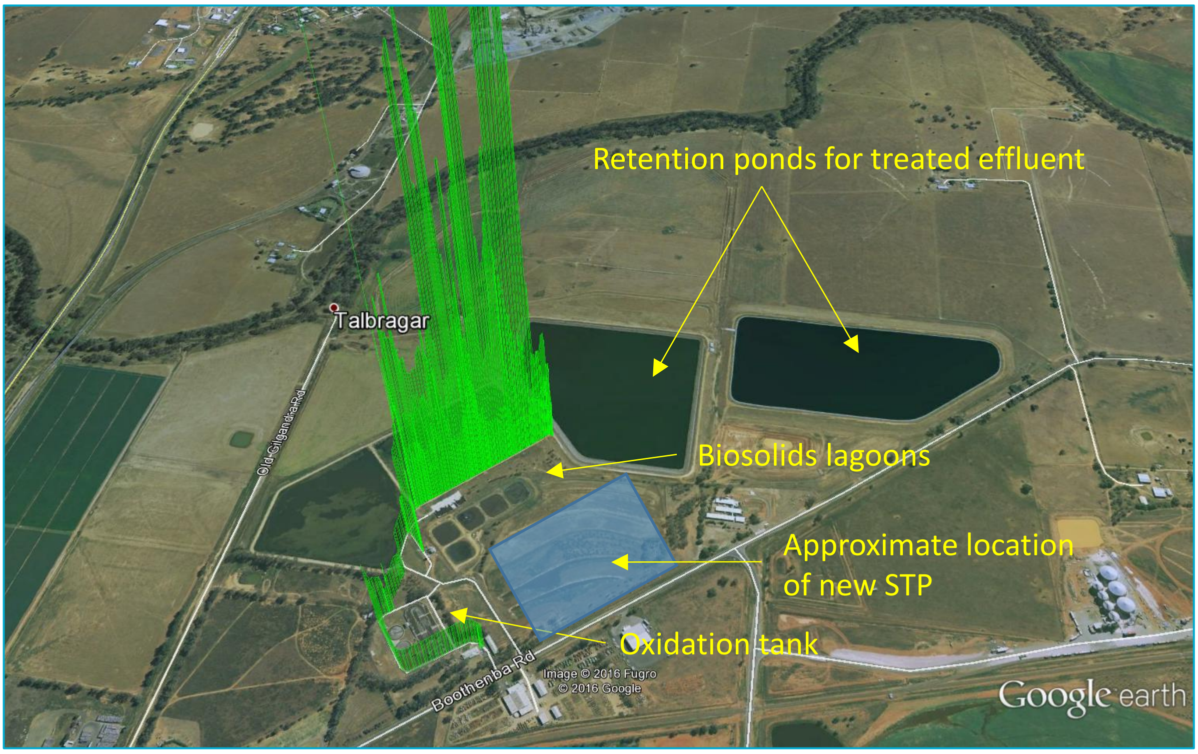

Figure 6.43. Mobile survey of the Dubbo STP made on 28th August 2014. The maximum CH_4 concentration measured downwind of the biosolids lagoons was approximately 3.5 ppm.

The traverses indicated the majority of CH_4 emissions were from the five biosolids lagoons. Circuits were also made of the retention ponds (not shown in Figure 6.43 for the sake of clarity) but the levels of CH_4 detected were close to background. Attempts to determine emission fluxes from biosolids lagoons using the vehicle traverses were unsuccessful because the traversing route (i.e. the line of high emissions indicated in Figure 6.43) was about 2 m below the level of the lagoons, so the ground level concentrations were unlikely to be the maximum concentrations within the plume. Because the ground level plume traversing method is based on the assumption that the maximum CH_4 concentrations are at ground level, hence when the plume originates above ground level, this method is not suitable for quantifying emission flux (see Section 5.2.2).

During later visits to the site, emissions measurements were made using the floating chambers in the biosolids lagoons, retention ponds and clarifier tanks located near the oxidation tank. While the oxidation tank was also a likely source of CH_4, access to the tank was limited and not well suited to the safe use of the flux chamber. Hence, direct measurements of the oxidation tanks were not made during the visits; however, mobile surveys suggested that relative to the biosolids lagoons it represented a relatively small proportion of the overall emission from the site.

Each of the biosolids lagoons had a small walkway that projected a short distance into the lagoon (Figure 6.44); all flux chamber measurements were made from these walkways for safety purposes.

Figure 6.44. Flux chamber measurements on one of the biosolids lagoons at Dubbo STP. Gas bubbles are visible on the surface of the lagoon.

The lagoons were a significant source of CH_4 with often vigorous bubbling evident on the surface. This ebullition also tended to contribute to sometimes wide variation in flux measurements, even on or near the same location within the lagoons. The results of the flux chamber measurements made on the biosolids lagoons is shown in Figure 6.45.

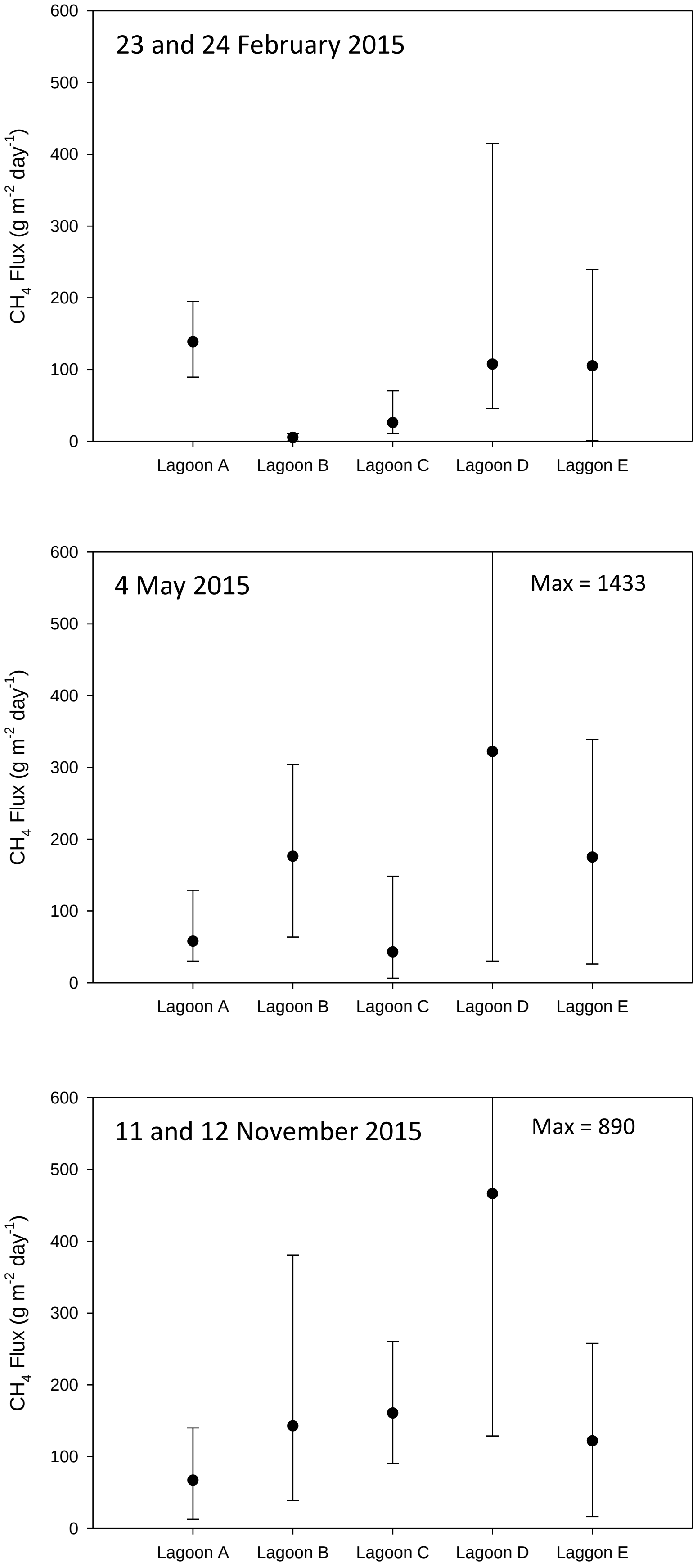

Figure 6.45. Summary of flux chamber measurement made in the biosolids lagoons at the Dubbo STP.

Compared to the Singleton and Wagga Wagga plants, where emissions were localised near the inlets of the reactor tanks, the emission fluxes from the Dubbo biosolids lagoons were high. The material in these lagoons is held for extended periods before disposal and during the site visits active bubbling was seen in each lagoon on most occasions.

At both the Singleton and Wagga Wagga sites, the maximum emission flux was less than 40 g CH_4 m^{-2} day^{-1} near the inlet to the reactors. However, the CH_4 fluxes from the biosolids lagoons were typically between 100 and 300 g CH_4 m^{-2} day^{-1}, although as shown in Figure 6.44, the variability was high. The high variability was probably due at least in part to the active bubbling of gas from the liquid. The overall average CH4 emission rate for all five lagoons measured during February, May and November 2015 was 137.5 g CH_4 m^{-2} day^{-1}.

Using the average emission flux for each lagoon and the approximate area (which was about 1,600 m^2 in each case), the total daily CH_4 emissions from the lagoons were estimated as shown in Table 6.10.

Table 6.10. Estimated daily CH_4 flux from the biosolids lagoons at Dubbo STP. All units are in kg day^{-1}.

	23rd and 24th February 2015	4th May 2015	11th and 12th November 2015	Average
Lagoon A	221	92	60	125
Lagoon B	8	282	228	173
Lagoon C	41	69	257	122
Lagoon D	172	516	746	478
Lagoon E	168	280	195	214
Total	610	1,238	1,486	1,111

Emission fluxes were also measured on the clarifier tanks and two large treated effluent retention ponds on the site. The CH_4 emissions from these components were much lower than the biosolids lagoons. In the case of the clarifier tanks, although emissions were measureable, the flux was trivial compared to the biosolids lagoons. Each of the two clarifier tanks were estimated to emit less than 0.05 kg CH_4 day^{-1}.

The retention ponds also yielded low emission rates of CH_4 but the area of these pond is large – the total area of the two ponds is approximately 22 ha so even small emission rates may contribute significant emissions. However, the emission rates from the ponds were found to be only slightly higher than the clarifier tanks at between 0.02 and 0.04 g CH_4 m^{-2} day^{-1}, so the total emission from the retention ponds was very minor compared to the total CH_4 emission from the facility. Total CH_4 emission from the two retention ponds were estimated to be 3.9 kg CH_4 day^{-1} during February, 6.4 kg CH_4 day^{-1} in May and 5.9 kg CH_4 day^{-1} in November.

6.8.4 PICTON

The Picton wastewater treatment plant is one of six operated by Sydney Water within the Hawksbury-Nepean catchment. The plant provides tertiary treatment with the treated water used for onsite irrigation. Site visits were made to the plant on 6th August 2014, 29th April 2015, 25th November 2015 and 13th January 2016. During the initial visit on 6th August 2014, measurements were limited to mobile ambient CH_4 concentration surveys and collection of samples for later analyses. Subsequent visits focussed on using the floating flux chamber method that was developed for the sewage treatment plants.

Like the other wastewater treatment facilities, elevated CH_4 concentrations were routinely measured within the plant. The highest ambient concentration measured during mobile surveys at the site was more than 18 ppm adjacent to one of the biosolids lagoons during the November 2015 visit. Surveys conducted in other parts of the facility generally showed low concentrations of CH_4, typical of background levels.

Figure 6.46 shows a plot of one of the mobile surveys made throughout the site on 6th August 2014. In this example, the maximum CH_4 concentration within the site was 3.1 ppm. However, note the narrow peak just south of Picton with a concentration of about 3.3 ppm, which was higher than in the wastewater treatment facility. A similar peak of 4.42 ppm CH_4 in the same location was also observed on 29th April 2015. The source of this peak is not known at this stage.

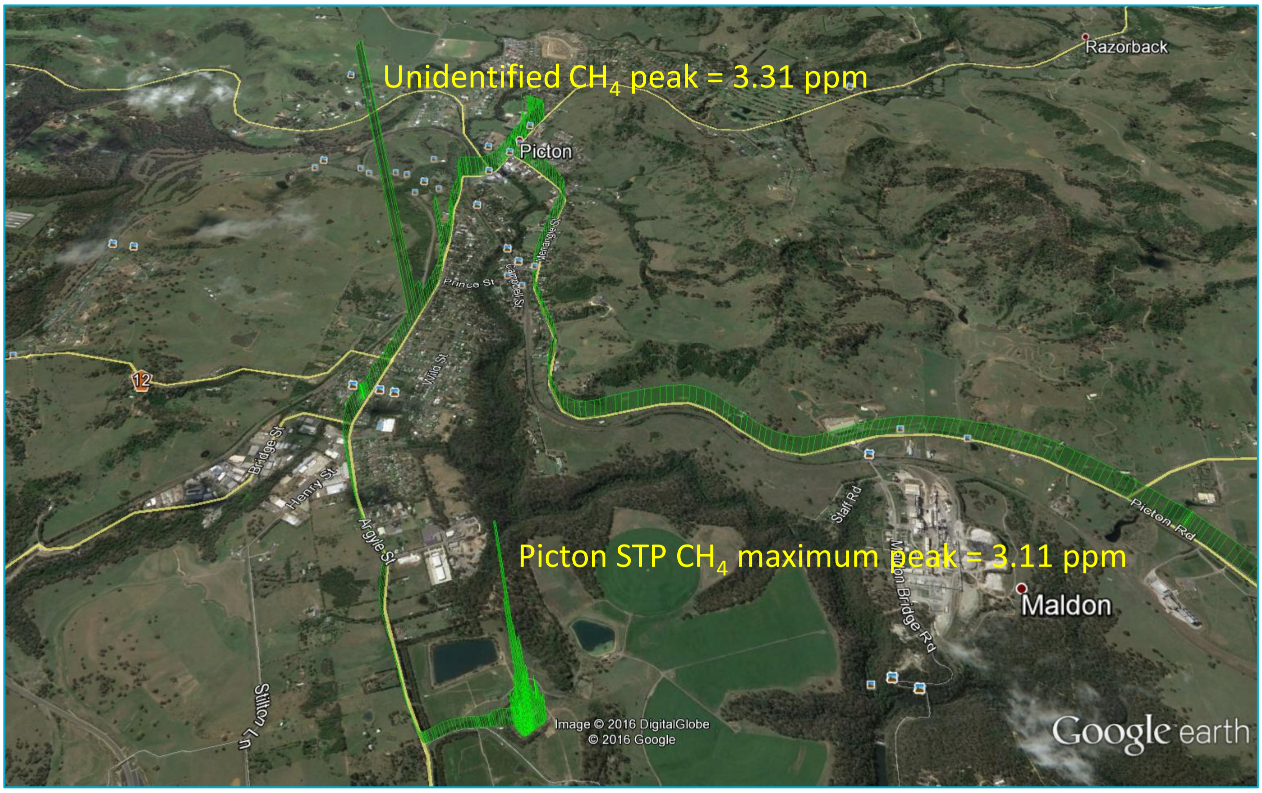

Figure 6.46. Mobile survey of the Picton wastewater treatment plant and surrounding area made on 6th August 2014. Note the unidentified peak of CH_4 unrelated to the facility located near Picton.

Access to downwind plumes at the site was generally poor and in any case, the wind conditions were unsuited to plume traverses during the visits so flux measurements using the plume traverse technique were not possible. Flux estimates were therefore based on the results of the floating chamber method.

The facility has two large retention ponds for treated effluent, which is used for irrigation. Like the ponds measured at the other sites, CH_4 emissions were low, typically less than 0.01 g CH_4 m^{-2} day^{-1} so that their contribution to the total site CH_4 emissions is very small; we estimated that the daily emission rate from the two retention ponds was less than 0.5 kg CH_4 day^{-1}. Carbon dioxide emissions from these ponds were also very low, in many cases showing negative flux, which is consistent with results observed at treated water impoundments in other sewage treatment facilities.

Methane emissions from the aeration/decanting reactors were also quite low; up to about 0.02 g CH_4 m^{-2} day^{-1} and again contributing only a relatively small amount of CH_4 to the overall site emissions. The bulk of the CH_4 emissions were produced in the two biosolids lagoons. These lagoons, like those at the Dubbo plant had much higher CH_4 emissions than all of the other sources combined. During the 29th April and 25th November 2015 visits, total emissions from the lagoons were estimated to be about 41 and 39 kg CH_4 day^{-1}, respectively. These rates were much lower than those seen at the Dubbo lagoons but still represented about 99 % of the emissions from the entire Picton site. However, on 13th January 2016, the emissions from the two lagoons were very much higher than on the two previous occasions. In this case, there was strong ebullition on the lagoon surfaces with emissions rates ranging from 370 to 2,500 g CH_4 m^{-2} day^{-1}. The average emission rate over the two lagoons was 1,140 g CH_4 m^{-2} day^{-1}, which corresponded to a daily emission rate from both lagoons of 2,960 kg CH_4 day^{-1}.

The reason for the very high emission rate in January compared to the other periods is not clear. While it is likely that the warmer temperatures in summer would result in higher emission rates (Toprak, 1993), it seems less likely that temperature effects alone could account for the difference. It is also possible that the rate of CH_4 generation is dependent upon how long the material is held in the lagoon before it is removed and disposed of. Whatever the reason for the large variation between individual results, the large differences observed over the monitoring period illustrate that extrapolating period measurements over long periods (e.g. annually) may introduce large errors into the estimate.

7 Results and Observations – VOC Emissions

Ambient monitoring for hydrocarbon and air toxics VOCs was undertaken for the source categories that were monitored for methane i.e. natural sources, the Camden region of CSG activity, animal feedlot, coal mining sites, CSG production facilities, landfills and wastewater treatment plants. Rice farming was excluded from VOC monitoring as this source was specifically selected for the purposes of its biogenic methane emissions and as such, ambient VOC determinations were not considered pertinent to this category. The results from ambient VOC determinations for each land-use source are discussed in the sections that follow and observations are made with respect to the source impact on ambient concentrations, the type of compounds present at each source and their likely origins. The basis for this evaluation is firstly introduced in Section 7.1 and the source locations are detailed in Section 7.2.

7.1 Basis for VOC Ambient and Source Evaluations

Terminology

Terminology and conventions used in the discussion, and which are of specific relevance to this project, are summarised as follows:

- Ambient concentration – reported as a mixing ratio in units of ppbv (parts per billion by volume).
- Ambient level – a more general description of concentration using the terms: "ultra-trace" < 0.1ppbv, "trace" < 1ppbv, "low" < 5-10ppbv, "significant" > 10ppbv, "high" > 50ppbv.
  Note that the concentration associated with each term will be dependent on the typical ambient concentration of a specific compound or that of the VOCs collectively.
- Data rounding – for ease of reading and to contextualise the discussion, concentration data at and above 0.1ppbv has been rounded to one decimal place. Appendix B reports this data at a higher level of accuracy. Data below 0.1ppbv and above 100ppbv has not been rounded past that reported in Appendix B.
- Data averaging – where a set of results to be averaged includes nil detects these are set to a value of the detection limit/2.
- Hydrocarbon – compound composed only of carbon and hydrogen atoms.
- Cn – a group of hydrocarbon compounds with "n" number of carbon atoms.
- Aliphatic hydrocarbon – compound with carbon atoms arranged in a chain. Includes the alkanes, alkenes and alkynes (see separate listing below).
- Alkane (saturated hydrocarbon, paraffin) – aliphatic hydrocarbon compound with single carbon-carbon bonds.
  Terms within this class include; n-alkane which has a straight carbon chain; iso-alkane which is any branched-chain alkane (especially one having a methyl group attached to the penultimate carbon atom of the main chain); cyclic alkane (naphthene) which has carbon atoms arranged in a ring.
- Alkene (olefin) – aliphatic hydrocarbon containing a double carbon-carbon bond in the carbon chain.
- Alkyne – aliphatic hydrocarbon containing a triple carbon-carbon bond in the carbon chain.
- Aromatic – planar cyclic compound consisting of conjugated double and single bonds. A monoaromatic compound contains a single ring.
- Cyclic - compound with carbon atoms joined in a ring; includes aromatic hydrocarbon compounds.
- Halocarbon or halogenated compound – organic compound containing chlorine, bromine or fluorine (the halogens specific to this study).
- Oxygenated compound – organic compound containing oxygen including aldehydes, ketones, alcohols, ethers and esters (the oxygenates specific to this study).
- Nitrogenous compound – organic compound containing nitrogen.

- Sulphur containing compounds – organic compound containing sulphur.

Source Recognition

Various studies undertaken by CSIRO Air Quality group in aspects of ambient and emissions monitoring have been used as a resource for the VOC component of this project. Publications sourced from the open literature have also been referenced with respect to the land-use sources investigated in this project and the specific compounds likely to be attributable to a source.

CSIRO studies which were used as a basis for our observations included those in ambient monitoring of ozone precursor VOCs in the Sydney region (Azzi et al., 2007), in diesel vehicle emissions testing undertaken with Diesel Test Australia and the Roads and Traffic Authority (Tibbett et al., 2005), in mixed petrol and ethanol-fuelled vehicle emissions testing with Orbital Australia (DEWHA, 2008), and in fuel composition and vapour studies (Tibbett et al., 2009) for a programme of work undertaken by NSW DECCW (DECCW (NSW), 2010 unpublished). The latter report included data from ambient monitoring conducted by a consulting laboratory, to which we had access, and aspects of which were included in the NSW State of the Environment report (NSW EPA, 2012). Projects undertaken in emissions from vegetation were also used as a resource (Nelson et al., 2000, Nelson et al., 2004). Together these studies provide a current understanding of ambient VOC concentrations in the Sydney region, the relationship of hydrocarbon VOCs with petrol and diesel fuelled vehicle emissions sources, and of biogenic contributions to source emissions.

Source recognition is based on the interpretation of the ambient VOC profile using the organic characteristics of, and relationships between, the compounds observed. As an introduction to the discussion of the results, the basis for this interpretation is described below. Where applicable, a summary of observations of relevance to the land-use monitoring undertaken in this project is included.

Biogenic emissions

Of importance to the evaluation of source emissions is the differentiation between compounds associated with natural emissions from surrounding vegetation and biological processes, and those biogenic emissions that are specific to the source but show similar characteristics, and possibly only an enhancement of emissions from the natural source. This relates to biological decomposition at waste treatment sites or that from biological processes associated with animal feedlots for example. Certain organic classes of compounds are characteristic of biogenic emissions and the following outlines their relevance for the specific compounds detected in this project.

Isoprene is a primary emission from vegetation and is enhanced during periods of plant growth. As such higher emissions will occur in the warmer months of the year when levels of photosynthetically active radiation (PAR) are higher. It is noted that isoprene reacts relatively quickly in the atmosphere (in the presence of sunlight and oxides of nitrogen) to methacrolein and methylvinylketone (Guenther et al., 1993). These oxidation products were not the focus of this study.

The compounds known as monoterpenes, such as the pinenes and cymenes, or monoterpeniods, such as eucalyptol (1,8-cineole), are emitted from trees and shrubs often in response to heat stress or to mitigate disease or insect attack.

Oxygenated compounds, such as alcohols, aldehydes, ketones and esters are commonly associated with emissions from both living and decaying vegetation and as such are commonly found in the atmosphere (Singh et al., 2004), and are commonly measured in ambient air (Kelly et al., 1993, Hunter et al., 2001). Ethanol is a major emission from natural environments (Kirstine and Galbally, 2012), as is acetone (ATSDR, 2015). The NSW EPA emissions inventory places a significant proportion of total ethanol and acetone emissions in the biogenic category of which most is from uncut grass (NSW EPA, 2008). Ethanol, acetone and other oxygenates are also components that would be expected in the vicinity of animals and their by-products (Le et al., 2005, Rabaud et al., 2003).

In this study, gaining an understanding of the typical concentration range for what could be termed ‘vegetative and biological induced background’ for these compounds allowed the land-use source contribution to be distinguished above this level.

- Isoprene was quantitatively measured and monoterpenes were qualitatively detected at many of the land-use sites and their concentration or prevalence tended to represent the density and type of vegetation and the season.
- Ethanol, acetone and isopropanol were observed in the ambient air at levels that tended to be consistent with the level of biological activity associated with nearby vegetation, soil or water. Higher ambient temperatures induced some increase in concentration, as would be expected for compounds with a biological origin.
    - Ethanol concentrations averaging 5ppbv and in the range of 1-25ppbv were present in moderately vegetated environments at the natural and semi-rural sites.
    - Acetone was present at average concentration 5ppbv and in the range 1-20ppbv in moderately vegetated environments.
    - Isopropanol was present at average concentration 1ppbv and in the range 0.1-4ppbv in moderately vegetated environments.
- Other biogenically derived oxygenates were source intensity and/or source dependent (such as acrolein, 2-butanone, methyl isobutyl ketone, methyl butyl ketone).
- Various C_4-C_{10} oxygenated compounds, primarily alcohols, aldehydes, ketones and esters, were qualitatively determined as likely to be of biological origin and were enhanced in ambient air at the feedlot, landfills and wastewater treatment sites.

Ubiquitous VOCs

The well-known atmospheric stability of the Freon™ group and similar halocarbons (Lilian et al., 1975) makes their presence likely to be detected as a constant ambient background even in relatively pristine environments.

Carbonyl sulphide is emitted from oceans and volcanoes and is known to be the most abundant sulphur-containing compound that is naturally present in the atmosphere (Andreae and Crutzen, 1997). Typical atmospheric concentrations of around 0.5ppbv are estimated (DeLeon-Rodrigueza, 2012). It is also a product of photo-oxidation of carbon disulphide (Newhook et al., 2002). Dimethyl sulphone is found in the atmosphere as a marine emission (Montzka et al., 2004*)*.

Compounds identified in ambient samples from this project that are regarded as ubiquitous to the atmosphere are:

- Dichlorodifluoromethane, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane and carbon tetrachloride. Relatively consistent ambient concentrations were measured at the natural source and semi-rural sites, and at all other land-use sites. An average ambient concentration of 0.5ppbv, 0.2ppbv, 0.05ppbv and 0.07ppbv was determined for these compounds, respectively, from site monitoring conducted in this study.

  Note 1: 1,1,2-trichloro-1,2,2-trifluoroethane was slightly more variable in its measured concentration than the other halocarbons and moved to concentrations close to its detection limit. It was therefore reported as "not detected" in some samples and for averaging purposes, a concentration of DL/2 was therefore assigned.

  Note 2: The compounds were not present as method related artefacts. Instrument background analysis and method blank samples (canisters that contain only the zero air used for sample pressurisation) did not yield these compounds, nor were they found in samples that did not contain ambient air (e.g. raw CSG sourced well gas). These compounds are therefore directly attributable to ambient air.
- Carbonyl sulphide and, tentatively, dimethyl sulphone were qualitatively identified in the ambient air from all land-use sources.

Vehicle emissions

It is pertinent to discuss the hydrocarbon VOC profile that typifies ambient air in environments impacted by vehicle emissions. This provides the basis for determining whether, or not, on-road or off-road vehicles were contributing to the emissions observed from the land-use activity under investigation.

The suite of hydrocarbon VOC targeted for assessment in this project comprises the major urban derived compounds contributing to emissions to ambient air. As such they are, in the main, directly attributable to vehicle emissions as products of fuel combustion, as fuel residuals in the exhaust, and from fuel evaporative losses (for both liquid and gaseous fuels). Certain industrial emissions (waste combustion and fuel refining for example) may also emit these compounds to ambient air in urban areas.

Notwithstanding the implications associated with vehicle technology, the efficiency of on-board catalytic converters and of vapour recovery devices for mitigation of VOC emissions, the following generalisations apply to the hydrocarbon profile typically observed for vehicle emissions to ambient air:

- The C_2 and C_3 hydrocarbons (ethane, ethene, acetylene, propane and propene) are products of liquid fuel combustion and these compounds are significant components in the composition of a typical raw petrol and diesel vehicle exhaust.
- Ethene and propene are products of combustion of higher alkanes and therefore generally dominate ethane and propane concentrations in raw exhaust.
- The relative levels of these compounds in exhaust emissions is effected by the efficiency of the vehicle catalyst with preferential removal of more reactive species (acetylene > alkenes > alkanes) in modern vehicles. Note once released to ambient air other processes such as photochemistry also effect the relative concentration of these and other exhaust components, as discussed further on.
- The major component in Australian LPG auto gas is propane. LPG is in common use as fuel and hence gas losses from vehicles, or other sources, will contribute to emissions of this compound to ambient air.
- The C_4 to C_6 aliphatic compounds, such as isobutane, n-butane, isopentane, n-pentane, 2-methylpentane and other C_6 isomers, are major components in petrol fuel. C_4 compounds are present as both combustion and fuel derived components in vehicle exhaust and C_5/C_6 compounds primarily as unburnt, or partially burnt, fuel in the exhaust. The higher concentration of these compounds in the fuel and their higher volatility make them significant components of vehicle evaporative emissions (refer later point).
- The n-butane component of petrol is reduced when formulating a summer grade fuel to reduce the fuel's vapour pressure. As such, this compound will vary in relative concentration in exhaust and evaporative emissions, dependent on season.
- The larger aliphatic hydrocarbons, C_7 through to C_{12}, are seen in petrol exhaust as unburnt fuel residuals. These are present at lower levels in the emissions than C_4-C_6 compounds, and at concentrations that roughly follow the composition of the fuel.
- Diesel fuel is composed of hydrocarbons from around C_9 to C_{26} and hence the VOC component (through to C_{12}) will be obvious in a diesel exhaust hydrocarbon profile as components of unburnt fuel. Their low vapour pressure minimises their emissions as vehicle evaporative emissions.
- Aromatic hydrocarbons (for example benzene, toluene, ethylbenzene, xylenes, trimethylbenzenes, ethyltoluenes) are components of petrol vehicle exhaust and evaporative emissions. In petrol-fuelled vehicles, these compounds are found primarily as fuel residuals. Toluene is a major component of petrol exhaust followed by xylenes. The activity of the vehicle catalyst also impacts on the relative concentration of these, and other of the more reactive compounds, in the exhaust.
- The mono-aromatics are not components of diesel fuel and are present in the exhaust of diesel-fuelled vehicles as products of combustion of higher alkyl-aromatics present in the raw fuel.

- The ratio of toluene to benzene can be indicative of vehicle-derived emissions. Based on a knowledge of the concentration of these compounds in raw petrol, and the activity of the on-board catalyst in preferential removal of these compounds from the exhaust, a ratio of around 2-3 is typically measured in the exhaust of mid-new model petrol-fuelled vehicles (DEWHA, 2008). Diesel derived emissions exhibit the opposite relationship with lower relative concentration of toluene over benzene in the exhaust (Tibbett et al., 2005).
- Isoprene, a primary emission from trees and other vegetation, is also a minor component of motor vehicle exhaust and can be detected as such when vehicle emissions are a major source (Borbon et al., 2003).
- Ethanol is present in vehicle emissions using ethanol mixed petrol fuel (DEWHA, 2008).
- Evaporative fuel losses from the vehicle are also a component of the overall vehicle related emissions mix to urban air. The vapour pressure of each compound and its concentration in the raw fuel primarily controls the relative mass emission for each compound (aside from temperature and various aspects of vehicle technology and emissions control). Toluene comprises the largest proportion of the aromatics in the composition of the raw fuel and as such is a dominant component of evaporative emission. Also significant are the more volatile and higher concentration aliphatic compounds, such as isobutane, n-butane, isopentane, n-pentane and 2-methylpentane (DEWHA, 2008, Tibbett et al., 2009).

The impact of photochemistry on ambient concentrations of hydrocarbon VOCs must also be taken into account in interpreting VOC profiles. Put simply, the effect of photodecomposition is most apparent for the more reactive compounds, such as the alkenes and aromatics, and the alkanes remain relatively stable after their emission to the atmosphere. Higher levels of sunlight and the intensity of radiation will enhance reactivity, in the presence of NO_x, resulting in lower ambient concentrations of the more reactive hydrocarbon VOCs relative to the less reactive compounds (where the source VOCs are the same). On this basis, the concentration of hydrocarbon VOCs in the atmosphere would be lower in summer than in winter for the same source and intensity. Conversely, warmer ambient temperatures enhance evaporative emissions of fuel-derived hydrocarbons from vehicles and other sources, thereby increasing ambient VOC concentrations of fuel volatiles. These aspects are discussed in Section 7.4.2 and 7.4.3 where the evidence for seasonal variability in vehicle-derived emissions is evaluated for the Camden campaign undertaken in spring and summer.

Odorous compounds

Sulphur containing compounds such as mercaptans (thiols) and organic sulphides are well known for their odorous properties. These compounds as well as volatile fatty acids, phenols, indoles and amines have been associated with animal husbandry (Le et al., 2005; Trabue et al., 2008).

The mercaptans and organic sulphides are commonly associated with sewer gases and biogas odours. The nitrogenous bicyclics, indole and skatole, are compounds known to be present in sewage waters as they occur naturally in human faecal matter. Despite their strong odour, these compounds have a high affinity for water and are therefore difficult to isolate from ambient air where they are present at low concentration (Godayol et al*.,* 2013).

Various alcohols, aldehydes, ketones and esters, mainly from biological processes (as discussed above) also contribute to odour. These compounds are found in the emissions from animal feedlots (Le et al., 2005, Rabaud et al., 2003) and landfill sites (Fang et al., 2012, Rodriguez-Navas et al., 2012). They have been reported to be commonly associated with raw sewage outfalls (Dewulf et al., 1999) and in the emissions from sewage treatment (Dincer and Muezzinoglu, 2008).

Major odorous source emissions observed at the sites monitored in this project included:

- The alkyl sulphides; dimethyl sulphide and dimethyl disulphide, nitrogenous compounds such as nitromethane and nitroethane, and numerous C_4 to C_8 aldehydes, ketones and alcohols associated with the cattle feedlot.

- The aldehydes such as butanal, pentanal, hexanal and heptanal were found at the landfill and wastewater treatment sites, along with various other C_4-C_{12} oxygenated compounds associated with biological decomposition.

Waste disposal and wastewater treatment

Various solvents are used in industrial processes, smaller operations such as cleaning and painting processes, and in household applications. Their disposal to waste is commonly observed in the emissions from landfill and wastewater treatment.

Trichloroethylene, tetrachloroethylene are dichloromethane are important chlorinated solvents that are classed as hazardous by health assessment agencies. These compounds are found in landfill emissions and are commonly used as markers for this source. The chlorinated solvents are less studied in relation to sewage treatment, however their occurrence has been reported at wastewater treatment plants (Atasoy et al., 2004), and as components of sewer gas (Haas and Herrmann, 1996, Pennell et al., 2013). Tetrachloroethylene has been reported in wastewaters in EU risk assessments (WHO, 2006).

Trichloroethylene is a commonly used solvent for extraction of greases, fats, oils, waxes and tars, as a vapour degreaser of metal parts, and as a chemical intermediate in chemical production. It has common household usage as a paint stripper, in adhesives and cleaning fluids, for example.

Tetrachloroethylene is a solvent used in various applications, including dry cleaning, textile processing, metal cleaning and as a chemical intermediate in industrial processes.

Dichloromethane is another common solvent used in many industrial and household applications and is present in emissions from landfills and wastewaters.

Other common solvents used in household and industrial applications include the aromatic compounds (xylenes for example), acetone and various other ketones and ethanol, to name a few. The aldehyde, acrolein, is also seen in waste emissions, generally from its use as biocide in various applications.

A number of monoterpenes, such as limonene and a-pinene, are used as fragrances in consumer products, and are found in emissions from solid waste disposal (Steinemann, 2015). Their use in household cleaning products makes these compounds common in the emissions from wastewater (Godayol et al., 2013).

Significant emissions from solid and liquid waste disposal and treatment originate from biological decomposition and the biological waste itself (such as sewage), as discussed in sub-sections dealing with biogenic emissions and odorous compounds, above. Emissions of various alcohols, aldehydes, ketones and esters originate from biological processes at landfill sites (Fang et al., 2012, Rodriguez-Navas et al., 2012) and are reported to be associated with raw sewage outfalls (Dewulf et al., 1999) and in the emissions from sewage treatment (Dincer and Muezzinoglu, 2008). Sulphur and nitrogen containing species are also common odorous emissions from waste sources.

Compounds specific to, or enhanced in, landfill and wastewater treatment at the sources monitored in this study included:

- Solvent emissions of acetone, 2-butanone, acrolein and methyl butyl ketone from landfill and enhanced ethanol and acetone from wastewater treatment.
- Chlorinated solvents; trichloroethylene, tetrachloroethylene, dichloromethane, chloroform and benzyl chloride at the landfill site; cis-1,2-dichloroethene, trichloroethylene, tetrachloroethylene at wastewater treatment sites.
- C_4 to C_{12} oxygenates as aldehydes, ketones, alcohols, phenol and esters from both landfill and wastewater treatment.
- Monoterpenes; limonene and a-pinene from landfill and wastewater treatment.
- Ethane originating from the methane gathering system at the landfill site.

CSG sourced well gas

The hydrocarbon characteristics of CSG sourced well gas was based on the development of a method for analysis of non-methane hydrocarbon (NMHC) VOCs with particular focus on the minor hydrocarbon compounds, i.e. those > C_5 including mono-aromatic compounds. The hydrocarbon concentrations obtained from this measurement were important in determining whether CSG emissions were impacting the ambient air at sites where CSG production was active.

Well gases exhibited the following hydrocarbon VOC characteristics:

- Compounds in the hydrocarbon range from C_2 through to C_8 were measurable to a detection limit of 0.007ppmv.
- Aliphatic hydrocarbons were present as the alkane class; as straight-chain, branched and cyclic alkanes.
- Alkenes were not observed in well gases.
- Aromatics compounds; benzene, toluene and xylenes, were detected and their concentration was positively correlated with the concentration of the non-methane hydrocarbons in the gas.

Aromatic compounds in coal seam gas are not unexpected as these compounds are generated under the processes involved in its thermogenic and/or microbial formation. Fragmentation of the basic coal structures during microbial decomposition will generate hydrocarbon intermediates including alkanes and related structures, benzene, toluene, ethylbenzene, xylenes and polycyclic aromatic hydrocarbons. These can undergo anaerobic oxidation and fermentation to form methanogenic substrates that finally undergo methanogenesis to produce the methane dominant gas (Strapoc et al., 2011). As these compounds are found in coal formation waters it is likely that residual aromatic compounds will be found in the coal seam gas. This is on the basis also that BTEX compounds are no longer used as additives to hydraulic fracturing fluids used in certain gas extraction operations (NSW Trade and Investment, 2012).

Air Toxics NEPM Priority Compounds

The aromatic compounds prioritised under the Australian National Environment Protection (Air Toxics) Measure (NEPM) are benzene, toluene and xylenes. Note that formaldehyde and benzo[a]pyrene are also NEPM priority air toxics but these were not the focus of this study, as discussed in the Section 5.3.1.

The current ambient concentrations designated as investigation levels under the NEPM (NEPC, 2011) for the aromatic compounds are:

Benzene	3ppbv (annual average as arithmetic mean of 24-hour average)
Toluene	100ppbv/1000ppbv (annual average/24-hour average)
Total xylenes	200ppbv/250ppbv total xylenes (annual average/24 hour average)

With respect to this report the NEPM levels are provided for information only. The ambient determinations in this study are point-in-time observations for source impact purposes and the sample was usually taken downwind of the source, often within the emission plume. The ambient concentration so obtained is likely to be higher than a 24-hour average as this averages the range in concentrations over a period which includes times when emissions may be low. The methodology employed in this study was adopted for source characterisation purposes and does not apply to ambient assessment for NEPM investigation purposes.

7.2 VOC Monitoring Campaigns

The source categories and sites monitored for ambient hydrocarbon and air toxics VOCs and the dates of the VOC monitoring campaigns are listed in Table 7.1. The sampling locations and selection criteria have been previously detailed in Section 5.1 and Table 5.1. A regional map of source locations can be found in Figure 6.1 and a description and map of individual sites can be found for each source in Section 6.

All sources assessed for methane were assessed for VOCs with the exception of rice farming. As this is an agricultural source of specific relevance in its emissions of methane, VOC determinations were not considered pertinent to this category. Each site was sampled for ambient VOCs at a number of locations that typify the source. The sample was taken as close as possible to the source and/or downwind of the source and at the time that was coincident with elevated ambient methane concentrations.

Canister collection was used at all sites for ambient VOC sampling of priority VOCs based on criteria described in Section 5.3.1 and using methodologies detailed in Section 5.3.4.

Further characterisation, for the determination of non-standard compounds, was undertaken for a number of representative sites, as discussed in Section 5.3.2. This involved the re-evaluation of the output from the VOC analysis using the methodology described in Section 5.3.5. Sorbent tube samples were also taken for further characterisation of source emissions using the sorbent methodology described in Section 5.3.5. Summerhill landfill, and Singleton and Picton wastewater treatment plants, were chosen for sampling using sorbent tube collection as these sites had shown, from canister results, a high potential for source related non-standard compounds. These are marked with (ST) in Table 7.1.

Table 7.1 Source categories and sites monitored for VOCs by canister sampling, including sites selected for sorbent tube sampling (the latter marked ST).

Source Category	Site Location	Monitoring Date	Vicinity / Sample Information
Natural	Yaegl Nature Reserve, Maclean	12-Jul-14	Forest
	Cuba State Forest, Leeton	14-Oct-14	River
		14-Oct-14	Bushland
		02-Dec-14	River
		02-Dec-14	Bushland
		04-Aug-15	Bushland
		04-Aug-15	Bushland (duplicate sample)
Camden Region	Site 1 Medhurst Rd, Gilead		Semi-rural; near AGL CSG plant, in vicinity of motorway
	Site 2 Glenlee Rd, Spring Farm		Composting facility; near train line, coal pits in vicinity
	Site 3 Glenlee Rd, Spring Farm		Waste disposal centre; outside SW boundary of landfill area
	Site 4 Adriana Lane, Mount Annan	10 sites 06-Aug-14	Suburban reserve; at northern edge of pond
	Site 5 Glenlee Rd, Spring Farm	10 sites 20-Nov-14	Rural farmland; at rail line underpass
	Site 6 Racecourse Rd, Menangle Park	10 sites 25-Feb-15	Racecourse; at entrance roadway, semi-rural surrounds
	Site 7 Glenlee Rd, Ambarvale	10 sites 29-Apr-15	Semi-rural; near Menangle Road intersection
	Site 8 Cummins Rd / Fitzpatrick St, Menangle Park		Semi-rural; low density housing to south
	Site 9 Menangle Road, Menangle		Semi-rural; off main road, in vicinity of woodland and river
	Site 10 Off Woodbridge Rd, Menangle		Semi-rural/scrub land; on road to agricultural college
Cattle Feedlot	Jindalee Feedlot, Springdale	26-Aug-14	Feedlot
		16-Feb-15	Feedlot
		22-Apr-15	Feedlot
Coal Mines	Rix's Creek Mine, Hunter Valley	15-Apr-15	In-pit
		22-Jul-15	In-pit
		22-Jul-15	ROM Pad
	Gunnedah Basin Mining Region	21-Jul-14	Roadside outside mine lease; within CH_4 plume from mine
CSG Facilities	AGL Camden	19-Aug-15	Well Pad C3
	AGL Gloucester	16-Jul-15	Well Pad G1
		16-Jul-15	Well Pad G2
		23-Sep-15	Well Pad G2
	Santos Narrabri	28-Jul-15	Compression plant
		29-Jul-15	Well Pad N7

Source Category	Site Location	Monitoring Date	Vicinity / Sample Information
Landfills	Parkes Waste Facility	28-Aug-14	Active tipping area
		23-Apr-15	Active tipping area
	Summerhill Waste Management Centre, Newcastle	16-Jul-14	Tip face
		09-Jul-15	Tip face
		09-Jul-15	Tip face (concurrent sample)
		09-Jul-15 (ST)	Tip face
Wastewater Treatment	Singleton Wastewater Treatment Plant	02-Jul-14	Settling pond #1
		02-Jul-14	Settling pond #2
		02-Jul-14	Site background
		08-Jul-15	Raw sewage inlet
		08-Jul-15 (ST)	Raw sewage inlet
	Wagga Wagga (Narrung Street) Sewage Treatment Plant	26-Aug-14	Aeration tank; during aeration cycle
		17-Feb-15	Raw sewage Inlet
		21-Apr-15	Raw sewage inlet
	Picton Wastewater Treatment Plant	06-Aug-14	Biosolids lagoon #2
		29-Apr-15	Biosolids lagoon #2
		25-Nov-15	Aeration tank
		25-Nov-15 (ST)	Aeration tank
CSG Sourced Well Gas	AGL Gloucester	16-Jul-15	Well G1
		16-Jul-15	Well G2
		23-Sep-15	Well G2
		23-Sep-15	Well G3
	AGL Camden	19-Aug-15	Well C1
		19-Aug-15	Well C2

7.3 Natural Sources

Yaegl Nature Reserve, near MacLean NSW, and Cuba State Forest, near Leeton NSW, were monitored as sites depicting natural environments that are minimally impacted by urban, industrial or other land-use activities.

The site locations of the natural source can be found in Table 5.1 and a detailed description of the sites can be found in Section 6.2. Details of the VOC site monitoring campaigns can be found in Table 7.1.

The quantitative results for PAMS hydrocarbon VOCs and TO-15 air toxic VOCs for the natural source sites are presented in Appendix B.1 in Tables B.1.1 and B.1.2, respectively. The results are also presented graphically in Figures 7.1 and 7.2 at the end of this sub-section.

7.3.1 YAEGL NATURE RESERVE

The VOC monitoring site at the Yaegl Nature Reserve (Yaegl NR) was located in a forested environment and canister sampling was undertaken on the 12th July 2014, as listed in Table 7.1. Further campaigns were not undertaken as this site showed a VOC profile consistent with traffic impact from the main roads bordering the site, as discussed below, and it was found that the Cuba State Forest Site provided a better signature of a natural source.

Priority VOCs

The Yaegl Nature Reserve showed evidence of a level of anthropogenic activity in that C_2-C_4 hydrocarbons (0.1ppbv butane through to 3.9ppbv ethene) were found from the PAMS hydrocarbon suite, along with toluene (0.3ppbv) and the larger substituted aromatics. Benzene was unusually high in relation to the other aromatics (0.8ppbv). Overall, these compounds and their relative concentrations are indicative of a vehicle emissions source. This reasoning is fully discussed in Section 7.1, where the hydrocarbon profile associated with vehicle emissions is described, and in Section 7.4 where traffic impact on Camden ambient air was observed. This finding is supported by Yaegl's location, which is bounded by the Pacific Highway to the northwest, and urban development and agricultural land on the other borders (refer Section 6.2 and Figure 6.5).

Examination of the TO-15 air toxics VOC suite found site emissions to be dominated by oxygenated compounds. Specifically; ethanol (4.4ppbv), acrolein (0.9ppbv), acetone (7.1ppbv) and isopropanol (3.6ppbv). These compounds were also dominant in the samples from the Cuba State Forest sites and a discussion of their likely biogenic origins is presented with the Cuba State Forest results in Section 7.3.2, on the basis outlined in Section 7.1. Trace concentrations of certain halogenated species were also detected at levels that were replicated in the Cuba State Forest samples. Their occurrence as ubiquitous atmospheric compounds is discussed with the Cuba State Forest results, below, on the basis outlined in Section 7.1.

Isoprene was not detected at the Yaegl site. This compound might be expected to be present in a forested area due to its origins as a primary emission from trees and vegetation. However, it is likely that isoprene concentrations would be low in winter when this sample was taken. It is noted that isoprene reacts relatively quickly in the atmosphere (in the presence of sunlight and oxides of nitrogen) to methacrolein and methylvinylketone (Guenther et al*.,* 1993). These oxidation products were not the focus of this study.

7.3.2 CUBA STATE FOREST

Cuba State Forest (Cuba SF) was monitored for VOCs in both river and bushland locations on 14th October 2014, 2nd December 2014 and 4th August 2015, as listed in Table 7.1.

Priority VOCs

Cuba State Forest showed very low levels of compounds from the hydrocarbon suite, the highest being isobutane (0.9ppbv) from the October sample and ethene (0.9ppbv) from the December sample. Benzene was not detected in most samples and toluene was not detected or found at trace concentration. Based on the results from the Camden surveys, detailed in Section 7.4, the overall hydrocarbon VOC profile is significantly lower than the levels found in semi-rural environments. As such, the Cuba SF sites appeared substantially free of traffic impacts, fuel or other combustion-derived hydrocarbons and hence provided a baseline for comparison of the source impacted sites monitored in this project.

Broadly similar oxygenate concentrations were measured at the Cuba SF as were found at the Yaegl NR. Specifically ethanol (1.4-7.2ppbv), acrolein (ND-0.5ppbv), acetone (2.0-18.7ppbv) and isopropanol (0.3-1.3ppbv). The Cuba SF ambient concentrations were somewhat variable over the six campaigns and generally showed lower levels in the October campaign and higher in the December campaign. The December campaign was the only sample where 2-butanone was detected (0.5ppbv at the river location and 0.9ppbv bushland). As referenced in Section 7.1, these oxygenated compounds are emitted by living plants and through vegetative decomposition and are commonly found in the atmosphere. Ethanol and acetone are major emissions from natural environments. The NSW EPA emissions inventory places a significant proportion of total ethanol and acetone emissions in the biogenic category of which most is from uncut grass. These compounds may also be emitted from various land-use and manufacturing activities. The higher concentrations at Cuba SF that were seen in both the bushland and river samples in the December campaign is indicative of elevated biogenic emissions that occurs on warmer days, and further evidence of the purely biogenic source of these compounds at this site.

The emissions of oxygenated compounds were accompanied by the presence of isoprene, a primary emission from vegetation, at around 1.5ppbv, at the Cuba State Forest river and bushland sites in Dec-14. This also suggests that higher biogenic emissions were apparent in summer when temperature and levels of photosynthetically active radiation (PAR) are higher. Monoterpenes are compounds that are emitted from trees and shrubs and these were detected from the characterisation studies, as discussed below. Eucalyptol was found at the bushland location at Cuba SF and another monoterpene (likely p-cymene) was found at both Yaegl Reserve and Cuba SF sites.

A number of halogenated species, specifically dichlorodifluoromethane, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane and carbon tetrachloride were present at both Yaegl and Cuba reserves. The concentration for each was fairly consistent across the sites and averaged 0.5, 0.3, ND/0.08, 0.09ppbv, respectively. Note that 1,1,2-trichloro-1,22-trifluoroethane is slightly more variable in its measured concentration than the other halocarbons and therefore moves to concentrations close to its detection limit. Hence it will show as not detected in some samples. For averaging purposes, a concentration of DL/2 is then assigned, yielding an average for this compound of 0.05ppbv at the natural sites. Comparison of the occurrence and levels of these compounds with that seen in semi-rural environments and indeed at the various other source locations show that these compounds tend to be ubiquitous in the ambient air.

Note that these compounds were not found from instrument background analysis or in canister blank samples (which contain only the zero air used to pressurise the sample), nor were they found in samples of CSG well gas indicating that they are not present as method related artefacts. The well-known atmospheric stability of the Freon™ group and similar halocarbons makes their presence as an ambient background likely even in relatively pristine environments, as referenced in Section 7.1.

Characterisation Studies

Characterisation studies were undertaken by chromatographic review and mass spectral interpretation of the results from VOC analysis, as described in Section 5.3.2. Samples from the Yaegl Nature Reserve and from Cuba State Forest at the river and bushland sites monitored in the 2014 campaigns were evaluated. A number of additional compounds to the PAMS and TO-15 suites were identified and this qualitative information is presented in Table 7.2. Together with the results for priority VOCs, this information has been used to predict anthropogenic source emissions versus those likely to originate from biogenic processes.

Two sulphur containing compounds; carbonyl sulphide and, tentatively, dimethyl sulphone were identified in both the Yaegl and Cuba SF samples. As discussed in Section 7.1, carbonyl sulphide is emitted from oceans and volcanoes and is known to be the most abundant sulphur containing compound that is naturally present in the atmosphere. Typical atmospheric concentrations of around 0.5ppbv are estimated (DeLeon-Rodrigueza, 2012). It is also a product of photo-oxidation of carbon disulphide in the atmosphere (Newhook et al., 2002). Dimethyl sulphone is found in the atmosphere as a marine emission (Montzka et al., 2004). In this project, these compounds were identified in all ambient samples and at a consistent chromatographic signal intensity (as concentration equivalent). On these bases, carbonyl sulphide and dimethyl sulphone are considered unrelated to the source emissions and are therefore classed as ubiquitous in ambient air.

Oxygenates, primarily as C_7 to C_{10} aldehydes, ketones and alcohols, were found at both sites with additional compounds isolated particularly from the bushland site at the Cuba State Forest. These compounds are commonly associated with emissions from both living and decaying vegetation, as referenced in Section 7.1. Eucalyptol (1,8-cineole) was found at the bushland location at Cuba SF and another monoterpene, likely p-cymene, was found at both Yaegl Reserve and Cuba SF sites. These common terpenes are known to be emitted from the leaves of trees and shrubs.

Table 7.2 Compounds identified from characterisation studies of canister samples for the natural souce sites

Compound Name or Class	Presence in Ambient Air		
	Yaegl Nature Reserve 12-July-14	Cuba State Forest river region 14-Oct-14	Cuba State Forest bushland area 14-Oct-14 and 2-Dec-14
Carbonyl sulphide	✓	✓	✓
Sulphur containing; likely dimethyl sulphone	✓	✓	✓
3-Heptanone	-	-	✓
Oxygenate; possibly 2-ethylhexanal	-	-	✓
Benzaldehyde	✓	✓	✓
C_7 oxygenate; likely alcohol	✓	✓	✓
C_8 alcohol; possibly 2-ethyl-1-hexanol	-	✓	✓
Monoterpene; likely p-cymene	✓	✓	✓
Eucalyptol (1,8-cineole)	-	-	✓
C_9 oxygenate; likely nonenol or nonanal	-	✓	✓
C_{10} oxygenate	-	-	✓

7.3.3 SUMMARY OBSERVATIONS

Yaegl Nature Reserve showed a minor traffic derived impact and therefore it was considered unsuitable to continue VOC monitoring campaigns at this site for the purposes of establishing a natural source baseline.

The Cuba State Forest sites showed trace level and generally consistent VOCs concentrations for all campaigns. The site is considered to be largely unaffected by anthropogenic activities and these results provide a baseline for comparison of ambient emissions from other land-use sources.

The natural source, exemplified by Cuba State Forest, was characterised by:

- Nil to trace levels of C_2 to C_{12} aliphatic and aromatic hydrocarbons associated with vehicle exhaust, other combustion products or fuel related components.
- Certain halocarbons and sulphur containing compounds ubiquitous to the atmosphere; specifically dichlorodifluoromethane, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane, carbon tetrachloride, carbonyl sulphide and, tentatively dimethyl sulphone. The halocarbons were found at trace level (< 0.5ppbv) at the natural source.
- Emissions associated with vegetation and biological processes such as isoprene, alcohols (ethanol, isopropanol and larger alcohols), aldehydes and ketones (acetone, acrolein and larger carbonyls), and monoterpenes (eucalyptol and p-cymene).

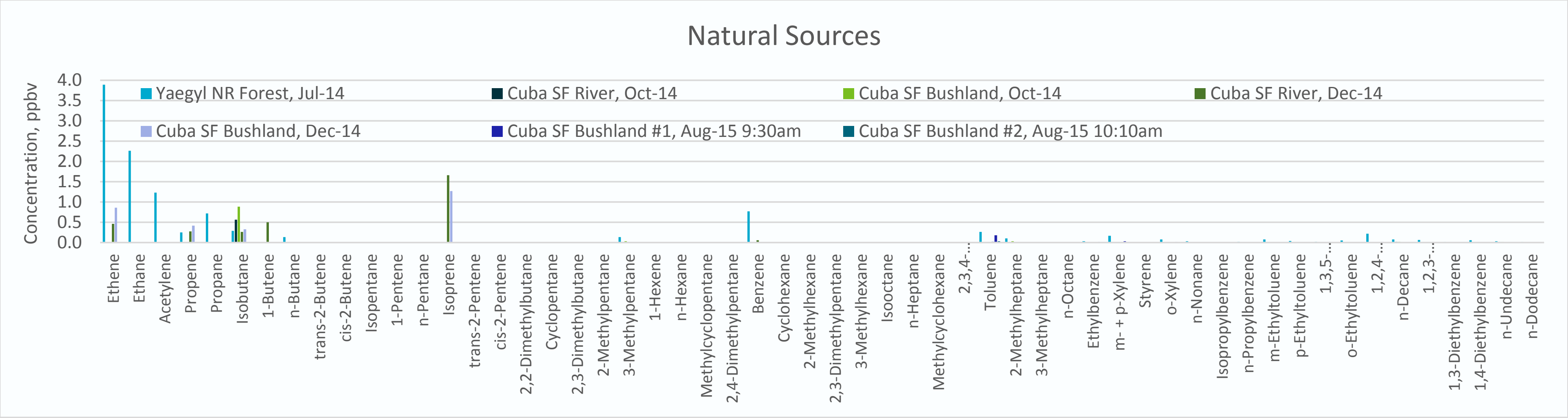

Figure 7.1 PAMS hydrocarbon VOCs measured at the natural source sites

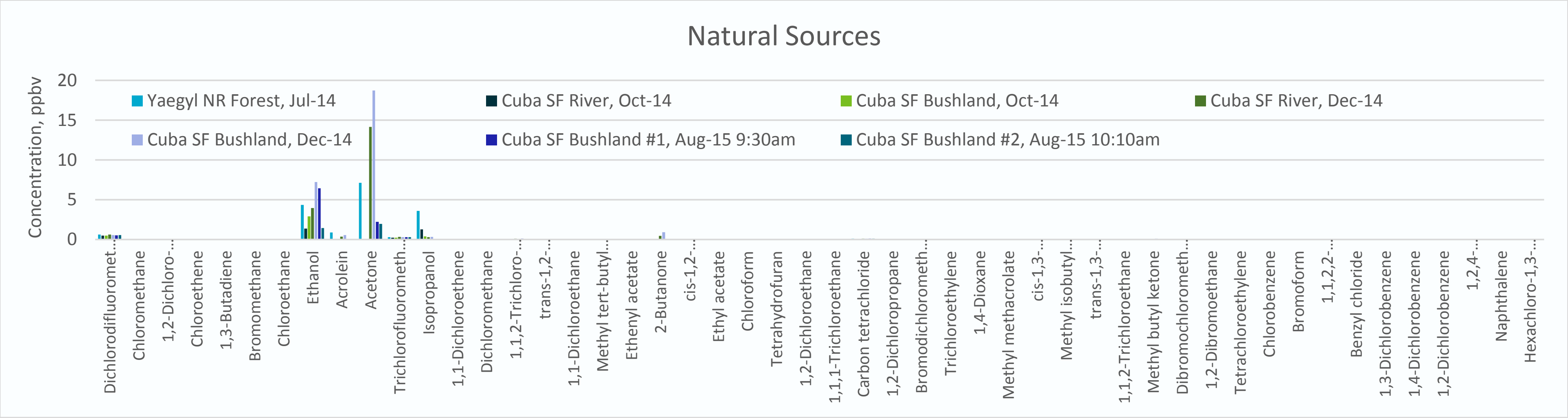

Figure 7.2 TO-15 air toxics VOCs measured at the natural source sites

7.4 Camden Region

Ten sites across the Camden region were monitored for priority VOCs. These sites were in suburban and semi-rural locations across a geographical area where CSG production was active. The site locations are shown in Figure 7.3 and the general characteristics of each site are listed in Table 7.3.

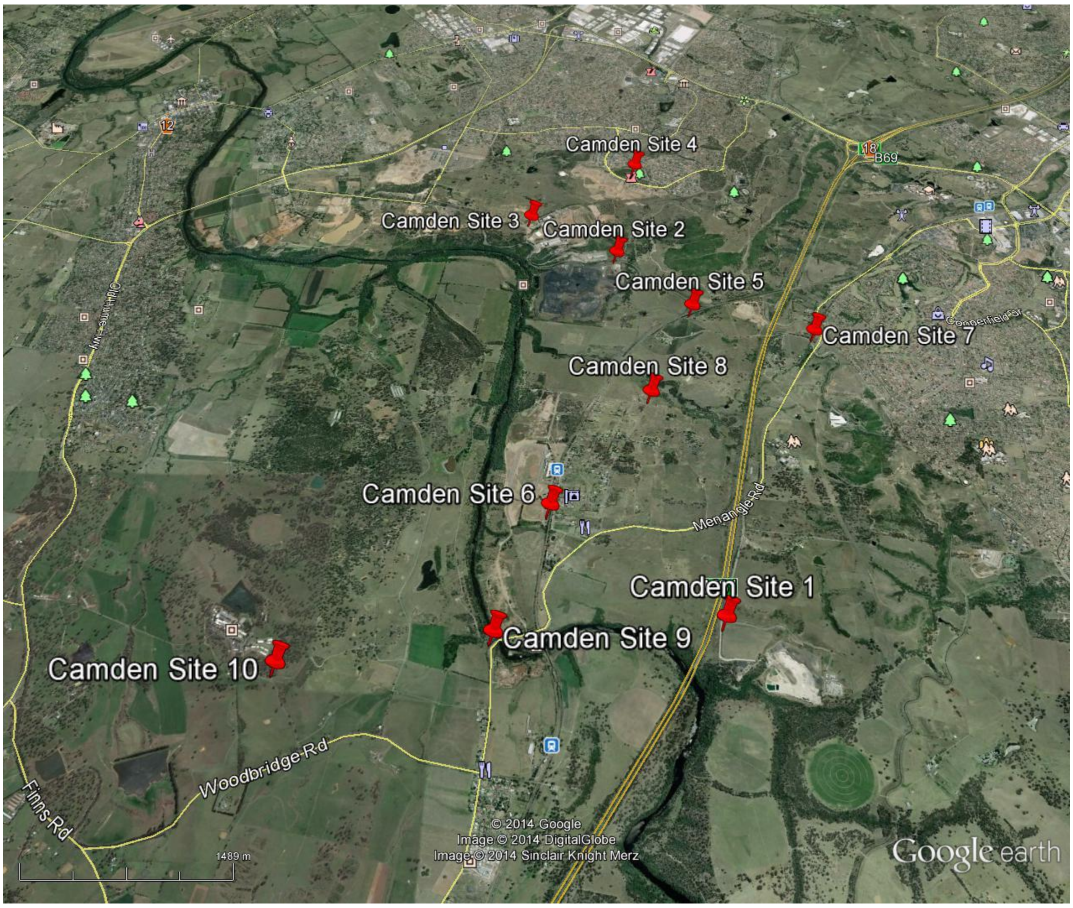

Figure 7.3 Geographical locations of the ten VOC monitoring sites in the Camden region (reference Google Earth)

Table 7.3 VOC monitoring sites for the Camden regional campaigns

Camden Sites and Location		Site Characteristics
Site 1	Medhurst Rd, Gilead	Semi-rural; near AGL CSG plant, in vicinity of motorway
Site 2	Glenlee Rd, Spring Farm	Composting facility; near train line, coal pits in vicinity
Site 3	Glenlee Rd, Spring Farm	Waste Centre; outside SW boundary of landfill area
Site 4	Adriana Lane, Mount Annan	Suburban reserve; at northern edge of pond
Site 5	Glenlee Rd, Spring Farm	Rural farmland; at rail line underpass
Site 6	Racecourse Rd, Menangle Park	Racecourse; at entrance roadway, semi-rural surrounds
Site 7	Glenlee Rd, Ambarvale	Semi-rural; near Menangle Road intersection
Site 8	Cummins Rd / Fitzpatrick St, Menangle Park	Semi-rural; low density housing to south
Site 9	Menangle Road, Menangle	Semi-rural; off main road, in vicinity of woodland and river
Site 10	Off Woodbridge Rd, Menangle	Semi-rural/scrub land; on road to agricultural college

The sites were monitored in the early morning on one day in winter, spring, summer and autumn to give some indication of seasonal variation in VOC concentration and to provide information on the general variability in VOC emissions that may be expected at, and between, each site. The Camden sites were monitored for priority VOCs by canister sampling. Campaign dates for the VOC monitoring are listed in Table 7.1.

Sampling was undertaken in the early morning to reduce the effects of mixing depth and to avoid changes in composition of VOCs that can occur later in the day when the effects of photochemical reactivity become apparent. In each campaign, the 10 sites were monitored between the hours of approximately 8:00 and 9:00 am. This period will also provide an indication of the impact of suburban traffic emissions during the morning peak.

7.4.1 WINTER CAMPAIGN

The winter monitoring campaign was undertaken between 8:15 and 9:00am on the 6th August 2014. During this period the average ambient temperature was 4.4°C, the wind direction was southerly at a speed of 0 to 6 km h^{-1}.

The results from VOC analysis of PAMS hydrocarbon and TO-15 air toxic VOCs for the winter campaign are presented in Appendix B.2.1 in Tables B.2.1.1 and B.2.1.2, respectively. The results are also presented graphically in Figures 7.4 and 7.5 at the end of Section 7.4.

Hydrocarbon VOCs from the Camden sites were found at relatively low concentrations across the hydrocarbon profile as would be expected from suburban and semi-rural environments compared with areas that are more densely urbanised (Azzi et al., 2007, NSW EPA, 2010). The concentration of individual compounds and the relative concentration between compounds were relatively consistent across all of the sites with the exception of Site 6, the racecourse, where a move away from trend was seen. At all Camden sites the ambient concentrations of the NEPM priority aromatic compounds (benzene, toluene and total xylenes) were well below the recommended investigation levels (refer Section 7.1), noting that the measurements reported here represent a morning traffic peak and are point-in-time concentrations which are very likely to be higher than the annual and 24-hour average levels specified in the NEPM guideline.

Based on our knowledge of the hydrocarbon characteristics of vehicle emissions (described in Section 7.1), it is apparent that vehicle exhaust is the primary source of anthropogenic emissions to ambient air in the Camden region. The following paragraphs detail these emissions.

Hydrocarbons in the C_2 to C_5 range dominated the emissions profile at all sites. Site 6, at the entrance to Menangle Park raceway, showed ambient concentrations that were significantly higher than the other sites, and this site will be discussed separately. The hydrocarbon VOC profile for the other nine sites showed that ethane was the major contributor to the C_2 to C_5 hydrocarbon subset with concentrations in the range of 4.4ppbv at Site 1 (semi-rural in the vicinity of the AGL plant) through to 11.0ppbv at Site 9 (just off Menangle Road). The other sites ranged from 5.2-8.3ppbv ethane. Site concentrations of ethene (0.7-2.0ppbv), propane (1.6-6.1ppbv) and propene (0.2-0.5ppbv) again tended towards higher concentration in the vicinity of main roads. The possible contribution of CSG activities to ethane and propane concentration is outlined in Section 7.4.5. The C_4 hydrocarbons were dominated by isobutane (0.7-2.3ppbv) and n-butane (0.9-2.6ppbv) and minor 1-butene (ND-0.5ppbv). 1,3-butadiene, an important combustion sourced ozone precursor and an air toxic from the TO-15 suite, was found at Site 5 (0.6ppbv) and its presence at the racecourse, at 0.4ppbv, is not unexpected based on the hydrocarbon profile exhibited there. Gas fuelled vehicles may contribute to emissions of C_3 and C_4 aliphatic hydrocarbons as these are major components of LPG. C_5 hydrocarbons, likely to be sourced from fuel residuals in exhaust, were isopentane (0.5-1.1ppbv) and n-pentane (0.2-0.9ppbv) and these were again consistent with the sites proximity to roads. Where detected, the aliphatic hydrocarbons C_6 through to C_{12} were at minimal concentration; the highest around 0.3ppbv for n-hexane and methylcyclohexane at Site 9. These larger hydrocarbons are generally associated with residual fuel in exhaust and are expected at lower concentration than the smaller hydrocarbons.

With the exception of Site 6, aromatic compounds were evident at trace levels in the Camden ambient air; benzene 0.07-0.35ppbv, toluene 0.16-0.37ppbv, total xylenes 0.09-0.36ppbv. The larger alky-substituted aromatics were variably present at trace concentration at most sites with highest concentration measured for 1,2,4-trimethylbenzene (0.01-0.36ppbv). The aromatics were correlated in relative concentration with the aliphatic hydrocarbons, which again indicated a petrol vehicle derived source. With the exception of Site 3, the toluene to benzene ratio of around 1.0-2.5 at the Camden sites was also indicative of petrol exhaust as the main source of the aromatic compounds. Naphthalene was found at trace concentrations (< 0.2ppbv) at Sites 6, 7, 8, 9, and 10. This compound can be found in exhaust emissions and from other sources of fuel and waste combustion.

Isoprene, a primary biogenic emission from trees and vegetation, was detected only at Site 7 (Menangle Road/semi-rural) and Site 6 (racecourse) at 0.2ppbv, despite the vegetated surroundings of most of the Camden sites. In winter, colder temperatures and lower levels of sunlight will reduce the growth of plants and hence the emissions of isoprene. Isoprene is also a component of motor vehicle exhaust and can be detected as such when vehicle emissions are a significant source (Borbon et al., 2003). Despite the higher than average hydrocarbon concentrations seen at the racecourse, the nature of both of these sites suggests that a biogenic source is more likely.

Ambient hydrocarbon concentrations at Site 6, at the entrance to Menangle Park raceway, were significantly higher than the other Camden sites and all targeted compounds were represented. This was particularly apparent in the range associated with petrol fuel residuals such as benzene (2.0ppbv), toluene (3.9ppbv), total xylenes (1.4ppbv) and the larger aromatic compounds (as discussed in Section 7.1). These compounds were around 5-10 times higher than those seen at other sites. Of the small aliphatic hydrocarbons, ethene (15.5ppbv) and propene (2.8ppbv) were also around 10-times higher than the average of other sites. 1,3-butadiene was measured at 0.4ppbv, and this was the only site where acetylene, another combustion product in engine exhaust, was found (10.0ppbv). Whilst these levels are not unusual where levels of traffic congestion are high, they are perhaps unexpected at a site in this location. The site is also near a railway line with occasional passing diesel locomotives and some motor vehicles were known to be operating within the raceway precinct. Whatever the exact source, there was certainly a level of on-road or off-road vehicle emissions impacting Site 6 at the time of the winter campaign.

Overall, the sites showed certain hydrocarbon characteristics. Site 1, closest to the AGL CSG plant, had the lowest overall levels of C_2-C_5 hydrocarbons compared with other sites, yet similar levels of aromatics. Hydrocarbons species and levels at the composting facility (Site 2) and Spring Farm tip (Site 3) were similar to those seen elsewhere and typical of a low level impact from on-site and passing vehicles. The reserve in the midst of Mount Annan housing area (Site 4) showed low level emissions characteristic of a suburban traffic source as did the semi-rural site 5, which was close to a rail-line underpass, Site 7 close to the Menangle road intersection, and Sites 8, 9, and 10 all of which have main or minor roads in their vicinity. The racecourse at Site 6 was higher is hydrocarbon VOCs than other sites and showed a profile consistent with nearby exhaust and fuel evaporative emissions.

The TO-15 air toxic VOCs in the Camden ambient air were primarily present as the oxygenated species, particularly ethanol (1.3-6.8ppbv across all sites), acetone (2.6-5.7ppbv) and isopropanol (0.7-3.4ppbv). As referenced in Section 7.1, these and other oxygenated VOCs are major biogenic emissions. However, they are also emitted from a number of anthropogenic sources, and ethanol is present in emissions from vehicles using E10 mixed petrol fuel (DEWHA, 2008). As the concentrations found in the Camden region are broadly similar to those from the natural source sites and in the knowledge that the traffic source is not intense, the biogenic origin of the oxygenated compounds is more likely.

Certain Freon™ compounds and other halocarbons were seen at a relatively constant level in the ambient air across all sites; specifically dichlorodifluoromethane (average 0.6ppbv), trichlorofluoromethane (average 0.3ppbv), 1,1,2-trichloro-1,2,2-trifluoroethane (average 0.06ppbv) and carbon tetrachloride (average 0.08ppbv). The atmospheric stability of these compounds was indicated by their concentration reproducibility across all Camden and other land-use campaigns and they were also measured at the natural source sites at similar concentrations, as discussed in Section 7.3. Of the other halogenated compounds, chloroform was measured at sites 4, 5 and 6 at < 0.1ppbv and a number were measured at ultra-trace levels (< 0.03ppbv) at some sites.

The contribution of CSG production to ambient hydrocarbons in the Camden region is also of relevance as the raw gas contains small amounts of ethane and propane. This aspect is evaluated fully in Section 7.4.5, where predictions of CSG source contribution is made based on the ambient methane measurements for the region, the measured concentration of ethane and propane in the gas and an estimate of resultant ambient concentrations for these compounds. In summary, this evaluation concluded that no correlation could be found to connect CSG emissions with observed ambient concentrations of ethane and propane and therefore that these emissions are primarily derived from other sources.

Major findings for the winter campaign and a basis for evaluation of on-going campaigns were:

- The Camden regional sites were primarily impacted by on-road vehicle sourced emissions based on the characteristics of hydrocarbon VOCs present in the ambient air at that time of sampling.
- The ambient concentrations of VOCs across the Camden region appear commensurate with levels expected in suburban and semi-rural environments. The racecourse at Site 6 showed higher concentrations of hydrocarbon VOCs than the other sites due to a nearby source of exhaust and fuel evaporative emissions.
- At the time of sampling the NEPM priority aromatics (benzene, toluene and xylenes) were present at concentrations well below the 24-hour average investigation levels at all Camden sites.
- A biogenic source of VOCs was also observed in the emissions profile. Compounds such as ethanol, acetone and isopropanol were found at ambient levels similar to the natural source sites. Isoprene was detected at only two sites due most likely to its reduced emissions intensity in the winter months.
- The halocarbons regarded as ubiquitous in the atmosphere; specifically dichlorodifluoromethane, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane and carbon tetrachloride showed concentration reproducibility for all sites in this campaign. These results were consistent with concentrations measured at the natural sites and those measured at Camden sites in all later campaigns.
- A major industrial source of emissions was not apparent.
- A source contribution from CSG activities to ambient VOCs in the Camden region was not evident.

7.4.2 SPRING CAMPAIGN

The spring monitoring campaign was undertaken between 8:00 and 9:00am on the 20th November 2014. During this period, the temperature averaged 21.7°C and the wind direction was northerly at 4-5 km h^{-1}.

The results from VOC analysis of PAMS hydrocarbon and TO-15 air toxic VOCs for the spring campaign are presented in Appendix B.2.2 in Tables B.2.2.1 and B.2.2.2, respectively. The results are also presented graphically in Figures 7.6 and 7.7 at the end of Section 7.4.

One significant difference to the results discussed for the winter campaign was the return of Site 6 (racecourse site) to ambient concentrations commensurate with the region's other sites. As such, the high hydrocarbon levels seen in the previous campaign were associated with a specific activity occurring at this site at that time, as has been discussed.

Also significant is the overall lower concentrations seen for the C_2-C_3 combustion derived hydrocarbons and most of the larger aliphatic hydrocarbons. 1,3-butadiene, seen at low concentration in three of the ten winter samples, was also not detected in the spring campaign. Ambient concentrations of these compounds are commonly seen to undergo seasonal and diurnal variation as discussed in Section 7.1. It must be noted that differences in absolute concentration levels are also affected by overall meteorological conditions at the time of sampling, such as mixing height and wind direction in relation to the source, and on source intensity etc.

The impact of photochemistry on ambient concentrations would be apparent for the more reactive compounds, such as the alkenes. Ethene and propene are present in vehicle impacted ambient air as combustion products of the larger alkanes present in the fuel. The alkenes dominate the alkanes in raw exhaust (DEWHA, 2008). Comparing the Camden winter and spring campaigns, it may be the case that the higher levels of ethene and propene over ethane and propane in winter showed that the alkenes had survived photodecomposition after their emission. In spring, when rates of photolysis are higher, the alkenes were generally lower than the alkanes in the ambient air. Isobutane was seen at similar ambient concentration in winter and spring across the sites (1.3-1.8ppbv). Compared to the alkenes, isobutane is relatively stable in the atmosphere. It is also a significant component in the composition of petrol and significant therefore in evaporative emissions. The aromatic compounds were also at similar levels in the winter and spring campaigns, with the possible exception of Site 2. For the other sites, benzene was found at levels of nil detected to 0.3ppbv, toluene 0.09-0.3ppbv and total xylenes 0.08-0.3ppbv. Site 2 (the composting facility) showed the highest ambient concentrations of the regional sites which may be consistent with on and off-road vehicles operating at this location (benzene 0.2ppbv, toluene 0.8ppbv, xylenes 1.0ppbv). Naphthalene was found at Sites 6-10 (0.02-0.4ppbv) at generally similar concentration to that measured across the sites in the winter campaign.

Isoprene was detected at levels of 0.04-0.3ppbv across all sites except Sites 5 and 8 in the spring campaign, whereas it was generally not detected in the winter campaign. This is indicative of warmer temperatures, increased sunlight, as photosynthetically active radiation, and the growth of plants in the spring.

The TO-15 oxygenates group showed increased levels overall compared to the winter campaign. Ethanol concentration increased by 2-3 fold at most sites; another possible indicator of increased biogenic activity in spring (1.7-15.5ppbv). This is particularly so for the composting facility (11.8ppbv compared to 2.4ppbv) where emissions from the degradation of plant matter would be apparent. The level of processing activity, the direction of the plume, or other downwind sources may also be explanations. Site 8 (semi-rural and woodland) also showed significantly higher levels of ethanol (15.5ppbv compared to 3.1ppbv). Acetone was measured at somewhat higher concentrations in spring compared to winter; 3.7-5.9ppbv and 8.4ppbv at Site 8, the latter likely to be associated with the higher ethanol measured at that site. Isopropanol was similar to winter concentrations at all sites (0.4-2.2ppbv).

Further to the biogenic emissions was the presence of methyl isobutyl ketone, which had not been detectable in the winter campaign, at a number of sites (0.03-0.08ppbv and 0.5ppbv at Site 1). Site 1, close to the AGL plant also showed comparatively high levels of methyl butyl ketone (1.0ppbv).

The halocarbons previously found as ubiquitous in a range of environments were again found at similar concentration at all sites in this campaign. Chloroform was again seen at sites 4, 5 and 6 at ultra-trace levels (< 0.05ppbv) and 1,4-dichlorobenzene was found at all sites, also at ultra-trace levels (< 0.02ppbv). Most of the larger halogenated air toxics were present at Site 1 near the AGL plant at concentrations < 0.3ppbv.

Major findings for the spring campaign were:

- Overall, the ambient concentrations of hydrocarbon VOCs were lower in spring compared with winter.
- Oxygenated compounds associated with biological processes (particularly ethanol and acetone), and isoprene emissions associated with plant growth, were higher in spring than in winter.
- It is possible that the spring campaign showed the impact of warmer temperatures and higher levels of sunlight in increased biogenic emissions, and of higher levels of photolysis in reducing ambient concentrations of the more photochemically active hydrocarbons from the vehicle source. However, atmospheric conditions generally and the intensity of the source and direction of the plume should not be underestimated in their impact on the observed concentrations and may be significant contributors to the variation in presence and levels of the observed emissions.

7.4.3 SUMMER CAMPAIGN

The summer monitoring campaign was undertaken between 7:40 and 8:30am on the 25th February 2015. During this period, the temperature averaged 20.4°C and the wind direction was northerly at 5-15 km h^{-1}.

The results from VOC analysis of PAMS hydrocarbon and TO-15 air toxic VOCs for the summer campaign are presented in Appendix B.2.3 in Tables B.2.3.1 and B.2.3.2, respectively. The results are also presented graphically in Figures 7.8 and 7.9 at the end of Section 7.4.

Ambient concentrations of hydrocarbon VOCs were generally in the range measured in the spring campaign across all sites in the Camden region. Note that temperature and wind direction were also similar in these campaigns. Vehicle exhaust emissions of ethane and propane dominated ethene and propene, the latter of which were not detectable at most sites and which is again consistent with their decomposition under conditions of higher photo-reactivity, as discussed previously. Isobutane from evaporative and exhaust emissions is somewhat higher than the spring and winter concentrations (2.5-4.0ppbv compared to 1.3-1.8ppbv in spring). Other aliphatics and the aromatics generally followed the average concentrations seen in the previous campaigns at all sites except Site 10 (roadside). This site showed an obvious impact from fuel evaporative emissions with the detection of most of the targeted C_5-C_{11} aliphatic and aromatic hydrocarbons associated with petrol fuel. Naphthalene was found at all sites at ultra-trace levels (0.01-0.07ppbv). Isoprene was found at Sites 4, 5, 8 and 10 at levels between 0.05ppbv and 0.5ppbv.

The TO-15 suite showed similar concentrations overall to those seen in the spring campaign. Ethanol was at similar levels as observed for spring campaign at most sites (1.4-6.5ppbv), this time with higher levels at Site 1 (19.8ppbv) and Site 10 (24.2ppbv). Acetone was also higher at Site 10 (11.0ppbv) than the other sites (1.8-5.4ppbv) which were at similar levels to the spring concentrations. Isopropanol showed similar or slightly lower levels overall (0.3-1.4ppbv) and ultra-trace levels of methyl isobutyl ketone was seen at Sites 1, 4 and 5 (around 0.02ppbv). This campaign also found 2-butanone at all sites (0.1-0.4ppbv); again this is likely to be biogenically derived in these environments.

The four halocarbons considered ubiquitous in a range of environments were again found at similar concentration at all sites in this campaign. Chloroform was found at ultra-trace level all sites (0.03-0.07ppbv). The suite of halogenated VOCs peculiar to Site 1 in the spring campaign were no longer present in samples from this campaign.

Characterisation Studies

The summer campaign samples were selected for further characterisation studies as the warmth of this season was likely to generate compounds associated with biological processes that typify the semi-rural environment of this region. The compounds identified are shown in Table 7.4.

The two ubiquitous sulphur containing compounds; carbonyl sulphide and likely dimethylsulfone were seen at all sites. Biogenic compounds were prevalent as aldehydes and alcohols (with isomers of C_4 and C_5 aldehydes also found at Site 1) along with the monoterpenes and monoterpenoids at various sites; a-pinene, p-cymene, limonene and eucalyptol. The prevalence of biogenically derived compounds and absence of compounds associated with odour or industrial activities is indicative of the semi-rural atmosphere at these sites.

Table 7.4 Compounds identified from characterisation studies of canister samples for the Camden regional sites monitored in the summer campaign, 25-Feb-15

Compound Name	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Carbonyl sulphide	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Sulphur containing; likely dimethyl sulfone	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
C_4 aldehyde; likely 2-methylpropanal	✓	-	-	-	-	-	-	-	-	-
C_5 aldehyde; likely 3-methylbutanal	✓	-	-	-	-	-	-	-	-	-

Compound Name	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
C_5 aldehyde; likely 2-methylbutanal	✓	-	-	-	-	-	-	-	-	-
a-Pinene (monoterpene)	-	-	✓	✓	✓	✓	-	✓	-	-
Benzaldehyde	✓	✓	✓	-	✓	✓	✓	-	✓	-
C_8 alcohol; possibly 2-ethyl-1-hexanol	✓	-	-	✓	✓	-	✓	-	-	-
Monoterpene; likely p-cymene	✓	-	-	✓	-	-	-	✓	-	-
Limonene (monoterpene)	✓	-	-	✓	✓	-	-	✓	-	-
Eucalyptol (1,8-cineole) (monoterpenoid)	✓	✓	✓	✓	✓	-	-	-	-	-
Phenyl alcohol or like	-	-	-	-	-	-	-	-	✓	✓
C_9 oxygenate; likely nonenol or nonanal	✓	✓	-	✓	✓	-	✓	-	-	-

Major findings for the summer campaign were:

- Hydrocarbon and air toxics VOCs for the summer campaign showed ambient concentrations similar to the spring levels and within the normal variation observed within the region.
- A strong biogenic component was observed in emissions of isoprene, ethanol and acetone along with C_4-C_9 aldehydes and alcohols, and monoterpenes (a-pinene, p-cymene, limonene and eucalyptol). These biogenic emissions, along with vehicle emissions, typify the region.
- As discussed in the findings for the spring campaign, it is possible that the effect of warmer temperatures and higher levels of sunlight in summer were seen in the concentration profiles of the biogenic and vehicle sourced compounds.

7.4.4 AUTUMN CAMPAIGN

The autumn monitoring campaign was undertaken between 8:00 and 9:00am on the 29th April 2015. During this period, the temperature averaged 10.6°C and the wind direction was northerly at 0 km h^{-1}.

The results from VOC analysis of PAMS hydrocarbon and TO-15 air toxic VOCs for the autumn campaign are presented in Appendix B.2.4 in Tables B.2.4.1 and B.2.4.2, respectively. The results are also presented graphically in Figures 7.10 and 7.11 at the end of Section 7.4.

Ambient concentrations of the hydrocarbon VOCs in autumn were broadly similar to the summer and spring campaigns and none of the sites stood out as varying from the overall intra-site trend. Again, ethene and propene were generally not detected with ethane and propane dominating this group, indicating a level of atmospheric decomposition of exhaust emissions. However, isobutane concentrations were low relative to ethane, which is a relationship, also observed in the winter campaign and indicative of reduced fuel evaporative emissions at lower ambient temperatures. Isoprene was still evident across all sites (0.03-0.1ppbv). Larger aliphatic and aromatic hydrocarbons followed typical regional concentrations.

The TO-15 suite also showed concentrations expected for the region with some variability in ethanol across the sites, as previously discussed. Some oxygenates seen in the summer campaign were no longer found, such as 2-butanone. All other compounds were within the concentration ranges expected for the region apart from a somewhat higher result for 1,1,2-trichloro-1,2,2-trifluorethane at Site 1 and 2 (0.3 and 0.2ppbv, respectively) above the average for this ubiquitous halocarbon (0.06ppbv).

Major findings from the autumn campaign were:

- VOC profiles of hydrocarbon and air toxics compounds, and their concentration range, are generally similar to that observed for the spring and summer seasons.
- Cooler temperatures were possibly responsible for reduced isobutane concentrations (on the assumption of a reduction in fuel evaporative emissions), and in 2-butanone (due to reduced biological activity) compared to the summer season. This effect was also observed in the results from the winter campaign.

7.4.5 IMPACT OF CSG OPERATIONS ON VOCS TO THE CAMDEN REGION

It is of interest to assess whether CSG production activities impact on ambient ethane and propane concentrations in the Camden region. Coal seam gas contains small amounts of ethane and propane (refer composition data in Appendix D.5) but it has been determined it is unlikely that CSG is a significant source of these compounds in the ambient air measured during the field campaigns. By way of example, during the winter campaign in August 2014, the average CH_4 concentration was 2.7ppmv (refer Section 6.6.3) or about 0.9ppmv above normal background levels. Assuming that this entire CH_4 enhancement was derived only from CSG fugitive emissions and based on average measured raw gas composition (ethane 1570ppmv and propane 21ppmv for 95% methane well gas); the estimated ambient concentrations of ethane and propane would be 1.5ppbv and 0.02ppbv, respectively. These estimated concentrations are much lower than the actual concentrations of 7.1ppbv for ethane and 3.3ppbv for propane that were measured in the field. Similar trends were found for the other campaigns where the estimated concentrations based on the CSG composition were often substantially lower than the observed concentrations. Also evident was the lack of correlation for ethane compared with propane for estimated and measured data. Moreover, the estimated concentrations are likely to be overestimates since we have assumed that the entire ambient CH_4 enhancement was due to CSG emissions, which is highly improbable. A similar approach can be used for the aromatic compounds. These compounds are at minimal concentration in the well gas, refer Section 7.8.1 and Appendix C; toluene can be 100,000-times lower than ethane for example. At these low concentrations, the aromatic compounds would be immeasurable as a CSG source to ambient air.

We conclude therefore, that ethane and propane emissions from CSG are negligible and that these compounds, and the aromatic compounds, are derived from other sources impacting the Camden region.

7.4.6 SUMMARY OBSERVATIONS

A clear impact from traffic related emissions was seen from the hydrocarbon VOC profile observed in the ambient air for all ten sites monitored in Camden region. The ambient concentrations of these compounds were low and consistent with levels expected for semi-rural and suburban environments. The NEPM priority aromatics (benzene, toluene and xylenes) as point-in-time concentration were below the 24-hour average guideline and the overall hydrocarbon VOC profile indicated motor vehicles as the major source of these compounds at all sites.

Emissions of biogenic compounds were apparent in the VOC profile and are indicative of the semi-rural atmosphere of the Camden regional sites. Compounds associated with biological processes included small oxygenates (ethanol, acetone and isopropanol) which were present at concentrations broadly similar to those observed in the natural environments. 2-butanone and the more complex C_4-C_9 aldehydes, ketones and alcohols were identified in the summer campaign and biogenic emissions of isoprene and monoterpenes were observed in the VOC profile at many sites.

The halocarbons regarded as ubiquitous in the atmosphere; specifically dichlorodifluoromethane, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane and carbon tetrachloride, were found at all Camden sites and showed concentration reproducibility across all campaigns. The average background concentration for these compounds for the Camden campaigns was 0.5ppbv, 0.2ppbv, 0.06ppbv and 0.07ppbv, respectively. These concentrations were also consistent with those measured at the natural sites and indeed all other land-use sources, as detailed in Section 7.1. Other halocarbons were found variably at the Camden sites at trace concentrations and were therefore considered to be of little consequence in the identification of a specific source of these compounds.

Based on ambient concentrations of ethane and propane and an estimation of ambient contribution of these compounds using ambient methane measurements and well gas composition, a source contribution from CSG activities to hydrocarbon VOCs in the Camden region was not evident.

Hydrocarbon and air toxics VOC profiles were not suggestive of a major industrial source of emissions in the vicinity of the Camden sites.

Seasonal monitoring of VOCs showed a general trend towards higher levels of biogenic compounds (such as oxygenated compounds, isoprene and monoterpenes) in the spring and summer campaigns which is consistent with warmer temperatures and higher intensity of photosynthetically active radiation. Vehicle related hydrocarbon VOCs were generally lower than the levels measured in winter and a reduction in the relative concentration of alkenes compared to alkanes is consistent with the effect of higher rates of photolysis on the more reactive species. Isobutane dominated the hydrocarbon emission profile in the warmer months, and this may be indicative of higher evaporative losses of fuel components from petrol-fuelled vehicles. A link to seasonal variation particularly in the change in emissions of the biogenic compounds and, tentatively, the transport related emissions could be surmised however, these observations must be tempered by the many other factors that are well known to affect source intensity, emissions transport and atmospheric fate.

The overall consistency in the results from ambient monitoring of locations across the Camden region establishes a database of expected concentrations of priority hydrocarbon and air toxics VOCs for the morning period at rural and semi-rural locations.

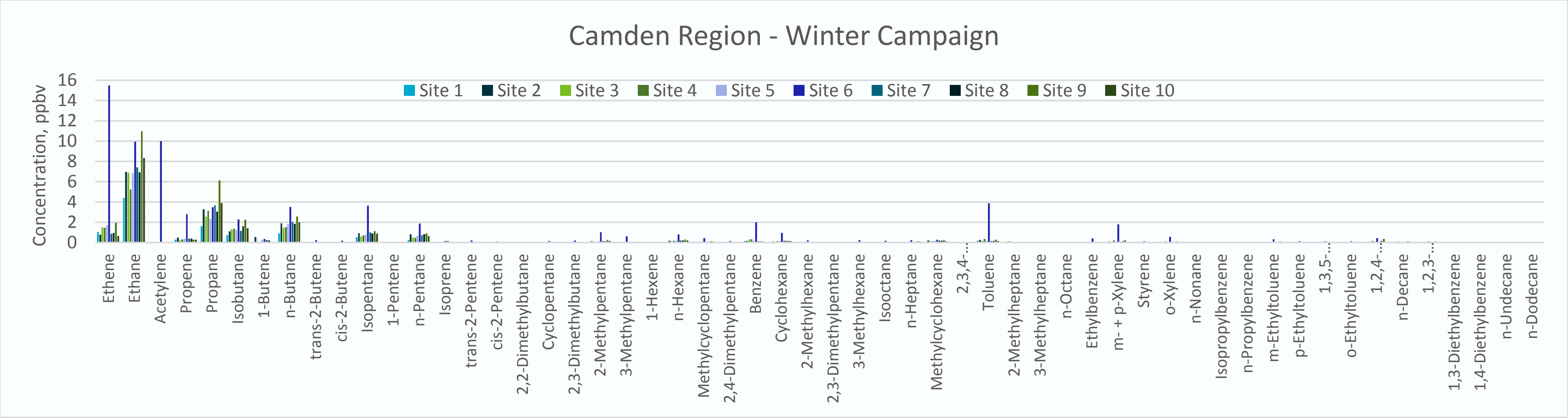

Figure 7.4 PAMS hydrocarbon VOCs measured at the Camden regional sites for the winter campaign, 06-Aug-14

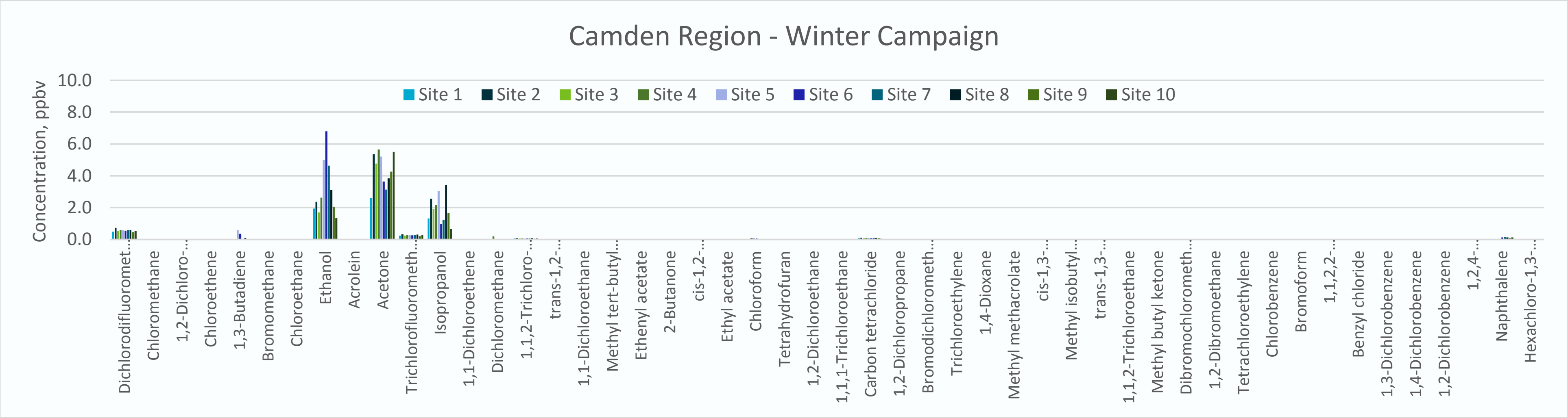

Figure 7.5 TO-15 air toxics VOCs measured at the Camden regional sites for the winter campaign, 06-Aug-14

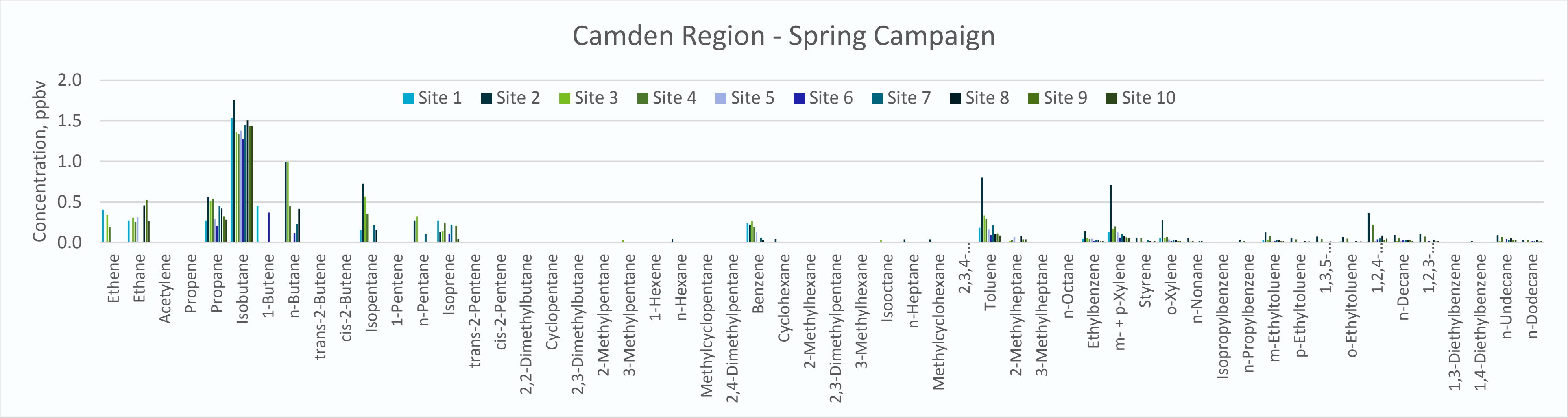

Figure 7.6 PAMS hydrocarbon VOCs measured at the Camden regional sites for the spring campaign, 20-Nov-14

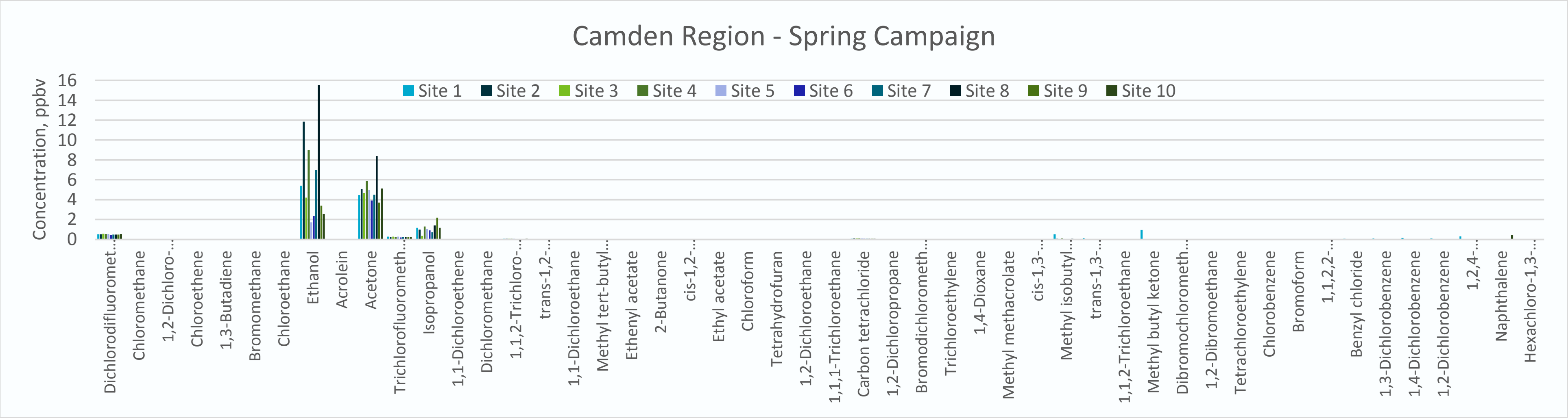

Figure 7.7 TO-15 air toxics VOCs measured at the Camden regional sites for the spring campaign, 20-Nov14

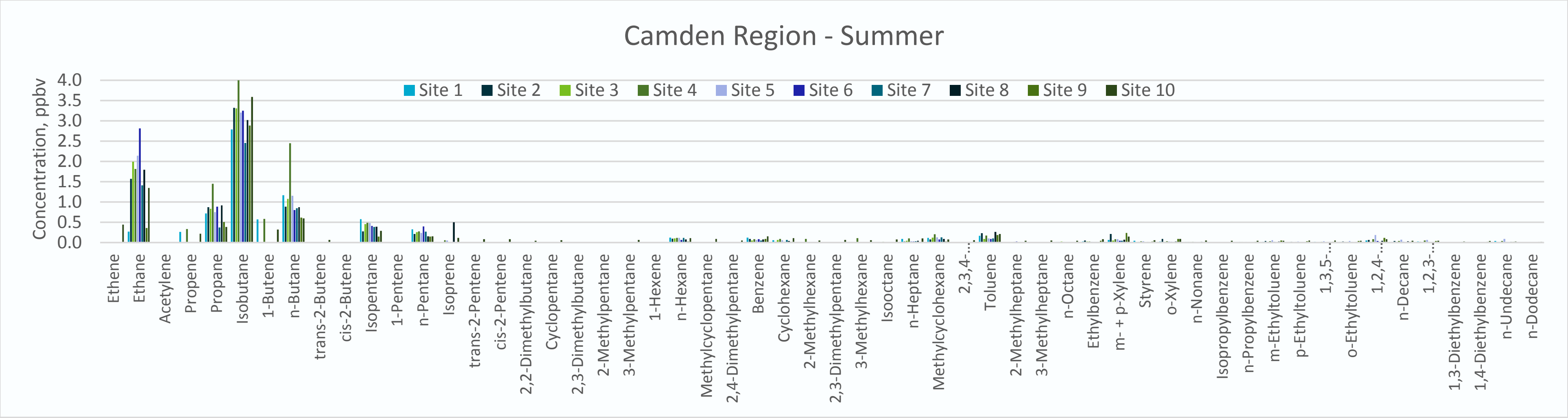

Figure 7.8 PAMS hydrocarbon VOCs measured at the Camden regional sites for the summer campaign, 25-Feb-15

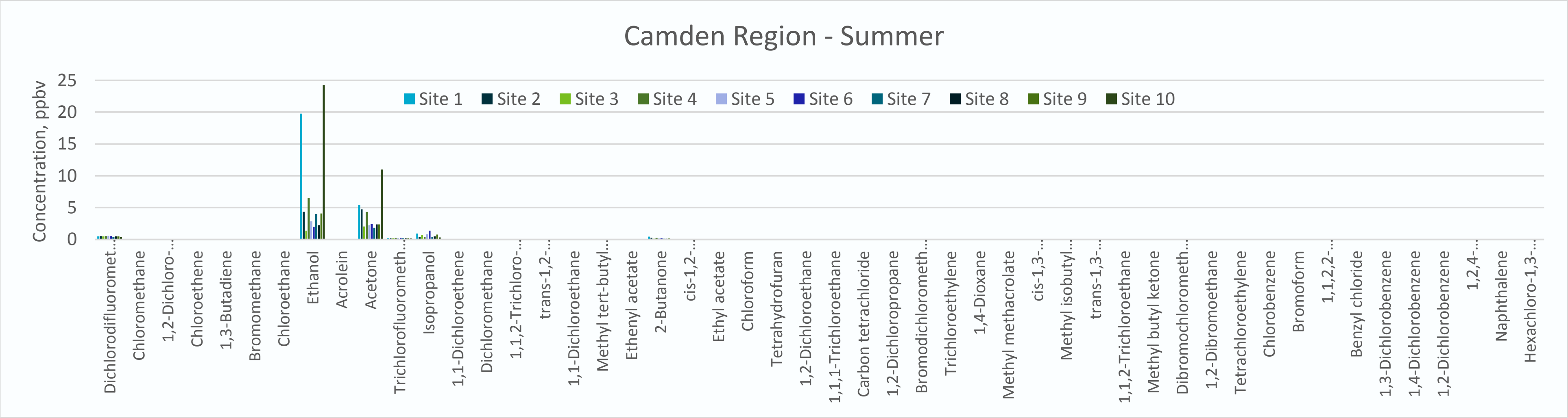

Figure 7.9 TO-15 air toxics VOCs measured at the Camden regional sites for the summer campaign, 25-Feb-15

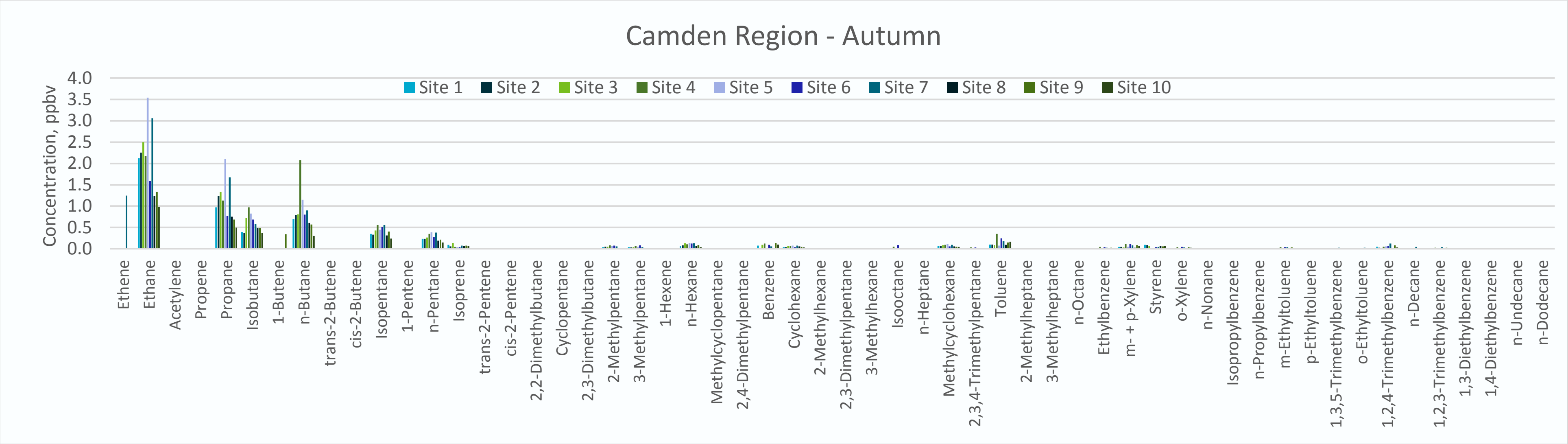

Figure 7.10 PAMS hydrocarbon VOCs measured at the Camden regional sites for the autumn campaign, 29-Apr-15

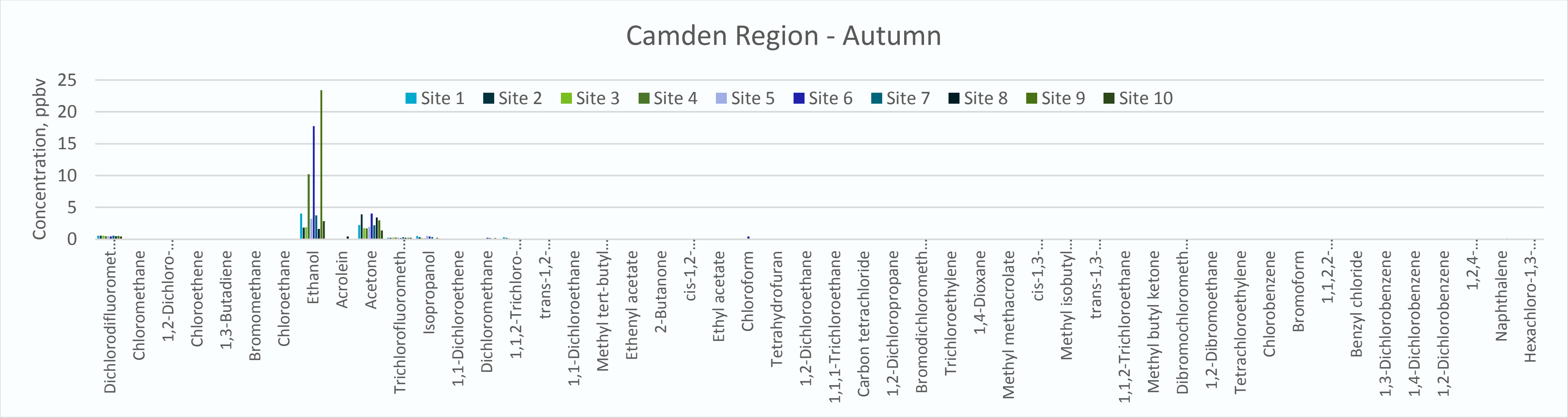

Figure 7.11 TO-15 air toxics VOCs measured at the Camden regional sites for the autumn campaign, 29-Apr-15

7.5 Cattle Feedlot

The Jindalee cattle feedlot at Springdale, NSW was monitored for VOCs and was selected to be an example of intensive agriculture, in this case of animal husbandry.

7.5.1 JINDALEE CATTLE FEEDLOT

Canister sampling campaigns were conducted on 26th August 2014, 16th February 2015 and 22nd April 2015 at a location in close vicinity to the feeding pens, as listed in Table 7.1. Details of the Jindalee site can be found in Section 5.1, Table 5.1, and a map of its location can be found in Section 6.4.

The quantitative results for PAMS hydrocarbon VOCs and the TO-15 air toxics suites are presented in Appendix B.3 in Tables B.3.1 and B.3.2, respectively. The results are also presented graphically in Figures 7.12 and 7.13 at the end of this section.

Priority VOCs

Hydrocarbon VOCs were not particularly prevalent at this site and those depicting a vehicle combustion derived emission were not evident in the Aug-14 campaign or were minimal in the other campaigns. Ethene and iso-butane were highest in the Feb-15 campaign (1.2 and 3.0ppbv, respectively). There was evidence of toluene (0.4ppbv), accompanied by xylenes (0.7ppbv) and higher aromatics, in the Aug-14 sample which may be indicative of petrol evaporative emissions from a parked vehicle (refer Section 7.1 for basis to vehicle derived emissions profiles). The two other campaigns showed only trace levels of a few aromatics and so these cannot be attributed to a particular source. Overall, it appears that the VOCs associated with the animal facilities were not high in aliphatic and aromatic hydrocarbons, which would be expected.

Site monitoring for the TO-15 suite showed oxygenated compounds (ethanol, acetone, acrolein, isopropanol and 2-butanone) likely to be derived from biological processes (Rabaud et al*.,* 2003). The concentrations measured were broadly in the range observed for the natural sites, Camden regional sites and the landfills. An exception was the high level of ethanol found in the Feb-15 sample (253ppbv) which was accompanied by a relatively significant level of acetone (26.4ppbv) and 2-butanone (4.1ppbv). This sample was taken when large numbers of cattle were in the feedlot and coincided with the measurement of high levels of methane. Ethanol and acetone would be expected in the vicinity of animals and their by-products (Le et al., 2005; Rabaud et al., 2003). The higher ambient temperature in February would also contribute to elevated levels of these biologically derived compounds. The only halogenated compounds of significance at this site were those considered ubiquitous in the environment, as previously discussed.

Characterisation Study

Qualitative results for identification of non-standard compounds in selected VOC canister samples is presented in Table 7.5. The August and February samples were selected as these showed greatest difference in compounds measured from the priority VOC analysis.

Sulphur containing compounds would be expected as contributors to odour at cattle feedlots along with volatile fatty acids, phenols, indoles, amines (Le et al., 2005; Trabue et al., 2008) as well as emission of alcohols, aldehydes, ketones and esters (Rabaud et al., 2003). Of the volatile subset of these compounds, the Jindalee feedlot was found to be rich in these classes of compounds. The sulphur containing compounds, carbonyl sulphide and dimethyl sulphone, have been seen in other source samples, these being naturally present in the atmosphere (refer discussion in section 7.1). However, the feedlot also showed the alkyl sulphides, dimethyl sulphide and dimethyl disulphide, both of which have disagreeable odours. Nitrogenous compounds (such as nitromethane and nitroethane), which were not found at other sites, were present as likely animal by-products and numerous C_4 to C_8 aldehydes, ketones and alcohols were identified. As referenced above, these compounds are all known to be associated with odour and their prevalence in the February sample in particular is likely related to cattle numbers, as well as the effect of elevated ambient temperature.

Table 7.5 Non-standard compounds identified from characterisation of VOCs in canister samples for the feedlot source

Compound Name or Class	Presence in Ambient Air Jindalee Cattle Feedlot 26-Aug-14	 16-Feb-15
Carbonyl sulphide	✓	✓
Sulphur containing; likely dimethyl sulphone	✓	✓
Dimethyl sulphide	-	✓
Nitromethane	-	✓
Butanal	-	✓
2-Pentanone	✓	✓
Pentanal	✓	✓
Nitroethane	-	✓
Nitrogenous unknown	✓	✓
Dimethyl disulphide	-	✓
Hexanal	-	✓
Furfural	✓	✓
3-Heptanone	✓	✓
Heptanal	✓	✓
Oxygenate; possibly 2-ethylhexanal	✓	✓
Benzaldehyde	✓	✓
a-Methylstyrene	-	✓
Oxygenate; likely C_7 alcohol	✓	✓
C_8 alcohol; possibly 2-ethyl-1-hexanol	✓	✓
Monoterpene, likely p-cymene	✓	✓
2-Chloroacetophenone	✓	✓
Phenyl alcohol or like	✓	✓

7.5.2 SUMMARY OBSERVATIONS

Oxygenated compounds dominated emissions from the feedlot and an excursion in ethanol was found in the February sample when large numbers of cattle were present in the feedlot. This along with higher than typical concentrations of acetone and 2-butanone, and the presence of various other oxygenated compounds, nitrogenous compounds and alkyl-sulphides indicates emissions directly attributable to the feedlot. The latter groups of compounds also would contribute to the odour associated with these facilities.

The feedlot was characterised by:

- Ethanol, acetone and 2-butanone at higher concentrations than typically found in vegetated environments.

- Odorous compounds particularly those related to animal by-products; dimethyl sulphide, dimethyl disulphide, nitromethane and nitroethane, and other biological processes; C_4 to C_8 aldehydes, ketones and alcohols.

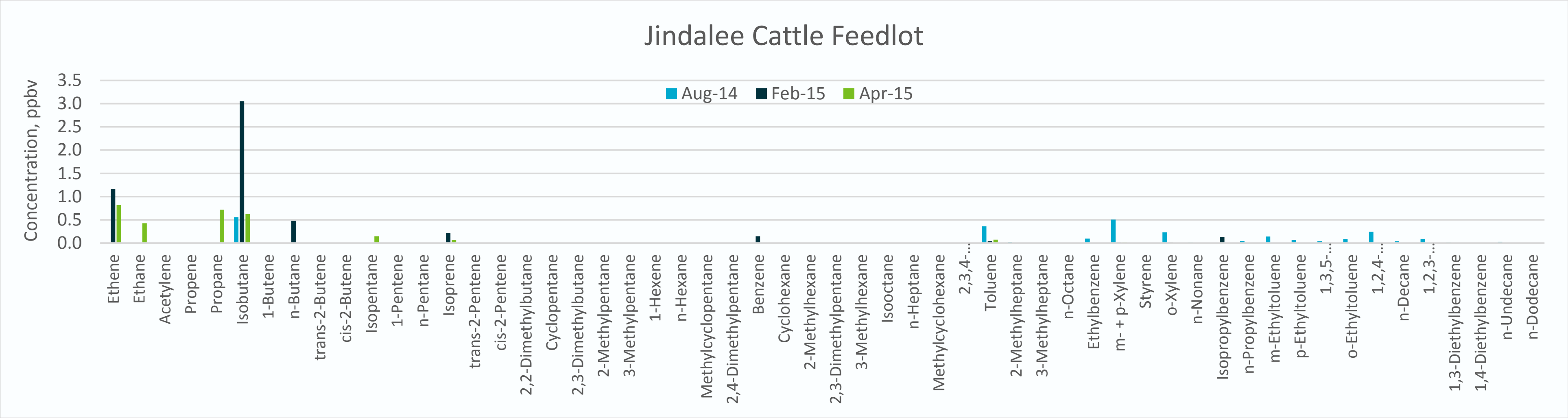

Figure 7.12 PAMS hydrocarbon VOCs measured at Jindalee cattle feedlot

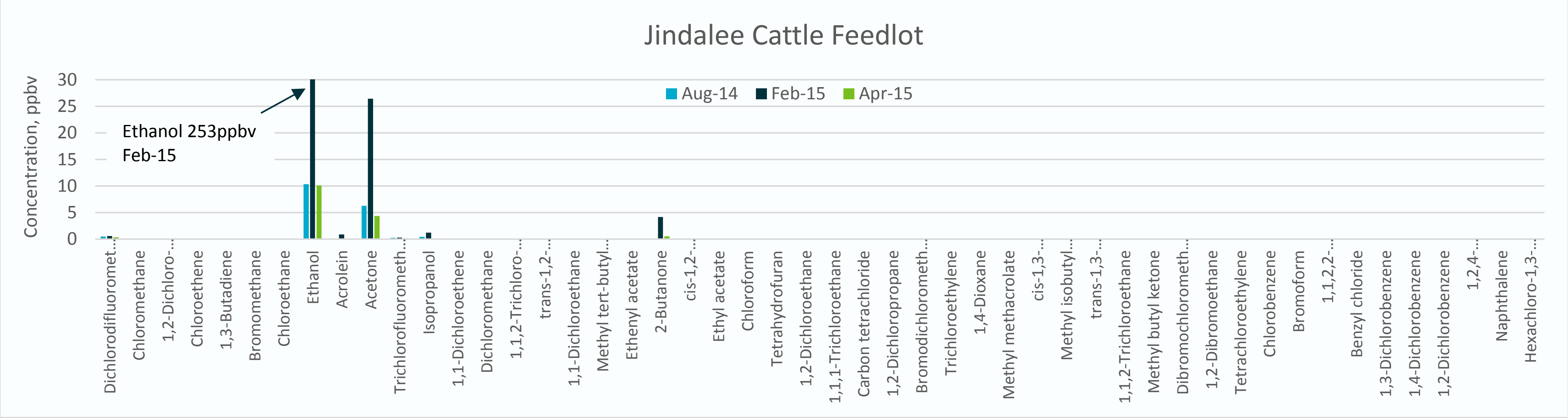

Figure 7.13 TO-15 air toxics VOCs measured at Jindalee cattle feedlot. *Note: The concentration of ethanol for the Feb-15 sample is off the plotted scale at 253ppbv.*

7.6 Coal Mines

Rix's Creek coal mine was monitored to assess VOCs that may be associated with fugitive emissions from open-cut mining. The site is located in the Hunter Valley and its exact location and description can be found in Section 5.1, Table 5.1. A map of the mine location can be found in Section 6.5.2, Figure 6.13.

A location at the edge of a mine lease in the Gunnedah Basin region was also monitored for VOCs. The VOC sample was taken within a methane plume, which had been established as originating directly from the mine at the time. Although this location was not an actual mine site, the ambient air sample possibly represented the VOC emissions from the mine.

The results of VOC analysis for PAMS hydrocarbons and TO-15 air toxics for Rix's Creek Mine and the Gunnedah Basin site are presented in Appendix B.4 in Tables B.4.1 and B.4.2, respectively. The results are also presented graphically in Figures 7.14 and 7.15 at the end of this section.

7.6.1 RIX'S CREEK COAL MINE

Rix's Creek coal mine was monitored for VOCs by canister sampling on 15th April 2015 and on 22nd July 2015 at an in-pit location. The latter campaign sampled also at the site of the ROM coal storage pad. The monitoring campaigns are listed in Table 7.1 and site locations are detailed in Section 5.1, Table 5.1. A description and map of the Rix's Creek mine site can be found in Section 6.5.2.

Priority VOCs

Hydrocarbon VOCs were generally measured at low concentration, compared to other land-use sites, for all monitoring campaigns at the mine and hence a definite source emission cannot be established. Fugitive emissions of mine gases may have contributed to the levels of smaller alkane hydrocarbons that were particularly apparent at the in-pit sample from the Jul-15 campaign, where only ethane was measured (at 2.3ppbv) in the C_2-C_6 range along with only trace contribution of large aliphatic and aromatic hydrocarbons. However, the contribution from seam gas would have been very low due to the low gas content of the coal extracted (see Section 6.5.2).

Where alkenes and larger alkanes are also present in the hydrocarbon profile, a diesel exhaust emission is indicated, possibly from off-road trucks or other machinery operating at the mine site. The ROM pad site monitored in the same campaign showed higher ethane (7.9ppbv) and similar smaller VOCs to those from the pit but with more significant aromatics, particularly xylenes (1.3ppbv) and ethylbenzene (0.2ppbv), and higher concentrations of the C_9-C_{11} alkanes and larger substituted aromatics. This profile may represent a diesel exhaust emission showing residual fuel volatiles. Isoprene was found at highest concentration in the February sample where a biogenic component may be enhanced with the higher summer temperature.

Oxygenated species were variable across the mine site campaigns and generally at the lower end of the concentration range observed in the Camden and natural source results, for example. Ethanol concentrations of 2.2-7.9ppbv were measured at the in-pit location and 10.8ppbv at the ROM pad, and acetone 2.2-8.1ppbv in-pit and 4.0ppbv at the ROM pad. Acrolein was measured only in the in-pit sample from the Feb-15 campaign at 0.8ppbv, respectively. This compound was seen at the natural sites at ND-0.9ppbv. These concentrations are suggestive of the remote and minimally vegetated nature of the site (refer discussion of biogenic emissions in Section 7.1). Other oxygenates were present at low concentration in most samples. The ROM pad site was highest with 2-butanone at 2.2ppbv and methyl isobutyl ketone at 0.4ppbv.

Halogenated compounds were at levels expected for the species now known to be consistently present as an ambient background (noting that the 1,1,2-trichloro-1,22-trifluoroethane is found close to its detection limit and hence will be reported as not detected in some samples, as noted in Section 7.1). Ultra-trace levels of a few other chlorinated species were also measured at the in-pit samples. Again, the ROM pad site showed higher levels, with chloroform present at 0.3ppbv and tetrachloroethylene at 2.7ppbv. The latter compound is used as an industrial solvent and was found in ambient samples from landfill and wastewater treatment sites; the reason for its presence at the ROM pad cannot be postulated.

7.6.2 GUNNEDAH BASIN

A location at the edge of a mine lease in the Gunnedah Basin was monitored for VOCs. The VOC sample was taken within a methane plume, which had been established as originating directly from the mine at the time. Although this location was not an actual mine site, the ambient air sample possibly represented the VOC emissions from the mine. The VOC sample was taken on 21st July 2014 at the roadside outside the boundary of the mine.

Priority VOCs

Hydrocarbon VOCs from this site were at low concentration but showed a hydrocarbon profile resembling that of exhaust emissions in that C_2-C_4 alkanes and alkenes, the larger aliphatics, toluene and the larger alkyl-aromatics were present. The roadside location of the sample is likely to have meant that a traffic source contributed to the observed emissions and possibly the emissions from on-site vehicles were present in the plume from the mine site.

Oxygenated VOCs were in the range expected for a natural source (refer discussion of biogenic emissions in Section 7.1) and generally higher than the levels seen at the Rix's Creek mine site, as may be expected for a vegetated roadside location. Halogenated VOCs were also at trace level.

Characterisation Study

Characterisation studies were undertaken by chromatographic review and mass spectral interpretation of the canister collected sample from the Gunnedah Basin sample using methodology described in Section 5.3.5.

A number of additional compounds to the PAMS and TO-15 suites were identified from the VOC characterisation study and this qualitative information is presented in Table 7.6. Two sulphur-containing compounds regarded as ubiquitous in the atmosphere (as discussed in Section 7.1) and identified in natural and other land-use sites were again identified as ambient background. Oxygenates were found as C_4 to C_7 aldehydes, 3-heptanone and various alcohols. Biogenic emission of the monoterpenes, p-cymene and limonene, were identified.

The non-standard compounds observed in the emissions are suggestive of a natural environment.

Table 7.6 Compounds identified from characterisation of VOC samples for the Gunnedah Basin mine plume

	Presence in Ambient Air
Compound Name or Class	Gunnedah Basin mine plume Jul-14
Carbonyl sulphide	✓
Sulphur containing; likely dimethyl sulphone	✓
Butanal	✓
Oxygenated, likely alcohol	✓
Pentanal	✓
Hexanal	✓
3-Heptanone	✓

	Presence in Ambient Air
Compound Name or Class	Gunnedah Basin mine plume Jul-14
Heptanal	✓
Benzaldehyde	✓
a-Methylstyrene	✓
C_7 alcohol	✓
C_8 alcohol; possibly 2-ethyl-1-hexanol	✓
Monoterpene, likely p-cymene	✓
Limonene	✓
C_9 alcohol, possibly 2-nonen-1-ol	✓

7.6.3 SUMMARY OBSERVATIONS

The ambient air at Rix's Creek coal mine was generally low in VOCs compared to semi-rural and the higher intensity land-use sites. Those hydrocarbons that were detected inferred a diesel emissions profile, which was more obvious at the ROM coal storage pad, which may be consistent with the machinery operating at the site. It is possible that fugitive emissions of ethane contributed to the hydrocarbon profile at the in-pit locations. Oxygenated and halogenated compounds were non-distinctive for the mine source, as would be expected for a remote site of this kind.

The ambient air in the vicinity of the mine in the Gunnedah Basin showed low levels of compounds associated with vehicle exhaust, and vegetation, which are likely consistent with on-site mining activities and the roadside location of the monitoring site.

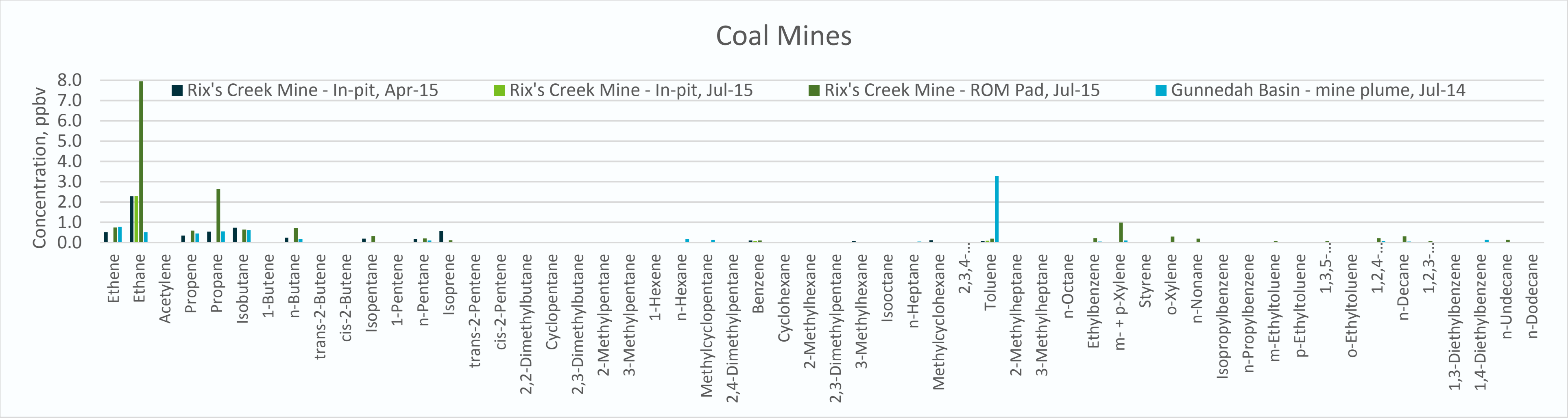

Figure 7.14 PAMS hydrocarbon VOCs measured at the coal mines

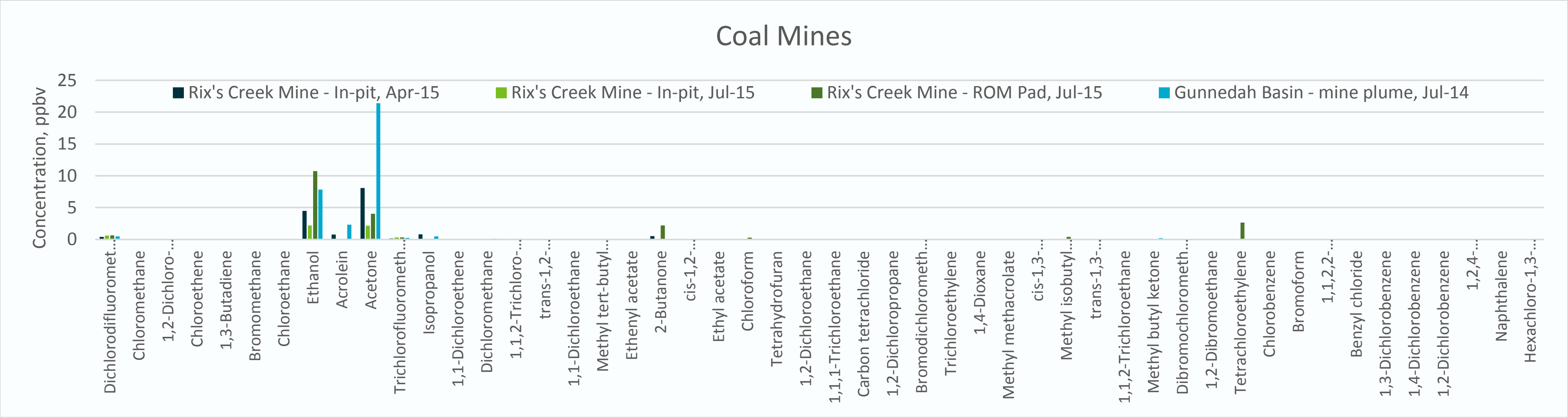

Figure 7.15 TO-15 air toxics VOCs measured at the coal mines

7.7 CSG Facilities

CSG production facilities were monitored to observe the impact of the gas wells and plant operations on ambient concentrations of VOCs.

The CSG production facilities from AGL operations at Camden and Gloucester, and the Santos operations in the Pilliga State Forest at Narrabri were monitored for ambient VOCs as listed in Table 7.7. A description of the sites and their location can be found in Section 5.1, Table 5.1. Note that the Santos Well N7 was sampled for VOCs only and is therefore not included in Table 5.1.

A description of CSG operations at the time of sampling can be found in Section 6.6 for each of the CSG facilities together with maps of the Camden (Figure 6.19) and Narrabri (Figure 6.23) fields.

VOC monitoring at the AGL sites were in the vicinity, and downwind of, active wells and generally where a methane perturbation was apparent. Note that the Santos facility is a pilot gas field that is not yet producing on a commercial basis and operates periodically. The activity of the wells and of plant operations at the Santos site was therefore unclear.

Table 7.7 VOC ambient monitoring campaigns at CSG production facilities

CSG Facility	Monitoring Site	Campaign Date
AGL Camden	Well Pad C3	19-Aug-15
AGL Gloucester	Well Pad G1	16-Jul-15
	Well Pad G2	16-Jul-15
	Well Pad G2	23-Sep-15
Santos Narrabri	Compression Plant (compressor inactive; upwind of gas flare)	28-Jul-15
	Well Pad N7	29-Jul-15

The results of VOC analysis for PAMS hydrocarbons and TO-15 air toxics for the CSG sites are presented in Appendix B.5 in Tables B.5.1 and B.5.2, respectively. The results are also presented graphically in Figures 7.16 and 7.17 at the end of this Section 7.7. Characterisation studies were not undertaken as this source was well characterised by the hydrocarbon VOCs.

The hydrocarbon profile obtained from the measurement of non-methane hydrocarbons in raw well gases (refer Section 7.10) was important in determining whether emissions from CSG operations were impacting the ambient air.

7.7.1 AGL CSG SITE, CAMDEN

Ambient monitoring for the hydrocarbon VOC suite in the vicinity of well pad C3 at the Camden gas field was dominated by C_2-C_4 alkanes; ethane (1.0ppbv), propane (1.0ppbv), isobutane (0.9ppbv) and n-butane (0.3ppbv) and minor higher aliphatics were also detected. Aromatics were present as benzene (0.6ppbv), toluene (0.7ppbv), total xylenes (1.0ppbv) and larger alkyl-aromatics (< 0.2ppbv). Alkenes were not detected in the hydrocarbon profile. This profile does not represent that typically associated with vehicle emissions, as described in Section 7.1, and one may consider therefore that the source of these compounds may be the CSG operations. However, on comparing the hydrocarbon profile for raw gas from Camden CSG wells C1 and C2 (refer Section 7.10 and reported well gas concentrations in Appendix C), the relative concentration of the hydrocarbons in the ambient samples is different to that measured in the well gas. For example, ethane is many orders of magnitude higher than propane in the well gas but at similar concentration in ambient air, and aromatic compounds were found at significantly higher concentrations in ambient air than would be expected from the well gas itself. This suggests an alternative source of hydrocarbons was impacting the ambient air at the Camden CSG site.

An additional consideration is that methane measurements, taken around the CSG well pad C3 during the same campaign as the VOC collection, showed only a small perturbation above ambient background (refer Section 6.6.3). The concentrations of hydrocarbons found in the ambient air at the well pad were not consistent with the measured levels of methane, if the methane was CSG derived. Hence, a link to the CSG source cannot be established for the compounds present in the ambient samples from the Camden CSG facility.

All oxygenated and halogenated compounds, which have been designated as ambient background from the monitoring of other sites, were present at low concentration, consistent with a natural environment.

7.7.2 AGL CSG SITE, GLOUCESTER

Monitoring at the AGL Gloucester CSG site showed trace concentrations and a minor prevalence of hydrocarbon VOCs. In the Jul-15 campaign, only isobutane was detected (0.3ppbv) in the vicinity of Well G1, and only ethane (0.3ppbv) and ultra-trace levels of toluene (0.04ppbv) were measured in the vicinity of Well G2. The Sep-15 campaign showed 0.2ppbv propane and 0.06ppbv isobutane in the vicinity of Well G2 along with benzene (0.4ppbv) and toluene (0.05ppbv). Methane concentrations at the well pads were generally close to background levels with spikes measured at wells G1 and G2 in the Jul-15 and Sept-15 campaigns. The methane levels measured at well pad G1 may be attributable to degassing from a nearby water tank and at G2 to a gas flare (refer Section 6.6.2). The hydrocarbon profile is not source specific at the low concentrations measured and hence no link to a CSG source can be found.

Oxygenated and halogenated compounds from the air toxics suite were in the concentration range expected for a natural environment with the addition of chloroform in all samples at ultra-trace levels (0.02-0.05ppbv).

7.7.3 SANTOS CSG SITE, NARRABRI

Hydrocarbon VOCs were not detected in the samples collected in the vicinity of the compression plant or the gas well at the Santos Narrabri CSG site. Compounds from the air toxics suite were in the range observed and expected for a natural site.

7.7.4 SUMMARY OBSERVATIONS

The AGL CSG well sites at Camden and Gloucester were characterised by a hydrocarbon profile that was dominated by C_2-C_4 alkane species, there was an absence of C_2 and larger alkenes, and aromatic compounds were also present. The dominance of alkanes in the hydrocarbon profile is consistent with that measured in raw CSG well gases however these, and the aromatics, were disproportionately represented in the ambient samples compared their profile in the well gases. Hydrocarbon concentrations were also not correlated with measured methane in the ambient air at the well pads. Hence, the hydrocarbon profile and concentrations found in the ambient air cannot be interpreted to be linked to CSG production at the AGL sites and an alternative source of VOCs is considered likely.

The overall ambient concentration of VOCs at the AGL Camden and Gloucester sites was low compared with semi-rural sites, for example.

There was no indication at all of a CSG source to ambient air at the Santos site and this site showed only those compounds consistent with a natural environment.

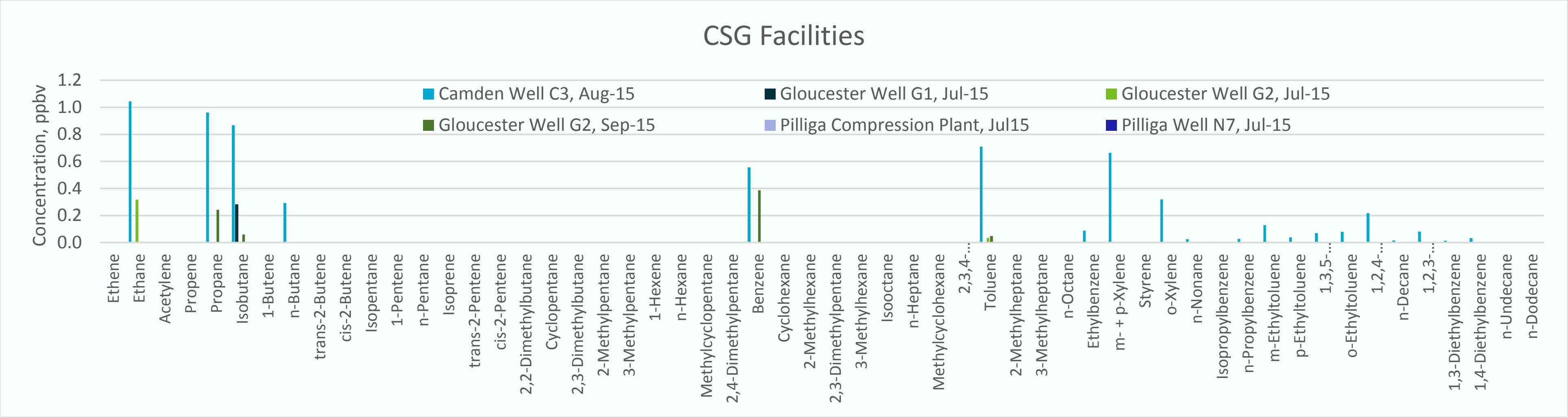

Figure 7.16 PAMS hydrocarbon VOCs measured at the CSG production facilities

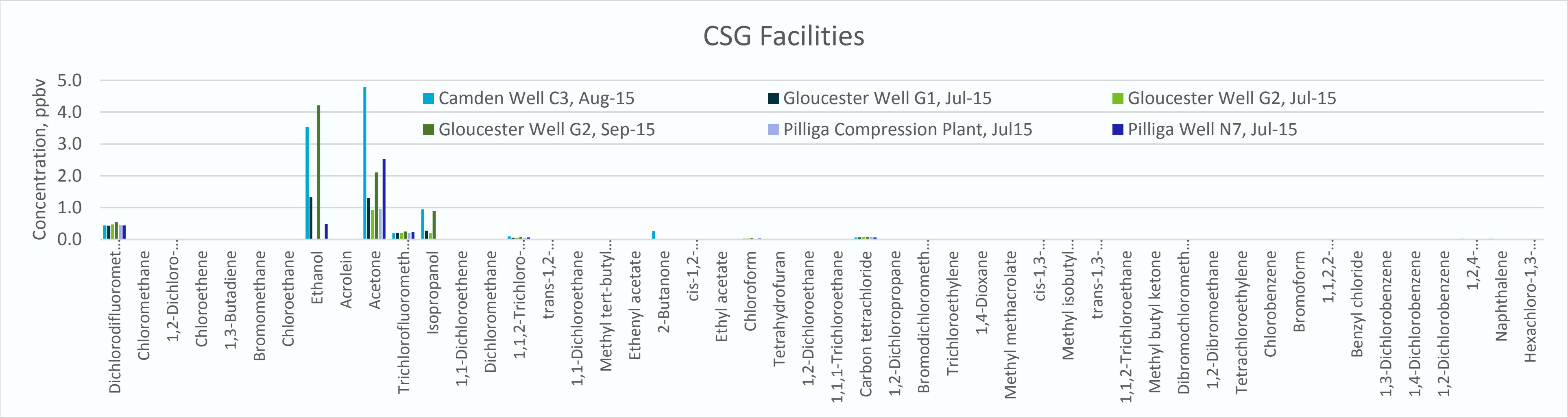

Figure 7.17 TO-15 air toxics VOCs measured at the CSG production facilities

7.8 Landfill Sites

VOC monitoring campaigns were undertaken at the Parkes Waste Facility and the Summerhill Waste Management Centre, Newcastle, by canister collection. The Summerhill Centre was also sampled using the sorbent tube collection technique, as listed in Table 7.1. Site locations can be found in Section 5.1, Table 5.1. Site descriptions and maps of the areas can be found in Section 6.7.

The results of VOC analysis for PAMS hydrocarbons and TO-15 air toxics for the landfill sites are presented in Appendix B.6 in Tables B.6.1 and B.6.2, respectively, and are presented graphically in Figures 7.18 and 7.19 at the end of this Section. The results of characterisation studies for selected samples from Parkes and Summerhill sites are presented in Table 7.8, at the end of this section.

7.8.1 PARKES WASTE FACILITY

The Parkes Waste Facility was monitored for ambient VOCs by canister sampling on 28th August 2014 and on 23rd April 2015, as listed in Table 7.1, at a location downwind of the active tipping area. Monitoring locations are detailed in Section 5.1, Table 5.1 and a description of the site can be found in Section 6.7.1. Figure 6.28 shows a map of the Parkes Waste Facility.

Priority VOCs

Parkes Waste Facility showed C_3-C_4 aliphatic hydrocarbons at a relative concentration which indicated that they originated from vehicle exhaust (refer Section 7.1). Residual fuel components were also evident in the larger aliphatic compounds (such as cyclopentane, 2-methylpentane and 3-methylpentane) and most aromatic compounds were represented including naphthalene at trace levels. The Aug-14 sample was generally slightly higher in these compounds than Apr-15 sample, and a somewhat higher toluene concentration was found (1.1ppbv). At the higher toluene concentration, benzene would be expected if the source were petrol or diesel exhaust so the presence of toluene may be associated with solvent disposal to the landfill. Isoprene was detected at < 0.08ppbv indicative of the sparse level of vegetation at the Parkes site. Overall, the hydrocarbon profile and ambient concentrations are typical of a site moderately impacted by vehicle emissions with perhaps a solvent contribution from the landfill.

Oxygenated compounds from the TO-15 suite dominated at the Parkes landfill site. Ethanol was measured in samples from both monitoring campaigns (24.9ppbv and 14.5ppbv for Aug-14 and Apr-15, respectively) and these levels were higher than the average, but within the range, measured at Camden semi-rural sites (average 5.9; range 1.3-24.2ppbv), and considerably higher than the natural sites (average 4.0; range 1.4-7.2). Acetone (1.2 and 11.4ppbv) was not dissimilar to concentrations measured at Camden (average 4.0ppbv; range 1.4-11.0ppbv) and natural sites (average 7.2ppbv; range 2.0-18.7ppbv). Isopropanol (0.6 and 0.4ppbv) was also within the range measured at Camden (average 1.0ppbv; range 0.14-3.4ppbv) and natural sites (average 1.2ppbv; range 0.3-3.6ppbv). These compounds would be expected to have a biogenic origin at a landfill site, from biological processes associated with decomposition for example, and based on the similarity in concentration to semi-rural and natural sites this could be surmised here. However, their association with household products, solvents and other chemical disposal (Steinemann, 2015) is possible. Ethyl acetate, another commonly used solvent, was found in the Aug-14 campaign at 0.4ppbv and was not detected in the Apr-15 campaign. This compound has not been found at semi-rural and natural sites.

The Freon™ compounds and other halocarbons (dichlorodifluoromethane, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane and carbon tetrachloride) have been observed at a relatively constant levels in the ambient air from all sources and again are present at both landfill sites at very similar concentrations to other source locations. As has been previously stated, 1,1,2-trichloro-1,2,2-trifluoroethane is somewhat more variable than the other compounds and importantly is present at a concentration close its detection limit. Therefore, it will sometimes be reported as not detected but this does not discount its status as ubiquitous.

Chlorinated hydrocarbons commonly used as markers for landfill emissions were found at the Parkes waste facility; trichloroethylene (0.8ppbv in Aug-14 campaign only) and tetrachloroethylene (0.4 and 0.2ppbv in Aug-14 and Apr-15 respectively). Trichloroethylene is an industrial solvent and tetrachloroethylene is a commonly used solvent in various applications, including as a dry cleaning fluid. Dichloromethane was found in the samples from both campaigns at concentrations 7.3 and 1.4ppbv, respectively. As a common industrial and household solvent (component of paint stripper, for example) its presence is not unexpected. The concentrations measured for these compounds at the landfill site were well below workplace exposure limits mandated by the US occupational health agency, NIOSH (NIOSH, current at 2016).

Characterisation Studies

Examination of the chromatographic results and mass spectral interpretation from the canister sample was undertaken for the Parkes landfill sample taken on 28th August 2014. Qualitative results are presented in Table 7.8, at the end of this section.

Carbonyl sulphide and dimethyl sulphone were found as ubiquitous compounds as discussed in Section 7.1. Bromopropane, a non-priority halocarbon was detected at the Parkes site. A number of C_4 to C_7 aldehydes were identified, such as butanal, hexanal, heptanal, and these compounds would contribute to odour associated with biological decomposition, as discussed in Section 7.1. Monoterpenes emissions of a-pinene, p-cymene, 3-carene and limonene were also identified. These compounds are emitted from trees and vegetation but they also present in the emissions from landfill due to their common usage as fragrances in consumer products (Steinemann, 2015).

7.8.2 SUMMERHILL WASTE MANAGEMENT CENTRE

The Summerhill Waste Management Centre (WMC) was monitored for VOCs by canister sampling on the 16th July 2014 at a location at the tip face. A sorbent tube sample was also taken at a similar time. A second campaign was undertaken on the 9th July 2015 at a similar location and on this occasion two concurrent canister samples were taken, 25 minutes apart. Monitoring locations are detailed in Section 5.1, Table 5.1 and a description of the site can be found in Section 6.7.2. Figure 6.34 shows a map of the Summerhill Waste Management Centre.

Priority VOCs

VOC emissions at Summerhill WMC showed a different hydrocarbon profile than that seen at Parkes WF, the major difference being the inclusion of significant levels of ethene in the July-15 profile and the absence of compounds more typical of petrol residuals in the exhaust. Unusual also, compared with urban vehicle derived emissions, is the relative concentration of toluene to benzene where, in the July-15 samples, benzene dominates toluene. These characteristics are indicative of a diesel exhaust profile, or another combustion source (refer Section 7.1). On the basis that tipping trucks were operating at the site at the time of sampling, a diesel engine emissions source was likely distinguished. Some variation in concentration of C_2-C_4 hydrocarbons, particularly, was seen for the concurrent samples taken on Jul-15. This is likely representing the variability in the level of exhaust emissions from on-site vehicles moving past the sampling point.

Ethane was higher at the Summerhill site than at the Parkes landfill and this may be associated with the methane gathering system operating at the Summerhill site.

Isoprene was evident (around 0.2ppbv) in the July-15 samples indicative of biogenic emissions from surrounding vegetation at the site.

The results for air toxics compounds for the concurrent samples were extremely reproducible and hence the average concentrations will be used in the following discussion. Ethanol was measured at 15.3ppbv in Jul-14 and averaged 12.2ppbv in the Jul-15 campaigns. These concentrations would be expected from vegetative decomposition (refer levels compared for Parkes landfill, semi-rural and natural sites in the preceding Section 7.8.1). Isopropanol (4.5ppbv and 1.4ppbv for Jul-14 and Jul-15 campaigns) was higher than Parkes landfill (around 0.5ppbv) but within the range found at semi-rural and natural sites. Acetone

(14.0ppbv) was within the expected range for the Jul-14 campaign only. High concentrations of acetone, averaging 200ppbv, were measured in samples from the Jul-15 Summerhill campaign. Acetone is a commonly used solvent, in paint thinner for example, and this higher level may indicate a large solvent disposal event around the time of the Jul-15 monitoring campaign. This was accompanied by high levels of 2-butanone (18.0ppbv average) which may be associated with the release of the same source solvent or material. Ultra-trace levels of methyl butyl ketone (0.07ppbv) were also found in the Jul-15 samples, which possibly originated from solvent disposal. Acrolein averaged 2.3ppbv in the Jul-15 campaign, which is above the levels measured for this compound in semi-rural and natural environments (ND – 0.9ppbv). This compound may arise from biological processes however, it is a chemical with various industrial applications, such as a biocide for example, and its disposal to landfill may be evident in the landfill emissions.

Dichloromethane (0.3ppbv, average) and benzyl chloride (0.01ppbv, average) were measured in samples from the Jul-15 campaign only. Ultra-trace levels of chloroform (0.06 and 0.04ppbv) and 1,4-dichlorobenzene (0.009 and 0.006ppbv) were measured in the Jul-14 and Jul-15 campaigns, respectively. The ubiquitous halocarbons were also found at the Summerhill site at similar concentrations as have been observed at all other locations.

Characterisation Studies

The sorbent-based technique for characterisation of non-standard compounds was undertaken using sorbent tube sampling at the Summerhill site on 16th July 2014. The sample was collected at a flow rate of 150 mls.min^{-1} for 15 minutes using methodology described in Section 5.3.5. The chromatographic output from VOC analysis of the canister sample from the same monitoring campaign was also examined. Qualitative results for the canister evaluation and semi-quantitative results for the sorbent tube analysis are presented in Table 7.8, at the end of this section.

Carbonyl sulphide and dimethyl sulphone were again identified as ambient background and, from the sorbent result, and an approximate concentration of between 0.5 and 1.0ppbv was estimated for dimethyl sulphone. Various oxygenated compounds, a nitrogenous compound and a monoterpene were identified from VOC mass spectral characterisation. Sorbent tube analysis extended the range of compounds found and many larger, lower volatility oxygenated compounds were isolated from this analysis. These included various C_8 to C_{12} aldehydes, ketones, including acetophenone, alcohols and phenol, and esters, all likely associated with biological decomposition at the landfill site and contributing to the characteristic odour of landfill, as discussed in Section 7.1. Concentrations generally less than 0.5ppbv and up to 1.0ppbv were estimated for these compounds. Limonene and a-pinene are common fragrances used in household products and these were identified at around 0.5-1.0ppbv and < 0.5ppbv respectively. Biogenic emissions of p-cymene at < 0.5ppbv and 3-carene at < 0.1ppbv were also found. Whilst some of these compounds are associated with household products and chemical disposal, a number will be generated from biological processes and all contribute to the characteristic odour associated with landfill (Fang et al., 2012, Rodriguez-Navas et al., 2012).

7.8.3 SUMMARY OBSERVATIONS

Ambient concentrations at the landfill sites were generally low or in the range expected for an intensive land-use site of this kind. An exception was the excursion in acetone of 200ppbv (0.2ppmv) on one occasion at the Summerhill Waste Centre.

The evaluation of VOCs at the landfill sites found a number of compounds that are somewhat characteristic of these sites and sorbent tube analysis extended the range of compounds identified to include lower volatility oxygenated compounds and a range of monoterpenes.

Compounds that appeared characteristic to the landfill source include:

- Acetone, 2-butanone and methyl butyl ketone associated with solvent disposal.
- Acrolein possibly from waste disposal (as biocide for example) or from biological processes.

- The chlorinated hydrocarbons; trichloroethylene and tetrachloroethylene. These are commonly specified as markers for landfill emissions based on their use as solvents in various applications. Ambient concentrations were well below the limits for workplace exposure.
- Other chlorinated solvent residues; dichloromethane, chloroform and benzyl chloride.
- C_4 to C_{12} oxygenates as aldehydes, ketones, including acetophenone, alcohols, phenol and esters, which are associated with biological processes more generally but likely enhanced in soil decomposition in landfills. All contribute to the characteristic odour associated with landfills.
- Monoterpenes; limonene and a-pinene as common fragrances used in household products.
- The exhaust emissions of hydrocarbons from on-site diesel vehicles were identified as a contributor to the source profile at the Summerhill site.
- Ethane was detected at levels that may be indicative of the methane gathering system operating at the Summerhill site.

Table 7.8 Compounds identified from characterisation studies for the Parkes and Summerhill landfill sites

Characterisation from Canister Analysis	**Presence in Ambient Air**		**Characterisation from Sorbent Tube Analysis**	**Approx. Ambient Concentration, ppbv**
Compound Name or Class	Parkes WF Aug-14	Summerhill WMC Jul-14	Compound Name or Class	Summerhill WMC Jul-14
Carbonyl sulphide	✓	✓	Sulphur containing, likely dimethyl sulphone	~ 0.5
Sulphur containing; likely dimethyl sulphone	✓	✓	Alcohol; likely 2-butanol	< 0.5
Butanal	✓	-	Butylester	< 0.5
Bromopropane	✓	-	Oxygenate, possibly alkylester	< 0.5
Nitrogenous	-	✓	Oxygenate, possibly alcohol	< 0.5
Hexanal	✓	✓	Benzaldehyde	0.5-1.0
3-Heptanone	-	✓	Monoterpene, likely a-pinene	< 0.5
Heptanal	✓	✓	Phenol	< 0.5
Oxygenate; possibly 2-ethylhexanal	-	✓	C_8 ketone, possibly 6-methylheptanone	< 0.5
a-Pinene	✓	-	C_8 oxygenate	< 0.5
Benzaldehyde	-	✓	Monoterpene, possibly 3-carene	< 0.1
a-Methylstyrene	-	-	C_8 aldehyde, likely octanal	< 0.5
Oxygenate; likely C_7 alcohol	-	✓	Monoterpene, likely p-cymene	< 0.5
C_9 oxygenate; likely nonenol or nonanal	✓	✓	Limonene	0.5-1.0
Monoterpene; likely p-cymene	✓	✓	Acetophenone (1-phenylethanone)	< 0.5
Limonene	✓	-	C_9 oxygenate, possibly nonanal or nonenol	0.5-1.0
			C_{10} oxygenate, possibly decanal or decenol	0.5-1.0
			C_{11} oxygenate, possibly undecanal	< 0.1
			C_{12} aldehyde	< 0.1
			C_{12} ketone	< 0.5

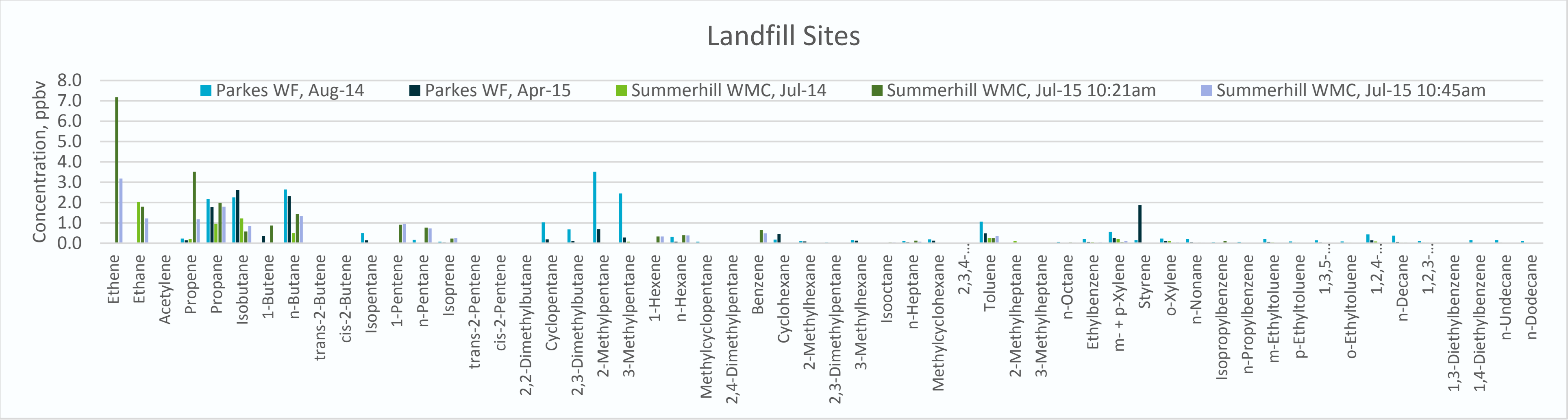

Figure 7.18 PAMS hydrocarbon VOCs measured at the landfill sites

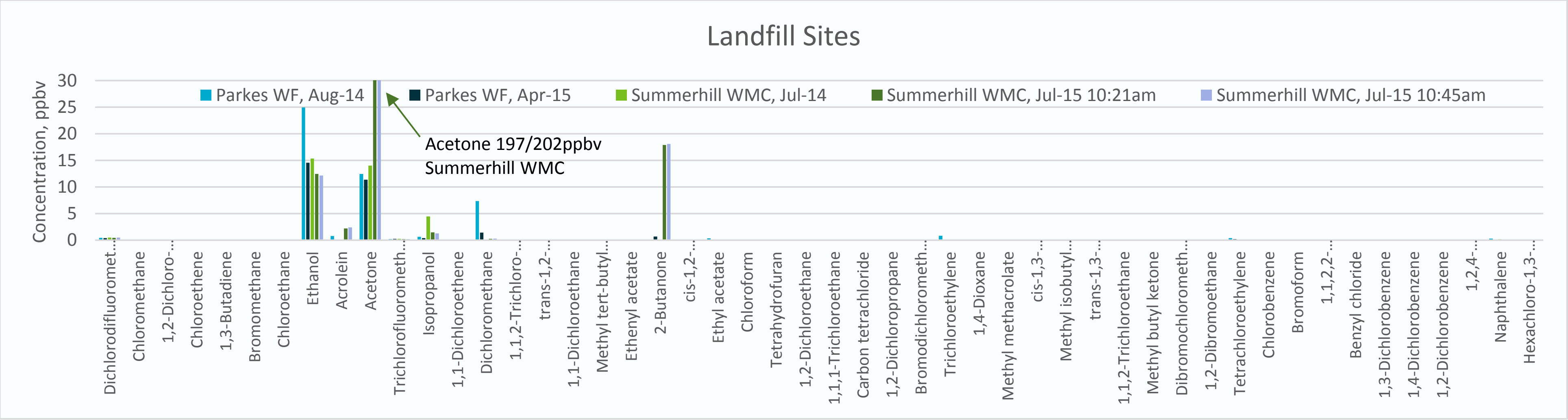

Figure 7.19 TO-15 air toxics VOCs measured at the landfill sites.

Note: The acetone concentrations at Summerhill WMC for the Jul-15 samples are off the plotted scale and are 197ppbv and 202ppbv.

7.9 Wastewater Treatment

VOC monitoring campaigns were undertaken at the Singleton Wastewater Treatment Plant, Wagga Wagga (Narrung Street) Wastewater Treatment Plant and Picton Wastewater Treatment Plant, for plant operations listed in Table 7.1. Details of the monitoring locations can be found in Table 5.1 and site descriptions and maps can be found in Section 6.8.

The results of VOC analysis for PAMS hydrocarbon and TO-15 air toxic compounds at the wastewater treatment sites are presented in Appendix B.7 in Tables B.7.1 and B.7.2, respectively, and the results of characterisation studies at selected sites is presented in Table 7.9. The VOC results are also presented graphically in Figures 7.20 and 7.21 at the end of this section.

7.9.1 SINGLETON WASTEWATER TREATMENT PLANT

The Singleton wastewater treatment plant (WWTP) was monitored for ambient VOCs by canister sampling on the 2nd July 2014 at two locations close to the settling ponds; Pond #1 and Pond #2. An ambient background sample was also taken during this campaign at a location upwind of, and some distance from, the active treatment sites.

A second VOC campaign was undertaken on the 8th July 2015 from near the raw sewage inlet to the plant and a sorbent tube sample was also taken at this location at this time, as listed in Table 7.1.

These campaigns were designed to provide some indication of the variation in emissions at different locations at the Singleton plant. A description of plant operations can be found in Section 6.8.1 and Figure 6.39 shows a map of the plant.

High odour levels were experienced by sampling personnel in campaigns at the Singleton plant.

Priority VOCs

Singleton WWTP showed no discernible impact from emissions associated with exhaust derived hydrocarbon VOCs in the Jul-14 campaign where only isobutane (0.4ppbv) was found in the C_2-C_4 hydrocarbon range at Ponds #1 and #2. The hydrocarbons 3-methylpentane (1.4 and 0.3ppbv at Ponds #1 and #2 respectively) and 2-methylheptane (4.0 and 0.7ppbv, respectively) were also measured. Benzene was not detected at Ponds #1 or #2 at concentrations above that measured in the background sample (0.02ppbv) and toluene was at, or slightly above, the background sample (maximum 0.2ppbv at Pond #2). The xylenes were at ultra-trace levels (< 0.03ppbv). 1,3-butadiene, a hydrocarbon from the TO-15 suite and uncommonly found at significant concentrations in the emissions at other source locations evaluated in this study, was also present in samples from Pond #1 (0.6ppbv) and the background sample (0.3ppbv). This compound is usually found in heavily trafficked areas as a fuel derived combustion product; its occurrence at the plant cannot be established.

The sample taken at the raw sewage inlet in the Jul-15 campaign showed relatively high levels of C_2-C_4 hydrocarbons (up to 10.2ppbv ethene and 7.6ppbv propene, 1.1ppbv ethane and 0.9ppbv propane, 0.4ppbv isobutane and 0.5ppbv butane). This profile was associated with larger aliphatic hydrocarbons, which included various alkenes. Benzene concentration was 0.6ppbv but other aromatics were at trace concentrations (e.g. toluene 0.1ppbv). This profile makes it difficult to infer a definite vehicle emissions impact. As the site is remote and service roads are not significantly trafficked, it is possible the hydrocarbons measured are associated with the source sewage or the operations at the treatment plant.

Isoprene was not found in any samples from the Singleton WWTP as would be expected from the sparsely vegetated environment at this site (refer Figure 6.39).

Analysis of the TO-15 suite found the site to be dominated by the oxygenated compounds; ethanol, acetone and isopropanol. The biological occurrence of these compounds is discussed in Section 7.1 and extensively in the source emissions evaluations in previous sections. It is useful to note though that their biological association is apparent at the Jul-14 sampling of this site in that average levels at the pond locations were consistently 4-fold higher than the background location (average pond concentrations for ethanol 7.6ppbv, acetone 24.5ppbv, isopropanol 12.7ppbv, 2-butanone 1.9ppbv). Isopropanol was found at 20ppbv at pond #2, which is significantly higher than typically found in natural and semi-rural environments (around 1ppbv). Methyl butyl ketone was also present in these samples (0.3ppbv and 0.07ppbv at ponds #1 and #2, respectively and ND in background).

The raw sewage inlet sampled in the Jul-15 campaign generally showed higher levels of the oxygenated compounds than at the ponds (albeit from different campaigns). Concentration of ethanol (13.7ppbv) was within the range found at other source locations evaluated in this study. Acetone (93.2ppbv) and 2-butanone (6.5ppbv) were significantly higher than other land-use sources, with the exception of an excursion in these compounds at a landfill site. Inlet levels of isopropanol (1.9ppbv) were lower than the ponds and within the range typically found from other sources. Acrolein was measured in the inlet sample at 1.0ppbv, which is again within the range measured at other source locations. Methyl butyl ketone (0.3ppbv) and methyl isobutyl ketone (0.1ppbv) were found at the inlet, which is slightly higher than the few occurrences seen at other source locations. These ketones may be associated with the acetone as a combined solvent release. All of the oxygenated compounds have been reported to be commonly associated with raw sewage outfalls and wastewater treatment, along with the alcohols and other ketones (Dewulf et al., 1999, Dincer and Muezzinoglu, 2008).

The Singleton WWTP site also stood out in the prevalence of certain chlorinated compounds, some of which have not been detected, or detected at significantly lower levels, at the various source locations evaluated in this project. This was apparent at the location of the settling ponds. The Singleton WWTP was significantly higher than other sources evaluated in this study in cis-1,2-dichloroethene (3.7ppbv at Pond #1 and at 13.5ppbv at Pond #2), trichloroethylene (1.2ppbv at Pond #1 and 4.4ppbv at Pond #2) and tetrachloroethylene (18.9ppbv at Pond #1 and 58.3ppbv at Pond #2). Other chlorinated residues included 1,1,1-trichloroethane, which was detected at Pond #1 at ultra-trace level (0.05ppbv), and chloroform that was found at around 0.2ppbv but this level is not uncommon from other sources. The concentration of trichloroethylene and tetrachloroethylene were well below occupational exposure limits (100ppmv as 8-hour time-weighted average), as recommended by NIOSH (NIOSH, 2016).

The chlorinated compounds are common industrial solvents and their release to wastewaters may not be uncommon. Halogenated compounds are less studied in relation to sewage treatment, however their occurrence has been reported at treatment plants (Atasoy et al., 2004), and as components of sewer gas (Haas and Herrmann, 1996, Pennell *et al.*, 2013). Tetrachloroethylene has been reported in wastewaters in EU risk assessments (WHO, 2006).

Of the ubiquitous halogenated compounds, 1,1,2-trichloro-1,2,2-trifluoroethane was measured at 0.2ppbv in the Pond #1 sample whereas 0.05ppbv has been established as ambient background from all other sources (refer Section 7.1). With the exception of dichlorodifluoromethane, the Singleton site showed all other ubiquitous halocarbons slightly above the average ambient levels. This may concur with the higher levels seen for the other chlorinated species.

The Singleton sewage inlet sample showed levels of halocarbons consistent with ambient background accompanied by trace levels of bromomethane (0.1ppbv) and ultra-trace levels of chloroform (0.03ppbv), chlorobenzene (0.01ppbv), benzyl chloride (0.01ppbv) and hexachloro-1,3-butadiene (0.002ppbv). As mentioned previously, an excursion in the typical levels of acetone was the main characteristic of the inlet section of the plant.

Characterisation Studies

Based on the higher concentrations and prevalence of compounds observed from VOC analysis for Singleton WWTP, as described above, it was selected for characterisation of non-standard compounds using sorbent tube collection and analysis. This technique also targets sulphur and nitrogen containing compounds (as described in the Section 5.3.2) which may contribute to the levels of odour apparent at the Singleton site. These results are presented in Table 7.9, along with the evaluation of non-standard compounds for Wagga and Picton WWTPs, at the end of this section.

The sulphur containing compounds carbonyl sulphide and dimethyl sulphone were identified as ambient background in these samples at a concentration estimated around 0.5 and 1.0ppbv, respectively. Sorbent tube analysis extended the range of compounds found and many more complex, lower volatility oxygenated compounds were isolated from this analysis. These included various aldehydes, ketones, alcohols including phenol, and esters. Concentrations generally less than 0.5ppbv and up to 1-2ppbv were estimated for these compounds. The monoterpenes a-pinene, limonene and p-cymene were also apparent. Aside from the biogenic sources of these compounds, they are commonly used in household cleaning products and hence have been shown to be present in the emissions from wastewater (Godayol et al., 2013). The absence of a biogenic emission of isoprene in the VOC profile indicates that the source of the monoterpenes is more likely to be the wastewater itself.

Due to the high odour levels apparent at the Singleton site, the pursuit of organic sulphur and nitrogen containing compounds was emphasised in the characterisation study. The mercaptans (thiols) and organic sulphides are commonly associated with sewer gases and biogas, and compounds belonging to these organic classes were mass spectrally searched in the characterisation process. However, they were not detected in the ambient air from these plants despite the successful isolation of organic sulphides from characterisation studies of the landfill source. Other odorous compounds known to be present in sewage waters include indole and skatole (nitrogenous bicyclics) which occur naturally in human faecal matter. These compounds were also mass spectrally searched but were not detected. These compounds have a high affinity for water and, despite their strong odour, they are therefore difficult to isolate from ambient air where they are present at low concentration (Godayol et al*.* 2013).

7.9.2 WAGGA WAGGA WASTEWATER TREATMENT PLANT

The Wagga Wagga wastewater treatment plant was monitored for ambient VOCs by canister sampling in three campaigns, as listed in Table 7.1. The first campaign was on the 26th August 2014 at a location adjacent to the aeration tank, and the sample was taken during an aeration cycle. Campaigns were undertaken on the 17th February 2015 at the raw sewage inlet to the plant and the 21st April 2015, also at the inlet. A description of the plant can be found in Section 6.8.2.

This plant is relatively new and domestic waste as well as pre-treated industrial waste is processed. Our sampling personnel noticed minimum odour at this site, compared to the Singleton treatment plant.

Priority VOCs

For all sampling campaigns, the occurrence of hydrocarbon VOCs was minimal in the ambient air at the Wagga Wagga wastewater treatment plant. Minor levels of isobutane were measured in the Aug-14 sample taken adjacent to the aeration tank (1.0ppbv) and at the raw sewage inlet (0.09ppbv). Somewhat higher isobutane concentration was seen at the inlet sample from the Feb-15 campaign (3.0ppbv) along with trace level n-butane (0.4ppbv) and benzene (0.2ppbv). Toluene was found in all campaigns and was significant only in the sample at the aeration tank (0.5ppbv) along with xylenes (1.0ppbv) and trace levels of larger aromatics and alkanes. The scarcity of compounds making up the hydrocarbon profile provides insufficient information to predict a source for these compounds. Isoprene emissions were measured in the February inlet sample (0.5ppbv) which was not seen in April indicating possibly, but not definitely, the higher biogenic emission of isoprene from surrounding vegetation in summer.

Of the oxygenated VOCs, the Wagga Wagga plant showed significant levels of ethanol for the inlet sample taken in the Feb-15 campaign (40.9ppbv). In Apr-15 the inlet sample concentration was 1.5ppbv. The aeration tank had 9.9ppbv ethanol in Aug-14. The latter concentrations are commensurate with ethanol measurements at the various locations at the Singleton wastewater treatment plant, and indeed are within the range found for most other sources. Acetone was also within the observed range of most sources but, as seen for ethanol, it was higher at the inlet in February (13.8ppbv) compared with April (2.5ppbv) at the Wagga plant. The higher concentration of both ethanol and acetone in February compared with April indicates their higher emission rate with warmer temperatures. Acetone at the aeration tank was 7.1ppbv in Aug-14. Acrolein was also found at higher concentration in the inlet sample taken in February (1.5ppbv) compared with the sample taken in April (0.4ppbv). Acrolein was not detected in the sample taken at the aeration tank. Isopropanol was measured at a concentration of 0.4ppbv at the inlet in February and was not detected at the inlet in April. Isopropanol was 0.4ppbv in the aeration tank sample. A trace level of 2-butanone was found at the inlet in the April sample only (0.2ppbv) and methyl butyl ketone was measured at ultra-trace levels (0.05ppbv) in the February inlet sample only.

Halogenated compounds were at background concentrations expected for the four compounds designated as ubiquitous in ambient air. Ultra-trace levels of only a few other halogenated species were detected (< 0.1ppbv) mainly in the February inlet sample. Tri- and tetrachloroethylene, which had been found at Singleton wastewater plant and characteristic in sewage emissions, were not detected in any samples from the Wagga Wagga plant.

Characterisation Studies

The Wagga Wagga wastewater plant was characterised for non-standard compounds using evaluation of the canister samples for the aeration tank (Aug-14) and the raw sewage inlet (Feb-15). These results are presented in Table 7.9, along with Singleton and Picton characterisation results.

Carbonyl sulphide and dimethyl sulphone were again identified as ambient background at this site. The inlet sample had higher prevalence of C_4 to C_7 aldehydes and 2-chloroacetophenone was also found.

7.9.3 PICTON WASTEWATER TREATMENT PLANT

The Picton wastewater treatment plant was monitored for ambient VOCS by canister sampling in three campaigns. On 6th August 2014, the VOC sample was taken at a vegetated area overlooking the biosolids lagoon #2, and again on 29th April 2015 in the same area overlooking lagoon #2. On 25th November 2015, VOCs were monitored at an area between the fluxing/aeration tanks at a time when the fluxing and aeration tanks were cycling. Monitoring by sorbent tube was also undertaken at the location of the aeration tanks in the same campaign. The VOC monitoring campaigns at the Picton site are listed in Table 7.1 and Table 5.1 details the site and its location. A description and map of the Picton plant can be found in Section 6.8.4.

The VOC campaigns monitored variations in ambient concentrations at lagoon #2 and differences due to plant processes. Odour levels were low at the Picton site.

Priority VOCs

Hydrocarbon VOCs were not prevalent at the Picton plant and only minimal concentrations were found in samples taken in the vicinity of the lagoon #2 and the aeration tanks. The lagoon sample from the Aug-14 campaign showed slightly higher concentrations than the Apr-14 lagoon and aeration tank samples. C_2-C_4 hydrocarbons were found at concentrations < 0.6ppbv (propane). Larger aliphatic and aromatic hydrocarbons were measured at trace concentration, the highest in this group being toluene at 0.2ppbv. Overall, the hydrocarbon profiles for samples from the three campaigns did not clearly indicate if a vehicle source was contributing and if so only the alkane component of the emissions were measurable.

Emissions of isoprene were found at highest concentration at the aeration tank (0.6ppbv) in the sample taken in summer. Isoprene was also identified in the Apr-15 lagoon sample (0.1ppbv). This site is surrounded by bushland and it is likely that the vegetation, rather than source emissions, generated the observed levels of isoprene.

Analysis for the TO-15 suite showed low concentrations of the oxygenated compounds, at levels typical of that found in other vegetated regions where emissions from biological processes are impacting the ambient air (refer Section 7.1). Ethanol concentrations were consistent across the three campaigns (around 2.5-4.0ppbv). Highest acetone concentration was found in the lagoon sample from the Aug-14 campaign (14.5ppbv). The Apr-15 campaign showed 4.0ppbv acetone and the Nov-15 campaign at the aeration tanks showed 7.7ppbv. Isopropanol was low (< 1.1ppbv) in lagoon and aeration tank samples. 2-butanone was also low, < 0.5ppbv. Methyl isobutyl ketone and methyl butyl ketone were not detected in all samples from these campaigns. Acrolein was present at this site at a concentration of 0.4ppbv from the lagoon in the Apr-15 campaign and at 0.8ppbv close to the aeration tanks in the Nov-15 campaign.

Halogenated compounds were at the background concentrations expected for the four compounds designated as ubiquitous in ambient air. Dichloromethane was found at 1.0ppbv and trace levels of only a few other halogenated species compounds were detected (< 0.2ppbv) in the Aug-14 lagoon sample. Tri- and tetrachloroethylene, which had been seen at Singleton wastewater treatment plant and characteristic in sewage emissions, were not seen in any samples from the Picton plant.

Characterisation Studies

The Picton STP was characterised for non-standard compounds by evaluation of the chromatographic output of samples from lagoon #2 for both the Aug-14 and April-15 campaigns. The aeration tank was sampled using the sorbent tube technique in Nov-15, at the same time as the canister sample was collected. These results are presented in Table 7.9.

Carbonyl sulphide and dimethyl sulphone were again identified as ambient background in these samples. Carbonyl sulphide was not detected from sorbent sampling as this compound is less efficiently collected in this manner. There was low prevalence of non-standard compounds from the lagoon samples, showing a few aldehydes, ketones and a nitrogenous compound. Sorbent tube revealed more about the sample from the aeration tank. Compounds associated with sewage treatment included phenol and limonene and the more complex C_8-C_{12} aldehydes and/or alcohols, as discussed in Section 7.1.

7.9.4 SUMMARY OBSERVATIONS

Apart from an excursion in the ambient concentration of ethanol on one occasion at the Wagga Wagga wastewater treatment plant, the Wagga Wagga and the Picton plants generally showed ambient VOC concentrations in the range measured at other land-use sources.

Certain operations at the Singleton plant generated oxygenated and halogenated VOCs at levels that were at the high end, or exceeded, those measured from other emissions sources, such as landfill and the cattle feedlot. At the sewage inlet to the plant, acetone (93.2ppbv) and 2-butanone (6.5ppbv) were significantly higher than other land-use sources, with the exception of an excursion in these compounds at a landfill site. The Singleton wastewater treatment plant was higher than other sources evaluated in this study in chlorinated compounds at the settling ponds; cis-1,2-dichloroethene (up to 13.5ppbv), trichloroethylene (up to 4.4ppbv) and tetrachloroethylene (up to 58.3ppbv). Compounds associated with odour, such as aldehydes, ketones, alcohols and nitrogenous compounds were apparent in the emissions profile at the Singleton site.

Emissions identification and concentration is affected by the proximity of the sampling point, amount and type of emissions, meteorological variables and a range of other factors. However, it is evident that the emissions from the Singleton wastewater treatment site were captured at a level that would allow certain oxygenated and halogenated VOCs to be used to characterise the operations at that site at that time. The high levels found at the Singleton site are also of importance when addressing air toxics along with odorous emissions from this source.

From a qualitative viewpoint, the oxygenated and chlorinated compounds isolated in the VOC determinations and from the characterisation work for the wastewater sites have been reported as attributable to emissions from wastewater treatment plants, as discussed in Section 7.1. However, this study has found that most of these compounds are also found in the emissions from other sources, particularly landfills, albeit at lower prevalence and concentration. Plant operations and processes also dictate the level and type of emissions attributable to the source.

The mercaptans (thiols) and organic sulphides that are commonly associated with odour from sewer gases and biogas were not detected in the ambient air from these plants, as discussed with reference to the Singleton plant in Section 7.9.1. The nitrogenous bicyclics, indole and skatole, were also not detected.

Despite their strong odour these compounds have a high affinity for water and will consequently be found at very low concentration in ambient air (Godayol et al., 2013).

Table 7.9 Compounds identified from characterisation studies for the wastewater treatment sites.

Note: Characterisation of Picton WWTP identified the same compounds in the samples from the two campaigns and the results have therefore been listed together.

Characterisation from Canister Analysis	Presence in Ambient Air			Characterisation from Sorbent Tube Analysis	Ambient Concentration, ppbv	
	Wagga STP Aeration Tanks	Wagga STP Inlet	Picton WWTP Lagoon #2		Singleton WWTP Inlet	Picton WWTP Aeration Tank
Compound Name or Class	26-Aug-14	17-Feb-15	6-Aug-14 and 29-Apr-15	Compound Name or Class	08-Jul-15	25-Nov-15
Carbonyl sulphide	✓	✓	✓	Carbonyl sulphide	~ 0.5	-
Sulphur containing; likely dimethyl sulphone	✓	✓	✓	Sulphur containing; likely dimethyl sulphone	~ 1.0	< 0.5
Butanal	-	✓	✓	Ketone; likely 4-methyl-4-penten-2-one	< 0.5	-
Pentanal	-	✓	-	Oxygenate, possibly alkylester	< 0.5	< 0.1
Nitrogenous	✓	✓	✓	Oxygenate, possibly alcohol	< 0.5	-
Hexanal	-	✓	-	Benzaldehyde	1.0-2.0	0.5-1.0
Furfural	-	✓	✓	a-Pinene	< 0.1	< 0.1
3-Heptanone	✓	✓	✓	Phenol	~ 0.5	< 0.5
Heptanal	-	✓	-	C_8 ketone; possibly 6-methylheptanone	< 0.5	-
Oxygenate; possibly 2-ethylhexanal	✓	✓	-	C_8 oxygenate	< 0.5	-
Benzaldehyde	✓	✓	✓	C_8 aldehyde; likely octanal	< 0.5	< 0.5
Oxygenate; likely C7 alcohol	✓	-	-	Monoterpene; likely p-cymene	< 0.1	< 0.1
Monoterpene; likely p-cymene	✓	✓	-	Limonene	< 0.5	< 0.1
2-Chloroacetophenone	-	✓	-	Acetophenone	0.5-1.0	~ 0.5
				C_9 oxygenate, likely nonanal or nonenol	1.0-2.0	< 0.5
				C_{10} oxygenate, likely decanal or decenol	1.0-2.0	< 0.5
				C_{11} oxygenate, likely undecanal	< 0.5	< 0.1
				C_{12} aldehyde	< 0.5	< 0.1
				C_{12} ketone	< 0.5	-

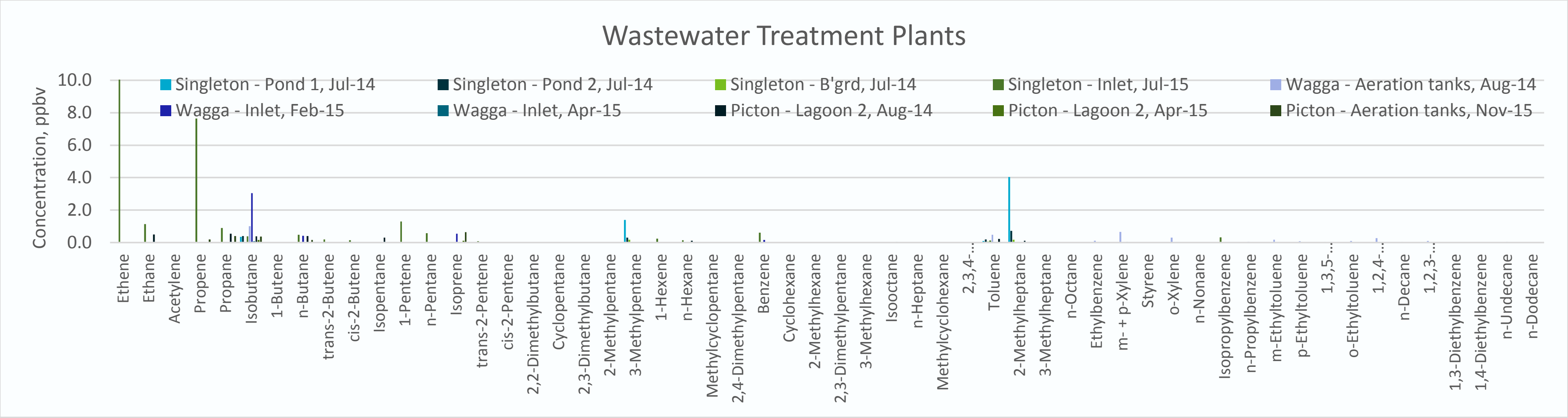

Figure 7.20 PAMS hydrocarbon VOCs measured at the wastewater treatment plants

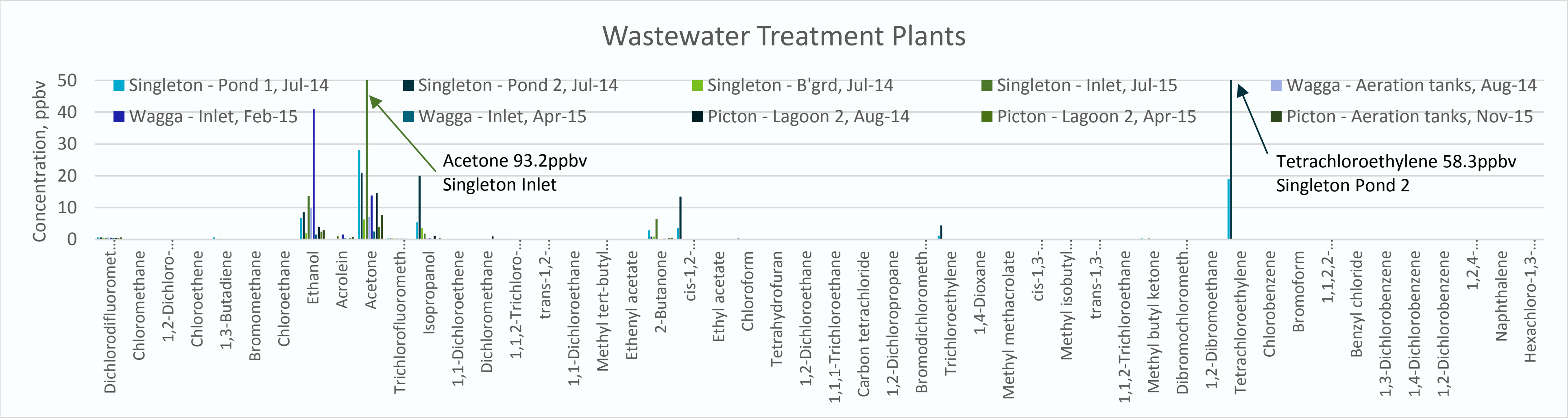

Figure 7.21 TO-15 air toxics VOCs measured at the wastewater treatment plants

Note: The acetone result for the Singleton inlet is off the plotted scale and is 93.2ppbv. The tetrachloroethylene result for Singleton pond 2 is 58.3ppbv.

7.10 CSG Sourced Well Gas

The minor hydrocarbon VOCs present in CSG sourced well gas, that is those above C_5, were the focus of this component of the work, and included the aromatic compounds; benzene, toluene and xylenes. The minor compounds are generally not measured in conventional gas composition analysis as the aim is more usually on determining the bulk components (methane and C_2-C_5 compounds). Non-methane hydrocarbons (NMHCs) in the range C_2 to C_5 were also determined in the same analysis as the minor hydrocarbons to provide a measure of relative concentration to the C_5-C_8 compounds.

Although VOC determination in well gases was not a requisite of this project, it was considered that this determination might be informative in the recognition of a CSG source and its impacts to ambient air and with respect to human and environmental health. An initial investigation for the analysis of NMHCs was undertaken using the IsoTube® samples of well gas that were collected for the molecular composition and isotope determinations.

Hydrocarbon VOCs were determined on samples from AGL Gloucester Wells G1 and G2, sampled on 16-Jul-15, Well G2 sampled again on 23-Sept-15 and Well G3 sampled on 23-Sep-15. AGL Camden well gases were from Well C1 and C2, sampled on 19-Aug-15. The monitoring campaigns are listed in Table 7.1 and well locations are detailed in Section 5.1, Table 5.1. Operations at the CSG facilities are described in Section 6.6.

7.10.1 HYDROCARBON VOC RESULTS

The non-methane hydrocarbon VOC results for the well gas samples are presented in Appendix C, Table C1.1. Note that the concentration unit for well gas is parts per million by volume (ppmv), rather than ppbv as is reported for ambient VOCs. For C_2 and C_3 bulk constituents the conversion to mole % requires division by 10,000. For C_2 to C_5 compounds with concentrations > 100ppmv in the well gas the analysis was considered to be semi-quantitative (as discussed in Section 5.3.6). The exact concentration of these bulk constituents is obtained from the molecular composition analysis (Appendix D.5).

The results for minor hydrocarbons, > C_5, are presented graphically in Figure 7.22. The detection limit for all compounds is 7.0ppbv (0.007ppmv) in the raw gas.

AGL Gloucester Wells

The well gases from the AGL Gloucester gas field showed non-methane hydrocarbons C_2 through to C_8 and aromatic compounds were detected for certain wells. The detection of aromatic compounds in the well gases correlated with those well gases with higher non-methane hydrocarbon concentration.

Well G1 showed low concentrations of C_2-C_4 hydrocarbons compared to the other wells and the larger hydrocarbons and aromatics were not detected. From the composition analysis (Appendix D.5, Table D.5.5.) this well was only 85% (by mole) methane, which would explain the low NMHC result.

Well G2 was significantly higher in C_2-C_4 hydrocarbons than Well G1 and a number of compounds in the range C_5-C_8 were detected. These presented as straight chain, branched or cyclic alkanes and benzene, toluene and xylenes. Very similar concentrations for the minor hydrocarbons were found for gas samples from Jul-15 and Sept-15 campaigns. This well was 90.3 and 93.9% methane, respectively. Concentrations of > C_5 minor alkanes from 28.3ppmv isopentane (average) down to 0.01ppmv for n-octane (Sep-15) were measured. Concentrations of aromatic compounds were; benzene (0.6 and 0.5ppmv), toluene (0.3 and 0.2ppmv) and m- + p-xylenes (0.03 and 0.01ppmv) for the Jul-15 and Sep-15 samples, respectively.

Well G3 (93.3% methane) was lower in non-methane alkanes overall, alkanes through to C_7 were measured, and toluene was the only aromatic detected at concentration 0.04ppmv.

AGL Camden Wells

Well C1 from the AGL Camden gas field showed hydrocarbons through to C_5 and two other as C_6 and C_7 cyclic alkanes at concentration 0.02 and 0.01ppmv respectively. Toluene was measured at trace level (0.009ppbv) and benzene and xylenes were not detected.

Well C2 was higher in NMHCs overall and a number of the minor alkanes through to C_7 were found. Toluene was found at concentration 0.09ppmv and benzene and xylenes were not detected in the gas from Well C2.

Ambient VOC Estimation

The impact of CSG well gas on the ambient air concentration of aromatic compounds can be estimated. Based on a worst-case scenario of high aromatic concentration in the well gas (0.5ppmv benzene) and high ambient methane in close proximity to a producing well (10ppmv), the emissions from a typical 95% methane gas would result in an ambient concentration of around 5pptv benzene (part per trillion by volume). By comparison, concentrations up to 1000pptv benzene are typically measured in semi-rural environments that are impacted by low volume on-road vehicle emissions.

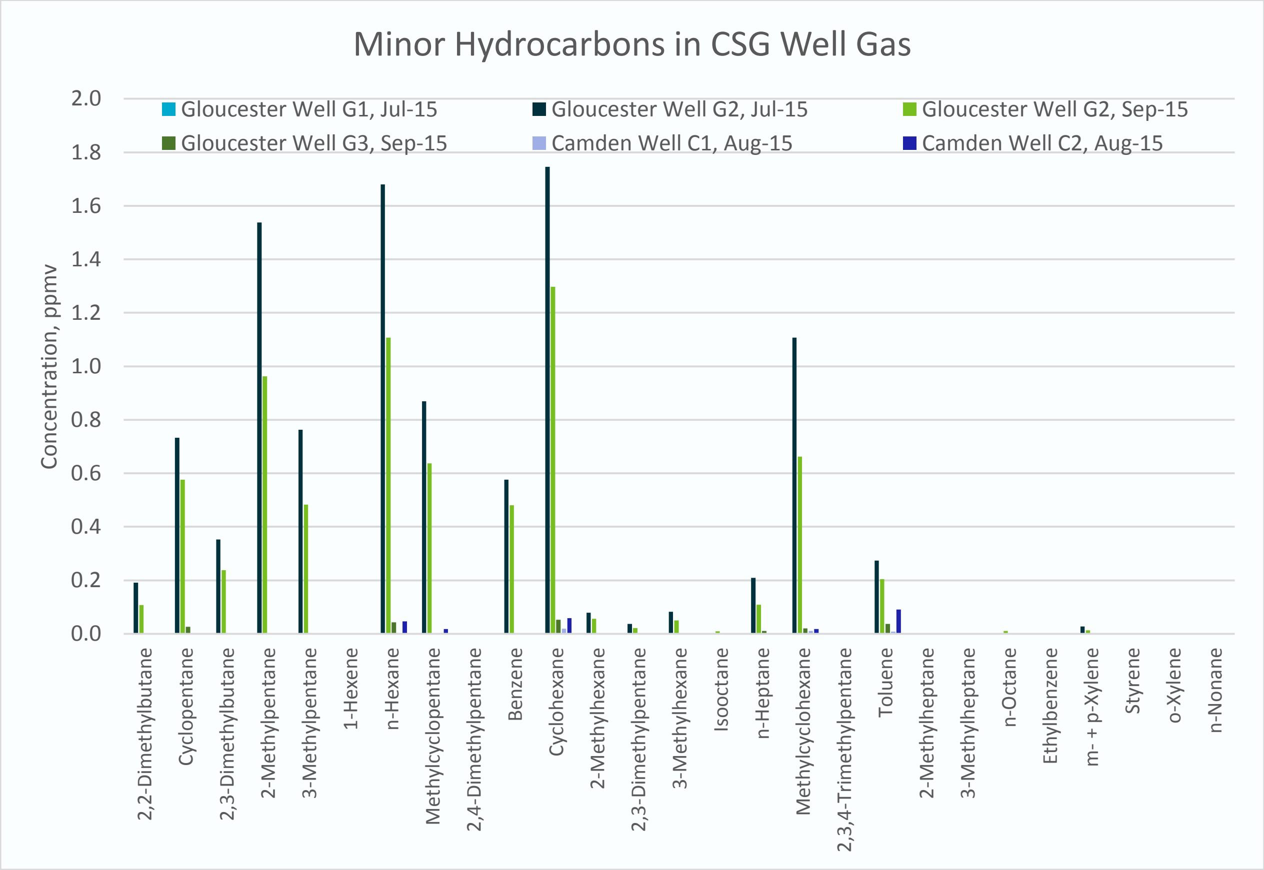

Figure 7.22. Hydrocarbon VOCs > C_5 measured in CSG well gases

7.10.2 SUMMARY OBSERVATIONS

The development of a method for analysis of minor hydrocarbon VOCs in well gases allowed the detection of non-methane hydrocarbon species through to C_8 which were found as straight-chain, branched and cyclic alkanes, and the aromatics; benzene, toluene and xylenes. The detection of aromatics compounds correlated with gases with higher non-methane alkane concentration. The highest aromatic content was measured in two samples of Well G2 gas from AGL operations at the Gloucester gas field (averaging 0.5ppmv benzene, 0.2ppmv toluene, 0.02ppmv xylenes).

The ambient air equivalent concentration for the aromatic compounds, based on a worst-case emissions scenario in close proximity to a producing well, would be low pptv (parts per trillion by volume). This compares favourably with low ppbv (parts per billion by volume) concentrations measured in the ambient air of semi-rural regions that are impacted by low-volume traffic.

Aromatic compounds in coal seam gas are not unexpected as these compounds are generated under thermogenic and/or microbial formation processes. Fragmentation of the basic coal structures during microbial decomposition will generate hydrocarbon intermediates including alkanes and related structures, benzene, toluene, ethylbenzene, xylenes and polycyclic aromatic hydrocarbons. These can undergo anaerobic oxidation and fermentation to form methanogenic substrates, which finally undergo methanogenesis to produce the methane dominant gas (Strapoc et al., 2011). As these compounds are found in coal formation waters it is likely that residual aromatic compounds will be found in the coal seam gas. The evaluation of the presence of aromatic compounds is also on the basis that BTEX compounds are no longer used as additives to hydraulic fracturing fluids used in certain gas extraction operations (NSW Trade and Investment, 2012).

8 Results – Isotopic Analyses

8.1 Source Gases

Samples of source gases were collected from a range of sites when this was practical (i.e. gas from CSG wells, sites that had gas collection facilities installed, or could be collected in chambers, for instance). At many of the sites, however, CH_4 emissions were diffuse and did not have facilities that allowed collection of concentrated source gas samples. Safe access to collect samples also placed some constraints on the ability to obtain samples at some sites. The results of the isotopic analyses of the source gas samples, and sample details, are tabulated in Appendix D (Tables D.1.1 → D.8.2). In certain sections and graphical plots, data from previous CSIRO research on fugitive emissions and from CSG basins outside of NSW, such as the Surat and Bowen basins are included to aid in the discussion.

8.1.1 CSG PRODUCTION GAS IN NSW

As part of the project, CH_4 and VOC emissions from CSG gas fields in NSW were identified for study. At the time the project was active, there were four CSG projects:

- Camden Gas Project (Sydney Basin, AGL Energy)
- Gloucester Gas Project (Gloucester Basin, AGL Energy)
- Narrabri Gas Project (Gunnedah Basin, Santos Limited)
- West Casino Gas Project (Clarence-Moreton Basin, Metgasco Limited)

In some cases, access to CSG sites was negotiated with operators early in the study; however in other cases issues related to safety and commercial confidentiality delayed well head gas sampling. All of the wells within the West Casino gas project had already been suspended or plugged and abandoned before this project had started and hence, gas samples were not available for bulk compositional or stable isotopic analyses. With respect to the Narrabri gas project, the final access agreement occurred after the end of the CSIRO study and hence CSG well head samples were not available at the time of writing.

The Camden samples were obtained from a number of production wells at various locations throughout the field and were geographically distributed over the Camden gas production area. Some consideration was given to operational issues in so much that only active gas producing wells were chosen for the study; there seemed little justification to analyse samples from inactive/plugged wells, which would have made well head gas sampling non-viable.

Sampling at Camden occurred before Gloucester since it was an established field with significant numbers of wells that were already in the production phase and had been so for many years. In contrast, at the start of the study, Gloucester had only four wells in development, with all of the gas produced being flared. The Gloucester well head gas samples were collected in late 2015 before the wells were suspended. On the last mobile survey for Gloucester, no further well head gas samples could be taken as the wells had already been shut in, awaiting a programme of agreed plugging and abandonment.

8.1.2 CSG MOLECULAR COMPOSITION

Thermogenic gas is produced when organic matter is deeply buried and consequently, the temperature of the buried strata rises. Therefore, increasing temperatures modify the organic matter due to various chemical reactions, such as cracking and hydrogen disproportionation in the kerogen (Hoefs, 2009). The gas generation potential of an organic-rich source rock (coal or shale) is a major factor in the formation of thermogenic gas and has an influence on the composition of the gas generated at different maturity levels (Tissot and Welte, 1984). Organic matter type and maturity are also important parameters in the formation of microbial gas, with lower rates of microbial gas production expected at higher maturity levels (Strapoc et al., 2011; Golding et al., 2013). These studies have shown that the relative proportions of microbial and thermogenic gas are depth related such that the deeper locations contain predominantly thermogenic gas, whereas shallower locations may contain a mixture of microbial and thermogenic CH_4 (Strapoc et al., 2011).

For producing CSG wells, the origin of the gas, which was mostly CH_4 with minor ethane and carbon dioxide at shallow depths (150 m to 600 m), was unknown in the early days, and occurred notwithstanding the rank of the coal (Golding et al., 2013). Carbon isotope studies that then followed indicated that much of the gas was biogenic, with microbial CH_4 generation linked to meteoric water ingress during uplift of the coal measures, and that methanogenesis is ongoing in shallow coal seams subject to meteoric recharge (Faiz and Hendry, 2006; Kinnon et al., 2010; Strapoc et al., 2011).

As source rocks, coal and shale share a similarity in that they are both a source and reservoir for the gases, notwithstanding the differing hydrocarbon generation potentials between them. For CSG, the main constituents are CH_4, ethane, CO_2 and nitrogen, with a general lack of ethane and higher hydrocarbon species in gases produced from shallow seams or more mature coal layers (Burruss and Laughrey, 2010; Faiz and Hendry, 2006).

The hydrocarbon composition of CSG can be quantified in a number of different ways such that it is important to define exactly what is meant by gas dryness or wetness (Golding et al., 2013). Most gas geochemical parameters revolve around the proportion of CH_4 to the heavier hydrocarbons, generally the lighter gas hydrocarbons up to the pentane isomers and various ratio calculations thereafter. Even though ethane to butane are gases at ambient conditions, common usage of gas dryness also includes the associated liquid hydrocarbons. Because gases from many CSG fields are relatively dry, the ratio of CH_4 to the sum of ethane and propane ($C_1/(C_2 + C_3)$) is widely used to distinguish between microbial and thermogenic gases (Strapoc et al., 2011; Whiticar, 1999). Ratios greater than 1,000 and less than 100 are considered to be definitive for microbial and thermogenic gas, respectively, especially when used in combination with CH_4 carbon isotope composition. In the specific case of wet gases commonly associated with oil, they tend to show $C_1/(C_2 + C_3) < 50$ (Golding et al., 2013; Bernard et al., 1978; Faiz and Hendry, 2006; Strapoc et al., 2011).

8.1.3 CSG PRODUCTION GAS FROM WELLHEADS

By plotting the carbon isotope number versus the gas hydrocarbon component, any trends in the gas hydrocarbons can be clearly observed (Figure 8.1).

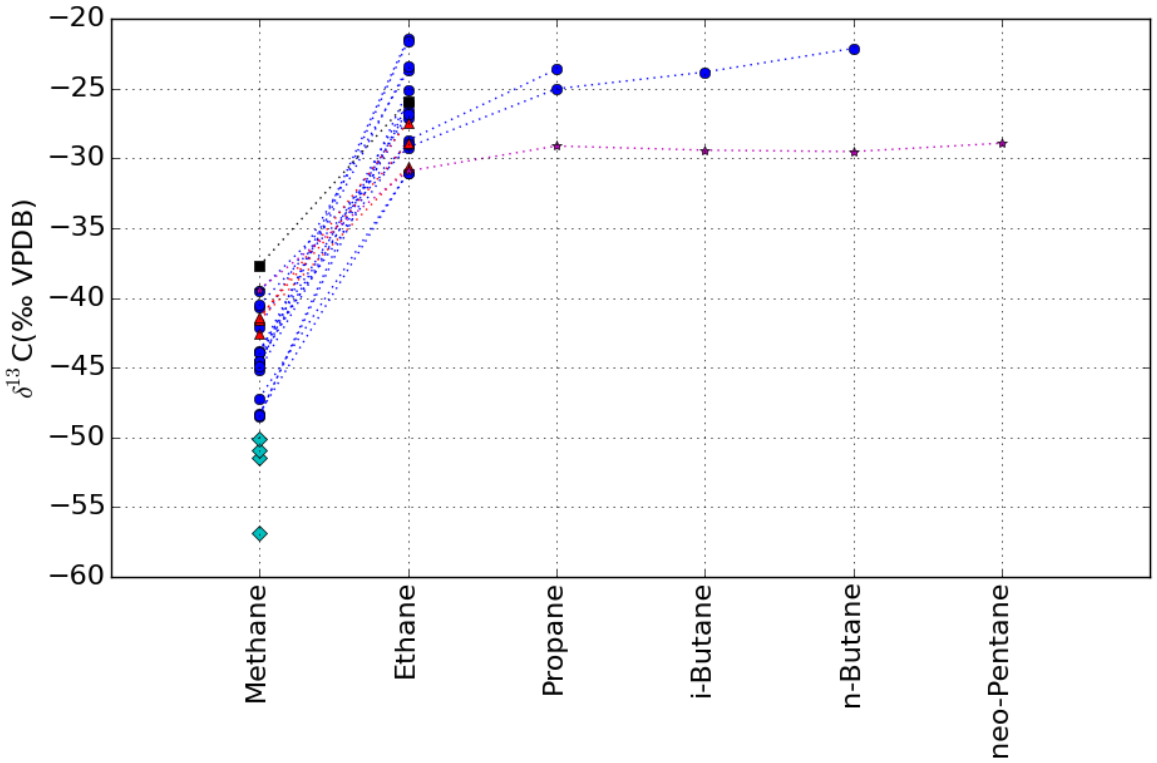

Figure 8.1. Plot of gas components versus its carbon isotopic signature. The dark blue circles represent Sydney Basin CSG samples, red triangles represents Gloucester Basin CSG, light blue diamonds represent Surat Basin, the black squares represent Bowen Basin and the red stars represent commercial NSW natural gas (Cooper Basin).

An examination of Figure 8.1 shows that most CSG samples are relatively ‘dry’ in that it is dominated mainly by methane and traces of ethane. A few rare samples do occasionally present with ‘wetter’ gas components (propane, *iso*-butane, *n*-butane). It is noted that the Camden and Gloucester CSG samples plot similarly with small differences, the Gloucester carbon isotope numbers are slightly more positive, reflecting a slight increasing percentage of more thermogenic gas which is to be expected when one considers the much deeper CSG well depths (~1 km deep) compared to the shallower Camden CSG coal layers (Balgownie and Bulli coal measures). These relatively ‘dry’ CSG samples contrast with the natural gas sample sampled from commercial sales gas in Sydney. The natural gas is largely derived from the Cooper Basin in SA and/or Bass Basin in Victoria; more ‘conventional’ oil and gas provinces. The interplay between depth and maturity differences is similarly highlighted by the Queensland samples from the shallower Surat Basin CSG (CH_4 with a significant biogenic overprint of-50 to -56 ‰ compared to the deeper Bowen basin CSG samples having both methane and ethane and a much more thermogenic signature at -37 ‰).

The carbon isotope plot in Figure 8.1 is also able to infer the bulk carbon isotope signature of the source material, the trend with carbon isotope numbers for the hydrocarbon gas components is that as the molecular weight increases, the carbon isotope numbers starts to reflect the bulk carbon isotope number of the coal or kerogen, a function of thermal maturity. Hence, by the time the gas components reach the butanes and pentanes, the number is indicative of the bulk carbon number. Hence, in the case of the one wetter Camden sample, the inferred bulk carbon isotope number of the parent coals is ~ -22 ‰, which is consistent with papers on Sydney Basin coal samples (Smith et al., 1982) run for bulk carbon isotope composition. The same trend holds true for the Cooper basin/Bass Basin sample, where the inferred bulk carbon isotope composition of the kerogen material that formed the majority of the gas in the deeper and more conventional oil and gas plays is ~ -29 ‰, also consistent with the literature (Boreham et al., 2001).

Figure 8.2 plots the carbon isotopic signature of CSG CH_4 versus the logarithm of the ratio of a gas dryness index (methane concentration/ ethane and propane concentrations). Also known as the Bernard diagram (modified after the Bernard et al., 1978), which compares the molecular ratio of $C_1/(C_2 + C_3)$ with ^{13}C CH_4 to distinguish between dry microbial and wet thermogenic gases. The shaded boundaries for the thermogenic gas field can vary and this largely reflects the effect of coal thermal maturity on the gas molecular and isotopic compositions.

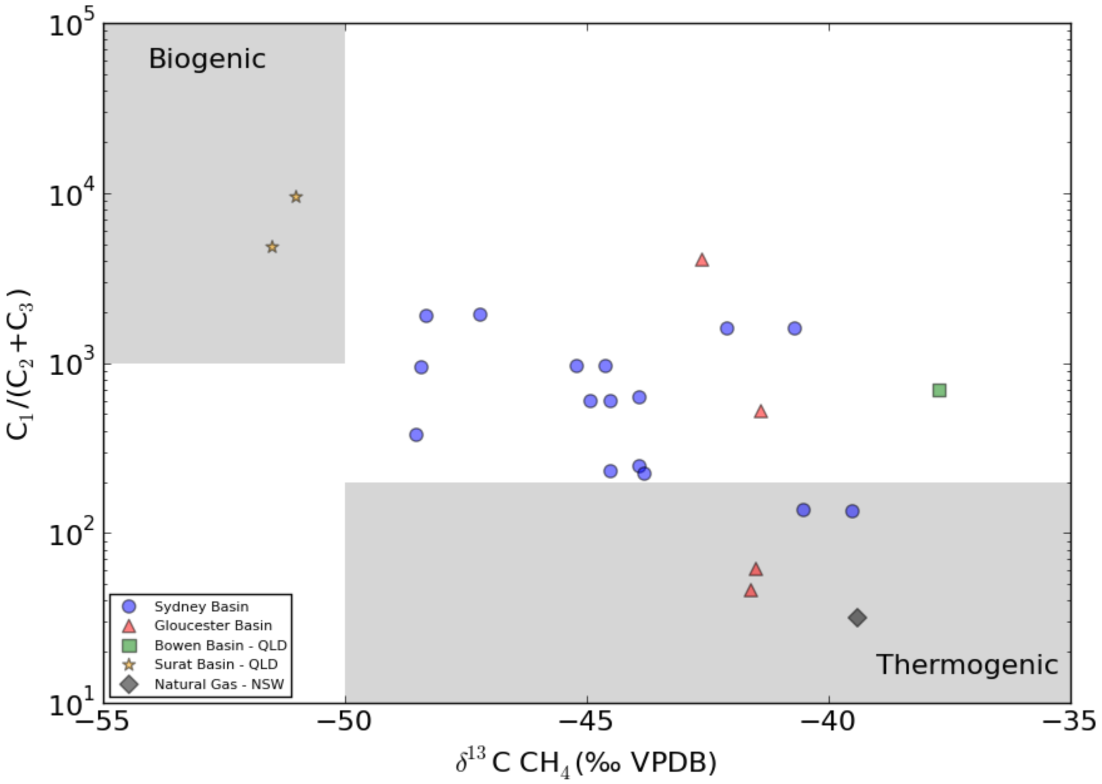

Figure 8.2. Plot of CSG methane carbon isotopic signature versus the log of a gas dryness index.

The CSG samples from Camden and Gloucester in NSW are contrasted with the Bowen and Surat CSG samples in Queensland and the natural gas sample representative of an almost pure thermogenic hydrocarbon gas. This gas dryness plot starts to extract the complex nature of CH_4 sources for CSG samples, an isotopic mixing line between biogenic gas and thermogenic end members (Golding et al., 2013, Faiz and Hendry, 2006). CSG samples usually have variable amounts of either end members mixing to give intermediate values. This is evident from Figure 8.2, where the Cooper Basin/Bass Strait sample is almost purely thermogenic and hence plots in the lowest quadrant of the classically derived thermogenic area for CH_4 gas. The Surat basin samples plot at the other end in the biogenic quadrant, which is consistent with the present day production gas, derived from the Walloon coal measures in the shallower Surat Basin. The deeper buried Bowen basin sample reflects the intermediate mixed zone of values between thermogenic and biogenic inputs into its total composition. The same is also true for the Sydney and Gloucester Basin samples, noting that a few of the probably deeper and more thermally mature coals have a stronger thermogenic signature. This spread of data reflects the real reality of CSG production gas from any particular CSG field, it is strongly influenced by local geological, stratigraphic and permeability factors that can change vastly for only several hundred metres lateral placement between adjacent wells.

In examining the biogenic source inputs to CSG gas and other geological samples, the biogenic production of CH_4 and its coupled CO_2 (microbial and archaeal anaerobic respiration products) can be further elucidated into two main biosynthetic pathways; CO_2 reduction to form CH_4 or acetoclastic and methylotropic fermentation of organics to form CH_4. A plot of ^{13}C CO_2 versus ^{13}C CH_4 values shows the carbon isotope fractionation lines for the various methanogenic pathways, where $\alpha CO_2\text{-}CH_4 = (1000 + \delta^{13}C\ CO_2) / (1000 + \delta^{13}C\ CH_4)$. Microbial gases from subsurface settings tend to have a similar carbon isotope fractionation between CH_4 and CO_2 even when the methane and carbon dioxide $\delta^{13}C$ values shift in response to progressive depletion of the substrate (Whiticar, 1999; Schlegel et al., 2011). Figure 8.3 has three alpha fractionation lines drawn in dotted lines. The red dotted line is α = 1.09, the black dotted line is α = 1.06 and the blue dotted line represents α = 1.03. Plotted values that fall between α = 1.09 and α = 1.06 represent the region mainly dominated by CO_2 reduction. Values that fall between α = 1.06 and α = 1.03 represent acetate and methyl fermentation.

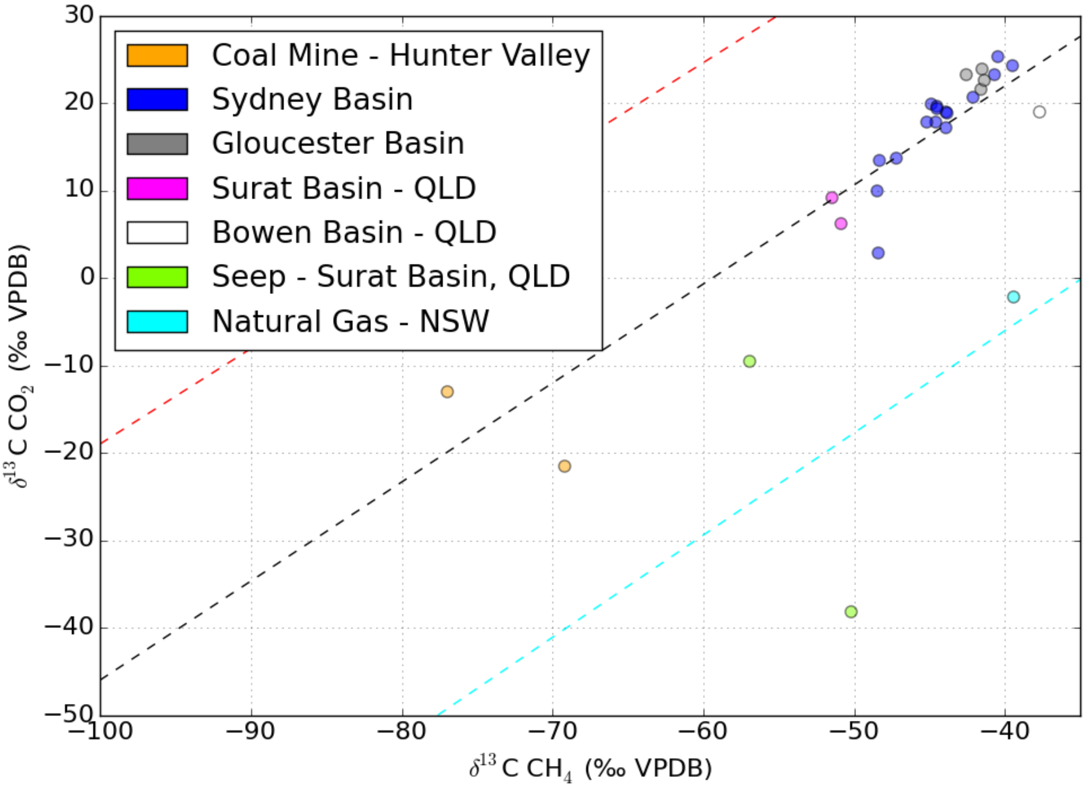

Figure 8.3. Plot of CSG and coal mine methane carbon isotopic signature versus the carbon dioxide isotopic signature.

Plotting the carbon isotope signatures of CH_4 versus CO_2 shows an interesting spread of data points. The Cooper/Bass Strait natural gas plots close to the lower edge of acetate and methyl fermentation inputs reflecting its strong organic (thermogenic source) signature. The two Surat Basin gas seeps from abandoned coal exploration holes plot in the same region and below it, demonstrating their more complex source nature. The fact that they are uncased results in gas inputs from not only the targeted coal formation layers but also any other gas prone geological units such as sandstones, shale layers and more shallow groundwater inputs, hence caution is applied to the varying results obtained. The vast majority of the Camden and Gloucester CSG samples display biogenic inputs from CO_2 reduction profiles consistent with (Li et al., 2008); although there are also samples that show a more organic rich (acetate and methyl fermentation signature) and seem to straddle the α = 1.06 demarcation line.

The two Hunter Valley coal mine samples are gas desorption samples obtained from coal chips collected at the mines and placing them into a desorption canister. Due to safety issues, freshly mined coal chips could not be accessed for immediate placement into the canisters, hence the results obtained have an undetermined prior degassing time before emplacement into the canister. It is well documented that the isotopic and molecular composition of coal desorption gas varies with time since being drilled or quarried (Strapoc et al., 2006). The apparent biogenic nature of the Hunter Valley coal mine desorption samples probably reflects the variable amounts of out-gassing and isotopic fractionation prior to canister emplacement. This plot helps to demonstrate that even biogenic inputs to the bulk gas have varying geological and microbiological controls with complex patterns of distribution.

8.1.4 MICROBIAL GAS SAMPLES

Using the same plotting variables (^{13}C CO_2 vs ^{13}C CH_4) samples of biogas were also analysed with the results shown in Figure 8.4. This time, the scatter of the plotted samples is more pronounced, reflecting the much more varied substrates that anaerobic methanogens can utilise to form CH_4 and CO_2 gas. Most samples plot between α = 1.06 and α = 1.03 representing acetate and methyl fermentation as the dominant methane pathway. It is interesting that the Sydney and Newcastle landfill samples plot above the α = 1.06 line in the CO_2 reduction zone. While the landfill derived methane is almost exclusively derived through acetoclastic and methylotrophic reaction pathways, the enriched CO_2 values must have a secondary pathway operating in tandem to push the carbon isotopic signature from depleted values to more enriched values. A landfill is quite a unique environment due to multiple redox zones in different stages producing quite variable amounts of gas. Fresher landfill material that has just been buried will initially have a more oxic profile as evident by significant oxygen and nitrogen gas being present in the landfill drainage gas. As organic decomposition proceeds, the oxygen is rapidly consumed and more anaerobic zones start to develop. With compaction and time, the older and hence deeper samples will have leachate layers develop, producing water saturated layers and strictly anaerobic zones (prime habitat for methanogenesis).

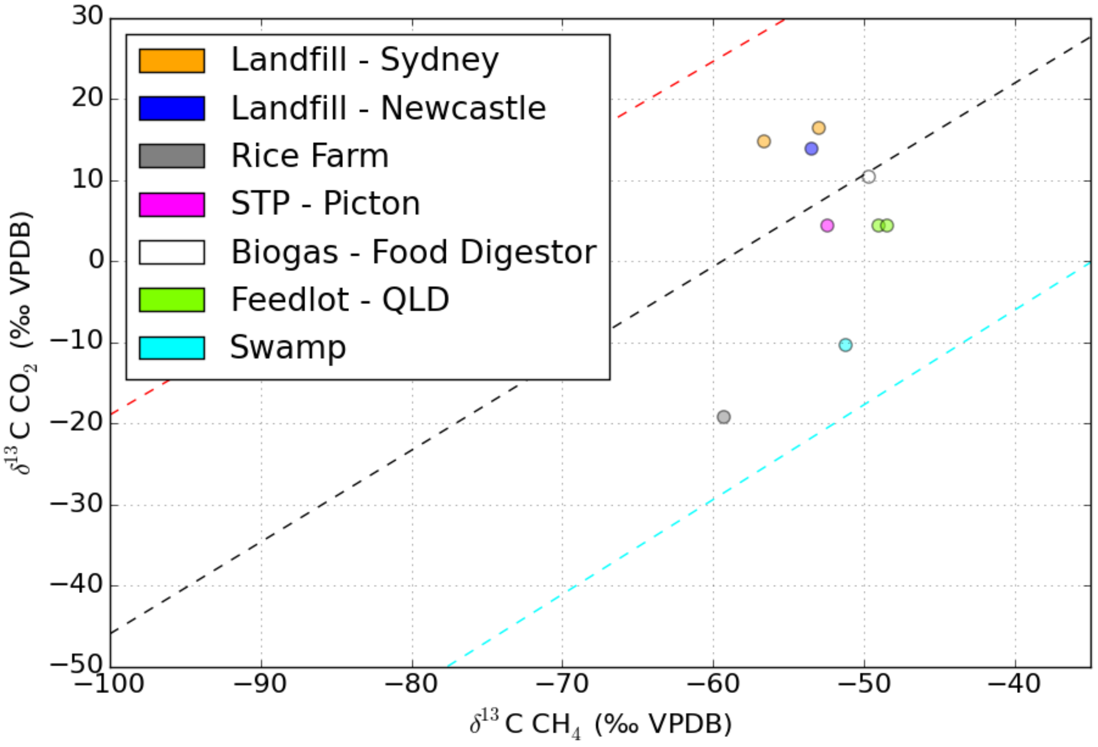

Figure 8.4. Plot of biogas derived CH_4 carbon isotopic signature versus the CO_2 isotopic signature.

In this stratified structure within multiple cells of a modern landfill, gases could easily be affected by in-landfill biodegradation, resulting in isotopically heavy carbon dioxide gas. This model is analogous to that seen in a small percentage of cases of conventional oil and gas reservoirs that do suffer biodegradation because of erosive uplift and faulting that can introduce meteoritic water and microorganisms that then start to preferentially consume the $^{12}CO_2$ leaving an enriched ^{13}C rich CO_2 gas cap. Shallow reservoir depths of < 1,500 m are a common characteristic of biodegraded gases as these reservoirs are generally at low temperatures (< 80°C) and have ready access to aquifer flow (Pallasser, 2000).

With reference to Figure 8.4, samples of biogas from food digesters, wastewater treatment plants, rice farms and feedlot samples from Queensland all plotted in the predicted acetoclastic and methylotrophic zone between α = 1.06 and α = 1.03 fractionation lines. Although the NSW feedlot sample had sampling difficulties due to insufficient gas generation from the manure lake, the corresponding Queensland sample (collected over several weeks) is analogous and the methane gas geochemical data is consistent with published data from other countries such as the United States of America (Monteil et al., 2011).

8.1.5 COMPARISON OF CSG PRODUCTION GAS AND MICROBIAL GASES

Figure 8.5 is a plot of the carbon isotopic signature of the CO_2 derived from various sources against its molecular composition. Carbon dioxide carbon isotope values above -3 ‰ to positive values are classified as having a biogenic nature or carbonate influence. Gases affected by in-reservoir biodegradation can also result in isotopically heavy CO_2 gas. Values in between -3 to -10 ‰ are generally designated as having an inorganic igneous and/or mantle origin. The remaining region below -10 ‰ are classified as being more organic in nature (thermogenic).

This plot demonstrates more clearly the conventional source definitions (described below) for different geological and biogas samples. This delineation is due in part to the strong effect on the carbon isotopic signature of the residual CO_2 left after anaerobic microbial processes have been allowed to proceed. In the case of CO_2 reduction, methanogens preferentially utilise ^{12}C CO_2 to form depleted CH_4 (larger negative numbers) and as a result the residual CO_2 fraction becomes more enriched in the less abundant ^{13}C CO_2 and hence results in more enriched delta values (positive values) for the CO_2 fraction. In contrast, the more organic derived CO_2 (acetoclastic and methylotrophic processing) results in using carbon from an organic source material that is already naturally depleted in the rarer ^{13}C isotopomers, hence the more negative carbon isotopic signatures.

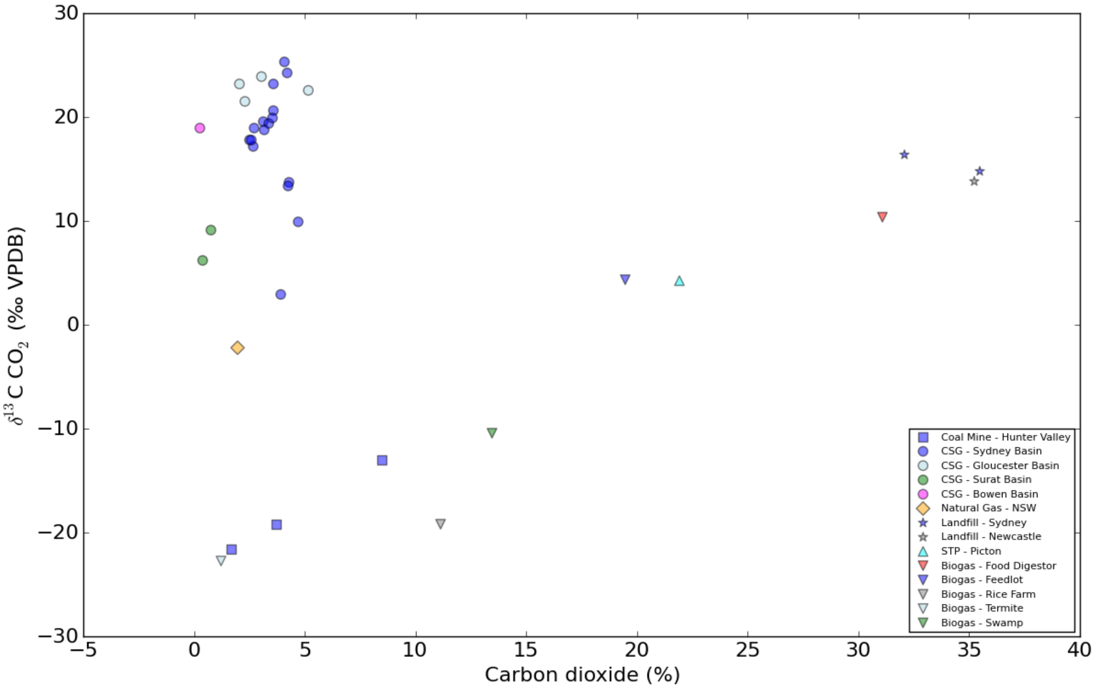

Figure 8.5. Plot of CSG, coal mine and biogas samples of CO_2 isotopic signature versus the CO_2 molecular composition.

The spread of samples displays patterns of clustering along some broad themes. In the top far right quadrant, the majority of the biogas samples can be found. The biogas samples include the Sydney and Newcastle landfills, the Sydney food waste digestor and the Picton wastewater treatment plant and are usually associated with substantial CO_2 levels. In the top left quadrant, the Sydney, Gloucester and Surat Basin CSG samples are all found with CO_2 levels generally below 10 %. The Gloucester, Sydney and Surat Basin CSG samples show a distinct preponderance for very enriched CO_2 gas and has been similarly linked to CO_2 reduction pathways (Golding et al., 2013). The other biogas samples clustered in the top right quadrant are all associated with acetoclastic and methylotropic pathways to produce CH_4. The natural gas sample, the Queensland feedlot and a portion of the gas seeps from Queensland are nestled within the inorganic region of contribution. The inorganic source of the CO_2 in the Cooper Basin natural gas is consistent with the very deep wells in the Cooper-Eromanga basins with significant bottom hole temperatures and igneous and/or mantle derived CO_2 inputs (Boreham et al., 2001).

The interesting anomaly is the Queensland feedlot biogas. This sample gas was collected using long duration bubble traps fixed to staked out poles within a manure pond. This may have allowed sufficient inorganic carbonate contribution over weeks to months of gas collection to overprint what should be strictly acetoclastic and methylotrophic fingerprinting that is characteristic of fermentation of organic materials (in the biogenic zone or above the inorganic CO_2 zone in Figure 8.5). Below the inorganic CO_2 zone in Figure 8.5, the Hunter Valley coal mine samples, the Bowen CSG and the rest of the Queensland gas seeps are found within the more organic (thermogenic) zone of contribution.

8.1.6 ISOTOPIC CH_4 CORRELATIONS FOR CSG AND MICROBIAL GASES

The carbon and hydrogen isotopic compositions of CH_4 and associated gases in combination with molecular composition are used to establish gas origin, particularly the relative role of thermal and microbial processes (Golding et al., 2013). Schoell (1980) showed that the different types of CH_4 have characteristic carbon and hydrogen isotope compositions, which also varied with source rock type and maturity in the case of thermogenic CH_4. Whiticar et al. (1986) extended this work to include the effect of CH_4 generation pathway on the molecular and isotopic compositions of microbial gases.

Primary thermogenic gases have CH_4 carbon isotope compositions greater than -50 ‰ and commonly fall on parallel trends that extrapolate to the isotope composition of the source material on a Schoell style plot of CH_4 δ^2H versus $\delta^{13}C$ (Golding et al., 2013). Microbial gases typically have CH_4 carbon isotope compositions less than -50 ‰ for acetoclastic/methylotrophic utilisation and less than -60 ‰ for the CO_2 reduction pathway. Mixing between microbial and thermogenic gases may produce intermediate CH_4 carbon isotope compositions between -50 and -60 ‰ that could also reflect secondary processes like water stripping or cracking of bitumen and liquid hydrocarbons (Faiz and Hendry, 2006). Another process that can also produce intermediate values is substrate depletion in a partially closed system (Whiticar, 1999).

The results of the analyses performed in this study along with a range of samples analysed in this laboratory previously are presented in Figure 8.6, where the hydrogen and carbon isotopic CH_4 compositions are plotted on a Schoell style plot. Figure 8.6 shows that the samples generally fit into clusters that are indicative of the CH_4 generation pathway. The Cooper Basin natural gas and the Bowen CSG Basin samples cluster in the thermogenic zone. Similarly, the Sydney Basin CSG samples are in the thermogenic zone but on the periphery, close to the mixing zone with the two primary microbial gas pathways (CO_2 reduction and acetoclastic/methylotrophic utilisation). The Gloucester Basin CSG samples are close to the Sydney Basin CSG but are in the mixing zone between the three main zones indicated in Figure 8.6.

All the microbial samples (i.e. the landfill composite samples, the wetland sample, the anaerobic food digester facility and the feedlot samples) consistently plotted within the acetoclastic/methylotrophic zone. Within the CO_2 reduction zone, the Surat Basin CSG and Surat Basin seeps plot toward the periphery of the mixing zone. The Hunter Valley coal mine desorption samples from coal chips collected at the surface are most probably subject to initial desorption gas loss and fractionation prior to canister emplacement.

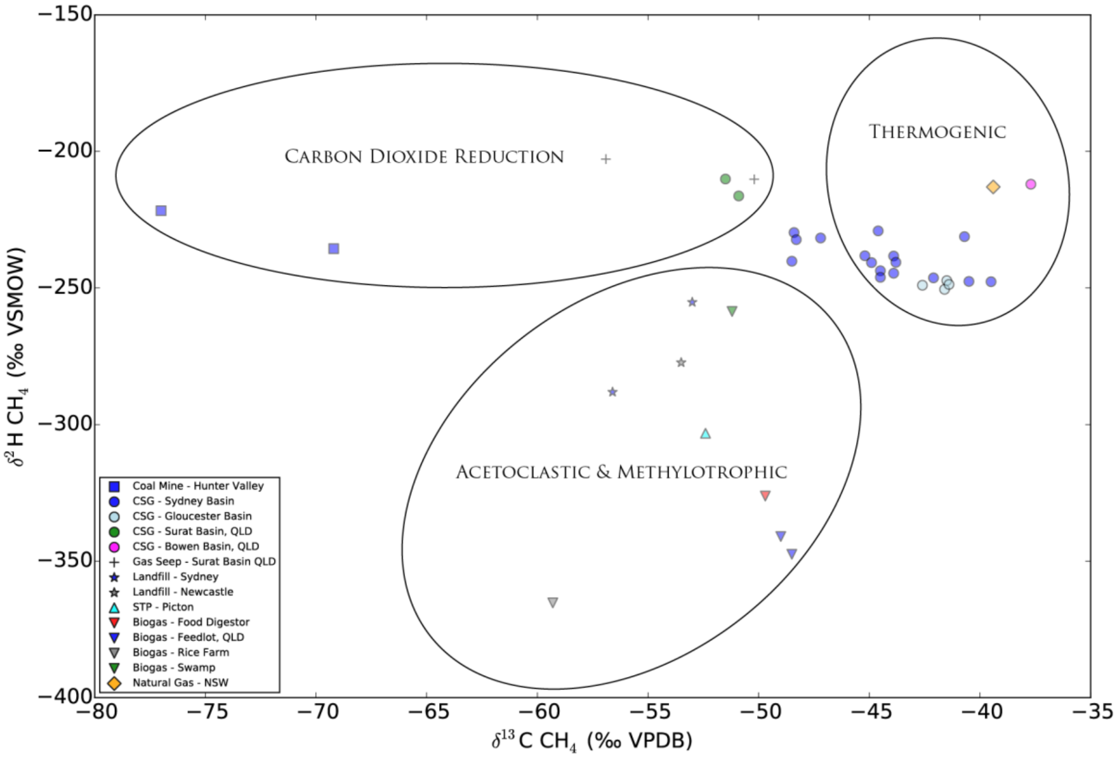

Figure 8.6. Plot of CSG, coal mine and microbial gas samples of CH_4 hydrogen isotopic composition as a function of CH_4 carbon isotopic composition.

8.1.7 SUMMARY OBSERVATIONS FOR SOURCE GASES

Although the gas sample set available for analysis was limited due to constraints mentioned previously, there is enough variation across the range of source gases measured to show how molecular and stable isotopic data can be used to group and classify CH_4 emissions. This is especially true for CSG samples that look similar based on molecular compositional data alone, but with the stable isotopic signatures, specifically the δ^2H and δ^{13}C isotopic ratios, the various CH_4 sources start to show distinct source attributes.

Although the possibility exists to use other isotope systems (i.e. N_2, H_2S, He, Ar) to provide additional information, there may be practical considerations that limit their widespread utilisation. For nitrogen species, contamination by air which contains ~78 % N_2 is a severe limitation and renders N_2 isotope analysis ineffective unless specialised sampling is undertaken. For hydrogen sulphide, the levels are usually at the trace level (ppb to ppm range) and suffers from rapid chemical reactivity with most container storage walls. Helium and argon are chemically stable, however, are usually at very low levels in sources gases and in the case of argon can be affected by atmospheric contamination (which is present in air at approximately 0.9 % by volume).

For the majority of the source gases analysed, it was identified that microbial sources such as landfill gas, food digester gas, feedlot manure pond gas, wetland gas and wastewater treatment gas are generally constrained by acetoclastic and methylotrophic utilisation pathways.

The Sydney Basin and Gloucester Basin CSG samples plotted as either mixed gases i.e. CH_4 source contributions from CO_2 reduction and thermogenic pathways. Other Basins outside of NSW such as the Cooper Basin in SA (natural gas) and the Bowen CSG basin in QLD, plotted with thermogenic source characteristics. The Surat Basin CSG and Surat Basin gas seeps also consistently had strong inputs utilising biogenic CO_2 reduction pathways.

Sampling methods are particularly important to ensure that isotopic analyses accurately reflect to true composition of the bulk gas. In particular, fractionation of the isotopes may occur within the sample if the sampling method is poorly executed. Fractionation can occur easily and results from leaks, diffusion of gases through organic materials, and sampling problems such as: insufficient flushing of sample containers, sampling gas below atmospheric pressure, and not allowing sufficient time to allow the gas source and sample container to reach isotopic equilibration. All these must be meticulously managed to ensure a representative sample is obtained (Eby et al., 2015).

8.2 Ambient Samples

Samples of ambient air, with a range of normal background to elevated CH_4 concentrations, were collected at most of the sites. The CO_2 $^{13}C/^{12}C$ isotopic ratios in these samples were analysed by GC-IRMS. It was also intended to analyse the carbon and isotope ratios of CH_4 in these samples but this required cryogenic pre-concentration of the sample before introduction to the isotope mass spectrometer. However, due to ongoing problems associated with the cryogenic concentrator system, analysis of ambient CH_4 for $\delta^{13}C$ and $\delta^{2}H$ analysis was not achieved. An alternative method based on cavity ringdown spectroscopy was investigated for ambient samples and is described in Section 8.3. Details of the prototype pre-concentrator system constructed for ambient air samples and procedures are discussed below.

8.2.1 CRYOGENIC CONCENTRATOR FOR AIR

The GC-IRMS system used for the isotope analyses conducted during this study requires a sample with an analyte concentration of at least 400 ppm to allow accurate quantitation. However, normal concentrations of CH_4 in ambient air are usually below about 2 ppm. Hence, to analyse atmospheric CH_4, a prototype cryogenic trap module was built to condense CH_4, which could then be presented to the GC-IRMS instrument with sufficient signal to noise ratio to allow normal analysis. Figure 8.7 is a schematic diagram of the prototype and Figure 8.8 shows the cryogenic trap module installed onto the front end of the GC-IRMS during trial runs.

The trap module was modified extensively throughout the study to improve its performance but despite these changes, the system proved to be unsuited to quantitative analyses of isotopic ratios. One of the problems encountered was that trace quantities of impurities in carrier gas collected in the cryogenic trap during the collection period which resulted in unacceptably high blanks for accurate analytical work. This was mitigated by more than a factor of 10 by installing a special hot metal getter helium purifier that increased the purity of 5.0 grade helium (99.999 %) to about ~7.0 grade (99.99999 %), although the blanks were still significant.

It was also found during testing that cryogenic concentration of CH_4 from air concomitantly trapped significant amounts of nitrogen and oxygen that eluted immediately before CH_4 and tailed into the CH_4 peak of the chromatogram, hence introducing variable amounts of interference. The variable N_2 peak tailing meant that it was not possible to achieve acceptable replicates of the same air sample. Post analysis of the design determined that a more complicated arrangement involving a second cryotrap with variable temperature control may reduce oxygen and nitrogen carry over to acceptable levels. This is an ongoing area of development.

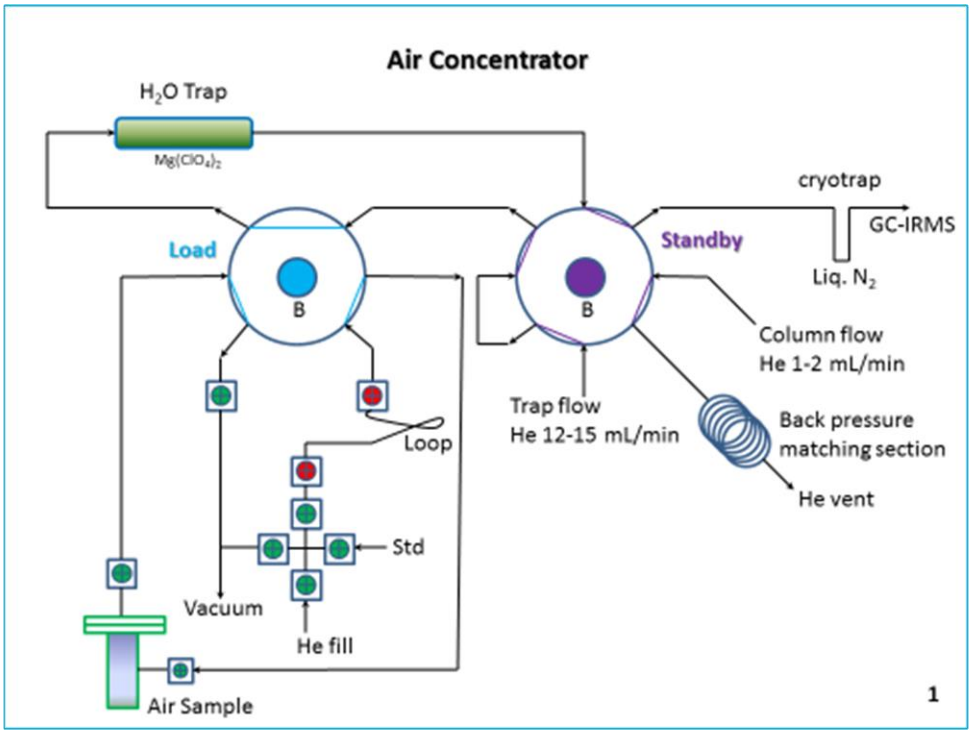

Figure 8.7. Schematic of prototype cryogenic trap module

Figure 8.8. Photograph of the prototype cryogenic trap module

Figures 8.9 and 8.10 are screen capture shots of the GC-IRMS runs during testing and the results obtained.

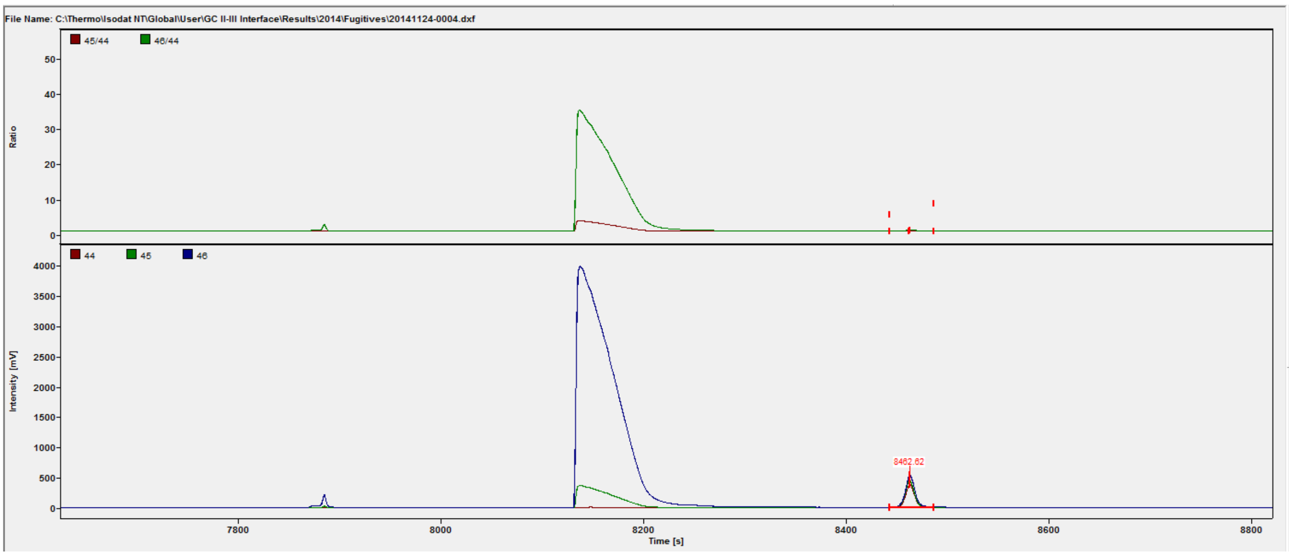

Figure 8.9. Screen capture of large air peak proceeding smaller CH_4 peak from cryogenic trap

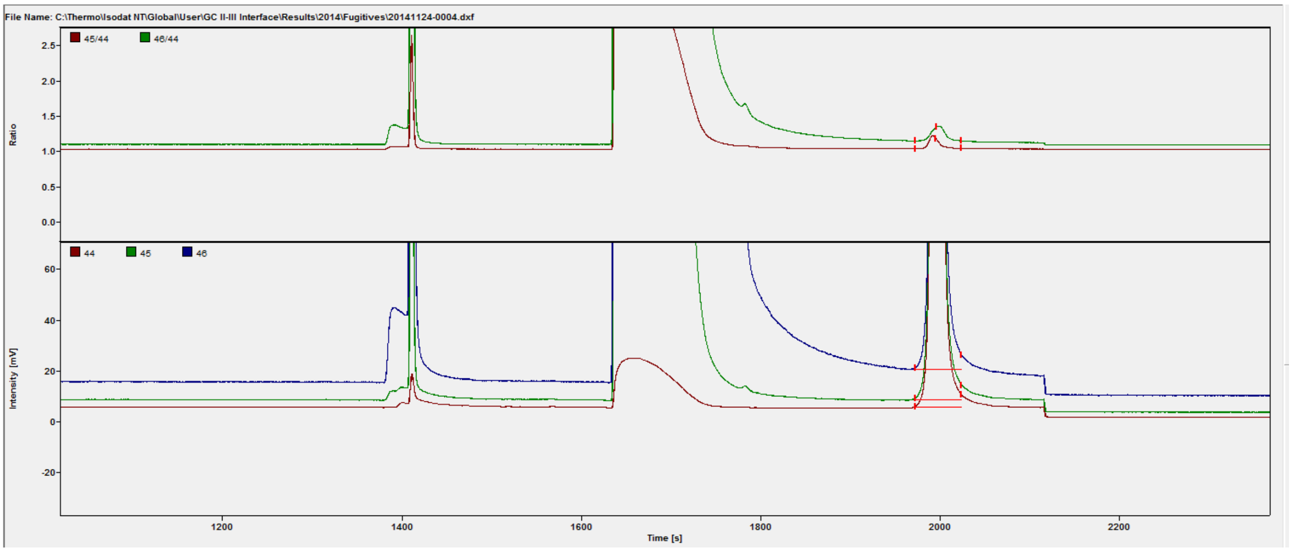

Figure 8.10. Screen capture of large air peak proceeding smaller CH_4 peak from cryogenic trap, expansion of baseline to show significant tailing into the start of the CH_4 peak that follows.

8.2.2 CARBON ISOTOPE ANALYSIS OF AMBIENT CO_2

With method development, it was found that a large volume injection of air onto the GC-IRMS could inject just enough of the ~400 ppm CO_2 in air sample to give a reproducible carbon isotope signal for analyses. The air canisters that had 1 atmosphere of air pressure were filled with 35 kPa of UHP helium to allow positive pressure to exist in the sample canister for subsequent aliquots without causing a vacuum in the stainless steel canisters upon repeated sample aliquot withdrawals, hence avoiding fractionation of the sample.

All the samples were analysed for bulk composition and carbon isotopes on atmospheric CO_2. Figure 8.11 is a plot of all the data acquired, including the 4 sets of 10 canisters taken around Camden during the four seasons. All the NSW EPA atmospheric samples were analysed by bulk composition and all but one were found to contain ~400 ppm (0.040 %) CO_2 in air. In addition to the NSW EPA samples, extra samples in air canisters taken in Queensland around slightly elevated methane seeps in the Surat basin were also plotted for comparison. One air sample taken on a farm just outside of Perth was also included in the plot.

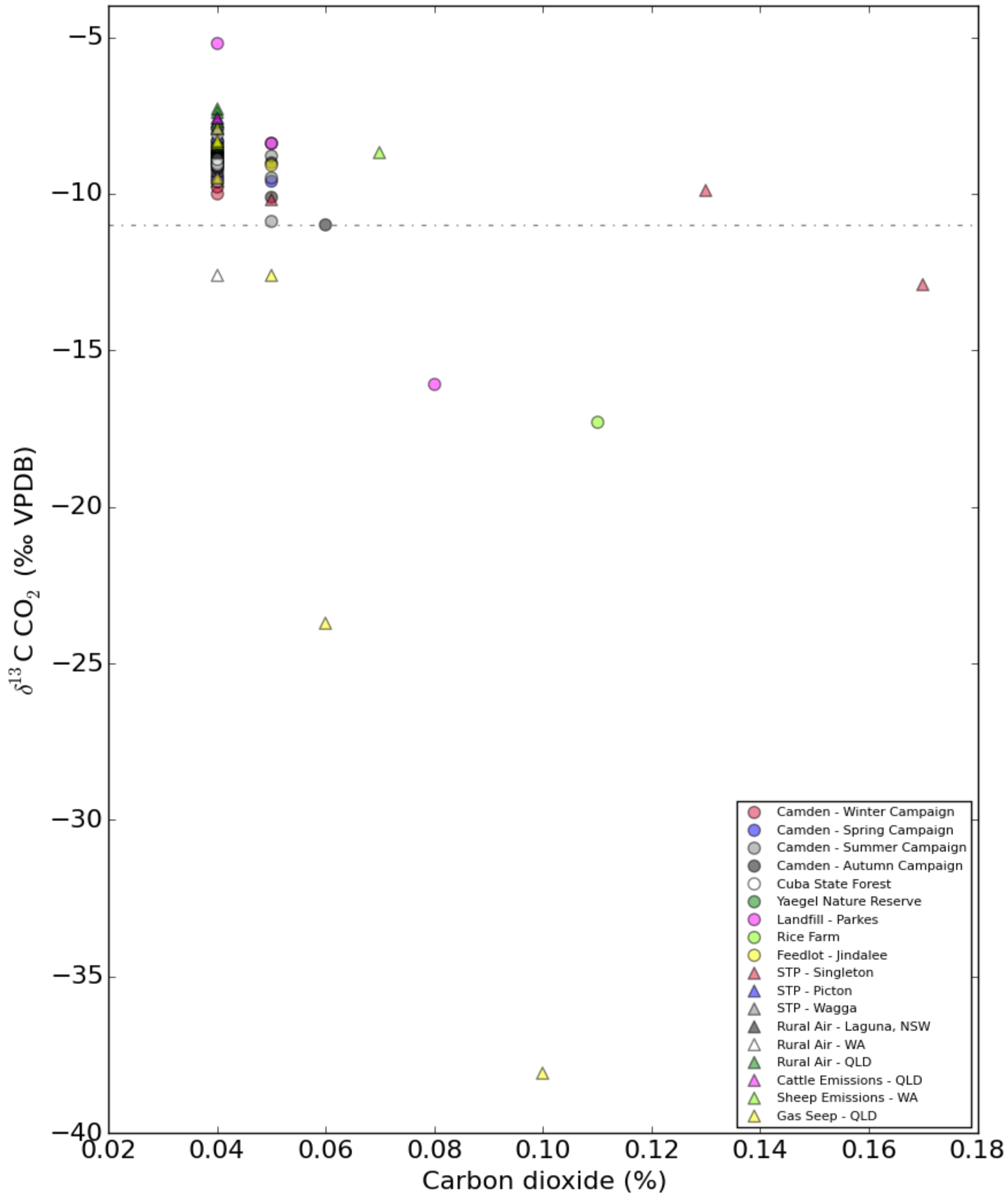

Figure 8.11. Plot of carbon isotopes of CO_2 in air versus the CO_2 concentration in air

From Figure 8.11, only one Camden air sample had a slightly elevated reading of 0.05 %, all the rest were at normal levels of 0.04 %. The CO_2 samples at 0.04 % all clustered between -7 to -10 ‰ which is indicative of clean air. One Camden air sample plotted slightly higher at 0.05 % and had an isotope value of -10.2 ‰. There is one data point for farm air taken just outside Perth, WA that has normal compositional levels of CO_2 but has a carbon isotope value of -12.6 ‰, indicative of CO_2 with a more organic derived source. The rest of the samples at 0.05 % and one at 0.06 % all came from Surat Basin seeps. The lowest isotope values at 0.05 and 0.06 % straddle the cut-off line at -11 ‰, i.e. heading to a more organic CO_2 source contribution, consistent with the thought that the seeps are CSG derived.

8.2.3 SUMMARY OBSERVATIONS FOR AMBIENT SAMPLES

It is currently not possible to directly determine carbon and hydrogen isotopes in ambient CH_4 on our GC-IRMS due to the low sample concentrations. Accordingly, we constructed a prototype cryogenic system designed to provide concentrated samples suitable for GC-IRMS analyses. However, the pre-concentrator also trapped large amounts of nitrogen and oxygen that co-eluted with the CH_4 during the analyses which prevent quantification. The system also tended to trap contaminants in carrier gas that resulted in unacceptably blanks. A development of the pre-concentrator using a second cryogenic trap to reduce these effects is currently under consideration.

Due to the higher concentration of CO_2 compared to CH_4, ambient air samples collected during the project were successfully analysed for bulk composition and for $\delta^{13}C$ CO_2. All of the NSW samples plotted in the normal zone for clean air samples with no significant overprinting of isotopic signatures observed for CO_2.

8.3 Isotope Analysis by Cavity Ringdown Spectroscopy

Owing to the difficulties encountered in analysing $\delta^{13}C$-CH_4 at ambient concentrations as described in Section 8.2, we trialled an alternative approach using two cavity ringdown spectrometers. The first of these instruments was a Picarro model G2201-i analyser, which reports carbon isotope ratios for CO_2 and CH_4. This instrument can operate in three modes: CO_2-isotope only mode, CH_4-isotope only mode and combined mode. Within the CH_4-isotope only operational mode there are two further modes depending on methane concentration ranges, a high dynamic range mode for concentrations between 1.8 and 1000 ppm, and a high precision mode for methane concentrations between 1.8 and 12 ppm. For this project, the instrument was operated in the CH_4-isotope only, high precision mode. Under these conditions, the instrument has a reported precision of 5 ppb ± 0.05% for $^{12}CH_4$ and 1 ppb ± 0.05% for $^{13}CH_4$. The $\delta^{13}C$-CH_4 precision over a one hour window using 5 minute averages is <0.4 ‰, and the maximum reported drift over 24 hours using a 1-hour average interval measurement is <1.5‰ at 10 ppm CH_4. The instrument reports a new measurement approximately once every 3 seconds.

The second instrument was a Picarro G2132-i analyser, which reports carbon isotope ratios for CH_4 only. This instrument was used after a failure during the project of the first instrument. Its specifications are similar to the G2201-i analyser described above when it is operating the CH_4-isotope only mode. The $\delta^{13}C$-CH_4 precision over a one hour window using 5 minute averages is <0.8 ‰ at 1.8 ppm, and <0.5 ‰ using 15 minute averages at 1.8 ppm. The maximum reported drift over 24 hours using a 1-hour average interval measurement is <1.5‰ at 10 ppm CH_4, and <2‰ at 1.8 ppm CH_4. The instrument reports a new measurement approximately once every 2 seconds. This instrument was sourced from AGL.

The spectrometers work similarly to the Picarro used for ambient monitoring (Section 5.2.1), but differ in that they analyse for $^{12}CH_4$ and $^{13}CH_4$ separately rather than just a peak for the $^{12}CH_4$ isotopologue. These results ultimately determine the $\delta^{13}C$ value once other background interferences from water and carbon dioxide are accounted for. They are prone to possible interferences from other non-measured species, such as ethane and other alkanes, nitrous oxide and ammonia.

The $^{13}CH_4$ concentration in ambient air is quite low, typically around 18-19 ppbv, compared with 1700-1800 ppbv for $^{12}CH_4$. Small changes in the measured $^{13}CH_4$ concentration will have a large impact on $\delta^{13}C$-CH_4. For example, a change on 0.1 ppbv in the ^{13}C response relative to a constant ^{12}C response will manifest as a 5 ‰ change in $\delta^{13}C$ for ambient CH_4 concentrations. The instrument noise at ambient levels for $^{13}CH_4$ on the Picarro G2201-i is around 0.3 ppbv, which when factored in with other instrumental uncertainties ($^{12}CH_4$, interferences from H_2O and CO_2) leads to high noise for $\delta^{13}C$-CH_4 of ±10‰ at ambient concentrations. The same noise in the 'raw' data was observed for the G2132-i instrument.

8.3.1 CALIBRATION

Calibration of the G2201-i instrument was performed by CSIRO Oceans and Atmosphere laboratories at Canberra. The instrument was calibrated against two known methane samples with different $\delta^{13}C$ values, each at 3 different concentration values (equivalent to 2, 4 and 10 ppm). The G2132-i instrument was not calibrated for isotope values, rather the calibration performed by the instrument manufacturer at date of shipping was relied on.

In order to calibrate isotope CRDS instruments, standards of methane with known $\delta^{13}C$ values need to be run at different concentrations. Pure standards of methane, which are more easily quantifiable, cannot be used as the operational range of the instrument is up to 1000 ppm only using the high range modes, and up to 12 ppm using the high precision range modes used in this study. As the instruments were being used to analyse ambient samples lower than 12 ppm, the high precision range modes were used for these analyses to minimise the instrumental error for methane. Using mass flow controllers to generate lower concentrations of methane from a higher concentration standard fractionates the isotopologues in the samples, leading to possibly incorrect $\delta^{13}C\text{-}CH_4$ values. Ideally, the instruments would be calibrated daily for $\delta^{13}C\text{-}CH_4$, however as suitable standards with known $\delta^{13}C$ values at these concentrations could not be sourced during this project, the earlier calibrations performed earlier at other locations by CSIRO Oceans and Atmosphere and Picarro were used.

To attempt to overcome these problems, methane standards were generated by diluting microlitre quantities of methane of known carbon isotopic ratio (-42.9 ‰) into Flexfoil® sample bags containing zero air. The concentration of methane in the zero air was below the detection limit of the instruments. The syringe was prepared identically to the calibrations performed for the IRMS instrument. Once the sample was injected into the flexible bag however, stabilisation and equilibration of the bag surface with the surrounding air might lead to fractionation. Flexfoil® was chosen over Tedlar® bags due to its suitability to store low molecular weight compounds such as methane. A sampling vessel with flexible volume was also desired to avoid issues with pressure differences within the cavity ring down spectrometer, which could occur with fixed volume sampling devices such as glass vials or canisters. Flexfoil® bags used in other CSIRO projects have showed little change in methane concentration over 2-3 months, albeit at much higher methane concentrations than that used in this work.

Where methane concentrations less than 5 ppm are measured by the instrument, the error in the raw $\delta^{13}C\text{-}CH_4$ values are reasonably high. As such, sample bags were run for 5-10 minutes to allow averages to be taken. Longer sample times for low concentration samples is advisable to improve instrument precision for the sensitive $^{13}CH_4$ measurement and $\delta^{13}C$ calculation (Palmer and Wahl, 2013).

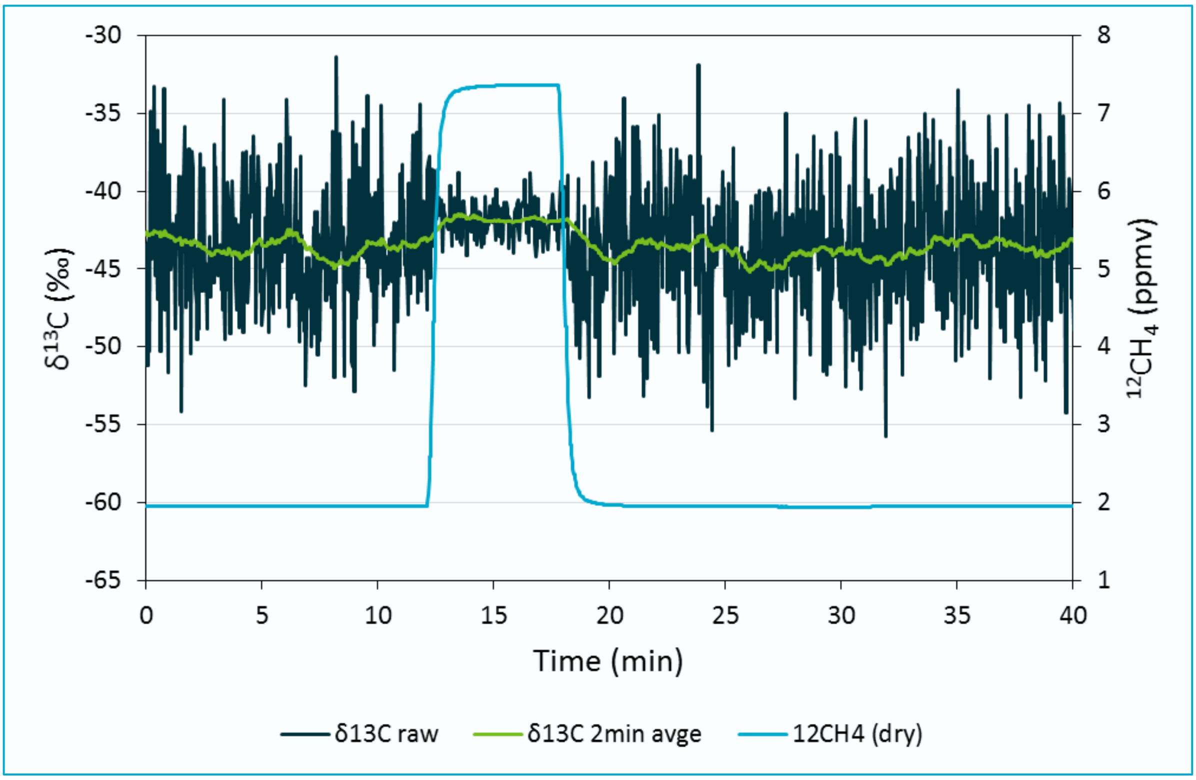

Figure 8.12. Standard bag sample run between 12 and 19 minutes for G2201-i, compared with background lab air.

Six standards were generated using the same reference pure methane standard gas. The sample bags were connected to the instrument inlet and analysed for a sufficient length of time to allow a stable concentration to occur (Figure 8.12). The results are summarised in Table 8.1.

Table 8.1. Results from bags prepared from methane standard

Standard	Picarro G2201-i			Picarro G2132-i	
	$[CH_4]$ (ppm)	Uncorrected $\delta^{13}C-CH_4$ (‰)	Corrected $\delta^{13}C-CH_4$ (‰)	$[CH_4]$ (ppm)	$\delta^{13}C-CH_4$ (‰)
A-background	1.80	-33.2 ± 1.8	-43.2 ± 1.8	-	-
A-instrument air	1.90	-34.7 ± 2.2	-44.7 ± 2.2	1.91	-44.7 ± 2.4
A1	7.51	-38.1 ± 0.7	-48.1 ± 0.7	-	-
A2*	18.5	-28.2 ± 0.4	-38.2 ± 0.4	-	-
B-background	1.82	-33.5 ± 2.4	-43.5 ± 2.4	1.79	-43.0 ± 2.6
B1	8.31	-27.9 ± 0.3	-37.9 ± 0.3	-	-
B2*	12.3	-25.9 ± 1.3	-35.9 ± 1.3	-	-
B3	11.6	-25.5 ± 1.5	-35.5 ± 1.5	10.0	-37.9 ± 0.4
B4	3.20	-35.7 ± 1.0	-45.7 ± 1.0	2.80	-45.9 ± 1.4

* Out of calibrated range of the instrument

The standards for the G2201-i were analysed 2-3 days after preparation, those with the G2132-i were analysed 6 weeks later. Some bags were not able to be re-analysed, either because the remaining air volume was not sufficiently large for a sample, or the type of bag used did not allow further analysis.

Across the standards, reported values varied -25 to -38 ‰ for the G2201-i analyser, and -37 to -46 ‰ for the G2132-i analyser. This difference in $\delta^{13}C\text{-}CH_4$ between standards was despite the standards being prepared similarly and from the same high concentration reference standard. The errors reported in $\delta^{13}C$ are the 95% confidence intervals for the 30 s averaged (boxcar) values. Background air obtained from an elevated position in Sydney during the early afternoon on a relatively unpolluted day was used for a background sample. In addition, instrument air (Coregas) containing methane was also analysed periodically. The instrument air was the stable base standard, which the instruments could be referenced against on days where sampling occurred.

The discrepancy in $\delta^{13}C\text{-}CH_4$ between the samples indicates that this method using Flexfoil® bags was not appropriate to generate standards in a reproducible manner.

The two Picarro instruments gave different $\delta^{13}C\text{-}CH_4$ values that were offset to each other by 10 ‰. Some instrumental drift over time is expected (Rella et al. 2015), but unlikely to the extent observed. A realignment of the water signal was performed on the G2201-i instrument after calibration but before analysis, which may be partially responsible for this discrepancy. As neither instrument could be calibrated for $\delta^{13}C\text{-}CH_4$ during this experimental program, it was assumed that the G2132-i results were accurate for $\delta^{13}C\text{-}CH_4$ as the alignment and calibration had not knowingly been altered since its last calibration.

In order to make the instrument results comparable, the G2201-i results were offset -10 ‰, so that the instrument air results were similar between the Picarro instruments (Table 8.1). Once the offset was applied, the corrected $\delta^{13}C\text{-}CH_4$ measurements for the G2201-i instrument compared favourably to the G2132-i results, even for the standard bags.

The total methane concentrations in the later analysed samples (G2132-i) are around 10 % lower than those observed not long after preparation. This was likely due to small methane losses from the Flexfoil® bag over time, which was observed for sample bags (see section 8.3.3)

8.3.2 INSTRUMENT STABILITY

To check the linearity of the instrument across the methane concentration range, one bag of standard methane was dissolved in zero air to a concentration of 10 ppmv. The sample was analysed with the G2201-i Picarro, then subsequently diluted further with zero air, stabilised over 8-24 hours and reanalysed. If differences were observed in $\delta^{13}C\text{-}CH_4$ as the bag was diluted and reanalysed, then this could have been attributed either to fractionation of the sample during dilution, or variation in the instrument calibration across different methane concentrations. As air was being added at each step, with no sample containing methane being removed, fractionation was not considered likely from dilution. Eleven samples of between 10.8 and 2.6 ppm were analysed. The $\delta^{13}C\text{-}CH_4$ recorded for each are shown on a Keeling plot in Figure 8.13. The uncertainty was determined as before: a 95% confidence interval of the 30s averages over a 5-15 minute sampling time. As expected, this uncertainty increased for lower methane concentrations.

Within the uncertainty of the method, no obvious deviation or trend in $\delta^{13}C$ was observed. As the same sample repeatedly diluted and reanalysed over 8 days gave the same $\delta^{13}C\text{-}CH_4$, the system was still considered linear for $^{12}CH_4$, $^{13}CH_4$ and subsequently $\delta^{13}C$. As time did not allow a proper analysis of the G2132-i instrument, the same cannot be said definitively for this instrument. However, the similarity of results for $\delta^{13}C\text{-}CH_4$ at different methane concentrations between the two instruments (see Tables 8.1 and 8.2) suggests that similar results may be likely.

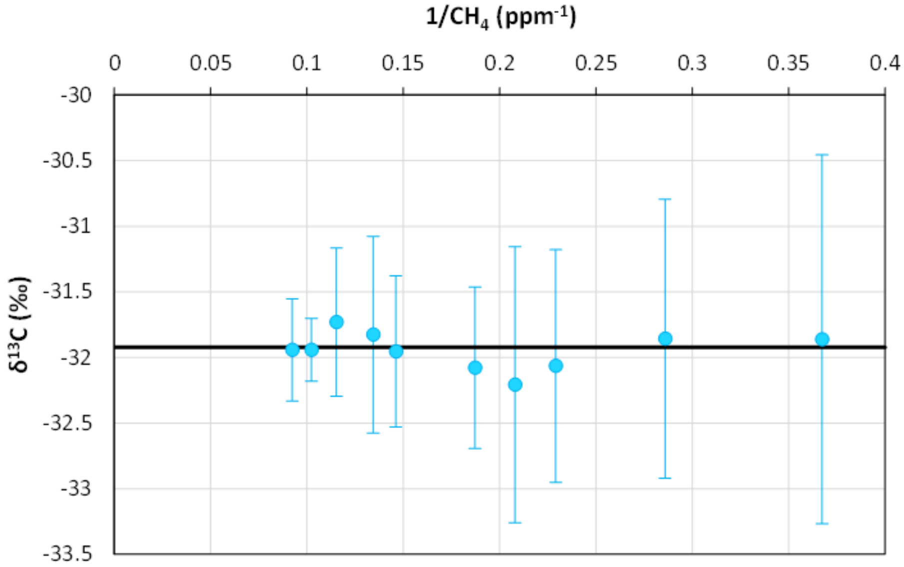

Figure 8.13 Analysis of δ^{13}C-CH$_4$ in bag of methane diluted with zero air. Line is weighted average of all data.

8.3.3 GAS SAMPLE BAGS

Flexfoil® bag samples were taken from ambient air surrounding two coal seam gas locations and a waste treatment facility (Table 8.2). In addition, a sample bag containing air sampled from the background location at North Ryde was also analysed.

The sample bags were analysed for δ^{13}C-CH$_4$ using the G2201-i instrument between 4-8 weeks after sampling. The reason for this delay between sampling and analysis was due to trying to calibrate the instrument with standard bags as described in Section 8.3.1. This method was unfortunately unsuccessful. The sample bags were then analysed approximately 4 weeks after the first analysis using the G2132-i instrument.

Some drift is expected due to sample storage (Eby et al., 2015), however the change measured in the aforementioned study for pure gas samples (± 0.2 ‰) is less than the instrumental uncertainty of the Picarro at these concentrations (± 0.4 ‰ for one hour run). However, the difference in behaviour of high methane concentration gas compared to ambient or slightly raised methane concentrations in flexible film bags is not known.

Table 8.2. Gas sample bags analysed with Picarro isotope instruments

		Picarro G2201-i		Picarro G2132-i	
Sample	Sample Details	[CH$_4$] (ppm)	δ^{13}C (‰)	[CH$_4$] (ppm)	δ^{13}C (‰)
Background	North Ryde	1.82	-43.6 ± 2.4	1.79	-43.0 ± 2.6
Inst.	Instrument air	1.90	-44.7 ± 2.2	1.91	-44.7 ± 2.4
Pic1	Picton 13/1/16; Upwind of lagoon #1	1.98	-43.4 ± 2.2	1.92	-45.0 ±2.9
Pic4	Picton 13/1/16; Near sludge tank	2.09	-44.0 ± 1.6	2.00	-43.5 ± 2.0

		Picarro G2201-i		Picarro G2132-i	
Sample	Sample Details	$[CH_4]$ (ppm)	$\delta^{13}C$ (‰)	$[CH_4]$ (ppm)	$\delta^{13}C$ (‰)
Pic2	Picton 13/1/16; Between lagoons	2.16	-43.3 ± 1.6	2.04	-45.3 ± 2.5
Pic3	Picton 13/1/16; Downwind lagoons	2.21	-44.1 ± 2.1	2.10	-43.5 ± 2.0
Cam6	Camden 12/1/16; 13:35	1.92	-44.2 ± 2.1	1.85	-43.6 ± 2.4
Cam1	Camden 12/1/16; 12:50	1.98	-43.3 ± 2.2	1.89	-44.3 ± 2.9
Cam5	Camden 12/1/16; 10:28	2.08	-42.7 ± 1.3	-	-
Cam3	Camden 12/1/16; 10:08	2.16	-40.4 ± 1.7	-	-
Cam4	Camden 12/1/16; 08:50	2.50	-37.2 ± 1.7	-	-
Cam2	Camden 12/1/16; 09:30	2.62	-39.8 ± 1.1	-	-
Nar1	Narrabri 8/2/16; Well N1	2.24	-45.4 ± 1.6	2.10	-45.4 ± 2.0
Nar2	Narrabri 8/2/16; Well N2	2.62	-46.7 ± 1.7	2.41	-46.4 ± 1.9

Camden CSG

The samples taken at Camden were collected on a single morning with elevated background CH_4 concentrations present across the Camden valley. Throughout the day the concentration of CH_4 decreased due to atmospheric mixing, which was often observed during field surveys (Section 6.6.3).

The results indicate a possible trend towards a higher $\delta^{13}C$-CH_4 than ambient on the particular day of sampling. If extrapolated to its source, the $\delta^{13}C$-CH_4 calculated (-22 ‰), which is improbable, and indicates some change in values from storage before analysis. The CH_4 concentrations determined in the samples Cam2 through Cam5 by the first instrument (G2201-i) were also around 20-40 % lower than that measured by the online vehicle Picarro (G2301) which was on site during sampling. This was found for all Flexfoil® sample bags where the CH_4 concentration sampled was higher than 2 ppmv. Further analysis a month later by the second isotope Picarro (G2132-i) showed further reduction in CH_4 concentration.

Direct comparison of the total methane response for all three Picarro instruments was not performed. The G2301 Picarro instrument used for real-time field measurements of methane was calibrated against a known methane standard constantly throughout the project. The other two Picarro instruments were not calibrated during this project for total methane, the original calibrations for total methane were used instead. The total methane measured by both instruments for instrument-grade cylinder air in Table 8.1 was within 10 ppb (0.5%). As the two instruments gave similar results for the same stable concentration of methane contained in the cylinder, the differences between total methane between the two isotope Picarro instruments for samples in Tables 8.1 and 8.2 is due most likely to variation in methane concentrations within the samples themselves over time.

The CH_4 loss from sample bags during storage was found to be rapid, and consistent with other studies (Akdeniz et al., 2011). The loss of CH_4 from the bags compromises the results obtained for the isotopes, as there is no way of measuring or quantifying the kinetic isotope effect of this desorption and equilibration likely occurring through the surface of the bag or the inlet.

Given these issues and the limited number of samples, it was not possible to draw conclusions from the Picarro results alone regarding the source of the elevated CH_4 background in the valley that particular day. The area involved has multiple CH_4 sources, which can result in variation in $\delta^{13}C\text{-}CH_4$ at different locations. This has been highlighted in studies of the area which show source elevated CH_4 concentrations observed in the area in the mornings are sourced from landfill, CSG, agricultural and sewage treatment facilities in differing amounts and concentrations depending on conditions (Pacific Environment, 2014).

Picton STP

The CH_4 results for the Picton STP differed little from expected ambient results, both in concentration and $\delta^{13}C\text{-}CH_4$. Similarly to the Camden results, no conclusions can be drawn. The concentrations ultimately determined in the sample by the isotope Picarro instruments were lower than the concentrations measured in the field at the same time by the vehicle Picarro.

Narrabri CSG

The two samples taken at the Narrabri wells were different than those from the Camden field, as they positively linked to direct emissions from two wells (N1 and N2), in that they were sampled in a methane plume originating from the wellheads. The exact sampling location was determined by monitoring the methane plume on the LGR instrument to ensure that the plume was captured in the sample.

The $\delta^{13}C\text{-}CH_4$ data obtained are lower than ambient values, in contrast to the Camden site results. Even with the aforementioned issues regarding sample storage, the values would correspond to a source $\delta^{13}C\text{-}CH_4$ of -54 ‰. These values are similar to those identified by Maher et al. (2014) in their assessment of the Tara and Casino gas fields (-55 to -57 ‰).

The convergence of these results is likely serendipitous. There is no data available on the $\delta^{13}C\text{-}CH_4$ of the Narrabri gas well samples. In addition, the measured CH_4 concentrations are much lower than those measured by the LGR instrument that was used to locate the CH_4 plume (around 4 to 6 ppmv). This indicates CH_4 loss from the bags over time, with the degree of possible fractionation uncertain. Possible fractionation of methane at the wellhead when compared to measured isotopic values for methane from the pure well gas is also unknown.

8.3.4 ISOTUBE® SAMPLES

As the Flexfoil® bag sample technique was not sufficient for sampling ambient air accurately, another technique was tested to check the precision of the numbers returned by the Picarro isotope instruments. These results could be compared against more precise data obtained using the isotope mass spectrometer (Section 8.1).

After the mass spectrometer analyses were performed, a small amount of the collected gas from selected IsoTubes® was released close to the inlet of the Picarro. This resulted in a response on the instrument from which a Keeling curve was generated. These results are summarised in Table 8.3.

In order to generate meaningful results, the analysis was limited to conditions where the CH_4 concentration was decreasing (i.e. not during release), and where the calculated methane concentration was between 2 and 10 ppm. This was because the rapid change in concentration during release returned unreliable $\delta^{13}C\text{-}CH_4$ data, and because the instrument operational and calibrated range was limited to 10 ppm. An example of some of the results are shown in Figure 8.14.

Table 8.3. Comparison of IsoTube® samples from isotope Picarro (G2132-i) to IRMS results

Description	Picarro δ^{13}C-CH_4	IRMS δ^{13}C-CH_4	Difference
Coregas CH_4 Cylinder grade 5.0	-43.3 ± 0.7	-42.0	+1.3 ± 0.7
Natural gas reticulated	-77.7 ± 3.5	-39.4	-38.3 ± 3.5
Gloucester Well G1	-44.8 ± 1.1	-42.4	-2.4 ± 1.1
Gloucester Well G2	-38.8 ± 6.5	-41.7	+2.9 ± 6.5
Eastern Creek	-74.6 ± 3.4	-56.6	-18.0 ± 3.4
Eastern Creek	-81.7 ± 1.9	-56.6	-25.1 ± 1.9
Summer Hill WMC	-68.9 ± 3.2	-53.5	-15.4 ± 3.2
Summer Hill WMC	-72.3 ± 2.5	-53.5	-18.8 ± 2.5

While the methane cylinder and CSG samples were similar between the two analytical methods, the other samples tested were not. The Picarro measurements for the natural gas and landfill samples indicate ^{13}C depleted by between -15 and -38 ‰.

The possible explanations for these differences were improper calibration, interference from other species, insufficient sample testing time or fractionation of the IsoTube® sample upon release. Calculation of other gas components of these samples (ethane, CO_2, water, ammonia) showed no trend that would indicate interference. The concentrations of these other species are unlikely to account for the magnitude in differences observed when compared to the cross-interference data provided by Rella et al. (2015).

Fractionation during release of gas from the IsoTube® cannot be ruled out, although it would seem unlikely that it would occur with some samples and not others. This would not be a factor in the isotope measurements however, as long stabilisation between the IsoTube® during instrument sampling overcomes any possible fractionation which may occur during brief venting through. Given these results, the method of analysing IsoTube® samples using the Picarro instruments cannot be recommended without further refinement.

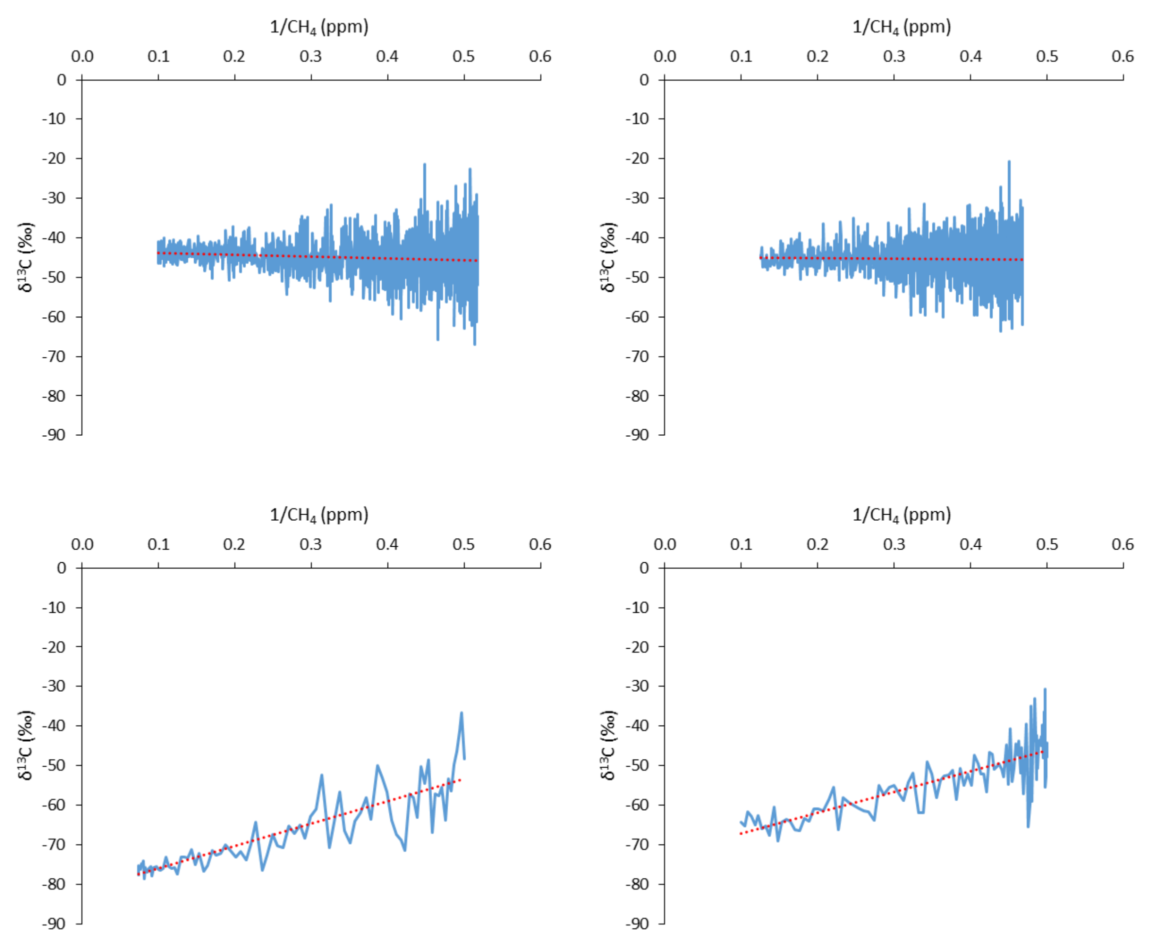

Figure 8.14. Example Keeling curves from IsoTube® samples analysed by Picarro G2132-i

8.3.5 TRAVERSE WORK

The G2132-i Picarro was used for two vehicle traverse runs at the AGL Camden and Gloucester sites. Because of limited battery power available to supply the unit, the instrument was turned on the mornings of use, and thus was stabilising during the early part of each day.

At Camden, the elevated CH_4 readings typical for early morning runs was observed. The instrument returned $\delta^{13}C$-CH_4 of -55 ± 3 ‰ in the morning when the CH_4 concentration was above 2 ppm. As the instrument was started from cold that morning, it could not be stabilised in time (Figure 8.15), and it is therefore possible that the general trend observed over a few hours was a reflection of instrument stabilisation and not representative of real $\delta^{13}C$-CH_4. This would also explain the reverse but similar trend observed at the Gloucester site the following week (Figure 8.16). For the Gloucester emissions test, the measured total CH_4 concentration did not vary much from expected ambient concentrations. Similar drifts in $\delta^{13}C$-CH_4 have been observed during the first three hours after the instrument has been restarted in the laboratory. Subsequently, it is not recommended that the Picarro instruments be used for isotope measurements in the first few hours of operation from a cold start.

As such, the usefulness of this instrument for determining $\delta^{13}C$ is limited for these traverse runs. A more stable dataset would be expected if the instrument were left running for some time (likely days) before real time analysis. These results do not affect the measurement of total CH_4 (or rather $^{12}CH_4$) from these instruments, which is much less prone to instrumental drift (Rella et al., 2015).

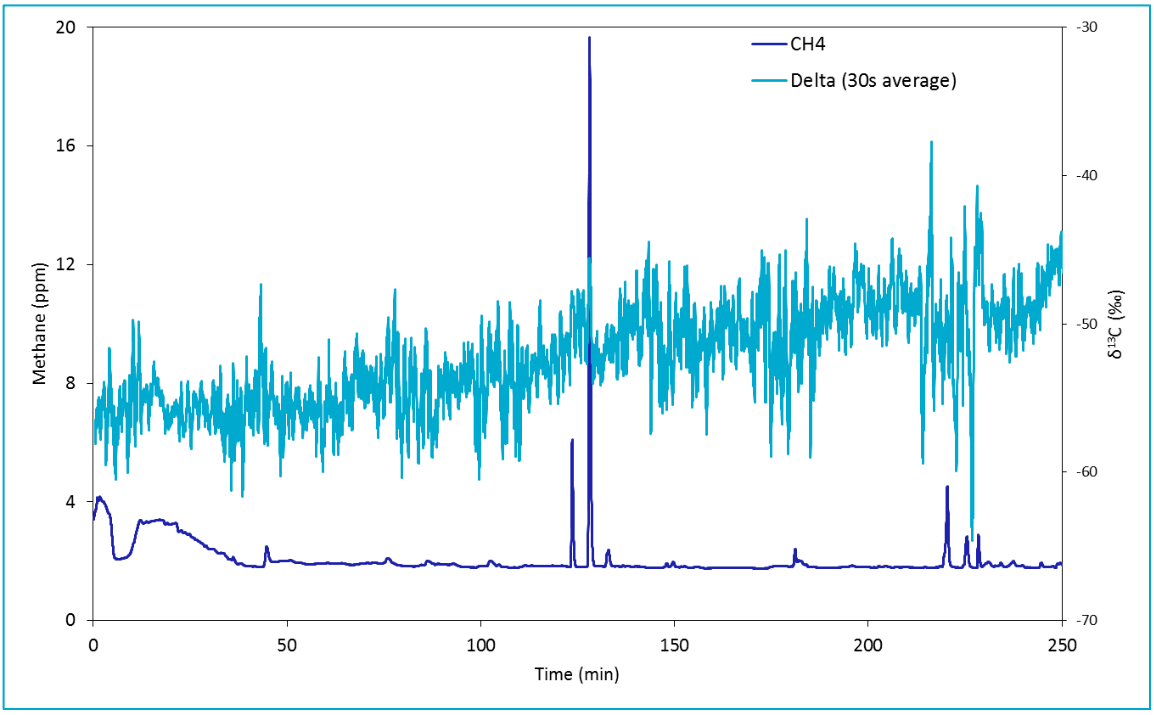

Figure 8.15. Methane and δ^{13}C measured on 16/3/16 at Camden.

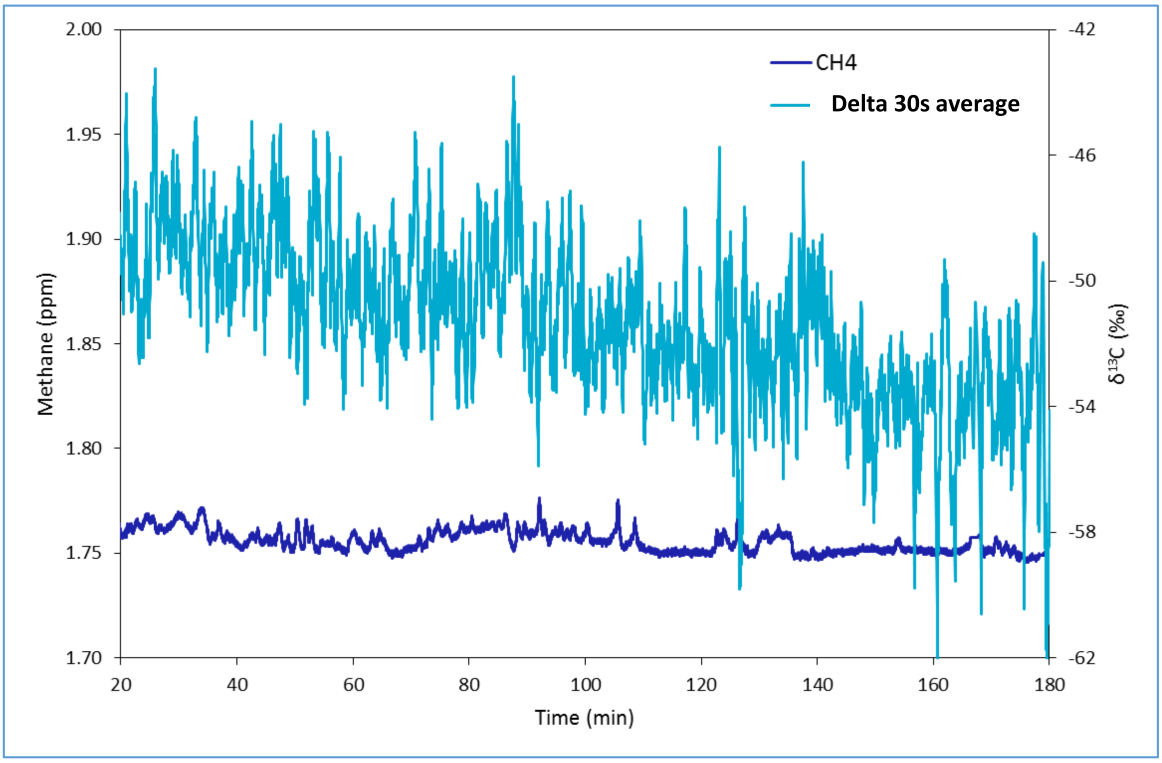

Figure 8.16. Methane and δ^{13}C measured on 21/3/16 at Gloucester.

9 Discussion

9.1 Methane Emissions

One of the key objectives of the project was to develop and trial methodology suitable for monitoring and differentiating CH_4 emissions from a range of sources across NSW. The first step in this process is to detect CH_4 sources reliably and with sufficient sensitivity to locate even small sources. Mobile surveying using a vehicle fitted with a cavity ringdown spectrometer (CRDS) has been shown to be a very versatile method in this regard; large areas can be surveyed at normal highway speed and when the data are combined with spatial information from GPS receiver, detailed maps of emission sources can be produced. The technique is now well established and the instrumentation is generally very reliable. CSIRO has used the method extensively in Queensland CSG fields previously (Day et al., 2015) and other Australian researchers have used mobile CDRS to map large areas of Queensland and NSW (Kelly et al., 2015; Iverach et al., 2014; Maher et al., 2014). The method has also been successfully in the U.S. and U.K. (Phillips et al., 2013; Zazzeri et al., 2015).

Measuring emissions rates of CH_4 from sources, however, is often more challenging, especially if the source is over a large area. Some atmospheric methods such as inverse modelling are capable of locating sources and determining emission fluxes over areas of up to 1 km^2 (e.g. Luhar et al., 2015) and eddy covariance methods can also cover similar sized areas. Research is currently underway in Queensland to extend the inverse modelling method to monitor emissions over much larger areas (Day et al., 2015). Such approaches also offer the prospect of providing long-term continuous monitoring which is important for baseline monitoring ahead of development or monitoring industrial activity. However, these techniques are complex, requiring fixed installations and high levels of data analyses and interpretation. Wide area applications of inverse modelling are still very much at the developmental stage but despite the complexities of such methods, they may be the most appropriate for longer term monitoring especially if information on seasonal or other temporal variation is required. Opportunities for further method development and longer term monitoring may exist in the GISERA partnership that has recently been expanded into NSW.

9.1.1 FLUX METHODOLOGY

During this project we focussed on CH_4 flux methods that did not require fixed systems on site. The measurements made using these methods were relatively rapid, and could usually be completed within a day. The downside to this approach, however, is that they do not generally provide high resolution temporal data unless a large number of measurements are made over a long period. Due to the large number of sites investigated in this project and their geographical distribution, it was not practical to make very frequent flux measurements at each site. Consequently, it was difficult to discern subtle temporal changes such as seasonal variation, except in a few instances such as the rice farm and possibly the natural wetland.

While the relative infrequency of the measurements made here complicated identification of seasonal effects, it was apparent that other factors tended to obscure seasonal variations, even if they existed. The natural wetland showed little variation in CH_4 flux over the monitoring period but there was an apparent effect on the CO_2 flux that corresponded to seasonality. However, the effect of heavy rain immediately prior to the site visits is unknown; it is possible that the observed variation in emission flux was due more to weather events than normal seasonal variation.

The same is true for other sites. Landfills, for example, may be expected to show some seasonal variation; however, it has been shown that CH_4 emissions from landfills are strongly influenced by periodic events such as drought and heavy rain (USEPA, 2012). In addition, even a small change in air pressure can have a large effect on emissions over a short period (Czepiel et al., 2003), which our results from the Summerhill site seem to confirm.

Although seasonal variability may be relevant to emissions in some situations, the results from this study suggest that seasonal variation may not be the most significant factor in flux variability for many of the emission sources investigated. Other factors, which are often site-specific, seem to have more influence on CH_4 emissions. For example, emissions from landfills were found to be sensitive to surface disturbances with significantly increased emissions rates occurring after removing even a small amount of the surface material. It seems likely therefore that the day-to-day operation of mobile machinery used to move and compact waste would affect emission rates. Coal mining CH_4 emissions are also strongly affected by operations within the mine (i.e. blasting, exposing coal seams, breaking and excavating of coal).

The potential for emissions to vary over time either through seasonal or other influences needs to be considered when designing suitable methodology for measuring emissions rates. This would include not only the measurement method but also the frequency of measurements. Extrapolating the results of infrequent periodic measurements over long periods (e.g. annually) may introduce large errors into the estimate. Hence for sources with emission rates that vary widely with time, continuous measurement systems may be more appropriate than the periodic techniques trialled in this project.

Some of the main points relating to the three flux estimation methods used throughout this project are discussed below.

Flux Chambers

Surface flux chambers were found to be suitable at some sites, although specialised purpose-built chambers were necessary in some cases. In particular, floating chambers were required for the sewage treatment plants and the CSG water treatment facility. Another variation on the flux chamber was required for the rice farm where the chamber was built with sufficient height to accommodate the plants at all stages throughout the growing season.

The flux chamber method is very versatile and individual measurements are accurate – the main problem with this approach is that many measurements are usually required to properly determine the emission flux from spatially large sites. The method yielded good results for the sewage treatment plant tanks provided suitable access (via walkways over the tanks) was available. In other parts of the plant, such as effluent retention ponds or biosolids lagoons sampling may not be practical over the entire surface, which introduces representativeness issues. Biosolids lagoons at some wastewater treatment plants were found to be strong gas emission sources, which was largely by ebullition and consequently with variable emission rates across the lagoon surface. Treated effluent ponds, on the other hand, were low emitters with the emission route probably by diffusion so were reasonably homogeneous across the surface. In these cases, the relatively small number of individual flux chamber measurements were less of an issue than at many other sites where large variations in emission rate were found.

Other sites such as landfills are also amenable to flux chambers and indeed this approach forms the basis of some standard methods for estimating emissions from landfills. However, landfills are especially inhomogeneous and it is therefore usually not practical to completely measure emissions over the entire surface due to the small area of ground covered by the chamber. There may also be other more prosaic problems such the ability of the operator to be able to safely access areas, which affect the viability of the method. The difficulty in obtaining representative sampling across the site therefore introduces a significant level of uncertainty into the flux chamber method. Hence, in these instances other methods for estimating emission flux may be more appropriate.

Flux chambers are generally an excellent method for measuring gas fluxes from natural surfaces. The chambers can provide very high sensitivity (provided a suitable gas analyser is used) for measuring the usually very low gas emission or uptake rates of soils. The principal limitation is the spatial coverage. While these surfaces are subject to significant variation, in absolute terms the variability is much less than often seen at some sites, such as landfills where emission rates can vary by several orders of magnitude within a short distance.

Although flux chambers are an extremely useful and well proven method for measuring emissions fluxes, they are limited to surface emissions. Other sources from industrial or intensive agricultural facilities, for instance, require alternative methods.

Plume Traverses

At the commencement of the project, we had intended to use ground based plume traverses for estimating fluxes from many of these sites. In this approach, the ground level concentration of CH_4 is measured across the plume using the Picarro or LGR analyser mounted in the field vehicle. The vertical concentration profile of the plume is calculated by assuming a Gaussian distribution and that the ground level concentration measured are the maximum concentrations. Local wind speed data are also required for the calculation. The plume traverse method requires that the emission source is at ground level and that the plume is not buoyant. Although CH_4 is lighter than air, under conditions where this method can be used (i.e. with at least a moderate wind speed), CH_4 emissions would be expected to mix rapidly into the surrounding so that plume rise due to buoyancy is negligible.

This method has several advantages in that it is simple to deploy in the field, is relatively rapid and can be used at over a wide range of distances from the source. In some cases, emission estimates may be made without access the facility under investigation. However, it is very dependent upon wind conditions and the ability to completely transect to the plume.

This method has been used previously by CSIRO and others for quantifying emissions from a wide range of sources, including coal mines and CSG infrastructure (Williams et al., 1993; Lilley et al., 2012; Day et al., 2014; Day et al., 2015), although it is acknowledged that there are relatively high uncertainties associated with this method. Individual traverses often yield wide variation in emission estimates, which is a consequence of the uncertainties of the method but also because of the meandering nature of the plumes, especially in light winds. Consequently, emission rate estimates based on this method should include a reasonable number of replicates from which to derive an average rate.

Some of the sites visited during the project were amenable to the ground level traversing approach and reasonable flux estimates were made for the Singleton wastewater treatment plant, several CSG wells and the Summerhill Waste Management Centre. However, these were the exception and more often we were unable to use the method for various reasons including lack of suitable wind conditions at the time of the field visits, inability to access the plume (usually due to restricted vehicle access), unsuitable terrain and the presence of buildings, fences or other obstructions.

Tracer Gas Method

Because of the limitations of the flux chamber and plume traversing methods, we investigated the use of a tracer gas to measure emission fluxes, which was shown to be a promising method. Small scale trials demonstrated that it can provide high accuracy with lower uncertainty than the plume traverse method. These trials showed that uncertainties of less than 10 % were achievable when measuring emissions from up to 50 m from the source. The method was subsequently used to measure emission rates of CH_4 from several CSG wells in the Narrabri gas field.

A major advantage of the tracer gas method is that accurate flux measurements can be made without the need to fully transect the plume (which is necessary for the plume traverse method). In addition, assumptions about vertical dispersion of the plume are not necessary. Because of this, the method can be used for measuring emission fluxes from a range of sites and under conditions where other methods may not but suitable. The main limitations are that the tracer must be released at the same location as the source and the tracer gas must be well mixed within the plume at the point where concentration measurements are made. For point sources or sources confined to relatively small areas (such as CSG well pads), the technique is ideal and can be deployed reasonably rapidly.

The method was used for making period measurements but in principle, measurements could also be made over longer periods, provided that sufficient tracer gas was available. Such extended measurements would provide information on rapidly changing emission rates that may be a feature of some emission sources (e.g. intermittently operating vents on gas infrastructure). This aspect was not examined during this project but would be a useful topic for further investigation.

Although the technique was predominantly used in this project to measure emissions from small emission sources, it can also be used at larger scales – some experiments on a landfill site provided reasonable results. However, larger sites that are more diffuse such a landfill, coal mines and other large area sources present a range of problems that must be considered. Firstly, it is difficult to co-release the tracer with the CH_4 sources, which may be numerous and spread across a relatively large area. This can be compensated for to a large extent by making the measurements at longer distances downwind, which has the effect of approximating a point source (i.e. the source is small compared to the downwind distance). While this is effective in principle, in practice it introduces another problem, namely that the concentration of the tracer becomes extremely low. Hence, the analytical system used for the measurements must have the necessary sensitivity and precision to be able to yield accurate results. The landfill measurements trialled using the LGR instrument to detect acetylene as the tracer gas were generally successful but were approaching the limit of the of the instrument’s capability. Alternative approaches using more sensitive analytical methods may be suitable. For example, it may be possible to achieve an order of magnitude greater sensitivity using canisters to sample the plume and analyse for CH_4 and acetylene using GCMS methods such as those used here for the ambient VOC analyses discussed in previous sections of this report. Other tracers (e.g. N_2O) and different analysers may also be suitable.

It should be noted that the validation experiments conducted on the tracer method during this project were made on point sources and at downwind distances of less than about 50 m. The larger scale experiments conducted at the landfill were at a much larger scale and at downwind distances of up to 2 km. As a consequence, it is likely that the uncertainty of the estimates of the landfill emission rates made with the tracer gas method are higher than the controlled validation experiment.

Coal Mining Methods

As discussed in Section 2.2, estimating fugitive emissions from coal mining is complex and while measurements were made at the two mines included in this study, the methodology employed was not suitable to provide robust emission estimates from the entire mines. However, in Australia, methodology already exists for estimating coal mining emissions and is used across the industry for the purposes of NGER reporting. Methods now used for estimating fugitive emissions from coal mines have improved significantly in recent years with the widespread adoption of NGER Method 2 for open-cut mines, which is based on mine specific gas content data. Underground mines are also now required to measure emissions directly according to Method 4, which has relatively low uncertainties. The methodology used for measuring underground mine emissions is well established and reliable, and because all mines routinely collect data for safety and greenhouse reporting (sometimes continuously), emission estimates for Australian underground coal mines are among the most accurately defined and with the lowest uncertainty of any CH_4 source.

Fugitive emissions from open-cut mines are also now reasonably well defined although the methodology, which is based on measuring the in-situ gas content of strata ahead of mining, is subject to higher uncertainty than the direct measurements used in underground operations. The accuracy of the open-cut method is determined to some extent by the representativeness of the gas content data for the entire mine since gas content may vary over the mine site. In addition, boreholes for gas content are usually only drilled infrequently, so the method is at best periodic. Research is currently underway in Australia into methods based on atmospheric science to measure fugitive emissions from open-cut coal mines continuously. One of the approaches under consideration is the use of the tracer gas method discussed above.

9.1.2 EMISSION ESTIMATES

Estimates of CH_4 emission rates were made at most of the sites visited during the project. However, due to various reasons, we were unable to generate flux estimates that could be considered representative; rather they represent snapshots at that moment in time. All of the estimates made must be considered within the limitations of the measurements made on each site, which often resulted in substantial uncertainty. The uncertainty of the emission flux estimates is derived not only from the measurements but also from the representativeness of the sample. For example, the uncertainty of the flux estimates made for individual CSG well pads is relatively low, especially when the tracer gas method was used. However, we only examined a small number of wells that represent only a few percent of the total number of wells in NSW; the CH_4 emission behaviour of the remaining wells is as yet unknown. Similarly, individual surface fluxes measured using the chamber method have low uncertainty but the heterogeneity of many sites may lead to large uncertainties if the results of a small number of individual measurements are extrapolated to estimate total emissions from large areas.

Other factors unrelated to measurement or sampling may also contribute to uncertainty of emission estimates. These include operational or management practices that may cause emissions to change over time (for instance, the leak testing and repair programmes conducted by CSG operators would be expected to reduce emissions). Changes to industry sectors (e.g. expansion or contration of particular industries or companies) would also affect emissions.

Despite the uncertainty of the emission estimates derived for the CSG operations, CH_4 emissions from the facilities examined during the project were low, especially compared to many other sites. Highest well pad emissions measured were from two wells in the Narrabri gas field, and were mainly due to the operation of gas-powered pneumatic equipment installed on the pads. The emissions rates for these wells were nevertheless within the range of a previous study of CSG well emissions (Day et al., 2014). In the Camden and Gloucester gas fields, well pad emissions on the wells examined were very low, with most showing no signs of CH_4 emissions. The low well pad emissions observed at these sites are probably due in part to the fact that all of the wells at the Gloucester site and some at the Camden site use compressed air to power any pneumatic devices used on the surface equipment. This is in contrast to the Narrabri wells that use the product gas, which contributes to emissions as these devices operate normally. Another feature of the Camden wells, especially, is that the wells produce very little water hence they do not require water pumps and the usual gas-powered engines, which are a common feature on most CSG well pads. These engines have been shown to be a significant source of CH_4 from well pads (Day et al., 2014).

Although only a relatively small number of CSG wells were examined during this project (5 at Casino; 4 at Glouscester; 9 at Camden; 6 at Narrabri; 24 total), the results of these measurements complement the previous study on Australian CSG well emissions (Day et al., 2014) and greatly expands the number of Australian CSG wells where CH_4 emissions have been directly measured. Collectively, the results are suggesting that CH_4 emissions from Australian CSG well pads are relatively minor; most emissions appear to be from equipment that is designed to vent small amounts of CH_4 rather than unintended leakage.

Water treatment facilities at CSG operations represent a potential source of CH_4. The extent to which these facilities contribute to the overall greenhouse gas emissions from gas production is not yet well defined and the measurements presented in this study only consider CH_4 that was degassing from water that had been in storage for some time. More work is required to better understand these emissions, which would include an investigation of the CH_4 content of seam water.

Although emission fluxes have been made at many of the facilities included in this study, it is acknowledged that in many cases, more detailed measurements will be required to provide accurate estimates with defined uncertainties. However, the purpose of this project was not to produce an inventory of emissions of all major CH_4 sources. Rather the primary aim was to develop appropriate methodology that can be used at a wide variety of sites within NSW to measure greenhouse gas emissions. The methods used in this study and especially the tracer gas technique, and the flux results obtained at the various sites point the way to further more detailed measurements at individual facilities that will aid in developing a comprehensive inventory of CH_4 and VOC emissions across the state. The outcome of this study also complements work that is currently underway in the Surat Basin in Queensland through the Gas Industry Social and Environmental Research Alliance (GISERA) aimed at longer term monitoring of greenhouse gas emissions within the CSG gas fields.

9.1.3 IMPLICATIONS FOR A NSW METHANE EMISSIONS INVENTORY

It is clear that developing an accurate CH_4 emissions inventory for NSW will be a major and challenging undertaking. There are numerous CH_4 sources across NSW and while some of these are reported to the federal Clean Energy Regulator under the current National Greenhouse and Energy Reporting legislation, emissions estimates are often subject to significant uncertainties. Moreover, some sources such as agriculture and natural sources are not reported while others may be below the current reporting thresholds. However, when considering the uncertainty of emissions estimates, it is also important to understand the relative contribution of each emission source to the total inventory. Small emission sources, even with very high uncertainty, contribute little to the overall uncertainty of an inventory. Conversely, large sources with high uncertainties (e.g. agriculture) will dominate the uncertainty of the inventory. If attempting to better define a statewide emission inventory, it is therefore worthwhile targeting in the first instance the larger sources.

During this project, several methodologies were examined and tested as to their applicability for directly measuring CH_4 emissions from various sources. The results have also yielded some preliminary flux estimates but these are still a long way from a robust NSW inventory. Some of the methods trialled show considerable promise for measuring emissions from some sources on a routine basis; however, other sources may require further development. In yet other cases, current practices or emission factors may yield sufficiently accurate data to develop an inventory, provided the necessary data can be obtained. A summary of the main sources identified in this project and the estimated relative contribution to overall state emissions is provided in Table 9.1. The relative size of the emission sources shown in Table 9.1 is a subjective estimate based on current national inventory data and the authors' knowledge of emissions and it is hence acknowlegeded that these magnitude estimates are at best a rough guide. Also shown in Table 9.1 are some methods for measuring or estimating emissions from these sources. It is noted that other sources of CH_4 exist in NSW (such as biomass burning) but these are not included in Table ES.1.

Table 9.1. Summary of the main sources of CH_4 emissions in NSW. Note that the relative magnitude of the emission sources is a rough guide only.

Source	Relative Emission Source Size	Uncertainty	Notes
Coal Mining	Large	Low to moderate	Fugitive emissions estimated and reported under NGERS. Underground mines measure emissions and have low uncertainty. Open-cut operations use gas content data from coring ahead of mining; moderate uncertainty.
CSG	Currently small in NSW	Moderate to high	Potential emissions from wells, processing plants, water treatment facilities, pipelines etc. Emissions reported under NGERS but some estimates have high uncertainty (although others may have lower uncertainty e.g. some venting and flaring operations). The tracer gas method has application for measuring emissions from well sites and some other infrastructure.
Agriculture	Large	High	Mostly from ruminant animals and liquid manure management. Feasible but difficult to measure; published emission factors for cattle more practical. Rice farming is a small source overall in NSW.
Landfills	Moderate	High	Difficult to measure but methods exist. The tracer gas method shows promise.

Source	Relative Emission Source Size	Uncertainty	Notes
Wastewater Treatment	Probably small	High	Feasible to measure with chambers and tracer; most emissions from biosolids storage.
Wetlands	Small	High	Likely to be a small component of NSW inventory. Difficult to measure directly but chambers or methods (e.g. eddy covariance) are feasible.

9.2 Volatile Organic Compounds

This study has brought together a volume of information on the levels of source related organic compounds likely to be present in the ambient air in the vicinity of land-use activities in regional NSW. Results from the Camden region, obtained from ten sites and four seasonal monitoring campaigns over the year, provides an ambient VOC database for the region. Each emissions source has also been evaluated from both quantitative and qualitative perspectives and the reader is referred to Section 7 for a fully referenced discussion of the prevalence and likely origins of the compounds found.

The results from this work have been evaluated from the perspective of ambient concentration and relevance to source impact on air quality, and compound type and relevance to source characterisation.

General findings from the ambient study are summarised in the following points and specific findings for each source category are outlined subsequently:

- A number of the Freon™ group and other halocarbons (specifically dichlorodifluoromethane, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane and carbon tetrachloride) and certain sulphur containing species (carbonyl sulphide and, tentatively, dimethyl sulphone) were observed at relatively consistent concentration at all sites. They are found at trace concentration (< 0.5ppbv) and are considered compounds which are ubiquitous in the atmosphere.
- The presence, or lack of, a hydrocarbon profile indicative of vehicle exhaust was informative in evaluating contributing sources to the ambient air at a particular site and petrol versus diesel hydrocarbon profiles could also be distinguished. Minor vehicular related impacts were apparent at semi-rural and suburban locations in the Camden region and the impact of on-site vehicles was apparent at a number of operational sites.
- Measurement of VOCs at the Cuba State Forest found minimal impact from anthropogenic activity and as such, this natural source established a baseline for biogenically derived compounds. This enabled land-use source emissions to be effectively allocated for compounds which were common to anthropogenic and biogenic sources (such as ethanol, acetone and other oxygenates).
- From an air quality perspective, ambient concentrations of priority hydrocarbon and air toxic VOCs were generally low (mixing ratios of low ppbv) and, with certain exceptions, in the range expected for the particular source and the location or processes within that environment. Measurements at natural and rural environments, and remote locations associated with mining or CSG activities, were in the trace to low ppbv concentration range and many of the priority VOCs could not be detected in these environments.
- Obvious impacts on ambient VOC concentrations were seen from more intensive sources such as those resulting from animal feeding, municipal solid waste disposal and wastewater treatment, where compounds specific to the activity were apparent, such as biologically derived oxygenates and nitrogenous compounds, solvent residues and chlorinated compounds.
- Source characterisation studies for non-standard VOCs identified additional compounds and organic classes of compounds to those from the priority VOC suites. The sorbent tube collection

methodology was found to extend the range of compounds that could be captured and isolated compared to those from VOC collection by the canister technique. Compounds with strong links to vegetation and biological processes, such as monoterpenes and more complex oxygenated compounds, were apparent at many sites. At higher intensity land-use sites these were overlain with compounds whose attributes were more specific to the source, such as odorous sulphur and nitrogen containing compounds for example.

- Within each source category, site-specific operations and processes also dictated the intensity of the emissions and excursions from more typical measured levels were seen for particular operations at the feedlot, landfill and wastewater treatment sites.
- The effect of the seasons on ambient VOC concentrations was investigated from four monitoring campaigns over a twelve-month period for ten sites across the Camden region. This evaluation showed a link to seasonal variability in the emissions of biogenic compounds and possibly, vehicle related emissions. However, these observations must be tempered by the many other factors, such as source intensity, emissions transport and atmospheric fate, which are well known to affect ambient concentrations of VOCs and other air pollutants.
- The analysis of non-methane hydrocarbon VOCs in CSG sourced well gases was effective in providing quantitative results for minor hydrocarbon compounds which are not commonly measured in these gases, i.e. those above C_5 and aromatic compounds; benzene, toluene and xylenes. Compounds at a concentration down to 0.007ppmv were measurable. The determination was informative in the recognition of a CSG source impact to ambient air and with respect to human and environmental health.

Specific findings for VOC emissions associated with each source category are summarised as follows:

- *Natural Sources* (Yaegl Nature Reserve, Cuba State Forest)
  Compounds with strong links to vegetation and biological processes (such as isoprene and monoterpenes) and the oxygenated species (such as ethanol, acetone, isopropanol and more complex oxygenates) were observed. The Yaegl site showed a minor traffic related impact from nearby roadways. There was no detectable impact from anthropogenic sources in the ambient air collected from Cuba State Forest. The monitoring of this natural source was used for allocation of biogenic versus anthropogenic activity to the emissions from other land-use sources.
- *Camden Region*
  The overall consistency in the results from ambient monitoring of the Camden sites establishes a database of expected concentrations of priority hydrocarbon and air toxics VOCs for the morning period at rural and semi-rural locations in the Camden region.

  A clear impact from traffic related emissions was seen in the hydrocarbon VOC profile observed in the ambient air for all ten sites monitored in the Camden region. The ambient concentrations of the hydrocarbon VOCs were in the low ppbv range and consistent with levels expected for semi-rural and suburban environments.

  Biogenic compounds were apparent in the VOC profile and their emissions are indicative of the semi-rural atmosphere of the Camden regional sites. Compounds associated with biological processes included small oxygenates (ethanol, acetone and isopropanol) which were present at concentrations broadly similar to those observed in the natural environments. 2-butanone and larger C_4 to C_9 aldehydes, ketones and alcohols were also identified in samples from the summer campaign and emissions of isoprene and monoterpenes from vegetation were observed in the VOC profile at many sites.

  Hydrocarbon and air toxics VOC profiles were not suggestive of a major industrial source of emissions in the vicinity of the Camden monitoring sites.

  - *CSG impact on ambient VOCs* – VOC monitoring in the Camden region encompassed a geographical area where CSG production was active. Ethane and propane were present in the ambient air in this region and these compounds are components of CSG sourced well gas. An evaluation was therefore made as to the likely impact of CSG as a source of these emissions to ambient air. Based on measured methane concentrations for the region and ethane and propane concentrations in the CSG sourced well gas, a predicted ambient concentration for these compounds was compared to measured ambient concentrations. This evaluation concluded that ethane and propane emissions from CSG were negligible and their presence in ambient air in the Camden region was derived from other sources. Aromatic compounds are present in the well gas at extremely low concentrations and as such were not a measurable source of aromatic compounds to ambient air in the Camden region (refer later point regarding well gas hydrocarbons).

  - *Seasonal Variability* – seasonal monitoring of VOCs across the Camden sites showed a general trend towards higher levels of biogenic compounds (such as oxygenated compounds, isoprene and monoterpenes) in the spring and summer campaigns which is consistent with warmer temperatures and a higher intensity of photosynthetically active radiation. Vehicle related hydrocarbon VOCs were generally lower in summer than the levels measured in winter and a reduction in the relative concentration of alkenes compared to alkanes is consistent with the effect of higher rates of photolysis on the more reactive species. Isobutane dominated the hydrocarbon emission profile in the warmer months, which may be indicative of higher evaporative losses from petrol-fuelled vehicles. These results indicate a possible link to seasonal variation particularly in the change in emissions of the biogenic compounds and, tentatively, the vehicle related emissions.

- *Cattle Feedlot* (Jindalee Cattle Feedlot).
  The ambient air at this site was rich in an array of oxygenated, nitrogenous and sulphur-containing compounds commonly associated with animal by-products and odour. Ethanol, acetone and 2-butanone were found at higher concentrations than typically observed in vegetated environments and an excursion in ethanol (253ppbv) was measured on one occasion at the feedlot site. Odorous compounds related to animal by-products such as dimethyl sulphide, dimethyl disulphide, nitromethane and nitroethane, and to other biological processes; C_4 to C_8 aldehydes, ketones and alcohols were apparent in the emissions from this source. There were minimal emissions indicative of a vehicular or other source impacting the site indicating that the compounds found were directly attributable to the feedlot.

  With the exception of an excursion in ethanol, the overall ambient concentration of the priority VOCs associated with this source was lower than other more intensive land-use activities; i.e. landfill and wastewater treatment.

- *Coal mining* (Rix's Creek Coal Mine, Gunnedah Basin mining region).
  Ambient concentrations at the Rix's Creek mine site were generally low in most VOCs compared to semi-rural and the higher intensity land-use sites. Those hydrocarbons that were identified inferred a diesel emissions profile, which is likely to be consistent with the machinery operating at the mine site. In the case of the Gunnedah Basin mine, it is possible that fugitive emissions of ethane from seam gas contributed to the hydrocarbon profile.

  The ambient air in the vicinity of the mine in the Gunnedah Basin showed low levels of compounds associated with vehicle exhaust and vegetation, which is likely to be consistent with on-site mining activities and the roadside location of the monitoring site.

- *CSG facilities* (AGL Camden, AGL Gloucester, Santos Narrabri).
  The AGL CSG production sites at Camden and Gloucester were characterised by a hydrocarbon profile that was dominated by C_2-C_4 alkane species, an absence in C_2 and larger alkenes and the presence of aromatics. The dominance of alkanes in the hydrocarbon profile is consistent with that measured in raw CSG well gases however these, and the aromatics, were disproportionately represented in the ambient samples compared to their profile in the well gases. Hydrocarbon concentrations were also not correlated with measured methane in the ambient air at the well pads. Hence, the hydrocarbon profile and concentrations found in the ambient air cannot be interpreted to be linked to CSG production at the AGL Camden and Gloucester sites and an

alternative source of VOCs is considered likely. The overall ambient concentration of VOCs measured at the AGL Camden and Gloucester facilities was low compared with semi-rural sites, for example.

The VOCs present in ambient air samples collected within the Narrabri CSG field and their concentrations were consistent with those found in a natural environment.

- *Landfills* (Summerhill Waste Management Centre, Parkes Waste Facility).
  Compounds associated with household and chemical disposal were elevated in the ambient air at the landfill sites. An excursion in the ambient concentration of acetone (200ppbv), accompanied by 2-butanone (18.0ppbv), were measured on one occasion at the Summerhill Centre. Chlorinated compounds such as trichloroethylene and tetrachloroethylene that are commonly used as markers for landfill emissions were identified at the Parkes Facility albeit at low (< 1ppbv) ambient concentrations. Other chlorinated solvent residues included dichloromethane, chloroform and benzyl chloride. The monoterpenes, limonene and a-pinene, which are used as fragrances in household products, were identified.

  Compounds derived from biological decomposition were also identified. C_4 to C_{12} oxygenates as aldehydes, ketones, alcohols, phenol and esters are associated with biological processes more generally but are likely enhanced due to soil decomposition in landfills. These compounds contribute to the characteristic odour associated with landfills.

  The impact of allied sources such as exhaust emissions from on-site diesel trucks and those from a methane generation system were identified at the Summerhill site.

- *Wastewater treatment* (Singleton Wastewater Treatment Works, Wagga Wagga Wastewater Treatment Plant, Picton Wastewater Treatment Plant).
  In certain aspects of the wastewater treatment process at the Singleton plant, VOCs were measured at ambient levels that were at the high end, or exceeded, those measured at other high intensity land-use sources, such as the landfill and the cattle feedlot. At the sewage inlet to the plant, emissions of acetone (93ppbv) accompanied by 2-butanone, were higher than other land-use sources, with the exception of an excursion in these compounds on one occasion at a landfill site. The Singleton WWTP was significantly higher than other sources in chlorinated compounds at the settling ponds; cis-1,2-dichloroethene (up to 13.5ppbv), trichloroethylene (up to 4.4ppbv) and tetrachloroethylene (up to 58.3ppbv). Compounds associated with odour, such as aldehydes, ketones, alcohols and nitrogenous compounds were apparent in the emissions profile at the Singleton site.

  Source identification and quantification is affected by the proximity of the sampling point, amount and type of emissions, meteorological variables and a range of other factors. However, it is evident that emissions from the Singleton wastewater treatment site were captured at a level that would allow certain oxygenated and halogenated VOCs to be used to characterise the operations at that site at that time. The high levels found at the Singleton site are also of importance when considering and assessing air toxics along with odorous emissions from this source.

  In contrast, ambient VOC concentrations at the Wagga and Picton plants were broadly in the range measured at other intensive land-use sources, apart from an excursion in ethanol (40.9ppbv) on one occasion at the inlet location of the Wagga Wagga wastewater treatment plant.

- *CSG sourced well gas* (AGL Camden, AGL Gloucester).
  Hydrocarbon VOCs were characteristically present as the alkane class and straight chain, cyclic and branched alkanes through to C_8 were measured. Alkenes were not present in the hydrocarbon profile of the well gases. Aromatic compounds were detected at low concentration; the highest aromatic content was measured in samples from AGL operations at the Gloucester gas field (around 0.5ppmv benzene, 0.2ppmv toluene, 0.02ppmv xylenes). The detection of the larger alkanes and aromatics correlated with those gases with higher non-methane hydrocarbon concentration. The aromatics are considered consistent with components originating from gas formation processes.

The ambient air equivalent concentration for the aromatic compounds, based on a worst-case emissions scenario in close proximity to a producing well, was estimated to be low pptv (parts per trillion by volume). This compares favourably with low ppbv (parts per billion by volume) concentrations measured in the ambient air of semi-rural regions that are impacted by low-volume traffic.

9.3 Isotopic Analyses

Stable isotopic analyses combined with bulk compositional work were able to allow some disentangling of source inputs, this is especially true for CSG samples that look very similar based on molecular compositional data alone, but add the embodied wealth of information locked up in the stable isotopic signatures, specifically the δ^2H and δ^{13}C isotopic ratios, and the various CH_4 emissions start to show distinct source attributes.

For the majority of the source gases analysed, it was identified that microbial sources such as landfill gas, food digester gas, feedlot manure pond gas, swamp gas and wastewater treatment gas was broadly speaking constrained by acetoclastic and methylotrophic generation pathways.

The Sydney Basin and Gloucester Basin CSG samples plotted as mixed gases (source contributions from thermogenic and carbon dioxide reduction pathways). Other Basins outside of NSW such as the Cooper Basin in SA (natural gas) and deep parts of the Bowen CSG basin in QLD, plotted with thermogenic source characteristics. The Surat Basin CSG and Surat Basin gas seeps also consistently had strong inputs utilising CO_2 reduction pathways.

Other important lessons learned deal with the stochastic nature of gas samples and their propensity for alteration by sampling problems, atmospheric contamination and leakage problems, all of which necessitate as large a sample set as possible to get a true population statistic of the median and range of values that truly define the methane source. The last and final point deals with isotopic fractionation of gas samples, something that occurs all too easily, especially with leaks, diffusion of gases through organic materials and sampling problems (insufficient rinsing/flushing of gas sample containers, sampling gas below atmospheric pressure and insufficient equilibration times to allow gas source and sample container to reach isotopic equilibration, thus ensuring a representative sample).

Although it was planned that ambient methane would be analysed for carbon and hydrogen isotopes it could not be technically achieved with the time and resources available, even though considerable effort was expended to build a prototype cryogenic trap module. The single trap design was shown to work but not reproducibly, due to the large concomitant nitrogen peak that elutes just before the concentrated methane peak. Subsequent design changes incorporating a possible second cryogenic trap should achieve a smaller carryover peak of nitrogen. The air samples were successfully analysed for bulk composition and for δ^{13}C CO_2, the NSW samples all plotted in the normal zone for clean air samples, no significant overprinting, at least not for CO_2.

The three main issues identified at the beginning of the short isotope Picarro campaign that needed to be investigated and ultimately overcome were:

- Less than ideal precision of δ^{13}C values at low methane concentrations;
- Verification and calibration of the instrument responses;
- Impact of sampling techniques on results.

The instrument noise in the δ^{13}C values (see Figure 8.12 for example) can be overcome by running consistent samples for extended periods of time, or by taking a large number of samples. Extended sampling can only overcome the high noise issue if the same air is able to be sampled consistently, which is difficult for vehicle monitoring of constantly moving airsheds. Repeated sampling for days and weeks is another method to overcome this problem, but this option may be expensive and could be difficult for remote locations.

Sampling air into static sampling vessels for longer analysis times was considered. The Flexfoil ® gas bags designed to store small molecular weight samples were not appropriate to store low concentration samples for either methane or isotope measurements. Solid metal vessels such as IsoTubes ® appear to be a better choice, however constant calibration of the instrument is required to make sure the numbers obtained are accurate. In addition, the effect of changing pressure that would occur in a solid inflexible vessel would need to be assessed and possibly accounted for during sample analysis.

One method that was not investigated due to time constraints is the MegaCore® sampling used by Rella et al. (2015). In this example, air is sampled in the field, while a concurrent system pumps the same ambient air into a very long storage tube. On returning to the sample to the lab, the air in the storage tube is connected to the Picarro and very slowly sampled, providing a replay of the ambient run. The instrument is constantly recalibrated during this laboratory run every 10-15 minutes.

The isotope Picarro instrument shows promise as an ambient method for measuring δ^{13}C, as it has a high temporal resolution compared to sampling for isotope mass spectrometry. It must be noted however that the sampling method requires very careful sampling methods, constant calibration and a thorough understanding of potential interferences to ensure it is both accurate and precise in measuring δ^{13}C. The method is also limited in that the instrument does not provide hydrogen isotope data, which limits to some degree its usefulness for source apportionment.

10 Conclusions

One of the primary aims of the project was to develop tractable methodology that could be applied across a range of activities to accurately measure CH_4 emissions. During the project, several methods were used in a range of applications. For detecting CH_4 sources, mobile surveys using a vehicle fitted with a cavity ringdown spectrometer was effective at locating even small sources while driving at highway speeds. Surveys of ambient CH_4 concentrations covering more than 25,000 km were made over the course of the project.

Flux measurements were made at most of the selected sites using several methods. While simple surface flux chamber methods are useful in many applications, they are labour intensive and are impractical for some very large sources due to the number of measurements necessary to characterise the emission source. Atmospheric methods often have application at some sites – for instance, eddy covariance and inverse modelling approaches have the potential to measure emissions over moderate to large-scale sources with fine temporal resolution but they require complex and specialised fixed installations with a large amount of data analyses and interpretation required to derive emission fluxes.

The tracer method used during this project shows considerable promise as a relatively simple and rapid yet accurate method for measuring emission rates from a wide range of sources. For small point sources such as CSG wells, it is a very robust method. For larger area sources, the tracer method is viable but consideration must be given to the area of the emission source and the distance downwind where measurements are made to ensure that adequate mixing of the tracer is achieved. It is also important to ensure that the analytical methods for determining the tracer concentration have sufficient sensitivity to cope with the potentially very low concentrations encountered in some applications.

The VOC component of the project has brought together a volume of information on the levels of source related organic compounds in the ambient air in the vicinity of land-use activities in regional NSW and provides an ambient VOC database for the Camden region. Emissions characterisation of the land-use sources, based on the prevalence and concentration of individual compounds, provides an insight into source recognition, emissions variability, and the processes that dictate source intensity. The determination of non-methane hydrocarbons, including aromatic compounds, in CSG sourced well gas allowed CSG operations, as a source of VOCs to ambient air, to be evaluated. A basis for future studies into the qualitative and quantitative impacts of various emission sources on air quality has now been established.

Analytical methods (molecular composition and stable isotope) used in gas geochemistry were successfully utilised for concentrated point source samples in the range 0.1 % to 100 % for CH_4 and/or carbon dioxide. Molecular composition using gas chromatography based natural gas analysers gave very reliable bulk composition results. A GC-IRMS was used to analyse carbon and hydrogen isotopes on CSG and microbial gases from landfill and wastewater treatment plants. Plots of stable isotope data allowed seemingly similar gas samples to be differentiated into different categories and contributing source characteristics identified. Contributions from thermogenic, CO_2 reduction and acetoclastic/methylotrophic utilisation were able to be made for samples with mixed origins.

Some gas sampling techniques were found to be unsuited for isotopic analyses because they tended to fractionate the isotopic signature of the gas yielding unreliable results. Extended periods of sample storage may also affect isotopic analyses and consideration must be given to the type of storage containers used for sample collection and storage.

Analyses of ambient CH_4 for carbon and hydrogen isotopes were not possible using the GC-IRMS system directly because of the low concentration of CH_4. A prototype device designed to cryogenically concentrate ambient CH_4 was trialled; however it was adversely affected by excessive co-trapping of ambient nitrogen. Further development of this system is required.

Trials were performed with cavity ringdown spectrometers to measure isotopic ratios of ^{13}C:^{12}C in ambient CH_4. Although this technique is now in widespread use, there are some limitations with respect to using these data for source apportionment. With the instruments trialled in this project, it was apparent that significantly elevated CH_4 concentrations were required to achieve meaningful results – at concentration much below about 5 ppm, there was a large amount of noise in the data making attribution difficult. Another problem related to calibrations. In both instruments, the measured $\delta^{13}C$ was significantly offset from the true value. Regular calibration of the isotope data of these instruments requires specialised standards which are not widely available. Hence, care must be exercised when interpreting the results, especially if instruments are used in mobile surveys.

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Appendix A – VOC Detection Limits

Appendix A Table Key:

IDL	Instrument Detection Limit; minimum detectable concentration in the sample as presented to the instrument
MDL	Method Detection Limit; accounts for parameters associated with sample preparation and analysis
LOR	Limit of Reporting; a conservative limit to account for sampling and analytical variables

A.1 Detection and reporting limits for PAMS hydrocarbon VOCs by GCFID and GCMS

Table A.1.1 Statistical and GCMS/GCFID signal derived detection and reporting limits for the hydrocarbon VOC suite

Hydrocarbon VOCs	Statistical Limits, ppbv			Chromatographic/Mass Spectral Limits, ppbv		
Compound	IDL	MDL	LOR	IDL	MDL	LOR
Ethene (GCFID)	0.3	0.6	1.9	0.4	0.7	2.2
Ethane (GCFID)	0.4	0.7	2.2	0.4	0.8	2.3
Acetylene (GCFID)	0.4	0.9	2.7	0.4	0.8	2.4
Propene	0.2	0.4	1.1	0.12	0.2	0.7
Propane	0.1	0.3	0.9	0.17	0.3	1.0
Isobutane	0.2	0.4	1.2	0.05	0.09	0.3
1-Butene	0.2	0.4	1.2	0.06	0.1	0.3
n-Butane	0.1	0.3	0.9	0.05	0.1	0.3
trans-2-Butene	0.1	0.3	0.9	0.05	0.1	0.3
cis-2-Butene	0.1	0.2	0.7	0.05	0.1	0.3
Isopentane	0.1	0.3	0.8	0.03	0.06	0.2
1-Pentene	0.07	0.1	0.4	0.04	0.08	0.2
n-Pentane	0.2	0.4	1.2	0.04	0.07	0.2
Isoprene	0.2	0.4	1.2	0.03	0.06	0.2
trans-2-Pentene	0.2	0.4	1.1	0.04	0.08	0.2
cis-2-Pentene	0.1	0.2	0.6	0.04	0.09	0.3
2,2-Dimethylbutane	0.1	0.2	0.7	0.02	0.04	0.1
Cyclopentane	0.2	0.3	1.0	0.04	0.08	0.2
2,3-Dimethylbutane	0.2	0.3	1.0	0.04	0.08	0.2
2-Methylpentane	0.1	0.2	0.7	0.03	0.07	0.2
3-Methylpentane	0.1	0.3	0.8	0.03	0.05	0.2
1-Hexene	0.07	0.1	0.4	0.03	0.07	0.2
n-Hexane	0.2	0.3	1.0	0.03	0.07	0.2

Hydrocarbon VOCs	Statistical Limits, ppbv			Chromatographic/Mass Spectral Limits, ppbv		
Compound	IDL	MDL	LOR	IDL	MDL	LOR
Methylcyclopentane	0.2	0.3	0.9	0.02	0.04	0.1
2,4-Dimethylpentane	0.2	0.3	0.9	0.01	0.03	0.09
Benzene	0.1	0.3	0.8	0.01	0.1	0.3
Cyclohexane	0.1	0.3	0.8	0.02	0.03	0.1
2-Methylhexane	0.1	0.3	0.8	0.02	0.03	0.09
2,3-Dimethylpentane	0.2	0.3	0.9	0.02	0.03	0.1
3-Methylhexane	0.1	0.2	0.6	0.01	0.02	0.06
Isooctane	0.1	0.3	0.8	0.01	0.02	0.06
n-Heptane	0.1	0.2	0.7	0.01	0.03	0.08
Methylcyclohexane	0.1	0.2	0.7	0.01	0.02	0.06
2,3,4-Trimethylpentane	0.1	0.2	0.6	0.01	0.02	0.05
Toluene	0.09	0.2	0.5	0.007	0.03	0.08
2-Methylheptane	0.08	0.2	0.5	0.01	0.02	0.07
3-Methylheptane	0.1	0.2	0.6	0.008	0.02	0.05
n-Octane	0.09	0.2	0.5	0.009	0.02	0.05
Ethylbenzene	0.07	0.1	0.4	0.002	0.009	0.03
m- + p-Xylene	0.09	0.2	0.5	0.002	0.009	0.03
Styrene	0.09	0.2	0.6	0.002	0.009	0.03
o-Xylene	0.07	0.1	0.4	0.002	0.007	0.02
n-Nonane	0.08	0.2	0.5	0.003	0.007	0.02
Isopropylbenzene	0.09	0.2	0.5	0.002	0.009	0.03
n-Propylbenzene	0.08	0.2	0.5	0.002	0.006	0.02
m-Ethyltoluene	0.05	0.1	0.3	0.002	0.007	0.02
p-Ethyltoluene	0.08	0.2	0.5	0.002	0.006	0.02
1,3,5-Trimethylbenzene	0.08	0.2	0.5	0.003	0.01	0.04
o-Ethyltoluene	0.07	0.1	0.4	0.002	0.008	0.02
1,2,4-Trimethylbenzene	0.05	0.09	0.3	0.002	0.007	0.02
n-Decane	0.07	0.1	0.4	0.005	0.01	0.03
1,2,3-Trimethylbenzene	0.04	0.08	0.2	0.002	0.008	0.02
1,3-Diethylbenzene	0.05	0.1	0.3	0.001	0.006	0.02
1,4-Diethylbenzene	0.04	0.07	0.2	0.001	0.006	0.02
n-Undecane	0.1	0.2	0.7	0.006	0.01	0.04
n-Dodecane	0.1	0.2	0.6	0.01	0.02	0.06
Average Limit (GCMS)	0.1	0.2	0.7	0.02	0.05	0.15

A.2 Detection and reporting limits for TO-15 air toxic VOCs by GCMS

Table A.2.1 Statistical and GCMS signal derived detection and reporting limits for the air toxics VOC suite

Air Toxics VOCs	Statistical Limit, ppbv			Chromatographic/Mass Spectral Limit, ppbv		
Compound	IDL	MDL	LOR	IDL	MDL	LOR
Dichlorodifluoromethane	0.1	0.2	0.7	0.009	0.02	0.05
Chloromethane	0.06	0.1	0.4	0.06	0.1	0.4
1,2-Dichloro-1,1,2,2-tetrafluoroethane	0.1	0.3	0.8	0.006	0.01	0.04
Chloroethene	0.09	0.2	0.5	0.06	0.1	0.4
1,3-Butadiene	0.1	0.2	0.7	0.06	0.1	0.3
Bromomethane	0.1	0.2	0.7	0.03	0.06	0.2
Chloroethane	0.3	0.7	2.0	0.3	0.7	2.0
Ethanol	0.2	0.4	1.3	0.2	0.4	1.3
Acrolein	0.1	0.2	0.6	0.1	0.2	0.6
Acetone	0.1	0.2	0.7	0.1	0.2	0.6
Trichlorofluoromethane	0.2	0.3	0.9	0.008	0.02	0.05
Isopropanol	0.4	0.7	2.1	0.1	0.2	0.7
1,1-Dichloroethene	0.1	0.2	0.7	0.01	0.02	0.07
Dichloromethane	0.2	0.3	1.0	0.02	0.04	0.1
1,1,2-Trichloro-1,2,2-trifluoroethane	0.1	0.3	0.9	0.004	0.009	0.03
trans-1,2-Dichloroethene	0.1	0.3	0.8	0.009	0.02	0.05
1,1-Dichloroethane	0.2	0.3	1.0	0.02	0.03	0.1
Methyl tert-butyl ether	0.2	0.3	0.9	0.01	0.03	0.09
Ethenyl acetate	0.3	0.6	1.8	0.09	0.2	0.5
2-Butanone	0.1	0.3	0.9	0.1	0.2	0.7
cis-1,2-Dichloroethene	0.1	0.2	0.7	0.009	0.02	0.06
Ethyl acetate	0.2	0.3	0.9	0.03	0.06	0.2
Chloroform	0.1	0.3	0.8	0.007	0.01	0.04
Tetrahydrofuran	0.1	0.3	0.8	0.02	0.05	0.1
1,2-Dichloroethane	0.08	0.2	0.5	0.02	0.03	0.1
1,1,1-Trichloroethane	0.2	0.3	1.0	0.005	0.01	0.03
Carbon tetrachloride	0.1	0.3	0.9	0.005	0.01	0.03
1,2-Dichloropropane	0.09	0.2	0.5	0.01	0.02	0.06
Bromodichloromethane	0.1	0.2	0.6	0.006	0.01	0.03

Air Toxics VOCs	Statistical Limit, ppbv			Chromatographic/Mass Spectral Limit, ppbv		
Compound	IDL	MDL	LOR	IDL	MDL	LOR
Trichloroethylene	0.1	0.3	0.8	0.005	0.01	0.03
1,4-Dioxane	0.06	0.1	0.4	0.06	0.1	0.4
Methyl methacrolate	0.06	0.1	0.4	0.02	0.04	0.1
cis-1,3-Dichloropropene	0.1	0.2	0.7	0.01	0.02	0.06
Methyl isobutyl ketone	0.1	0.3	0.8	0.02	0.03	0.09
trans-1,3-Dichloropropene	0.1	0.2	0.7	0.01	0.02	0.07
1,1,2-Trichloroethane	0.1	0.2	0.7	0.004	0.007	0.02
Methyl butyl ketone	0.2	0.4	1.1	0.02	0.04	0.1
Dibromochloromethane	0.09	0.2	0.6	0.004	0.008	0.02
1,2-Dibromoethane	0.08	0.2	0.5	0.006	0.01	0.04
Tetrachloroethylene	0.1	0.2	0.7	0.003	0.005	0.02
Chlorobenzene	0.07	0.1	0.4	0.004	0.008	0.02
Bromoform	0.07	0.1	0.4	0.003	0.007	0.02
1,1,2,2-Tetrachloroethane	0.1	0.3	0.8	0.003	0.006	0.02
Benzyl chloride	0.2	0.3	1.0	0.003	0.006	0.02
1,3-Dichlorobenzene	0.1	0.2	0.6	0.003	0.005	0.02
1,4-Dichlorobenzene	0.1	0.2	0.7	0.002	0.004	0.01
1,2-Dichlorobenzene	0.1	0.2	0.7	0.002	0.004	0.01
1,2,4-Trichlorobenzene	0.2	0.3	1.0	0.003	0.005	0.02
Naphthalene	0.08	0.2	0.5	0.004	0.008	0.02
Hexachloro-1,3-butadiene	0.1	0.2	0.6	0.001	0.003	0.009
Average Limit	0.1	0.3	0.8	0.03	0.07	0.2

Appendix B – Ambient VOCs Site Results

Appendix B Table Key:
ND Not detected at or above the method detection limit (refer detection limit data, Appendix A)
< MDL Less than the method detection limit; result reported for use in characterisation studies only

B.1 Natural Sources

Table B.1.1 PAMS hydrocarbon VOCs measured at Yaegl Nature Reserve and Cuba State Forest

Hydrocarbon VOCs	Ambient Concentration, ppbv						
	Yaegl Reserve	Cuba State Forest					
	Forest	River	Bushland	River	Bushland	Bushland	Bushland
	12-Jul-14	14-Oct-14	14-Oct-14	02-Dec-14	02-Dec-14	04-Aug-15 #1 9:30am	04-Aug-15 #2 10:10am
Ethene	3.9	ND	ND	0.46 (< MDL)	0.86	ND	ND
Ethane	2.3	ND	ND	ND	ND	ND	ND
Acetylene	1.2	ND	ND	ND	ND	ND	ND
Propene	0.25	ND	ND	0.28	0.42	ND	ND
Propane	0.72	ND	ND	ND	ND	ND	ND
Isobutane	0.29	0.56	0.88	0.27	0.33	ND	ND
1-Butene	ND	ND	ND	0.50	ND	ND	ND
n-Butane	0.14	ND	ND	ND	ND	ND	ND
trans-2-Butene	ND	ND	ND	ND	ND	ND	ND
cis-2-Butene	ND	ND	ND	ND	ND	ND	ND
Isopentane	ND	ND	ND	ND	ND	ND	ND
1-Pentene	ND	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND	ND
Isoprene	ND	ND	ND	1.7	1.3	ND	ND
trans-2-Pentene	ND	ND	ND	ND	ND	ND	ND
cis-2-Pentene	ND	ND	ND	ND	ND	ND	ND
2,2-Dimethylbutane	ND	ND	ND	ND	ND	ND	ND
Cyclopentane	ND	ND	ND	ND	ND	ND	ND
2,3-Dimethylbutane	ND	ND	ND	ND	ND	ND	ND
2-Methylpentane	ND	ND	ND	ND	ND	ND	ND

Hydrocarbon VOCs	Ambient Concentration, ppbv						
	Yaegl Reserve	Cuba State Forest					
	Forest	River	Bushland	River	Bushland	Bushland	Bushland
	12-Jul-14	14-Oct-14	14-Oct-14	02-Dec-14	02-Dec-14	04-Aug-15 #1 9:30am	04-Aug-15 #2 10:10am
3-Methylpentane	0.14	ND	0.03 (< MDL)	ND	ND	ND	ND
1-Hexene	ND	ND	ND	ND	ND	ND	ND
n-Hexane	ND	ND	ND	ND	ND	ND	ND
Methylcyclopentane	ND	ND	ND	ND	ND	ND	ND
2,4-Dimethylpentane	ND	ND	ND	ND	ND	ND	ND
Benzene	0.77	ND	ND	0.06 (< MDL)	ND	ND	ND
Cyclohexane	ND	ND	ND	ND	ND	ND	ND
2-Methylhexane	ND	ND	ND	ND	ND	ND	ND
2,3-Dimethylpentane	ND	ND	ND	ND	ND	ND	ND
3-Methylhexane	ND	ND	ND	ND	ND	ND	ND
Isooctane	ND	ND	ND	ND	ND	ND	ND
n-Heptane	ND	ND	ND	ND	ND	ND	ND
Methylcyclohexane	ND	ND	ND	ND	ND	ND	ND
2,3,4-Trimethylpentane	ND	ND	ND	ND	ND	ND	ND
Toluene	0.26	ND	0.01 (< MDL)	0.007 (< MDL)	0.03 (< MDL)	0.18	0.04
2-Methylheptane	0.11	ND	0.03	ND	ND	ND	ND
3-Methylheptane	ND	ND	ND	ND	ND	ND	ND
n-Octane	ND	ND	ND	ND	ND	ND	ND
Ethylbenzene	0.04	ND	ND	0.002 (< MDL)	ND	0.01	ND
m- + p-Xylene	0.17	ND	ND	0.004 (< MDL)	ND	0.03	ND
Styrene	ND	ND	ND	ND	ND	ND	ND
o-Xylene	0.08	ND	ND	ND	ND	0.01	ND
n-Nonane	0.03	ND	0.008	ND	ND	ND	ND
Isopropylbenzene	ND	ND	ND	ND	ND	ND	ND
n-Propylbenzene	0.02	ND	ND	ND	ND	ND	ND
m-Ethyltoluene	0.08	ND	ND	ND	ND	ND	ND
p-Ethyltoluene	0.04	ND	ND	ND	ND	ND	ND
1,3,5-Trimethylbenzene	0.02	ND	ND	ND	ND	ND	ND

Hydrocarbon VOCs	Ambient Concentration, ppbv						
	Yaegl Reserve	Cuba State Forest					
	Forest	River	Bushland	River	Bushland	Bushland	Bushland
	12-Jul-14	14-Oct-14	14-Oct-14	02-Dec-14	02-Dec-14	04-Aug-15 #1 9:30am	04-Aug-15 #2 10:10am
o-Ethyltoluene	0.05	ND	ND	ND	ND	ND	ND
1,2,4-Trimethylbenzene	0.22	ND	ND	ND	ND	0.01	ND
n-Decane	0.08	0.02	0.02	ND	ND	ND	ND
1,2,3-Trimethylbenzene	0.06	ND	ND	ND	ND	ND	ND
1,3-Diethylbenzene	0.01	ND	ND	ND	ND	ND	ND
1,4-Diethylbenzene	0.06	ND	ND	ND	ND	ND	ND
n-Undecane	0.03	0.02	0.01	ND	ND	ND	ND
n-Dodecane	0.02 (< MDL)	ND	0.01 (< MDL)	ND	ND	ND	ND

Table B.1.2 TO-15 air toxics VOCs measured at Yaegl Nature Reserve and Cuba State Forest

Air Toxics VOCs	Ambient Concentration, ppbv						
	Yaegl Reserve	Cuba State Forest					
	Forest	River	Bushland	River	Bushland	Bushland	Bushland
	12-Jul-14	14-Oct-14	14-Oct-14	02-Dec-14	02-Dec-14	04-Aug-15 #1 9:30am	04-Aug-15 #2 10:10am
Dichlorodifluoromethane	0.62	0.48	0.47	0.62	0.56	0.51	0.54
Chloromethane	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloro-1,1,2,2-tetrafluoroethane	ND	ND	ND	ND	ND	ND	ND
Chloroethene	ND	ND	ND	ND	ND	ND	ND
1,3-Butadiene	ND	ND	ND	ND	ND	ND	ND
Bromomethane	ND	ND	ND	0.05 (< MDL)	0.04 (< MDL)	ND	ND
Chloroethane	ND	ND	ND	ND	ND	ND	ND
Ethanol	4.4	1.4	2.9	4.0	7.2	6.4	1.4
Acrolein	0.87	ND	ND	0.36	0.54	ND	ND
Acetone	7.1	2.9	3.0	14.1	18.7	2.2	2.0
Trichlorofluoromethane	0.28	0.24	0.23	0.31	0.30	0.30	0.27
Isopropanol	3.6	1.3	0.39	0.30	0.33	ND	ND
1,1-Dichloroethene	ND	ND	ND	ND	ND	ND	ND
Dichloromethane	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichloro-1,2,2-trifluoroethane	ND	ND	ND	0.09	0.07	0.09	0.05
trans-1,2-Dichloroethene	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND	ND	ND	ND
Methyl tert-butyl ether	ND	ND	ND	ND	ND	ND	ND
Ethenyl acetate	ND	ND	ND	ND	ND	ND	ND
2-Butanone	ND	ND	ND	0.45	0.93	ND	ND
cis-1,2-Dichloroethene	ND	ND	ND	ND	ND	ND	ND
Ethyl acetate	ND	ND	ND	ND	ND	ND	ND
Chloroform	0.06	ND	ND	ND	ND	ND	ND
Tetrahydrofuran	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.09	0.07	0.08	0.10	0.10	0.08	0.09
1,2-Dichloropropane	ND	ND	ND	ND	ND	ND	ND

Air Toxics VOCs	Ambient Concentration, ppbv						
	Yaegl Reserve	Cuba State Forest					
	Forest	River	Bushland	River	Bushland	Bushland	Bushland
	12-Jul-14	14-Oct-14	14-Oct-14	02-Dec-14	02-Dec-14	04-Aug-15 #1 9:30am	04-Aug-15 #2 10:10am
Bromodichloromethane	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene	ND	ND	ND	ND	ND	ND	ND
1,4-Dioxane	ND	ND	ND	ND	ND	ND	ND
Methyl methacrolate	ND	ND	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND
Methyl isobutyl ketone	ND	ND	ND	ND	ND	ND	ND
trans-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND	ND	ND
Methyl butyl ketone	ND	ND	ND	0.04 (< MDL)	0.08	ND	ND
Dibromochloromethane	ND	ND	ND	ND	ND	ND	ND
1,2-Dibromoethane	ND	ND	ND	ND	ND	ND	ND
Tetrachloroethylene	ND	ND	ND	ND	ND	ND	ND
Chlorobenzene	ND	ND	ND	ND	ND	ND	ND
Bromoform	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	ND	ND	ND	0.01	0.007	ND	ND
1,3-Dichlorobenzene	0.008	ND	0.008	0.01	0.007	ND	ND
1,4-Dichlorobenzene	0.02	0.010	0.01	0.01	0.005	ND	ND
1,2-Dichlorobenzene	ND	ND	ND	0.009	0.005	ND	ND
1,2,4-Trichlorobenzene	ND	0.02	0.03	0.03	0.009	0.01	0.009
Naphthalene	ND	ND	ND	0.04	0.01	0.03	0.03
Hexachloro-1,3-butadiene	ND	ND	ND	ND	ND	ND	ND

B.2 Camden Region

Appendix B.2 Site Information:

Site 1	Medhurst Rd, Gilead	Semi-rural; near AGL CSG plant, in vicinity of motorway
Site 2	Glenlee Rd, Spring Farm	Composting facility; near train line, coal pits in vicinity
Site 3	Glenlee Rd, Spring Farm	Waste Centre; at SW boundary of landfill area
Site 4	Adriana Lane, Mount Annan	Suburban reserve; at northern edge of pond
Site 5	Glenlee Rd, Spring Farm	Rural farmland; at rail line underpass
Site 6	Racecourse Rd, Menangle Park	Racecourse; entrance roadway, semi-rural surrounds
Site 7	Glenlee Rd, Ambarvale	Semi-rural; near Menangle Rd intersection
Site 8	Cummins Rd / Fitzpatrick St, Menangle Park	Semi-rural; low density housing to south
Site 9	Menangle Road, Menangle	Semi-rural; off main road, in vicinity of woodland & river
Site 10	Off Woodbridge Rd, Menangle	Semi-rural/scrub land; on road to agricultural college

B.2.1 CAMDEN WINTER CAMPAIGN

Table B.2.1.1 PAMS hydrocarbon VOCs measured at the Camden regional sites for the winter monitoring campaign on 06-Aug-14

Hydrocarbon VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Ethene	1.0	0.79	1.5	1.5	1.7	15.5	0.89	0.97	2.0	0.66 (< MDL)
Ethane	4.4	7.0	6.9	5.2	6.8	10.0	7.4	6.9	11.0	8.3
Acetylene	ND	ND	ND	ND	ND	10.0	ND	ND	ND	ND
Propene	0.30	0.50	0.24	0.33	0.36	2.8	0.38	0.39	0.30	0.30
Propane	1.6	3.3	2.6	3.1	2.3	3.5	3.7	3.1	6.1	3.9
Isobutane	0.73	1.1	1.3	1.4	1.2	2.3	1.2	1.6	2.3	1.4
1-Butene	ND	0.54	ND	ND	0.28	0.38	0.27	0.22	ND	ND
n-Butane	0.91	1.9	1.5	1.5	1.8	3.5	2.0	1.9	2.6	2.0
trans-2-Butene	ND	ND	ND	ND	ND	0.25	ND	ND	ND	ND
cis-2-Butene	ND	ND	ND	ND	ND	0.19	ND	ND	ND	ND
Isopentane	0.53	0.94	0.59	0.73	0.81	3.7	1.0	0.90	1.1	0.89
1-Pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	0.25	0.82	0.52	0.46	0.67	1.9	0.74	0.84	0.91	0.65
Isoprene	ND	ND	ND	ND	ND	0.18	0.17	ND	ND	ND
trans-2-Pentene	ND	ND	ND	ND	ND	0.22	ND	ND	ND	ND
cis-2-Pentene	ND	ND	ND	ND	ND	0.10	ND	ND	ND	ND
2,2-Dimethylbutane	ND	ND	ND	ND	ND	0.08	ND	ND	ND	ND
Cyclopentane	ND	ND	ND	ND	ND	0.16	ND	ND	ND	ND

Hydrocarbon VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
2,3-Dimethylbutane	ND	ND	ND	ND	ND	0.21	ND	ND	ND	ND
2-Methylpentane	ND	0.14	ND	ND	0.15	1.0	0.15	0.15	0.26	0.15
3-Methylpentane	ND	0.09	ND	ND	0.06	0.63	0.09	0.06	0.10	0.08
1-Hexene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Hexane	0.09	0.20	0.15	0.19	0.19	0.82	0.21	0.22	0.31	0.20
Methylcyclopentane	ND	ND	ND	0.08	0.12	0.45	0.09	0.08	0.15	0.10
2,4-Dimethylpentane	ND	ND	ND	ND	ND	0.18	ND	ND	ND	ND
Benzene	0.16	0.17	0.33	0.35	0.19	2.0	0.14	0.12	0.12	0.07 (< MDL)
Cyclohexane	ND	0.11	0.10	0.14	0.14	0.97	0.18	0.16	0.19	0.15
2-Methylhexane	ND	ND	0.03 (< MDL)	ND	ND	0.24	0.04	0.03 (< MDL)	0.05	0.04
2,3-Dimethylpentane	ND	ND	ND	ND	ND	0.08	ND	ND	ND	ND
3-Methylhexane	ND	0.03	ND	ND	ND	0.23	0.03	ND	0.06	0.04
Isooctane	0.02 (< MDL)	ND	ND	0.04	0.02	0.19	ND	ND	0.03	0.04
n-Heptane	ND	0.08	ND	0.06	0.07	0.24	0.07	0.08	0.13	0.08
Methylcyclohexane	0.07	0.21	0.13	0.12	0.19	0.30	0.21	0.19	0.26	0.14
2,3,4-Trimethylpentane	ND	ND	ND	ND	ND	0.05	ND	ND	ND	ND
Toluene	0.18	0.27	0.17	0.37	0.16	3.9	0.18	0.18	0.30	0.16
2-Methylheptane	ND	ND	0.14	0.11	ND	ND	ND	ND	0.07	0.06
3-Methylheptane	ND	ND	ND	ND	ND	0.06	ND	ND	ND	ND
n-Octane	ND	0.03	ND	ND	0.02	0.09	0.02	0.02	0.04	0.03
Ethylbenzene	0.02	0.03	0.02	0.06	0.03	0.43	0.02	0.03	0.07	0.03

Hydrocarbon VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
m- + p-Xylene	0.06	0.11	0.04	0.22	0.09	1.8	0.06	0.13	0.24	0.02
Styrene	0.01	0.03	0.01	0.03	0.03	0.15	0.01	0.03	0.02	0.03
o-Xylene	0.03	0.05	0.03	0.10	0.04	0.58	0.02	0.06	0.12	0.03
n-Nonane	ND	0.03	ND	0.04	0.02	0.04	0.02	0.03	0.05	0.03
Isopropylbenzene	ND	ND	ND	0.005 (< MDL)	ND	0.02	ND	ND	0.02	0.02
n-Propylbenzene	0.005 (< MDL)	0.01	0.01	0.02	0.01	0.10	0.007	0.02	0.04	0.02
m-Ethyltoluene	0.02	0.03	0.01	0.07	0.04	0.34	0.02	0.06	0.10	0.02
p-Ethyltoluene	0.007	0.01	0.007	0.03	0.02	0.13	0.005 (< MDL)	0.03	0.06	0.02
1,3,5-Trimethylbenzene	0.005 (< MDL)	0.02	0.002 (< MDL)	0.03	0.02	0.14	0.007 (< MDL)	0.03	0.05	0.01 (< MDL)
o-Ethyltoluene	0.009	0.02	0.009	0.05	0.02	0.13	0.008 (< MDL)	0.04	0.07	0.02
1,2,4-Trimethylbenzene	0.02	0.06	0.02	0.16	0.12	0.46	0.03	0.17	0.36	0.01
n-Decane	0.03	0.06	0.05	0.11	0.07	0.06	0.02	0.11	0.12	0.03
1,2,3-Trimethylbenzene	0.008 (< MDL)	0.06	0.01	0.06	0.05	0.10	0.01	0.06	0.11	0.02
1,3-Diethylbenzene	ND	ND	ND	ND	ND	0.02	ND	ND	0.02	0.01
1,4-Diethylbenzene	ND	ND	ND	ND	ND	0.06	ND	ND	0.08	0.01
n-Undecane	0.02	0.05	0.05	0.09	0.05	0.06	0.01 (< MDL)	0.09	0.05	0.03
n-Dodecane	0.01 (< MDL)	0.02	0.02	0.03	0.04	0.03	0.009 (< MDL)	0.07	ND	0.03

Table B.2.1.2 TO-15 air toxics VOCs measured at the Camden regional sites for the winter monitoring campaign on 06-Aug-14

Air Toxics VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Dichlorodifluoromethane	0.49	0.74	0.52	0.60	0.57	0.55	0.59	0.59	0.45	0.54
Chloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloro-1,1,2,2-tetrafluoroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Butadiene	ND	ND	ND	ND	0.59	0.35	ND	0.10 (< MDL)	ND	ND
Bromomethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethanol	1.9	2.4	1.7	2.6	5.0	6.8	4.6	3.1	2.1	1.3
Acrolein	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acetone	2.6	5.4	4.8	5.7	5.2	3.6	3.1	3.8	4.3	5.5
Trichlorofluoromethane	0.24	0.32	0.24	0.29	0.30	0.26	0.29	0.30	0.21	0.27
Isopropanol	1.3	2.6	1.9	2.1	3.1	0.98	1.2	3.4	1.7	0.68
1,1-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloromethane	ND	ND	ND	0.20	ND	ND	ND	ND	ND	ND
1,1,2-Trichloro-1,2,2-trifluoroethane	0.06	0.08	0.06	0.07	0.06	0.06	0.06	0.07	0.04	0.07
trans-1,2-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl tert-butyl ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethenyl acetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Butanone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Air Toxics VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
cis-1,2-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethyl acetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroform	0.03	ND	ND	0.09	0.10	0.06	ND	ND	ND	ND
Tetrahydrofuran	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.07	0.11	0.08	0.09	0.09	0.09	0.09	0.09	0.07	0.05
1,2-Dichloropropane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene	ND	ND	ND	ND	ND	ND	ND	ND	0.03	ND
1,4-Dioxane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl methacrolate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl isobutyl ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
trans-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl butyl ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromochloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dibromoethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tetrachloroethylene	0.01	ND	ND	ND	ND	ND	ND	ND	0.01	ND
Chlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	0.02	ND

Air Toxics VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Bromoform	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	0.01	ND
1,4-Dichlorobenzene	ND	ND	ND	0.01	0.006	ND	ND	0.010	0.02	0.007
1,2-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	0.01	ND
1,2,4-Trichlorobenzene	ND	ND	ND	ND	ND	ND	ND	0.03	ND	ND
Naphthalene	ND	ND	ND	ND	ND	0.14	0.15	0.13	0.08	0.13
Hexachloro-1,3-butadiene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

B.2.2 CAMDEN SPRING CAMPAIGN

Table B.2.2.1 PAMS hydrocarbon VOCs measured at the Camden regional sites for the spring monitoring campaign on 20-Nov-14

Hydrocarbon VOCS	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Ethene	0.41 (< MDL)	ND	0.34 (< MDL)	0.19 (< MDL)	ND	ND	ND	ND	ND	ND
Ethane	0.27 (< MDL)	ND	0.31 (< MDL)	0.25 (< MDL)	0.32 (< MDL)	ND	ND	0.46 (< MDL)	0.52 (< MDL)	0.27 (< MDL)
Acetylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propane	0.27 (< MDL)	0.56	0.51	0.54	0.29 (< MDL)	0.21 (< MDL)	0.45	0.42	0.32 (< MDL)	0.28 (< MDL)
Isobutane	1.5	1.8	1.4	1.3	1.4	1.3	1.4	1.5	1.4	1.4
1-Butene	0.46	ND	ND	ND	ND	0.37	ND	ND	ND	ND
n-Butane	ND	1.00	1.00	0.45	ND	0.12	0.23	0.42	ND	ND
trans-2-Butene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-2-Butene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Isopentane	0.15	0.73	0.57	0.35	ND	ND	0.21	0.16	ND	ND
1-Pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	ND	0.27	0.33	ND	ND	ND	0.11	ND	ND	ND
Isoprene	0.27	0.13	0.14	0.24	ND	0.11	0.22	ND	0.20	0.04 (< MDL)
trans-2-Pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-2-Pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,2-Dimethylbutane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cyclopentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Hydrocarbon VOCS	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
2,3-Dimethylbutane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Methylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylpentane	ND	ND	0.03 (< MDL)	ND	ND	ND	ND	ND	ND	ND
1-Hexene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Hexane	ND	0.05 (< MDL)	ND	ND	ND	ND	ND	ND	ND	ND
Methylcyclopentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-Dimethylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzene	0.24	0.22	0.26	0.19	0.14	ND	0.06 (< MDL)	0.03 (< MDL)	ND	ND
Cyclohexane	ND	0.04	ND	ND	ND	ND	ND	ND	ND	ND
2-Methylhexane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,3-Dimethylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylhexane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Isooctane	ND	ND	0.03	ND	ND	ND	ND	ND	ND	ND
n-Heptane	ND	0.04	ND	ND	ND	ND	ND	ND	ND	ND
Methylcyclohexane	ND	0.04	ND	ND	ND	ND	ND	ND	ND	ND
2,3,4-Trimethylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Toluene	0.18	0.81	0.33	0.29	0.16	0.09	0.22	0.11	0.11	0.09
2-Methylheptane	ND	ND	0.02 (< MDL)	0.03	0.07	ND	ND	0.08	0.04	0.04
3-Methylheptane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Octane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Hydrocarbon VOCS	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Ethylbenzene	0.04	0.15	0.05	0.05	0.05	0.02	0.04	0.03	0.02	0.02
m- + p-Xylene	0.13	0.71	0.17	0.20	0.13	0.06	0.11	0.08	0.07	0.06
Styrene	ND	0.06	ND	0.06	0.01	0.009	0.03	0.02	0.009	0.02
o-Xylene	0.05	0.28	0.06	0.07	0.04	0.02	0.04	0.03	0.02	0.02
n-Nonane	ND	0.06	0.02	0.02	ND	ND	0.02	0.02	ND	ND
Isopropylbenzene	ND	0.007 (< MDL)	ND	0.005 (< MDL)	ND	ND	ND	ND	ND	ND
n-Propylbenzene	0.01	0.04	0.01	0.02	0.007	0.003 (< MDL)	0.01	0.01	0.003 (< MDL)	0.005 (< MDL)
m-Ethyltoluene	0.03	0.13	0.04	0.08	0.01	0.02	0.03	0.03	0.02	0.02
p-Ethyltoluene	ND	0.06	ND	0.04	0.005 (< MDL)	0.01	ND	0.02	0.01	0.01
1,3,5-Trimethylbenzene	ND	0.07	ND	0.05	0.003 (< MDL)	0.006 (< MDL)	ND	0.01	0.005 (< MDL)	0.006 (< MDL)
o-Ethyltoluene	0.02	0.07	ND	0.05	0.007 (< MDL)	0.01	ND	0.02	0.01	0.01
1,2,4-Trimethylbenzene	ND	0.36	ND	0.22	0.02	0.04	0.05	0.09	0.04	0.05
n-Decane	ND	0.09	0.02	0.06	0.02	0.03	0.03	0.04	0.03	0.02
1,2,3-Trimethylbenzene	ND	0.11	ND	0.07	0.009	0.02	ND	0.04	0.02	0.02
1,3-Diethylbenzene	ND	0.01	ND	ND	ND	ND	ND	ND	ND	ND
1,4-Diethylbenzene	ND	0.02	ND	ND	ND	ND	ND	ND	ND	ND
n-Undecane	ND	0.09	0.02	0.07	ND	0.04	0.04	0.05	0.04	0.03
n-Dodecane	ND	0.03	0.008 (< MDL)	0.03	ND	0.02	0.02 (< MDL)	0.03	0.01 (< MDL)	0.02

Table B.2.2.2 TO-15 air toxic VOCs measured at the Camden regional sites for the spring monitoring campaign on 20-Nov-14

Air Toxic VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Dichlorodifluoromethane	0.51	0.52	0.56	0.54	0.54	0.43	0.50	0.50	0.50	0.55
Chloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloro-1,1,2,2-tetrafluoroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Butadiene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromomethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethanol	5.4	11.8	4.2	9.0	1.7	2.4	7.0	15.5	3.4	2.5
Acrolein	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acetone	4.5	5.1	4.7	5.9	5.0	3.9	4.5	8.4	3.7	5.1
Trichlorofluoromethane	0.27	0.25	0.28	0.26	0.28	0.21	0.25	0.25	0.23	0.27
Isopropanol	1.2	0.99	0.35	1.3	1.1	0.92	0.73	1.4	2.2	1.2
1,1-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichloro-1,2,2-trifluoroethane	0.07	0.08	0.07	0.06	0.06	0.05	0.06	0.06	0.05	0.07
trans-1,2-Dichloroethene	0.01 (< MDL)	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl tert-butyl ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethenyl acetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Butanone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Air Toxic VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
cis-1,2-Dichloroethene	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethyl acetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroform	ND	ND	ND	0.04	0.05	0.04	ND	ND	ND	ND
Tetrahydrofuran	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.08	0.09	0.09	0.09	0.09	0.07	0.08	0.08	0.08	0.08
1,2-Dichloropropane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene	0.01 (< MDL)	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,4-Dioxane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl methacrolate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	0.03	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl isobutyl ketone	0.52	0.07	ND	0.10	ND	0.03 (< MDL)	0.05	0.07	ND	ND
trans-1,3-Dichloropropene	0.14	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl butyl ketone	0.96	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromochloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dibromoethane	0.06	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tetrachloroethylene	0.009	0.008	ND	0.02	ND	ND	ND	ND	0.02	ND

Air Toxic VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Chlorobenzene	0.05	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoform	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	0.04	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.08	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	0.10	0.005 (< MDL)	ND	ND	ND	ND	ND	ND	ND	0.008
1,4-Dichlorobenzene	0.14	0.03	0.008	0.02	0.005	0.005	0.005	0.009	0.007	0.02
1,2-Dichlorobenzene	0.10	ND	ND	ND	ND	ND	ND	ND	ND	0.01
1,2,4-Trichlorobenzene	0.32	ND	ND	ND	ND	0.009	0.008	ND	0.007	0.04
Naphthalene	ND	ND	ND	ND	ND	0.04	0.02	0.04	0.05	0.44
Hexachloro-1,3-butadiene	0.06	ND	ND	ND	ND	ND	ND	ND	ND	ND

B.2.3 CAMDEN SUMMER CAMPAIGN

Table B.2.3.1 PAMS hydrocarbon VOCs measured at Camden regional sites for the summer monitoring campaign on 25-Feb-15

Hydrocarbon VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Ethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.44 (< MDL)
Ethane	0.27 (< MDL)	1.6	2.0	1.8	2.1	2.8	1.4	1.8	0.36 (< MDL)	1.3
Acetylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propene	0.27	ND	ND	0.33	ND	ND	ND	ND	ND	0.22 (< MDL)
Propane	0.72	0.88	0.83	1.5	0.75	0.89	0.38	0.92	0.51	0.39
Isobutane	2.8	3.3	3.3	4.0	3.2	3.2	2.5	3.0	2.9	3.6
1-Butene	0.57	ND	ND	0.59	ND	ND	ND	ND	ND	0.32
n-Butane	1.2	0.89	1.1	2.4	1.2	0.80	0.85	0.87	0.61	0.60
trans-2-Butene	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.06 (< MDL)
cis-2-Butene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Isopentane	0.58	0.28	0.46	0.49	0.48	0.41	0.39	0.39	0.15	0.29
1-Pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	0.33	0.21	0.26	0.28	0.24	0.40	0.27	0.16	0.15	0.16
Isoprene	ND	ND	ND	0.06	0.05 (< MDL)	ND	ND	0.50	ND	0.12
trans-2-Pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.08
cis-2-Pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.09

Hydrocarbon VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
2,2-Dimethylbutane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05
Cyclopentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.06 (< MDL)
2,3-Dimethylbutane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Methylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.07
1-Hexene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Hexane	0.12	0.10	0.11	0.12	0.12	0.07 (< MDL)	0.12	0.08	0.03 (< MDL)	0.11
Methylcyclopentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.09
2,4-Dimethylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05
Benzene	0.12	0.09 (< MDL)	0.05 (< MDL)	0.09 (< MDL)	0.07 (< MDL)	0.09 (< MDL)	0.05 (< MDL)	0.08 (< MDL)	0.09 (< MDL)	0.16
Cyclohexane	0.06	0.02 (< MDL)	0.07	0.09	0.06	0.02 (< MDL)	0.07	0.04	0.02 (< MDL)	0.11
2-Methylhexane	ND	ND	ND	0.09	ND	ND	ND	ND	ND	0.05
2,3-Dimethylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.07
3-Methylhexane	ND	ND	ND	0.11	ND	ND	ND	ND	ND	0.06
Isooctane	ND	ND	ND	0.02 (< MDL)	ND	ND	ND	ND	ND	0.08
n-Heptane	0.09	0.03	0.05	0.10	0.04	0.03 (< MDL)	0.03	0.05	0.02 (< MDL)	0.10
Methylcyclohexane	0.12	0.08	0.13	0.21	0.13	0.08	0.13	0.09	0.03	0.08
2,3,4-Trimethylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.06

Hydrocarbon VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Toluene	0.17	0.24	0.09	0.18	0.11	0.09	0.10	0.26	0.19	0.21
2-Methylheptane	ND	ND	ND	ND	0.02 (< MDL)	0.03	ND	ND	ND	0.05
3-Methylheptane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05
n-Octane	0.02 (< MDL)	0.02 (< MDL)	0.03	0.02	0.01 (< MDL)	ND	ND	ND	ND	0.04
Ethylbenzene	0.03	0.06	0.03	0.03	0.02	0.01	0.02	0.02	0.05	0.09
m- + p-Xylene	0.06	0.21	0.05	0.09	0.08	0.05	0.04	0.07	0.24	0.15
Styrene	0.04	0.007 (< MDL)	0.02	0.04	0.03	0.01	0.02	0.01	0.03	0.06
o-Xylene	0.03	0.09	0.02	0.03	0.03	0.02	0.02	0.03	0.09	0.09
n-Nonane	0.02	0.02	0.02	0.02	0.01	0.009	0.01	0.02	0.01	0.05
Isopropylbenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05
n-Propylbenzene	0.01	0.02	0.01	0.007	0.02	0.007	0.003 (< MDL)	0.008	0.02	0.04
m-Ethyltoluene	0.02	0.04	0.01	0.03	0.06	0.02	0.01	0.03	0.05	0.05
p-Ethyltoluene	0.01	0.02	0.01	0.02	0.03	0.01	0.004 (< MDL)	0.01	0.04	0.05
1,3,5-Trimethylbenzene	0.02	0.005 (< MDL)	0.010 (< MDL)	0.02	0.03	0.009 (< MDL)	0.005 (< MDL)	0.01	0.02	0.05
o-Ethyltoluene	0.01	0.03	0.01	0.02	0.04	0.01	0.005 (< MDL)	0.01	0.04	0.05
1,2,4-Trimethylbenzene	0.05	0.07	0.02	0.08	0.19	0.04	0.02	0.05	0.12	0.09
n-Decane	0.02	0.04	0.02	0.04	0.07	0.02	0.008 (< MDL)	0.04	0.02	0.04

Hydrocarbon VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
1,2,3-Trimethylbenzene	0.03	0.02	0.01	0.05	0.07	0.01	0.006 (< MDL)	0.02	0.04	0.05
1,3-Diethylbenzene	ND	ND	ND	ND	ND	ND	ND	ND	0.01	0.03
1,4-Diethylbenzene	ND	ND	ND	ND	ND	ND	ND	ND	0.02	0.04
n-Undecane	0.04	0.02	0.02	0.04	0.09	0.01	0.01 (< MDL)	0.02	0.02	0.03
n-Dodecane	ND	ND	ND	ND	ND	ND	ND	ND	0.02 (< MDL)	0.02

Table B.2.3.2 TO-15 compounds measured at the Camden regional sites for the summer monitoring campaign on 25-Feb-15

Air Toxic VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Dichlorodifluoromethane	0.49	0.51	0.50	0.51	0.55	0.52	0.42	0.47	0.48	0.37
Chloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloro-1,1,2,2-tetrafluoroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Butadiene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromomethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethanol	19.8	4.4	1.4	6.5	2.9	2.0	4.0	2.2	4.1	24.2
Acrolein	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acetone	5.4	4.7	2.0	4.3	2.3	2.4	1.8	2.4	2.4	11.0
Trichlorofluoromethane	0.22	0.22	0.21	0.22	0.21	0.23	0.18	0.20	0.20	0.17
Isopropanol	0.95	0.36	0.73	0.41	0.81	1.4	0.35	0.49	0.76	0.33
1,1-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.03
Dichloromethane	ND	0.05	ND	ND	0.07	0.03 (< MDL)	0.08	ND	ND	0.07
1,1,2-Trichloro-1,2,2-trifluoroethane	0.05	0.05	0.05	0.05	0.06	0.05	0.04	0.05	0.05	0.07
trans-1,2-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl tert-butyl ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethenyl acetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Air Toxic VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
2-Butanone	0.44	0.26	0.12 (< MDL)	0.22 < MDL)	0.15 (< MDL)	0.18 (< MDL)	0.13 < MDL)	0.10 (< MDL)	0.14 (< MDL)	0.10 (< MDL)
cis-1,2-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethyl acetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroform	0.03	0.07	0.03	0.06	0.06	0.06	0.03	0.04	0.04	0.03
Tetrahydrofuran	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.04
1,1,1-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.03
Carbon tetrachloride	0.06	0.06	0.07	0.06	0.07	0.07	0.05	0.06	0.06	0.06
1,2-Dichloropropane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
Trichloroethylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05
1,4-Dioxane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl methacrolate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl isobutyl ketone	0.03 (< MDL)	ND	ND	0.03	0.02 (< MDL)	ND	ND	ND	ND	ND
trans-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
Methyl butyl ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromochloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
1,2-Dibromoethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01

Air Toxic VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Tetrachloroethylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
Chlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
Bromoform	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,4-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,4-Trichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Naphthalene	0.07	0.02	0.009	0.02	0.03	0.02	0.009	0.008 (< MDL)	0.07	0.04
Hexachloro-1,3-butadiene	0.009	ND	ND	ND	ND	ND	ND	ND	ND	0.03

B.2.4 CAMDEN AUTUMN CAMPAIGN

Table B.2.4.1 PAMS hydrocarbon VOCs measured at the Camden regional sites for the autumn monitoring campaign on 29-Apr-15

Hydrocarbon VOCs	**Ambient Concentration, ppbv**									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Ethene	ND	ND	ND	ND	ND	ND	1.2	ND	ND	ND
Ethane	2.1	2.3	2.5	2.2	3.5	1.6	3.1	1.2	1.3	0.98
Acetylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propane	0.97	1.2	1.3	1.1	2.1	0.77	1.7	0.75	0.68	0.50
Isobutane	0.39	0.37	0.73	0.97	0.82	0.69	0.57	0.48	0.48	0.37
1-Butene	ND	ND	ND	ND	ND	ND	ND	ND	0.34	ND
n-Butane	0.70	0.79	0.81	2.1	1.1	0.80	0.90	0.61	0.57	0.30
trans-2-Butene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-2-Butene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Isopentane	0.35	0.33	0.43	0.55	0.44	0.51	0.55	0.31	0.41	0.24
1-Pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	0.23	0.23	0.26	0.35	0.38	0.27	0.38	0.19	0.22	0.15
Isoprene	0.09	0.05 (< MDL)	0.13	0.05 (< MDL)	0.03 (< MDL)	0.04 (< MDL)	0.07	0.06	0.08	0.07
trans-2-Pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-2-Pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,2-Dimethylbutane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cyclopentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,3-Dimethylbutane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Hydrocarbon VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
2-Methylpentane	0.04 (< MDL)	0.05 (< MDL)	0.05 (< MDL)	0.08	0.07	0.07	0.05 (< MDL)	ND	ND	ND
3-Methylpentane	0.04 (< MDL)	0.03 (< MDL)	0.04 (< MDL)	0.06	0.05 (< MDL)	0.08	0.04 (< MDL)	ND	ND	ND
1-Hexene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Hexane	0.07 (< MDL)	0.08	0.13	0.10	0.14	0.12	0.13	0.06 (< MDL)	0.08	0.04 (< MDL)
Methylcyclopentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-Dimethylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzene	0.07 (< MDL)	ND	0.09 (< MDL)	0.12	ND	0.09 (< MDL)	0.06 (< MDL)	ND	0.14	0.10
Cyclohexane	0.04	0.04	0.06	0.06	0.07	0.04	0.08	0.06	0.05	0.03 (< MDL)
2-Methylhexane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,3-Dimethylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylhexane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Isooctane	ND	ND	ND	0.05	ND	0.09	0.02 (< MDL)	ND	ND	ND
n-Heptane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methylcyclohexane	0.07	0.07	0.09	0.09	0.12	0.06	0.09	0.06	0.05	0.04
2,3,4-Trimethylpentane	ND	ND	ND	0.03	ND	0.03	ND	ND	0.009 (< MDL)	ND
Toluene	0.10	0.10	0.09	0.35	0.08	0.24	0.18	0.09	0.15	0.16
2-Methylheptane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylheptane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Octane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Hydrocarbon VOCs	**Ambient Concentration, ppbv**									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Ethylbenzene	0.01	0.01	0.01	0.04	0.01	0.04	0.02	0.01	0.02	0.02
m- + p-Xylene	0.04	0.04	0.03	0.11	0.05	0.11	0.08	0.02	0.08	0.06
Styrene	0.09	0.09	0.06	0.02	0.01	0.04	0.04	0.06	0.06	0.07
o-Xylene	0.02	0.02	0.01	0.04	0.02	0.04	0.03	0.01	0.04	0.02
n-Nonane	ND	ND	ND	0.01	ND	ND	ND	ND	ND	ND
Isopropylbenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Propylbenzene	0.004 (< MDL)	0.004 (< MDL)	0.002 (< MDL)	0.01	0.004 (< MDL)	0.008	0.009	0.002 (< MDL)	0.006	0.004 (< MDL)
m-Ethyltoluene	0.02	0.01	0.008	0.04	0.01	0.04	0.04	0.004 (< MDL)	0.03	0.02
p-Ethyltoluene	0.009	0.007	0.003 (< MDL)	0.01	0.007	0.01	0.02	0.001 (< MDL)	0.01	0.007
1,3,5-Trimethylbenzene	0.01 (< MDL)	0.009 (< MDL)	0.003 (< MDL)	0.02	0.01	0.02	0.02	0.003 (< MDL)	0.02	0.009 (< MDL)
o-Ethyltoluene	0.008	0.008	0.004 (< MDL)	0.01	0.01	0.02	0.02	0.002 (< MDL)	0.02	0.01
1,2,4-Trimethylbenzene	0.05	0.03	0.008	0.05	0.05	0.06	0.12	0.006 (< MDL)	0.08	0.03
n-Decane	ND	ND	ND	ND	ND	ND	0.04	ND	ND	ND
1,2,3-Trimethylbenzene	0.02	0.01	0.003 (< MDL)	0.02	0.02	0.02	0.04	0.003 (< MDL)	0.03	0.009
1,3-Diethylbenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,4-Diethylbenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Undecane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Dodecane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table B.2.4.2 TO-15 air toxics VOCs measured at the Camden regional sites for the autumn monitoring campaign on 29-Apr-15

Air Toxic VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Dichlorodifluoromethane	0.55	0.55	0.59	0.48	0.50	0.44	0.57	0.48	0.54	0.45
Chloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloro-1,1,2,2-tetrafluoroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Butadiene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromomethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethanol	4.0	1.8	1.9	10.2	3.2	17.8	3.7	1.6	23.4	2.8
Acrolein	ND	ND	ND	ND	ND	ND	ND	0.44	ND	ND
Acetone	2.2	3.9	1.8	1.7	1.9	4.0	2.2	3.4	3.0	1.4
Trichlorofluoromethane	0.25	0.25	0.28	0.27	0.26	0.22	0.30	0.24	0.26	0.22
Isopropanol	0.54	0.31	0.21 (< MDL)	0.16 (< MDL)	0.53	0.46	0.36	ND	0.24	0.14 (< MDL)
1,1-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloromethane	ND	ND	ND	ND	ND	0.25	0.19	ND	0.18	ND
1,1,2-Trichloro-1,2,2-trifluoroethane	0.31	0.19	0.16	0.09	0.12	0.07	0.10	0.06	0.08	0.05
trans-1,2-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl tert-butyl ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethenyl acetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Butanone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Air Toxic VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
cis-1,2-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethyl acetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroform	0.05	0.008 (< MDL)	0.05	0.02	0.09	0.43	0.08	0.01 (< MDL)	0.06	0.03
Tetrahydrofuran	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloroethane	0.07	0.02	0.02	ND	0.02	ND	ND	ND	ND	ND
Carbon tetrachloride	0.07	0.07	0.08	0.06	0.07	0.06	0.08	0.07	0.07	0.06
1,2-Dichloropropane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,4-Dioxane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl methacrolate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl isobutyl ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
trans-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl butyl ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromochloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dibromoethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tetrachloroethylene	ND	ND	0.010	0.008	ND	ND	ND	ND	ND	ND
Chlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Air Toxic VOCs	Ambient Concentration, ppbv									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Bromoform	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	0.008	0.006	ND	ND	ND	ND	ND	ND	0.006	ND
1,4-Dichlorobenzene	0.01	0.007	ND	0.001 (< MDL)	ND	ND	0.005	ND	0.008	0.003 (< MDL)
1,2-Dichlorobenzene	0.006	0.006	ND	ND	ND	ND	ND	ND	ND	ND
1,2,4-Trichlorobenzene	0.02	0.009	ND	ND	0.001 (< MDL)	ND	ND	ND	0.01	ND
Naphthalene	0.04	0.03	0.02	0.05	0.01	0.02	0.04	0.12	0.04	0.01
Hexachloro-1,3-butadiene	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND

B.3 Cattle Feedlot

Table B.3.1 PAMS Hydrocarbon VOCs measured at Jindalee cattle feedlot

Hydrocarbon VOCs	Ambient Concentration, ppbv		
	Jindalee Cattle Feedlot		
	26-Aug-14	16-Feb-15	22-Apr-15
Ethene	ND	1.2	0.82
Ethane	ND	ND	0.43 (< MDL)
Acetylene	ND	ND	ND
Propene	ND	ND	ND
Propane	ND	ND	0.72
Isobutane	0.56	3.0	0.62
1-Butene	ND	ND	ND
n-Butane	ND	0.48	ND
trans-2-Butene	ND	ND	ND
cis-2-Butene	ND	ND	ND
Isopentane	ND	ND	0.15
1-Pentene	ND	ND	ND
n-Pentane	ND	ND	ND
Isoprene	ND	0.22	0.07
trans-2-Pentene	ND	ND	ND
cis-2-Pentene	ND	ND	ND
2,2-Dimethylbutane	ND	ND	ND
Cyclopentane	ND	ND	ND
2,3-Dimethylbutane	ND	ND	ND
2-Methylpentane	ND	ND	ND
3-Methylpentane	ND	ND	ND
1-Hexene	ND	ND	ND
n-Hexane	ND	ND	ND
Methylcyclopentane	ND	ND	ND
2,4-Dimethylpentane	ND	ND	ND
Benzene	ND	0.15	ND
Cyclohexane	ND	ND	ND
2-Methylhexane	ND	ND	ND
2,3-Dimethylpentane	ND	ND	ND

Hydrocarbon VOCs	**Ambient Concentration, ppbv**		
	Jindalee Cattle Feedlot		
	26-Aug-14	16-Feb-15	22-Apr-15
3-Methylhexane	ND	ND	ND
Isooctane	ND	ND	ND
n-Heptane	ND	ND	ND
Methylcyclohexane	ND	ND	ND
2,3,4-Trimethylpentane	ND	ND	ND
Toluene	0.36	0.04	0.07
2-Methylheptane	0.02 (< MDL)	ND	ND
3-Methylheptane	ND	ND	ND
n-Octane	0.007 (< MDL)	ND	ND
Ethylbenzene	0.09	ND	ND
m- + p-Xylene	0.50	0.02	0.02
Styrene	ND	ND	ND
o-Xylene	0.23	0.01	ND
n-Nonane	0.02	ND	ND
Isopropylbenzene	0.007 (< MDL)	0.13	ND
n-Propylbenzene	0.05	ND	ND
m-Ethyltoluene	0.14	ND	ND
p-Ethyltoluene	0.07	ND	ND
1,3,5-Trimethylbenzene	0.04	ND	ND
o-Ethyltoluene	0.09	ND	ND
1,2,4-Trimethylbenzene	0.24	ND	ND
n-Decane	0.04	ND	ND
1,2,3-Trimethylbenzene	0.09	ND	ND
1,3-Diethylbenzene	0.01	ND	ND
1,4-Diethylbenzene	ND	ND	ND
n-Undecane	0.03	ND	ND
n-Dodecane	ND	ND	ND

Table B.3.2 TO-15 air toxics VOCs measured at Jindalee cattle feedlot

Air Toxics VOCs	Ambient Concentration, ppbv		
	Jindalee Cattle Feedlot		
	26-Aug-14	16-Feb-15	22-Apr-15
Dichlorodifluoromethane	0.47	0.57	0.35
Chloromethane	ND	ND	ND
1,2-Dichloro-1,1,2,2-tetrafluoroethane	ND	ND	ND
Chloroethene	ND	ND	ND
1,3-Butadiene	ND	ND	ND
Bromomethane	ND	ND	ND
Chloroethane	ND	ND	ND
Ethanol	10.3	253	10.1
Acrolein	ND	0.87	ND
Acetone	6.3	26.4	4.4
Trichlorofluoromethane	0.22	0.28	0.15
Isopropanol	0.42	1.2	ND
1,1-Dichloroethene	ND	ND	ND
Dichloromethane	ND	ND	ND
1,1,2-Trichloro-1,2,2-trifluoroethane	ND	0.04	0.02
trans-1,2-Dichloroethene	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND
Methyl tert-butyl ether	ND	ND	ND
Ethenyl acetate	ND	ND	ND
2-Butanone	ND	4.1	0.53
cis-1,2-Dichloroethene	ND	ND	ND
Ethyl acetate	ND	ND	ND
Chloroform	ND	0.02	ND
Tetrahydrofuran	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND
Carbon tetrachloride	0.07	0.07	0.04
1,2-Dichloropropane	ND	ND	ND
Bromodichloromethane	ND	ND	ND
Trichloroethylene	ND	ND	ND
1,4-Dioxane	ND	ND	ND
Methyl methacrolate	ND	ND	ND

Air Toxics VOCs	**Ambient Concentration, ppbv**		
	Jindalee Cattle Feedlot		
	26-Aug-14	16-Feb-15	22-Apr-15
cis-1,3-Dichloropropene	ND	ND	ND
Methyl isobutyl ketone	ND	ND	ND
trans-1,3-Dichloropropene	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND
Methyl butyl ketone	ND	ND	ND
Dibromochloromethane	ND	ND	ND
1,2-Dibromoethane	ND	ND	ND
Tetrachloroethylene	ND	ND	ND
Chlorobenzene	ND	ND	ND
Bromoform	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	ND
Benzyl chloride	ND	ND	ND
1,3-Dichlorobenzene	ND	ND	ND
1,4-Dichlorobenzene	0.007	ND	ND
1,2-Dichlorobenzene	ND	ND	ND
1,2,4-Trichlorobenzene	ND	ND	ND
Naphthalene	ND	0.02	ND
Hexachloro-1,3-butadiene	ND	ND	0.05

B.4 Coal Mines

Table B.4.1 PAMS hydrocarbon VOCs measured at Rix's Creek coal mine, Hunter Valley, and in the vicinity of a mine in the Gunnedah Basin region, NSW

Hydrocarbon VOCs	Ambient Concentration, ppbv			
	Rix's Creek Mine			Gunnedah Basin
	In-pit 15-Apr-15	In-pit 22-Jul-15	ROM Pad 22-Jul-15	Mine plume 21-Jul-14
Ethene	0.52 (< MDL)	ND	0.74	0.79
Ethane	2.3	2.3	7.9	0.52 (< MDL)
Acetylene	ND	ND	ND	ND
Propene	0.35	ND	0.60	0.45
Propane	0.55	ND	2.6	0.56
Isobutane	0.74	ND	0.65	0.62
1-Butene	ND	ND	ND	ND
n-Butane	0.25	ND	0.71	0.18
trans-2-Butene	ND	ND	ND	ND
cis-2-Butene	ND	ND	ND	ND
Isopentane	0.20	ND	0.33	ND
1-Pentene	ND	ND	ND	ND
n-Pentane	0.18	ND	0.21	0.11
Isoprene	0.58	ND	0.12	0.04 (< MDL)
trans-2-Pentene	ND	ND	ND	ND
cis-2-Pentene	ND	ND	ND	ND
2,2-Dimethylbutane	ND	ND	ND	ND
Cyclopentane	ND	ND	ND	ND
2,3-Dimethylbutane	ND	ND	ND	ND
2-Methylpentane	ND	ND	ND	ND
3-Methylpentane	0.04 (< MDL)	ND	ND	ND
1-Hexene	ND	ND	ND	ND
n-Hexane	0.04 (< MDL)	ND	ND	0.18
Methylcyclopentane	ND	ND	ND	0.13
2,4-Dimethylpentane	ND	ND	ND	ND
Benzene	0.11	0.06 (< MDL)	0.10	ND
Cyclohexane	ND	ND	ND	ND
2-Methylhexane	ND	ND	ND	ND

Hydrocarbon VOCs	Ambient Concentration, ppbv			
	Rix's Creek Mine			Gunnedah Basin
	In-pit 15-Apr-15	In-pit 22-Jul-15	ROM Pad 22-Jul-15	Mine plume 21-Jul-14
2,3-Dimethylpentane	ND	ND	ND	ND
3-Methylhexane	0.06	ND	ND	ND
Isooctane	ND	ND	ND	0.02 (< MDL)
n-Heptane	0.03	ND	ND	0.06
Methylcyclohexane	0.12	ND	ND	0.04
2,3,4-Trimethylpentane	ND	ND	ND	ND
Toluene	0.08	0.09	0.20	3.3
2-Methylheptane	ND	ND	ND	ND
3-Methylheptane	ND	ND	ND	ND
n-Octane	0.01 (< MDL)	ND	ND	ND
Ethylbenzene	ND	ND	0.22	0.06
m- + p-Xylene	0.03	0.02	0.99	0.11
Styrene	ND	ND	0.01	0.02
o-Xylene	ND	ND	0.30	0.04
n-Nonane	0.01	ND	0.20	ND
Isopropylbenzene	ND	ND	0.01	0.005 (< MDL)
n-Propylbenzene	ND	ND	0.03	0.02
m-Ethyltoluene	ND	ND	0.08	0.03
p-Ethyltoluene	ND	ND	0.03	0.02
1,3,5-Trimethylbenzene	ND	ND	0.08	0.02
o-Ethyltoluene	ND	ND	0.03	0.02
1,2,4-Trimethylbenzene	ND	0.01	0.22	0.06
n-Decane	0.02	ND	0.31	0.06
1,2,3-Trimethylbenzene	ND	ND	0.08	0.02
1,3-Diethylbenzene	ND	ND	0.006	0.003 (< MDL)
1,4-Diethylbenzene	ND	ND	0.03	0.14
n-Undecane	0.03	ND	0.14	0.04
n-Dodecane	0.02	ND	0.04	0.03

Table B.4.2 TO-15 air toxics VOCs measured at Rix's Creek coal mine, Hunter Valley and in the vicinity of a mine in the Gunnedah Basin region, NSW

Air Toxics VOCs	**Concentration, ppbv**			
	Rix's Creek Mine			Gunnedah Basin
	In-pit 15-Apr-15	In-pit 22-Jul-15	ROM Pad 22-Jul-15	Mine plume 21-Jul-14
Dichlorodifluoromethane	0.40	0.62	0.64	0.49
Chloromethane	ND	ND	ND	ND
1,2-Dichloro-1,1,2,2-tetrafluoroethane	ND	ND	ND	ND
Chloroethene	ND	ND	ND	ND
1,3-Butadiene	ND	ND	ND	ND
Bromomethane	ND	ND	ND	ND
Chloroethane	ND	ND	ND	ND
Ethanol	4.5	2.2	10.8	7.9
Acrolein	0.79	ND	ND	2.3
Acetone	8.1	2.2	4.0	21.4
Trichlorofluoromethane	0.18	0.32	0.30	0.25
Isopropanol	0.81	ND	ND	0.47
1,1-Dichloroethene	ND	ND	ND	ND
Dichloromethane	ND	ND	ND	0.10
1,1,2-Trichloro-1,2,2-trifluoroethane	0.04	0.07	0.07	ND
trans-1,2-Dichloroethene	ND	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND
Methyl tert-butyl ether	ND	ND	ND	ND
Ethenyl acetate	ND	ND	ND	ND
2-Butanone	0.51	ND	2.2	ND
cis-1,2-Dichloroethene	ND	ND	ND	ND
Ethyl acetate	ND	ND	ND	ND
Chloroform	ND	0.04	0.27	ND
Tetrahydrofuran	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND	ND
Carbon tetrachloride	0.05	0.10	0.08	0.05
1,2-Dichloropropane	ND	ND	ND	ND
Bromodichloromethane	ND	ND	ND	ND
Trichloroethylene	ND	ND	ND	ND

Air Toxics VOCs	**Concentration, ppbv**			
	Rix's Creek Mine			Gunnedah Basin
	In-pit 15-Apr-15	In-pit 22-Jul-15	ROM Pad 22-Jul-15	Mine plume 21-Jul-14
1,4-Dioxane	ND	ND	ND	ND
Methyl methacrolate	ND	ND	ND	ND
cis-1,3-Dichloropropene	ND	ND	ND	ND
Methyl isobutyl ketone	ND	ND	0.39	0.09
trans-1,3-Dichloropropene	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND
Methyl butyl ketone	0.04	ND	ND	0.19
Dibromochloromethane	ND	ND	ND	ND
1,2-Dibromoethane	ND	ND	ND	ND
Tetrachloroethylene	ND	ND	2.7	ND
Chlorobenzene	0.006 (< MDL)	ND	ND	ND
Bromoform	0.008	ND	ND	ND
1,1,2,2-Tetrachloroethane	0.006 (< MDL)	ND	ND	ND
Benzyl chloride	ND	ND	ND	ND
1,3-Dichlorobenzene	0.02	ND	ND	ND
1,4-Dichlorobenzene	0.02	ND	ND	0.008
1,2-Dichlorobenzene	0.02	ND	ND	ND
1,2,4-Trichlorobenzene	0.04	0.004 (< MDL)	0.006	ND
Naphthalene	0.06	0.01	0.04	ND
Hexachloro-1,3-butadiene	0.02	ND	ND	ND

B.5 CSG Facilities

Table B.5.1 PAMS hydrocarbon VOCs measured at CSG production facilities

Hydrocarbon VOCs	**Ambient Concentration, ppbv**					
	Camden	Gloucester			Narrabri	
	Well C3	Well G1	Well G2	Well G2	Compression Plant	Well N7
	19-Aug-15	16-Jul-15	16-Jul-15	23-Sep-15	28-Jul-15	29-Jul-15
Ethene	ND	ND	ND	ND	ND	ND
Ethane	1.0	ND	0.32 (< MDL)	ND	ND	ND
Acetylene	ND	ND	ND	ND	ND	ND
Propene	ND	ND	ND	ND	ND	ND
Propane	0.96	ND	ND	0.24 (< MDL)	ND	ND
Isobutane	0.87	0.28	ND	0.06 (< MDL)	ND	ND
1-Butene	ND	ND	ND	ND	ND	ND
n-Butane	0.29	ND	ND	ND	ND	ND
trans-2-Butene	ND	ND	ND	ND	ND	ND
cis-2-Butene	ND	ND	ND	ND	ND	ND
Isopentane	ND	ND	ND	ND	ND	ND
1-Pentene	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND
Isoprene	ND	ND	ND	ND	ND	ND
trans-2-Pentene	ND	ND	ND	ND	ND	ND
cis-2-Pentene	ND	ND	ND	ND	ND	ND
2,2-Dimethylbutane	ND	ND	ND	ND	ND	ND
Cyclopentane	ND	ND	ND	ND	ND	ND
2,3-Dimethylbutane	ND	ND	ND	ND	ND	ND
2-Methylpentane	ND	ND	ND	ND	ND	ND
3-Methylpentane	ND	ND	ND	ND	ND	ND
1-Hexene	ND	ND	ND	ND	ND	ND
n-Hexane	ND	ND	ND	ND	ND	ND
Methylcyclopentane	ND	ND	ND	ND	ND	ND
2,4-Dimethylpentane	ND	ND	ND	ND	ND	ND
Benzene	0.56	ND	ND	0.39	ND	ND
Cyclohexane	ND	ND	ND	ND	ND	ND

Hydrocarbon VOCs	Ambient Concentration, ppbv					
	Camden	Gloucester			Narrabri	
	Well C3	Well G1	Well G2	Well G2	Compression Plant	Well N7
	19-Aug-15	16-Jul-15	16-Jul-15	23-Sep-15	28-Jul-15	29-Jul-15
2-Methylhexane	ND	ND	ND	ND	ND	ND
2,3-Dimethylpentane	ND	ND	ND	ND	ND	ND
3-Methylhexane	ND	ND	ND	ND	ND	ND
Isooctane	ND	ND	ND	ND	ND	ND
n-Heptane	ND	ND	ND	ND	ND	ND
Methylcyclohexane	ND	ND	ND	ND	ND	ND
2,3,4-Trimethylpentane	ND	ND	ND	ND	ND	ND
Toluene	0.71	ND	0.04	0.05	ND	ND
2-Methylheptane	ND	ND	ND	ND	ND	ND
3-Methylheptane	ND	ND	ND	ND	ND	ND
n-Octane	ND	ND	ND	ND	ND	ND
Ethylbenzene	0.09	ND	ND	ND	ND	ND
m- + p-Xylene	0.66	ND	ND	ND	ND	ND
Styrene	ND	ND	ND	ND	ND	ND
o-Xylene	0.32	ND	ND	ND	ND	ND
n-Nonane	0.03	ND	ND	ND	ND	ND
Isopropylbenzene	0.006 (< MDL)	ND	ND	ND	ND	ND
n-Propylbenzene	0.03	ND	ND	ND	ND	ND
m-Ethyltoluene	0.13	ND	ND	ND	ND	ND
p-Ethyltoluene	0.04	ND	ND	ND	ND	ND
1,3,5-Trimethylbenzene	0.07	ND	ND	ND	ND	ND
o-Ethyltoluene	0.08	ND	ND	ND	ND	ND
1,2,4-Trimethylbenzene	0.22	ND	ND	ND	ND	ND
n-Decane	0.02	ND	ND	ND	ND	ND
1,2,3-Trimethylbenzene	0.08	ND	ND	ND	ND	ND
1,3-Diethylbenzene	0.01	ND	ND	ND	ND	ND
1,4-Diethylbenzene	0.03	ND	ND	ND	ND	ND
n-Undecane	ND	ND	ND	ND	ND	ND
n-Dodecane	ND	ND	ND	ND	ND	ND

Table B.5.2 TO-15 air toxics VOCs measured at CSG production facilities

Air Toxics VOCs	Ambient Concentration, ppbv					
	Camden	Gloucester			Narrabri	
	Well C3	Well G1	Well G2	Well G2	Compression Plant	Well N7
	19-Aug-15	16-Jul-15	16-Jul-15	23-Sep-15	28-Jul-05	29-Jul-15
Dichlorodifluoromethane	0.44	0.43	0.47	0.54	0.45	0.44
Chloromethane	ND	ND	ND	ND	ND	ND
1,2-Dichloro-1,1,2,2-tetrafluoroethane	ND	ND	ND	0.010 (< MDL)	ND	ND
Chloroethene	ND	ND	ND	ND	ND	ND
1,3-Butadiene	ND	ND	ND	ND	ND	ND
Bromomethane	ND	ND	ND	ND	ND	ND
Chloroethane	ND	ND	ND	ND	ND	ND
Ethanol	3.5	1.3	ND	4.2	ND	0.48
Acrolein	ND	ND	ND	ND	ND	ND
Acetone	4.8	1.3	0.92	2.1	0.96	2.5
Trichlorofluoromethane	0.20	0.21	0.21	0.25	0.21	0.23
Isopropanol	0.94	0.28	0.19 (< MDL)	0.89	ND	ND
1,1-Dichloroethene	ND	ND	ND	ND	ND	ND
Dichloromethane	ND	ND	ND	ND	ND	ND
1,1,2-Trichloro-1,2,2-trifluoroethane	0.10	0.05	0.06	0.08	0.06	0.06
trans-1,2-Dichloroethene	ND	ND	ND	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND	ND	ND
Methyl tert-butyl ether	ND	ND	ND	ND	ND	ND
Ethenyl acetate	ND	ND	ND	ND	ND	ND
2-Butanone	0.27	ND	ND	ND	ND	ND
cis-1,2-Dichloroethene	ND	ND	ND	ND	ND	ND
Ethyl acetate	ND	ND	ND	ND	ND	ND
Chloroform	ND	0.02	0.03	0.05	0.02	0.03
Tetrahydrofuran	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	0.06	0.08	0.08	0.08	0.07
1,2-Dichloropropane	ND	ND	ND	ND	ND	ND
Bromodichloromethane	ND	ND	ND	ND	ND	ND

Air Toxics VOCs	Ambient Concentration, ppbv					
	Camden	Gloucester			Narrabri	
	Well C3	Well G1	Well G2	Well G2	Compression Plant	Well N7
	19-Aug-15	16-Jul-15	16-Jul-15	23-Sep-15	28-Jul-05	29-Jul-15
Trichloroethylene	ND	ND	ND	ND	ND	ND
1,4-Dioxane	ND	ND	ND	ND	ND	ND
Methyl methacrolate	ND	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND
Methyl isobutyl ketone	ND	ND	ND	ND	ND	ND
trans-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND	ND
Methyl butyl ketone	ND	ND	ND	ND	ND	ND
Dibromochloromethane	ND	ND	ND	ND	ND	ND
1,2-Dibromoethane	ND	ND	ND	ND	ND	ND
Tetrachloroethylene	ND	ND	ND	ND	ND	ND
Chlorobenzene	ND	ND	ND	ND	ND	ND
Bromoform	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND	ND
Benzyl chloride	ND	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	0.01	ND	ND	ND	ND	ND
1,4-Dichlorobenzene	0.02	ND	ND	ND	ND	ND
1,2-Dichlorobenzene	0.010	ND	ND	ND	ND	ND
1,2,4-Trichlorobenzene	0.02	ND	ND	0.01	ND	ND
Naphthalene	0.02	0.01	0.01	ND	ND	0.01
Hexachloro-1,3-butadiene	0.010	ND	ND	ND	ND	ND

B.6 Landfill Sites

Table B.6.1 PAMS hydrocarbon VOCs measured at landfill sites

Hydrocarbon VOCs	**Ambient Concentration, ppbv**				
	Parkes Waste Facility		Summerhill Waste Management Centre		
	28-Aug-14	23-Apr-15	16-Jul-14	09-Jul-15 10:21am	09-Jul-15 10:45am
Ethene	ND	ND	ND	7.2	3.2
Ethane	ND	ND	2.0	1.8	1.2
Acetylene	ND	ND	ND	ND	ND
Propene	0.24	0.14 (< MDL)	0.21 (< MDL)	3.5	1.2
Propane	2.2	1.8	0.96	2.0	1.8
Isobutane	2.3	2.6	1.2	0.58	0.86
1-Butene	ND	0.35	ND	0.87	ND
n-Butane	2.6	2.3	0.51	1.4	1.3
trans-2-Butene	ND	ND	ND	ND	ND
cis-2-Butene	ND	ND	ND	ND	ND
Isopentane	0.50	0.15	ND	ND	ND
1-Pentene	ND	ND	ND	0.91	0.95
n-Pentane	0.17	ND	ND	0.78	0.73
Isoprene	0.08	0.04 (< MDL)	ND	0.24	0.25
trans-2-Pentene	ND	ND	ND	ND	ND
cis-2-Pentene	ND	ND	ND	ND	ND
2,2-Dimethylbutane	ND	ND	ND	ND	ND
Cyclopentane	1.0	0.20	ND	ND	ND
2,3-Dimethylbutane	0.69	0.12	ND	ND	ND
2-Methylpentane	3.5	0.69	0.03 (< MDL)	ND	ND
3-Methylpentane	2.5	0.28	0.08	ND	ND
1-Hexene	ND	ND	ND	0.33	0.34
n-Hexane	0.32	0.08	0.05 (< MDL)	0.40	0.39
Methylcyclopentane	0.09	ND	ND	ND	ND
2,4-Dimethylpentane	ND	ND	ND	ND	ND
Benzene	ND	ND	ND	0.65	0.50
Cyclohexane	0.18	0.45	ND	ND	ND
2-Methylhexane	0.12	0.09	ND	ND	ND
2,3-Dimethylpentane	0.04	ND	ND	ND	ND

Hydrocarbon VOCs	Ambient Concentration, ppbv				
	Parkes Waste Facility		Summerhill Waste Management Centre		
	28-Aug-14	23-Apr-15	16-Jul-14	09-Jul-15 10:21am	09-Jul-15 10:45am
3-Methylhexane	0.16	0.13	ND	ND	ND
Isooctane	ND	0.02 (< MDL)	ND	0.04	0.04
n-Heptane	0.11	0.05	0.02 (< MDL)	0.13	0.08
Methylcyclohexane	0.20	0.13	ND	ND	ND
2,3,4-Trimethylpentane	ND	ND	ND	ND	ND
Toluene	1.1	0.50	0.26	0.25	0.35
2-Methylheptane	ND	ND	0.12	ND	ND
3-Methylheptane	ND	ND	ND	ND	ND
n-Octane	0.07	ND	0.02	0.04	0.03
Ethylbenzene	0.21	0.07	0.06	0.02	0.04
m- + p-Xylene	0.57	0.25	0.21	0.06	0.12
Styrene	0.16	1.9	ND	0.01	0.02
o-Xylene	0.24	0.11	0.10	0.03	0.04
n-Nonane	0.21	0.06	0.02	0.03	0.03
Isopropylbenzene	0.05	0.01	ND	0.13	0.006 (< MDL)
n-Propylbenzene	0.07	0.02	0.02	0.01	0.008
m-Ethyltoluene	0.22	0.07	0.05	0.01	0.01
p-Ethyltoluene	0.10	0.03	0.03	0.006 (< MDL)	0.01
1,3,5-Trimethylbenzene	0.15	0.05	ND	0.004 (< MDL)	0.008 (< MDL)
o-Ethyltoluene	0.10	0.03	0.04	ND	0.006 (< MDL)
1,2,4-Trimethylbenzene	0.45	0.14	0.09	0.02	0.03
n-Decane	0.38	0.07	0.03	0.03	0.02
1,2,3-Trimethylbenzene	0.12	0.03	0.03	0.006 (< MDL)	0.01
1,3-Diethylbenzene	0.01	ND	0.006 (< MDL)	ND	ND
1,4-Diethylbenzene	0.17	ND	0.02	ND	ND
n-Undecane	0.16	0.03	0.02	ND	ND
n-Dodecane	0.13	0.01 (< MDL)	0.01 (< MDL)	ND	ND

Table B.6.2 TO-15 air toxics VOCs measured at landfill sites

Air Toxics VOCs	Ambient Concentration, ppbv				
	Parkes Waste Facility		Summerhill Waste Management Centre		
	28-Aug-14	23-Apr-15	16-Jul-14	09-Jul-15 10:21am	09-Jul-15 10:45am
Dichlorodifluoromethane	0.44	0.38	0.47	0.43	0.47
Chloromethane	ND	ND	ND	ND	ND
1,2-Dichloro-1,1,2,2-tetrafluoroethane	ND	ND	ND	ND	ND
Chloroethene	ND	ND	ND	ND	ND
1,3-Butadiene	ND	ND	ND	ND	ND
Bromomethane	ND	ND	ND	0.11	0.10
Chloroethane	ND	ND	ND	ND	ND
Ethanol	24.9	14.5	15.3	12.4	12.1
Acrolein	0.79	ND	ND	2.2	2.4
Acetone	12.5	11.4	14.0	197	202
Trichlorofluoromethane	0.21	0.25	0.24	0.18	0.21
Isopropanol	0.64	0.37	4.5	1.5	1.3
1,1-Dichloroethene	ND	ND	ND	ND	ND
Dichloromethane	7.3	1.4	ND	0.24	0.27
1,1,2-Trichloro-1,2,2-trifluoroethane	ND	0.02	ND	0.06	0.06
trans-1,2-Dichloroethene	ND	ND	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND	ND
Methyl tert-butyl ether	ND	ND	ND	ND	ND
Ethenyl acetate	ND	ND	ND	ND	ND
2-Butanone	ND	0.66	ND	17.9	18.1
cis-1,2-Dichloroethene	ND	ND	ND	ND	ND
Ethyl acetate	0.36	ND	ND	ND	ND
Chloroform	ND	ND	0.06	0.03	0.04
Tetrahydrofuran	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	0.05	0.07	0.05	0.05
1,2-Dichloropropane	ND	ND	ND	ND	ND
Bromodichloromethane	ND	ND	ND	ND	ND
Trichloroethylene	0.82	ND	ND	ND	ND

Air Toxics VOCs	Ambient Concentration, ppbv				
	Parkes Waste Facility		Summerhill Waste Management Centre		
	28-Aug-14	23-Apr-15	16-Jul-14	09-Jul-15 10:21am	09-Jul-15 10:45am
1,4-Dioxane	ND	ND	ND	ND	ND
Methyl methacrolate	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	ND	ND	ND	ND	ND
Methyl isobutyl ketone	0.07	0.11	ND	ND	ND
trans-1,3-Dichloropropene	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND
Methyl butyl ketone	ND	ND	0.03 (< MDL)	0.07	0.07
Dibromochloromethane	ND	ND	ND	ND	ND
1,2-Dibromoethane	ND	ND	ND	ND	ND
Tetrachloroethylene	0.41	0.20	ND	ND	ND
Chlorobenzene	ND	ND	ND	ND	ND
Bromoform	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND
Benzyl chloride	ND	ND	ND	0.008	0.01
1,3-Dichlorobenzene	ND	ND	ND	ND	ND
1,4-Dichlorobenzene	0.010	ND	0.009	0.006	0.006
1,2-Dichlorobenzene	ND	ND	ND	ND	ND
1,2,4-Trichlorobenzene	ND	ND	0.01	0.006	0.004 (< MDL)
Naphthalene	0.31	0.01	0.12	0.01	0.008 (< MDL)
Hexachloro-1,3-butadiene	ND	ND	ND	ND	ND

B.7 Wastewater Treatment Plants

Table B.7.1 PAMS hydrocarbon VOCs measured at wastewater treatment sites

Hydrocarbon VOCs	**Ambient Concentration, ppbv**									
	Singleton Wastewater Treatment Plant				Wagga Wagga Sewage Treatment Plant			Picton Wastewater Treatment Plant		
	Pond #1	Pond #2	Background	Inlet	Aeration Tank	Inlet	Inlet	Lagoon #2	Lagoon #2	Aeration Tank
	02-Jul-14	02-Jul-14	02-Jul-14	08-Jul-15	26-Aug-14	17-Feb-15	21-Apr-15	06-Aug-14	29-Apr-15	25-Nov-15
Ethene	ND	ND	ND	10.2	ND	ND	ND	ND	ND	ND
Ethane	ND	ND	ND	1.1	ND	ND	ND	0.50 (< MDL)	ND	ND
Acetylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propene	ND	ND	ND	7.6	ND	ND	ND	ND	ND	0.20 (< MDL)
Propane	ND	ND	ND	0.90	ND	ND	ND	0.55	ND	0.41
Isobutane	0.36	0.41	ND	0.39	1.0	3.0	0.09 (< MDL)	0.38	0.17	0.38
1-Butene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	0.49	ND	0.43	ND	0.41	ND	0.17
trans-2-Butene	ND	ND	ND	0.19	ND	ND	ND	ND	ND	ND
cis-2-Butene	ND	ND	ND	0.15	ND	ND	ND	ND	ND	ND
Isopentane	ND	ND	ND	ND	ND	ND	ND	0.31	ND	ND
1-Pentene	ND	ND	ND	1.3	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	0.58	ND	ND	ND	ND	ND	ND
Isoprene	ND	ND	ND	ND	ND	0.54	ND	ND	0.11	0.65

Hydrocarbon VOCs	**Ambient Concentration, ppbv**									
	Singleton Wastewater Treatment Plant				Wagga Wagga Sewage Treatment Plant			Picton Wastewater Treatment Plant		
	Pond #1	Pond #2	Background	Inlet	Aeration Tank	Inlet	Inlet	Lagoon #2	Lagoon #2	Aeration Tank
	02-Jul-14	02-Jul-14	02-Jul-14	08-Jul-15	26-Aug-14	17-Feb-15	21-Apr-15	06-Aug-14	29-Apr-15	25-Nov-15
trans-2-Pentene	ND	ND	ND	0.09	ND	ND	ND	ND	ND	ND
cis-2-Pentene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,2-Dimethylbutane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cyclopentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,3-Dimethylbutane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Methylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylpentane	1.4	0.31	0.18	ND	ND	ND	ND	ND	ND	ND
1-Hexene	ND	ND	ND	0.25	ND	ND	ND	ND	ND	ND
n-Hexane	ND	ND	ND	0.15	ND	ND	ND	0.12	ND	ND
Methylcyclopentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-Dimethylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzene	ND	0.02 (< MDL)	0.02 (< MDL)	0.61	ND	0.17	ND	ND	ND	ND
Cyclohexane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Methylhexane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,3-Dimethylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylhexane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Isooctane	ND	ND	ND	0.02	ND	ND	ND	0.04	ND	ND
n-Heptane	ND	ND	ND	ND	ND	ND	ND	0.02 (< MDL)	ND	ND

Hydrocarbon VOCs	**Ambient Concentration, ppbv**									
	Singleton Wastewater Treatment Plant				Wagga Wagga Sewage Treatment Plant			Picton Wastewater Treatment Plant		
	Pond #1	Pond #2	Background	Inlet	Aeration Tank	Inlet	Inlet	Lagoon #2	Lagoon #2	Aeration Tank
	02-Jul-14	02-Jul-14	02-Jul-14	08-Jul-15	26-Aug-14	17-Feb-15	21-Apr-15	06-Aug-14	29-Apr-15	25-Nov-15
Methylcyclohexane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,3,4-Trimethylpentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Toluene	0.10	0.21	0.07	0.14	0.48	0.03	0.005 (< MDL)	0.23	ND	0.02 (< MDL)
2-Methylheptane	4.0	0.72	0.18	ND	0.03	ND	ND	0.12	ND	ND
3-Methylheptane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Octane	ND	ND	ND	ND	0.01 (< MDL)	ND	ND	0.01 (< MDL)	ND	ND
Ethylbenzene	ND	0.02	ND	0.01	0.13	ND	ND	0.03	ND	ND
m- + p-Xylene	0.01	0.03	0.005 (< MDL)	0.03	0.66	0.006 (< MDL)	ND	0.05	ND	ND
Styrene	0.009	0.005 (< MDL)	0.02	0.01	ND	ND	ND	ND	ND	ND
o-Xylene	ND	0.02	ND	0.02	0.30	ND	ND	0.03	ND	ND
n-Nonane	ND	ND	ND	ND	0.02	ND	ND	0.009	ND	ND
Isopropylbenzene	ND	ND	ND	0.33	0.01	ND	ND	ND	ND	ND
n-Propylbenzene	ND	ND	ND	ND	0.05	ND	ND	0.009	ND	ND
m-Ethyltoluene	ND	ND	ND	ND	0.18	ND	ND	ND	ND	ND
p-Ethyltoluene	ND	ND	ND	ND	0.08	ND	ND	ND	ND	ND
1,3,5-Trimethylbenzene	ND	ND	ND	ND	0.04	ND	ND	ND	ND	ND
o-Ethyltoluene	ND	ND	ND	ND	0.11	ND	ND	ND	ND	ND

Hydrocarbon VOCs	Ambient Concentration, ppbv									
	Singleton Wastewater Treatment Plant				Wagga Wagga Sewage Treatment Plant			Picton Wastewater Treatment Plant		
	Pond #1	Pond #2	Background	Inlet	Aeration Tank	Inlet	Inlet	Lagoon #2	Lagoon #2	Aeration Tank
	02-Jul-14	02-Jul-14	02-Jul-14	08-Jul-15	26-Aug-14	17-Feb-15	21-Apr-15	06-Aug-14	29-Apr-15	25-Nov-15
1,2,4-Trimethylbenzene	ND	ND	ND	0.009	0.28	ND	ND	ND	ND	ND
n-Decane	ND	ND	ND	ND	0.04	0.02	ND	0.02	ND	ND
1,2,3-Trimethylbenzene	ND	ND	ND	ND	0.10	ND	ND	ND	ND	ND
1,3-Diethylbenzene	ND	ND	ND	ND	0.02	ND	ND	ND	ND	ND
1,4-Diethylbenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Undecane	ND	ND	ND	ND	0.02	0.04	ND	ND	ND	ND
n-Dodecane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table B.7.2 TO-15 air toxics VOCs measured at wastewater treatment sites

Air Toxics VOCs	**Ambient Concentration, ppbv**									
	Singleton Wastewater Treatment Plant				Wagga Wagga Sewage Treatment Plant			Picton Wastewater Treatment Plant		
	Pond #1	Pond #2	Background	Inlet	Aeration Tank	Inlet	Inlet	Lagoon #2	Lagoon #2	Aeration Tank
	02-Jul-14	02-Jul-14	02-Jul-14	08-Jul-15	26-Aug-14	17-Feb-15	21-Apr-15	06-Aug-14	29-Apr-15	25-Nov-15
Dichlorodifluoromethane	0.62	0.61	0.59	0.44	0.61	0.59	0.44	0.48	0.41	0.64
Chloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloro-1,1,2,2-tetrafluoroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Butadiene	0.61	ND	0.26	ND	ND	ND	ND	ND	ND	ND
Bromomethane	ND	ND	ND	0.10	ND	ND	ND	ND	ND	ND
Chloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethanol	6.7	8.5	1.9	13.7	9.9	40.9	1.5	4.0	2.4	3.0
Acrolein	ND	ND	ND	1.0	ND	1.5	0.41	ND	0.43	0.80
Acetone	28.0	21.0	6.3	93.2	7.1	13.8	2.5	14.5	4.0	7.7
Trichlorofluoromethane	0.30	0.30	0.29	0.19	0.29	0.27	0.20	0.22	0.18	ND
Isopropanol	5.4	20.0	3.5	1.9	0.35	0.43	ND	1.1	ND	0.37
1,1-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloromethane	ND	0.17	ND	ND	ND	0.09	ND	1.0	ND	ND
1,1,2-Trichloro-1,2,2-trifluoroethane	0.24	0.10	0.10	0.06	ND	0.05	0.04	ND	0.02	ND
trans-1,2-Dichloroethene	ND	0.03	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Air Toxics VOCs	**Ambient Concentration, ppbv**									
	Singleton Wastewater Treatment Plant				Wagga Wagga Sewage Treatment Plant			Picton Wastewater Treatment Plant		
	Pond #1	Pond #2	Background	Inlet	Aeration Tank	Inlet	Inlet	Lagoon #2	Lagoon #2	Aeration Tank
	02-Jul-14	02-Jul-14	02-Jul-14	08-Jul-15	26-Aug-14	17-Feb-15	21-Apr-15	06-Aug-14	29-Apr-15	25-Nov-15
Methyl tert-butyl ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethenyl acetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Butanone	2.9	0.87	0.93	6.5	ND	ND	0.23	ND	0.48	0.53
cis-1,2-Dichloroethene	3.7	13.5	ND	ND	ND	ND	ND	ND	ND	ND
Ethyl acetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroform	0.11	0.30	ND	0.03	ND	0.06	ND	0.18	ND	ND
Tetrahydrofuran	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloroethane	0.05	ND	ND	ND	ND	ND	ND	0.01	ND	ND
Carbon tetrachloride	0.08	0.10	0.09	0.04	0.10	0.07	0.06	0.07	0.05	0.08
1,2-Dichloropropane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene	1.2	4.4	ND	ND	ND	ND	ND	ND	ND	ND
1,4-Dioxane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl methacrolate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl isobutyl ketone	ND	ND	ND	0.13	ND	ND	ND	ND	ND	ND
trans-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Air Toxics VOCs	Ambient Concentration, ppbv									
	Singleton Wastewater Treatment Plant				Wagga Wagga Sewage Treatment Plant			Picton Wastewater Treatment Plant		
	Pond #1	Pond #2	Background	Inlet	Aeration Tank	Inlet	Inlet	Lagoon #2	Lagoon #2	Aeration Tank
	02-Jul-14	02-Jul-14	02-Jul-14	08-Jul-15	26-Aug-14	17-Feb-15	21-Apr-15	06-Aug-14	29-Apr-15	25-Nov-15
Methyl butyl ketone	0.32	0.07	ND	0.30	ND	0.04	ND	ND	ND	ND
Dibromochloromethane	ND	ND	ND	ND	ND	0.007 (< MDL)	ND	ND	ND	ND
1,2-Dibromoethane	ND	ND	ND	ND	ND	0.008 (< MDL)	ND	ND	ND	ND
Tetrachloroethylene	18.9	58.3	ND	ND	ND	ND	ND	ND	ND	ND
Chlorobenzene	ND	ND	ND	0.008 (< MDL)	ND	ND	ND	ND	ND	ND
Bromoform	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	ND	ND	ND	0.008	ND	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,4-Dichlorobenzene	0.02	0.04	0.006	0.02	0.008	ND	ND	ND	ND	ND
1,2-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,4-Trichlorobenzene	ND	ND	ND	0.02	ND	ND	ND	ND	ND	ND
Naphthalene	0.02	0.03	0.05	0.06	ND	0.05	0.02	ND	ND	ND
Hexachloro-1,3-butadiene	ND	ND	ND	0.002 (< MDL)	ND	0.01	0.009	ND	ND	ND

Appendix C - Non-methane Hydrocarbon VOCs in CSG Sourced Well Gas

Appendix C Table Key:
ND Not detected at or above the method detection limit (0.007ppmv)

Note: The analytical parameters were optimised for minor hydrocarbon components in the well gas at concentrations > 100ppmv. Hence reported concentrations for C_2-C_4 hydrocarbons which are greater than 100ppmv are included for information only and as a guide to the relative concentration of the minor hydrocarbon species, as discussed in Section 5.3.6 and 7.10.

C.1 AGL Gloucester and AGL Camden CSG Wells

Table C.1.1 Non-methane hydrocarbon (NMHC) VOCs measured in CSG sourced well gases

NMHC VOCs	Well Concentration, ppmv					
	AGL Gloucester				AGL Camden	
	Well G1 16-Jul-15	Well G2 16-Jul-15	Well G2 23-Sep-15	Well G3 23-Sep-15	Well C1 19-Aug-15	Well C2 19-Aug-15
Ethene	ND	ND	ND	ND	ND	ND
Ethane	136	19316	20885	1840	2669	6323
Acetylene	ND	ND	ND	ND	ND	ND
Propene	ND	ND	ND	ND	ND	ND
Propane	7.3	3174	3440	104	18.4	161
Isobutane	ND	182	194	9.7	2.4	10.7
1-Butene	ND	ND	ND	ND	ND	ND
n-Butane	0.76	248	251	9.3	1.0	5.7
trans-2-Butene	ND	ND	ND	ND	ND	ND
cis-2-Butene	ND	ND	ND	ND	ND	ND
Isopentane	ND	29.0	27.6	1.5	0.27	0.67
1-Pentene	ND	ND	ND	ND	ND	ND
n-Pentane	ND	24.0	23.5	0.87	0.09	0.49
Isoprene	ND	ND	ND	ND	ND	ND
trans-2-Pentene	ND	ND	ND	ND	ND	ND
cis-2-Pentene	ND	ND	ND	ND	ND	ND
2,2-Dimethylbutane	ND	0.19	0.11	ND	ND	ND
Cyclopentane	ND	0.73	0.58	0.03	ND	ND
2,3-Dimethylbutane	ND	0.35	0.24	ND	ND	ND
2-Methylpentane	ND	1.5	0.96	ND	ND	ND
3-Methylpentane	ND	0.76	0.48	ND	ND	ND

NMHC VOCs	Well Concentration, ppmv					
	AGL Gloucester				AGL Camden	
	Well G1 16-Jul-15	Well G2 16-Jul-15	Well G2 23-Sep-15	Well G3 23-Sep-15	Well C1 19-Aug-15	Well C2 19-Aug-15
1-Hexene	ND	ND	ND	ND	ND	ND
n-Hexane	ND	1.7	1.1	0.04	ND	0.05
Methylcyclopentane	ND	0.87	0.64	ND	ND	0.02
2,4-Dimethylpentane	ND	ND	ND	ND	ND	ND
Benzene	ND	0.58	0.48	ND	ND	ND
Cyclohexane	ND	1.7	1.3	0.05	0.02	0.06
2-Methylhexane	ND	0.08	0.06	ND	ND	ND
2,3-Dimethylpentane	ND	0.04	0.02	ND	ND	ND
3-Methylhexane	ND	0.08	0.05	ND	ND	ND
Isooctane	ND	ND	0.009	ND	ND	ND
n-Heptane	ND	0.21	0.11	0.01	ND	ND
Methylcyclohexane	ND	1.1	0.66	0.02	0.01	0.02
2,3,4-Trimethylpentane	ND	ND	ND	ND	ND	ND
Toluene	ND	0.27	0.20	0.04	0.009	0.09
2-Methylheptane	ND	ND	ND	ND	ND	ND
3-Methylheptane	ND	ND	ND	ND	ND	ND
n-Octane	ND	ND	0.01	ND	ND	ND
Ethylbenzene	ND	ND	ND	ND	ND	ND
m- + p-Xylene	ND	0.03	0.01	ND	ND	ND
Styrene	ND	ND	ND	ND	ND	ND
o-Xylene	ND	ND	ND	ND	ND	ND
n-Nonane	ND	ND	ND	ND	ND	ND
Isopropylbenzene	ND	ND	ND	ND	ND	ND
n-Propylbenzene	ND	ND	ND	ND	ND	ND
m-Ethyltoluene	ND	ND	ND	ND	ND	ND
p-Ethyltoluene	ND	ND	ND	ND	ND	ND
1,3,5-Trimethylbenzene	ND	ND	ND	ND	ND	ND
o-Ethyltoluene	ND	ND	ND	ND	ND	ND
1,2,4-Trimethylbenzene	ND	ND	ND	ND	ND	ND
n-Decane	ND	ND	ND	ND	ND	ND
1,2,3-Trimethylbenzene	ND	ND	ND	ND	ND	ND
1,3-Diethylbenzene	ND	ND	ND	ND	ND	ND
1,4-Diethylbenzene	ND	ND	ND	ND	ND	ND
n-Undecane	ND	ND	ND	ND	ND	ND
n-Dodecane	ND	ND	ND	ND	ND	ND

Appendix D – Molecular and Isotopic Composition

Appendix D Table Key:

ND	Not Detected above the method detection limit
NA	Not Analysed, usually due to insufficient sample or sample container failure
<MDL	Less than the Method Detection Limit
FR	Fractionated, isotopic alteration caused by sampling below atmospheric pressure, diffusion or leakage

D.1 Natural Sources

Table D.1.1 Molecular gas composition measured at Yaegl Nature Reserve and Cuba State Forest

Component	**Bulk Composition (mol %)**					
	Yaegl Reserve	Cuba State Forest (Camden Regional Survey)				
	Forest	River	Bushland	River	Bushland	River
	12-Jul-14	14-Oct-14	14-Oct-14	02-Dec-14	02-Dec-14	18-Feb-15 3:49 pm
Methane	ND	ND	ND	ND	ND	ND
Ethane	ND	ND	ND	ND	ND	ND
Propane	ND	ND	ND	ND	ND	ND
iso-Butane	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	ND	ND	ND
neo-Pentane	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND
Carbon dioxide	0.04	0.04	0.04	0.04	0.04	0.04
Nitrogen	78.19	78.50	78.47	78.92	79.72	78.39
Oxygen + Argon	21.77	21.46	21.5	21.04	20.24	21.57

Table D.1.2 Isotopic composition measured at Yaegl Nature Reserve and Cuba State Forest

Isotope	Isotopic Composition					
	Yaegl Reserve	Cuba State Forest (Camden Regional Survey)				
	Forest	River	Bushland	River	Bushland	River
	12-Jul-14	14-Oct-14	14-Oct-14	02-Dec-14	02-Dec-14	18-Feb-15 3:49 pm
$\delta^{13}C$ CO_2 (‰ VPDB)	-8.5	-9.6	-8.1	-9.1	-8.9	-9.0
$\delta^{13}C$ C_1 (‰ VPDB)	ND	ND	ND	ND	ND	ND
$\delta^{2}H$ C_1 (‰ VSMOW)	ND	ND	ND	ND	ND	ND

Table D.1.3 Molecular gas composition measured for air samples

Component	Bulk Composition (mol %)										
	Bell (QLD)	Tennyson (QLD)	Tara Airport (rural, QLD)	Quires road Hopeland (QLD)	Cattle grazing nearby, Hopeland (QLD)	Hopeland (flux chamber 18)(QLD)	Hopeland (flux chamber 21)(QLD)	Sturgess Baking Board road, Greenswamp (Sample 2)(QLD)	Sturgess Baking Board road, Greenswamp (Sample 1)(QLD	Farm Air, Perth (WA)	Farm Air, Laguna (NSW)
	10-Jul-14	10-Jul-14	10-Jul-14	22-May-14	22-Jan-14	23-Jan-14	23-Jan-14	21-Jan-14	21-Jan-14	28-May-14	11-Feb-14
Methane	ND	ND	ND	0.11	0.10	0.13	0.16	0.05	0.14	ND	ND
Ethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
iso-Butane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
neo-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon dioxide	0.04	0.04	0.04	0.04	0.04	0.05	0.06	0.04	0.04	0.04	0.04
Nitrogen	77.82	78.05	77.95	81.86	81.75	81.82	81.59	82.24	82.41	82.06	80.83
Oxygen + Argon	22.14	21.91	22.01	17.98	18.11	18.01	18.19	17.67	17.41	17.9	19.13

Table D.1.4 Isotopic composition measured for air samples

Isotope	Isotopic Composition										
	Bell (QLD)*	Tennyson (QLD)*	Tara Airport (rural, QLD)*	Quires road Hopeland (QLD)*¥	Cattle grazing nearby, Hopeland (QLD) *¥	Hopeland (flux chamber 18)(QLD) *¥	Hopeland (flux chamber 21)(QLD) *¥	Sturgess Baking Board road, Greenswamp (Sample 2)(QLD) *¥	Sturgess Baking Board road, Greenswamp (Sample 1)(QLD*¥	Farm Air, Perth (WA)#	Farm Air, Laguna (NSW)#
	10-Jul-14	10-Jul-14	10-Jul-14	22-May-14	22-Jan-14	23-Jan-14	23-Jan-14	21-Jan-14	21-Jan-14	28-May-14	11-Feb-14
δ^{13}C CO_2 (‰ VPDB)	-7.7	-7.4	-7.3	-8.4	-7.6	-12.6	-23.7	-7.9	-8.3	-12.6	-8.7
δ^{13}C C_1 (‰ VPDB)	ND	ND	ND	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	ND	ND
δ^2H C_1 (‰ VSMOW)	ND	ND	ND	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	ND	ND

*Gas samples from CSIRO internally funded projects and/or GISERA (Gas Industry Social & Environmental Research Alliance) projects with freedom to use data publically but with some caveats on identifying exact well locations. Reference: Day, S., Ong, C., Rodger, A., Etheridge, D., Hibberd, D., van Gorsel, E., Spencer, D., Krummel, P., Zegelin, S., Fry, R., Dell'Amico, M., Sestak, S., Williams, D., Loh, Z. and Barrett, D., (2015). Characterisation of Regional Fluxes of Methane in the Surat Basin, Queensland, Phase 2: A pilot study of methodology to detect and quantify methane sources. CSIRO Report No. EP 15369. Report for the Gas Industry Social and Environmental Research Alliance (GISERA), Project No. GAS1315. Published online at the GISERA website.

¥Natural gas seepage sites found emanating from the ground near Chinchilla, QLD. Sites were found using truck mounted Picarro instrument in survey mode looking only for methane at ambient air concentrations; once an anomaly was detected, repeated passes were then used to localise the seepage site, including the use of hand held instrumentation.

#Gas samples were taken in 2014 as part of a CSIRO Innovation Science Fund (ISF) project on fugitive emissions.

D.2 Cattle Feedlot

Table D.2.1 Molecular gas composition measured at Jindalee and Kerwee cattle feedlots

Component	Bulk Composition (mol %)				
	Jindalee Feedlot			Kerwee Feedlot (QLD)[#]	
	26-Aug-14	17-Feb-15*	22-Apr-15	01-Aug-13 (1)	01-Aug-13 (2)
Methane	ND	NA	0.01	70.67	69.98
Ethane	ND	NA	ND	ND	ND
Propane	ND	NA	ND	ND	ND
iso-Butane	ND	NA	ND	ND	ND
n-Butane	ND	NA	ND	ND	ND
neo-Pentane	ND	NA	ND	ND	ND
iso-Pentane	ND	NA	ND	ND	ND
n-Pentane	ND	NA	ND	ND	ND
C_{6+}	ND	NA	ND	ND	ND
Carbon dioxide	0.05	NA	1.56	19.45	20.16
Nitrogen	78.21	NA	77.97	8.80	8.01
Oxygen + Argon	21.74	NA	20.46	1.08	1.85

*Insufficient sample remained after analysis for carbon isotopes.

[#]Kerwee Feedlot samples (Jondaryan, QLD) were undertaken by long term bubble traps from a manure pond, taken in 2013 as part of a CSIRO project funded by Meat & Livestock Australia (MLA) B. FLT.0362.

Table D.2.2 Isotopic composition measured at the Jindalee and Kerwee cattle feedlots

Isotope	Isotopic Composition				
	Jindalee Feedlot			Kerwee Feedlot (QLD)	
	26-Aug-14	17-Feb-15	22-Apr-15	01-Aug-13 (1)	01-Aug-13 (2)
$\delta^{13}C$ CO_2 (‰ VPDB)	-9.1	-9.0	FR	4.4	4.4
$\delta^{13}C$ C_1 (‰ VPDB)	ND	ND	FR	-49.0	-48.5
$\delta^{2}H$ C_1 (‰ VSMOW)	ND	ND	FR	-341.0	-347.5

FR - Fractionated, isotopic alteration most likely caused by insufficient gas sample or equilibration during sampling.

D.3 Camden Region

Appendix D.3 Site Information:

Site 1	Medhurst Rd, Gilead	Semi-rural; near AGL CSG plant, in vicinity of motorway
Site 2	Glenlee Rd, Spring Farm	Composting facility; near train line, coal pits in vicinity
Site 3	Glenlee Rd, Spring Farm	Waste Centre; at SW boundary of landfill area
Site 4	Adriana Lane, Mount Annan	Suburban reserve; at northern edge of pond
Site 5	Glenlee Rd, Spring Farm	Rural farmland; at rail line underpass
Site 6	Racecourse Rd, Menangle Park	Racecourse; entrance roadway, semi-rural surrounds
Site 7	Glenlee Rd, Ambarvale	Semi-rural; near Menangle Rd intersection
Site 8	Cummins Rd / Fitzpatrick St, Menangle Park	Semi-rural; low density housing to south
Site 9	Menangle Road, Menangle	Semi-rural; off main road, in vicinity of woodland & river
Site 10	Off Woodbridge Rd, Menangle	Semi-rural/scrub land; on road to agricultural college

D.3.1 CAMDEN WINTER CAMPAIGN

Table D.3.1.1 Molecular composition measured at the Camden regional sites for the winter monitoring campaign

Component	Bulk Composition (mol %)									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Methane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
iso-Butane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
neo-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon dioxide	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Nitrogen	78.36	75.96	77.42	77.15	78.37	78.37	75.89	78.24	77.22	77.31
Oxygen + Argon	21.60	24.00	22.54	22.80	21.59	21.58	24.07	21.72	22.73	22.65

Table D.3.1.2 Isotopic composition measured at the Camden regional sites for the winter monitoring campaign

Isotope	Isotopic Composition									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
δ^{13}C CO_2 (‰ VPDB)	-9.1	-10.0	-8.7	-9.0	-8.9	-8.7	-9.4	-8.7	-9.6	-9.8
δ^{13}C C_1 (‰ VPDB)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
δ^{2}H C_1 (‰ VSMOW)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

D.3.2 CAMDEN SPRING CAMPAIGN

Table D.3.2.1 Molecular composition measured at the Camden regional sites for the spring monitoring campaign

Component	Bulk Composition (mol %)									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Methane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
iso-Butane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
neo-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon dioxide	0.04	0.04	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Nitrogen	78.60	78.52	78.28	78.57	78.54	78.59	78.52	78.57	78.48	78.68
Oxygen + Argon	21.36	21.44	21.67	21.38	21.42	21.37	21.44	21.39	21.48	21.29

Table D.3.2.2 Isotopic composition measured at the Camden regional sites for the spring monitoring campaign

Isotope	Isotopic Composition									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
$\delta^{13}C$ CO_2 (‰ VPDB)	-9.0	-8.5	-9.6	-8.8	-8.4	-8.3	-9.5	-8.8	-9.0	-9.2
$\delta^{13}C$ C_1 (‰ VPDB)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
$\delta^{2}H$ C_1 (‰ VSMOW)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

D.3.3 CAMDEN SUMMER CAMPAIGN

Table D.3.3.1 Molecular composition measured at Camden regional sites for the summer monitoring campaign

Component	Bulk Composition (mol %)									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Methane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
iso-Butane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
neo-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon dioxide	0.05	0.04	0.05	0.04	0.04	0.05	0.05	0.05	0.04	0.04
Nitrogen	78.15	78.15	78.26	78.13	78.19	78.29	78.15	78.22	78.12	78.08
Oxygen + Argon	21.80	21.81	21.70	21.83	21.77	21.66	21.81	21.73	21.84	21.88

Table D.3.3.2 Isotopic composition measured at the Camden regional sites for the summer monitoring campaign

Isotope	Isotopic Composition									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
$\delta^{13}C$ CO_2 (‰ VPDB)	-10.1	-8.9	-8.8	-8.3	-9.3	-10.9	-9.5	-8.4	-7.9	-7.9
$\delta^{13}C$ C_1 (‰ VPDB)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
$\delta^{2}H$ C_1 (‰ VSMOW)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

D.3.4 CAMDEN AUTUMN CAMPAIGN

Table D.3.4.1 Molecular composition measured at the Camden regional sites for the autumn monitoring campaign

Component	Bulk Composition (mol %)									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
Methane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
iso-Butane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
neo-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon dioxide	0.04	0.04	0.04	0.05	0.06	0.04	0.04	0.04	0.05	0.04
Nitrogen	78.33	78.40	78.40	78.51	78.66	78.49	78.63	78.22	78.58	78.50
Oxygen + Argon	21.63	21.56	21.56	21.44	21.28	21.46	21.33	21.74	21.38	21.45

Table D.3.4.2 Isotopic composition measured at the Camden regional sites for the autumn campaign

Isotope	Isotopic Composition									
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
$\delta^{13}C$ CO_2 (‰ VPDB)	-8.6	-8.7	-8.8	-10.1	-11.0	-9.2	-8.6	-8.9	-9.0	-9.1
$\delta^{13}C$ C_1 (‰ VPDB)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
$\delta^{2}H$ C_1 (‰ VSMOW)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

D.4 Coal Mines

Table D.4.1 Molecular composition measured for coal desorption gas from Rix's Creek coal mine, Hunter Valley

Component	Bulk Composition (mol %)		
	Rix’s Creek Coal Mine (desorption gas)*		
	In-pit 10-Oct-14	In-pit 14-Apr-15	ROM Pad# 22-Jul-15
Methane	0.74	0.02	6.97
Ethane	ND	ND	ND
Propane	ND	ND	ND
iso-Butane	ND	ND	ND
n-Butane	ND	ND	ND
neo-Pentane	ND	ND	ND
iso-Pentane	ND	ND	ND
n-Pentane	ND	ND	ND
C_{6+}	ND	ND	ND
Carbon dioxide	1.67	3.73	8.48
Nitrogen	97.59	86.07	84.56
Oxygen + Argon	ND	10.18	ND

*Coal samples are crushed chips of coal on the surface of indeterminate age since release from the coal seam, hence an unknown amount of desorbed gas has been lost prior to sampling into the canisters. The mine operators deemed it too unsafe to go near the freshly excavated coal due to the massive machines working there.

#ROM Pad – Run of mine, refers to coal in its natural, unprocessed state just as it is when mined and placed on a pad.

Table D.4.2 Isotopic composition measured for coal desorption gas from Rix's Creek coal mine, Hunter Valley

Isotope	Isotopic Composition		
	Rix’s Creek Coal Mine (desorption gas)		
	10-Oct-14	14-Apr-15	22-Jul-15
$\delta^{13}C\ CO_2$ (‰ VPDB)	-21.6	-19.2	-13.0
$\delta^{13}C\ C_1$ (‰ VPDB)	-69.2	ND	-77.0
$\delta^{2}H\ C_1$ (‰ VSMOW)	-235.6	ND	-221.7

D.5 CSG Well Gas

Table D.5.1 Molecular composition of CSG well gas

Component	Molecular Composition (mol %)							
	Sydney Basin (Camden)*							
	Well C4	Well C4	Well C5	Well C6	Well C3	Well C3	Well C7	Well C7
	20-Nov-15	12-Jan-16	20-Nov-15	12-Jan-16	20-Nov-15	12-Jan-16	20-Nov-15	12-Jan-16
Methane	95.97	95.93	94.36	95.06	96.61	96.34	95.28	95.62
Ethane	0.06	0.06	0.25	0.10	0.10	0.10	0.05	0.05
Propane	ND	ND	ND	ND	ND	ND	ND	ND
iso-Butane	ND	ND	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	ND	ND	ND	ND	ND
neo-Pentane	ND	ND	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND	ND	ND
Carbon dioxide	3.58	3.57	4.69	3.93	2.59	2.5	4.26	4.29
Nitrogen	0.35	0.39	0.64	0.83	0.61	0.94	0.37	0.37
Oxygen + Argon	0.01	0.05	0.06	0.07	0.09	0.13	0.04	0.04

*CSG well gas samples were only undertaken in the latter stages of the project once access agreements were finalised, hence not all site visits had corresponding CSG well samples.

Table D.5.2 Isotopic composition of CSG well gas

Isotope	Isotopic Composition							
	Sydney Basin (Camden)							
	Well C4	Well C4	Well C5	Well C6	Well C3	Well C3	Well C7	Well C7
	20-Nov-15	12-Jan-16	20-Nov-15	12-Jan-16	20-Nov-15	12-Jan-16	20-Nov-15	12-Jan-16
δ^{13}C CO_2 (‰ VPDB)	20.6	23.2	9.9	2.9	17.8	17.8	13.4	13.7
δ^{13}C C_1 (‰ VPDB)	-42.1	-40.7	-48.5	-48.4	-45.2	-44.6	-48.3	-47.2
δ^{13}C C_2 (‰ VPDB)	-23.7	ND	-25.1	-26.0	-26.5	-26.0	-31.0	-31.0
δ^{2}H C_1 (‰ VSMOW)	-246.3	-231.2	-240.2	-229.7	-238.2	-229.1	-232.3	-231.7
δ^{2}H C_2 (‰ VSMOW)	ND	ND	ND	ND	ND	ND	ND	ND

Table D.5.3 Molecular composition of CSG well gas

Component	Molecular Composition (mol %)							
	Sydney Basin (Camden)*							
	Well C2	Well C2	Well C2	Well C1	Well C1	Well C1	Well C8 (1)#	Well C8 (2)#
	19-Aug-15	20-Nov-15	12-Jan-16	19-Aug-15	20-Nov-15	12-Jan-16	18-Apr-13	18-Apr-13
Methane	96.19	95.31	96.61	95.94	96.13	96.38	84.60	87.40
Ethane	0.42	0.40	0.38	0.16	0.16	0.15	0.58	0.60
Propane	0.01	0.01	0.01	0.001	ND	ND	0.04	0.05
iso-Butane	ND	ND	ND	ND	ND	ND	<MDL	ND
n-Butane	ND	ND	ND	ND	ND	ND	<MDL	ND
neo-Pentane	ND	ND	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND	ND	ND
Carbon dioxide	3.17	3.11	2.7	3.55	3.36	2.69	4.09	4.19
Nitrogen	0.20	0.94	0.28	0.35	0.34	0.70	8.26	5.84
Oxygen + Argon	0.01	0.22	0.02	ND	0.01	0.08	2.40	1.94

*CSG well gas samples were only undertaken in the latter stages of the project once access agreements were finalised, hence not all site visits had corresponding CSG well samples.

#Well 8 samples were Camden CSG well head gas venting from pneumatic controls (initially well gas was used to run pneumatic valves); taken in 2013 as part of a CSIRO Innovation Science Fund (ISF) project on fugitive emissions. Since that sample collection in 2013, the Well 8 pneumatic controls have since been converted to run on compressed air instead of using the CSG well gas pressure, hence no more CSG emissions from the control valve vent lines.

Table D.5.4 Isotopic composition of CSG well gas

Isotope	Isotopic Composition							
	Sydney Basin (Camden)							
	Well C2	Well C2	Well C2	Well C1	Well C1	Well C1	Well C8 (1)	Well C8 (2)
	19-Aug-15	20-Nov-15	12-Jan-16	19-Aug-15	20-Nov-15	12-Jan-16	18-Apr-13	18-Apr-13
$\delta^{13}C$ CO_2 (‰ VPDB)	18.8	19.6	19.0	19.9	19.4	17.2	25.3	24.3
$\delta^{13}C$ C_1 (‰ VPDB)	-43.8	-44.5	-43.9	-44.9	-44.5	-43.9	-40.5	-39.5
$\delta^{13}C$ C_2 (‰ VPDB)	-26.8	-27.1	-28.7	-21.6	-21.4	-23.4	-29.2	-29.0
$\delta^{13}C$ C_3 (‰ VPDB)	ND	ND	-23.6	ND	ND	ND	-25.0	ND
$\delta^{13}C$ i-C_4 (‰ VPDB)	ND	ND	ND	ND	ND	ND	-23.8	ND
$\delta^{13}C$ n-C_4 (‰ VPDB)	ND	ND	ND	ND	ND	ND	-22.1	ND
$\delta^{2}H$ C_1 (‰ VSMOW)	-240.6	-243.7	-238.3	-240.7	-246.1	-244.6	-247.6	-247.7
$\delta^{2}H$ C_2 (‰ VSMOW)	ND	ND	-170.2	ND	ND	ND	-201.2	<MDL
$\delta^{2}H$ C_3 (‰ VSMOW)	ND	ND	ND	ND	ND	ND	-150.2	<MDL

Table D.5.5 Molecular composition of CSG well gas

Component	Molecular Composition (mol %)			
	Gloucester Basin*			
	Well G1	Well G2	Well G2	Well G3
	16-Jul-15	16-Jul-15	23-Sep-15	23-Sep-15
Methane	84.75	90.29	93.88	93.28
Ethane	0.02	1.70	1.32	0.17
Propane	ND	0.26	0.21	0.01
iso-Butane	ND	0.02	0.01	ND
n-Butane	ND	0.02	0.02	ND
neo-Pentane	ND	ND	ND	ND
iso-Pentane	ND	ND	0.001	ND
n-Pentane	ND	ND	0.001	ND
C_{6+}	ND	ND	ND	ND
Carbon dioxide	2.04	2.28	3.06	5.16
Nitrogen	13.04	4.94	1.24	1.07
Oxygen + Argon	0.15	0.49	0.26	0.31

*CSG well gas samples were only undertaken in the latter stages of the project once access agreements were finalised. The final site visit had no gas samples taken as the wells had already been suspended, pending decommissioning and abandonment.

Table D.5.6 Isotopic composition of CSG well gas

Isotope	Isotopic Composition			
	Gloucester Basin			
	Well G1	Well G2	Well G2	Well G3
	16-Jul-15	16-Jul-15	23-Sep-15	23-Sep-15
$\delta^{13}C$ CO_2 (‰ VPDB)	23.2	21.5	23.9	22.6
$\delta^{13}C$ C_1 (‰ VPDB)	-42.6	-41.6	-41.5	-41.4
$\delta^{13}C$ C_2 (‰ VPDB)	ND	-30.6	-27.4	-28.9
$\delta^{13}C$ C_3 (‰ VPDB)	ND	ND	ND	ND
$\delta^{2}H$ C_1 (‰ VSMOW)	-249.0	-250.5	-247.3	-248.7
$\delta^{2}H$ C_2 (‰ VSMOW)	ND	ND	-200.3	-204.7
$\delta^{2}H$ C_3 (‰ VSMOW)	ND	ND	ND	ND

Table D.5.7 Molecular composition of fugitive CSG well venting, abandoned coreholes, natural gas and LPG

Component	Bulk Composition (mol %)						
	Bowen Basin*	Surat Basin*				Bass Basin	Cooper Basin
	BB1	SB1	SB2	Greenswamp abandoned coal corehole, QLD	Tara abandoned coal corehole, QLD	Domestic LPG, NSW	Commercial Natural Gas, NSW
	26-Nov-13	27-Sep-13	27-Sep-13	10-Sep-13	10-Sep-13	10-Feb-2014	10-Feb-14
Methane	97.39	96.33	95.06	3.05	3.18	ND	93.44
Ethane	0.14	0.02	0.01	ND	ND	5.62	2.67
Propane	ND	ND	ND	ND	ND	93.58	0.26
iso-Butane	ND	ND	ND	ND	ND	0.12	0.02
n-Butane	ND	ND	ND	ND	ND	0.01	0.03
neo-Pentane	ND	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND	ND
Carbon dioxide	0.28	0.78	0.38	0.04	0.1	0.001	1.95
Nitrogen	1.73	2.34	3.98	77.84	77.74	0.52	1.41
Oxygen + Argon	0.46	0.53	0.57	19.06	18.99	0.15	0.21

*Gas samples from CSIRO internally funded projects and/or GISERA (Gas Industry Social & Environmental Research Alliance) projects with freedom to use data publically but with some caveats on identifying exact well locations. Reference: Day, S., Ong, C., Rodger, A., Etheridge, D., Hibberd, D., van Gorsel, E., Spencer, D., Krummel, P., Zegelin, S., Fry, R., Dell'Amico, M., Sestak, S., Williams, D., Loh, Z. and Barrett, D., (2015). Characterisation of Regional Fluxes of Methane in the Surat Basin, Queensland, Phase 2: A pilot study of methodology to detect and quantify methane sources. CSIRO Report No. EP 15369. Report for the Gas Industry Social and Environmental Research Alliance (GISERA), Project No. GAS1315. Published online at the GISERA website.

Table D.5.8 Isotopic composition of fugitive CSG well venting, abandoned coreholes, natural gas and LPG

Isotope	Isotopic Composition						
	Bowen Basin	Surat Basin				Bass Basin[#]	Cooper Basin[#]
	BB1	SB1	SB2	Greenswamp, abandoned coal corehole, QLD	Tara, abandoned coal corehole, QLD	Domestic LPG, NSW	Commercial Natural Gas, NSW
	26-Nov-13	27-Sep-13	27-Sep-13	10-Sep-13	10-Sep-13	10-Feb-2014	10-Feb-14
δ^{13}C CO_2 (‰ VPDB)	19.0	9.1	6.2	-9.5	-38.2	ND	-2.2
δ^{13}C C_1 (‰ VPDB)	-37.7	-51.5	-50.9	-56.9	-50.2	ND	-39.4
δ^{13}C C_2 (‰ VPDB)	-25.9	ND	ND	ND	ND	-34.6	-30.9
δ^{13}C C_3 (‰ VPDB)	ND	ND	ND	ND	ND	-31.7	-29.1
δ^{13}C *i*-C_4 (‰ VPDB)	ND	ND	ND	ND	ND	ND	-29.4
δ^{13}C *n*-C_4 (‰ VPDB)	ND	ND	ND	ND	ND	ND	-29.5
δ^{13}C *neo*-C_5 (‰ VPDB)	ND	ND	ND	ND	ND	ND	-28.9
δ^{2}H C_1 (‰ VSMOW)	-212.0	-210.1	-216.3	-202.8	-210.2	ND	-213.0
δ^{2}H C_2 (‰ VSMOW)	ND	ND	ND	ND	ND	-199.0	ND
δ^{2}H C_3 (‰ VSMOW)	ND	ND	ND	ND	ND	-117.5	ND

[#] Gas samples were taken in 2013 as part of a CSIRO Innovation Science Fund (ISF) project on fugitive emissions. Domestic liquefied propane gas (LPG) was sampled from a 9 kg LPG cylinder sold in Sydney. Commercial natural gas was sampled from the reticulated natural gas network piped to the CSIRO site at North Ryde, Sydney.

D.6 Landfill Sites

Table D.6.1 Molecular composition measured of landfill well gas and flux chamber samples

Component	Bulk Composition (mol %)									
	Sydney Landfill 1	Parkes Waste Facility			Summerhill Waste Management Centre (Newcastle)					
	Composite 250 wells	Seepage (342 ppm)	Flux chamber	Air sample	Composite 100 wells	Gas analyser	Unnamed well	Flux chamber	Well 5	Well 6
	29-Jan-16	19-Feb-15	28-Aug-14	28-Aug-14	9-Feb-16	28-Feb-15	16-Jul-14	16-Jul-14	16-Jul-14	16-Jul-14
Methane	51.89	ND	ND	ND	51.38	4.51	26.73	0.07	22.36	22.27
Ethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
iso-Butane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
neo-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon dioxide	35.47	0.05	0.08	0.04	35.23	5.41	22.14	0.3	19.39	22.03
Nitrogen	10.45	78.35	79.11	78.15	12.40	74.77	44.03	81.74	49.45	49.97
Oxygen + Argon	2.19	21.61	20.81	21.81	0.98	15.31	7.1	17.89	8.79	5.72

Table D.6.2 Isotopic composition measured of landfill well gas and flux chamber samples

Isotope	Isotopic Composition									
	Sydney Landfill 1	Parkes Waste Facility			Summerhill Waste Management Centre (Newcastle)					
	Composite 250 wells*	Seepage (342 ppm)	Flux chamber	Air sample	Composite 100 wells[#]	Gas analyser	Unnamed well	Flux chamber	Well 5	Well 6
	29-Jan-16	19-Feb-15	28-Aug-14	28-Aug-14	9-Feb-16	28-Feb-15	16-Jul-14	16-Jul-14	16-Jul-14	16-Jul-14
$\delta^{13}C\ CO_2$ (‰ VPDB)	14.8	-8.4	-16.1	-5.2	13.8	FR	FR	FR	FR	FR
$\delta^{13}C\ C_1$ (‰ VPDB)	-56.6	< MDL	< MDL	< MDL	-53.5	FR	FR	FR	FR	FR
$\delta^{2}H\ C_1$ (‰ VSMOW)	-288.1	< MDL	< MDL	< MDL	-277.3	FR	FR	FR	FR	FR

*Gas sample was taken after the compressor which was fed from the main distribution manifold, and was a composite of ~250 landfill gas drainage wells. This positive pressure sample did not suffer any isotopic fractionation effects and is the best average signature of the whole landfill gas at Sydney Landfill 1 site.

[#] Gas sample was taken after the compressor which is fed from the main distribution manifold, and was a composite of ~100 landfill gas drainage wells . This positive pressure sample did not suffer any isotopic fractionation effects and is the best average signature of the whole landfill gas at the Summerhill Waste Management Centre site. The other sampling locations and well head samples did suffer fractionation effects due to the slight vacuum applied on the drainage wells to aid in gas drainage. Achieving representative gas sampling while under suction does not work, either for bulk compositional or stable isotopic analyses. The only way around this would be to shut in the well and allow positive pressure to build which does raise concerns of possible over-pressurisation of the waste cell membrane.

Table D.6.3 Molecular composition measured of landfill well gas

Component	Bulk Composition (mol %)					
	Summerhill Waste Management Centre (Newcastle)					Sydney Landfill 2
	Well 1	Well 2	Well 3	Well 4	Unnamed Well	Composite 450 wells
	7-Aug-2014	7-Aug-2014	7-Aug-2014	7-Aug-2014	7-Aug-2014	7-Mar-14
Methane	28.38	35.82	33.54	30.02	27.14	48.35
Ethane	ND	ND	ND	ND	ND	ND
Propane	ND	ND	ND	ND	ND	ND
iso-Butane	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	ND	ND	ND
neo-Pentane	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND
Carbon dioxide	20.77	25.82	25.44	27.47	22.66	32.07
Nitrogen	41.13	30.83	33.54	34.25	40.77	16.48
Oxygen + Argon	9.71	7.53	7.50	8.27	9.42	3.09

Table D.6.4 Isotopic composition measured of landfill well gas

Component	Bulk Composition (mol %)					
	Summerhill Waste Management Centre (Newcastle)					Sydney Landfill 2
	Well 1	Well 2	Well 3	Well 4	Unnamed Well	Composite 450 wells*
	7-Aug-2014	7-Aug-2014	7-Aug-2014	7-Aug-2014	7-Aug-2014	7-Mar-14
$\delta^{13}C$ CO_2 (‰ VPDB)	FR	FR	FR	FR	FR	16.4
$\delta^{13}C$ C_1 (‰ VPDB)	FR	FR	FR	FR	FR	-53.0
$\delta^{2}H$ C_1 (‰ VSMOW)	FR	FR	FR	FR	FR	-255.2

*Gas sample was taken after the compressor which was fed from the main distribution manifold, and is a composite of ~450 landfill gas drainage wells. This positive pressure sample did not suffer any isotopic fractionation effects and is the best average signature of the whole landfill gas at Sydney Landfill 2 site. Gas samples were taken in 2014 as part of a CSIRO Innovation Science Fund (ISF) project on fugitive emissions.

D.7 Wastewater Treatment Sites

Table D.7.1 Molecular composition measured of air samples, flux chambers and diffuse bubbling at wastewater treatment sites

Component	Bulk Composition (mol %)					
	Singleton Wastewater Treatment Plant*			Wagga Wagga Wastewater Treatment Plant*		Dubbo Wastewater Treatment Plant*
	Pond 1 (East)	Pond 2 (West)	Influent	Aeration Tank	Inlet	Aeration Tank
	31-Oct-14	31-Oct-14	31-Oct-14	26-Aug-14	21-Apr-15	4-May-15
Methane	ND	ND	ND	ND	0.06	0.09
Ethane	ND	ND	ND	ND	ND	ND
Propane	ND	ND	ND	ND	ND	ND
iso-Butane	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	ND	ND	ND
neo-Pentane	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND
Carbon dioxide	0.12	0.16	0.05	0.04	0.07	0.06
Nitrogen	78.83	78.89	78.74	78.27	83.31	83.39
Oxygen + Argon	21.05	20.95	21.21	21.69	16.56	16.47

*The Singleton, Waga Waga and Dubbo plants did not have any gas harvesting tanks or systems, the main emissions were due to diffuse venting from the water tanks and lagoons. The samples collected as grab samples from air or floating flux chambers met with sampling difficulties; either not having sufficient methane levels or suffering isotopic fractionation effects due to very long transfer lines resulting in insufficient gas equilibration times during collection.

Table D.7.2 Isotopic composition measured of air samples, flux chambers and diffuse bubbling at wastewater treatment sites

Component	Bulk Composition (mol %)					
	Singleton Wastewater Treatment Plant			Wagga Wagga Wastewater Treatment Plant		Dubbo Wastewater Treatment Plant
	Pond 1 (East)	Pond 2 (West)	Influent	Aeration Tank	Inlet	Aeration Tank
	31-Oct-14	31-Oct-14	31-Oct-14	26-Aug-14	21-Apr-15	4-May-15
$\delta^{13}C$ CO_2 (‰ VPDB)	-9.9	-12.9	-10.2	-9.6	FR	FR
$\delta^{13}C$ C_1 (‰ VPDB)	ND	ND	ND	ND	FR	FR
$\delta^{2}H$ C_1 (‰ VSMOW)	ND	ND	ND	ND	FR	FR

Table D.7.3 Molecular composition measured of air samples, flux chambers and diffuse bubbling at wastewater treatment sites

Component	Bulk Composition (mol %)							
	Picton Wastewater Treatment Plant							
	Raw Sewerage Inlet Suction Pipe	Lagoon 2	Raw Sewerage Inlet	Lagoon 1 (Flux Chamber)	Lagoon 2 (Flux Chamber)	Lagoon 1 (Isojar)	Lagoon 1 (Bubble Trap)	Lagoon 1 (Bubble Trap)
	6-Aug-14	6-Aug-14	6-Aug-14	29-Apr-15	29-Apr-15	13-Jan-2016	13-Jan-2016	13-Jan-2016
Methane	ND	ND	ND	0.05	0.01	57.86	0.001	1.77
Ethane	ND	ND	ND	ND	ND	ND	ND	ND
Propane	ND	ND	ND	ND	ND	ND	ND	ND
iso-Butane	ND	ND	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	ND	ND	ND	ND	ND
neo-Pentane	ND	ND	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND	ND	ND
Carbon dioxide	0.04	0.04	0.04	0.16	0.07	21.91	0.05	0.89
Nitrogen	78.46	78.15	82.40	83.33	83.44	20.23	85.15	82.82
Oxygen + Argon	21.50	21.81	17.55	16.47	16.48	ND	14.8	14.53

Table D.7.4 Isotopic composition measured of air samples, flux chambers and diffuse bubbling at wastewater treatment sites

Component	Bulk Composition (mol %)							
	Picton Wastewater Treatment Plant							
	Raw Sewerage Inlet Suction Pipe	Lagoon 2	Raw Sewerage Inlet	Lagoon 1 (Flux Chamber)	Lagoon 2 (Flux Chamber)	Lagoon 1 (Isojar)*	Lagoon 1 (Bubble Trap)	Lagoon 1 (Bubble Trap)
	6-Aug-14	6-Aug-14	6-Aug-14	29-Apr-15	29-Apr-15	13-Jan-2016	13-Jan-2016	13-Jan-2016
$\delta^{13}C$ CO_2 (‰ VPDB)	-7.9	-7.6	-8.5	FR	FR	4.3	<MDL	FR
$\delta^{13}C$ C_1 (‰ VPDB)	ND	ND	ND	FR	FR	-52.4	<MDL	FR
$\delta^{2}H$ C_1 (‰ VSMOW)	ND	ND	ND	FR	FR	-303.2	<MDL	FR

*The Isojar sample contained three phases (water, gas bubbles and suspended sludge) and did not appear to suffer any isotopic fractionation effects; and is probably the best signature profile of the diffuse gas emissions at the Picton wastewater treatment plant. The Picton plant did not have any gas harvesting tanks or systems other than odour control filters on the raw sewerage inlet suction line. The Picton plant relies primarily on mechanical aeration to promote aerobic bacterial decomposition followed by aluminium sulphate flocculation and sludge decomposition in lagoons open to the air. The other samples collected as grab samples from air, flux chambers or short term bubble traps met with sampling difficulties; either not having sufficient methane levels or suffering isotopic fractionation effects due to insufficient gas equilibration times during collection.

D.8 Biogas Samples

Table D.8.1 Molecular composition measured of biogas samples

Component	Bulk Composition (mol %)					
	Biogas Samples					
	Yanco Rice Farm (bubble trap)	Yanco Rice Farm (Isojar)*	Yanco Rice Farm (bubble trap)	Freshwater Swamp (Isojar)	Food Digestor	Termite Mound
	2-Dec-14	23-Dec-14	18-Feb-15	11-Feb-2014	12-Aug-13	11-Feb-2014
Methane	ND	16.82	6.54	34.58	62.6	0.01
Ethane	ND	ND	ND	ND	ND	ND
Propane	ND	ND	ND	ND	ND	ND
iso-Butane	ND	ND	ND	ND	ND	ND
n-Butane	ND	ND	ND	ND	ND	ND
neo-Pentane	ND	ND	ND	ND	ND	ND
iso-Pentane	ND	ND	ND	ND	ND	ND
n-Pentane	ND	ND	ND	ND	ND	ND
C_{6+}	ND	ND	ND	ND	ND	ND
Carbon dioxide	0.11	11.13	0.73	13.47	31.08	1.22
Nitrogen	78.67	72.05	77.93	51.98	4.98	80.55
Oxygen + Argon	21.22	ND	14.8	ND	1.34	18.22

*The Isojar sample contained three phases (water, gas bubbles and suspended mud/organic matter) and did not appear to suffer any isotopic fractionation effects; and is probably the best signature profile of the diffuse gas emissions at the Yanco rice farm. During the height of the growing season when the rice plants are flooded, although bubbles can be seen emanating randomly from the submerged roots of the rice, collecting enough quantitative gas proved very difficult. The other samples collected as grab samples from flux chambers or short term bubble traps met with sampling difficulties; either not having sufficient methane levels or suffering isotopic fractionation effects due to insufficient gas equilibration times during collection.

Table D.8.2 Isotopic composition measured of biogas samples

Component	Bulk Composition (mol %)					
	Biogas Samples					
	Yanco Rice Farm	Yanco Rice Farm (Isojar)*	Yanco Rice Farm	Freshwater Swamp (Isojar)[#]	Food Digestor[¤]	Termite Mound[¥]
	2-Dec-14	23-Dec-14	18-Feb-15	11-Feb-2014	12-Aug-13	11-Feb-2014
δ^{13}C CO_2 (‰ VPDB)	-17.3	-19.2	FR	-10.4	10.4	-22.7
δ^{13}C C_1 (‰ VPDB)	ND	-59.3	FR	-51.2	-49.7	<MDL
δ^{2}H C_1 (‰ VSMOW)	ND	-365.3	FR	-258.6	-326.2	<MDL

[#] The Isojar sample contained three phases (water, gas bubbles and suspended mud/organic matter) and did not appear to suffer any isotopic fractionation effects; and is probably the best signature profile of the diffuse gas emissions from a swampy, black mud habitat. Gas samples were taken in 2014 as part of a CSIRO Innovation Science Fund (ISF) project on fugitive emissions.

[*#] The Isojar samples contained a small amount of oxygen at the time of collection that was subsequently consumed (chemically and/or microbially) leaving an elevated nitrogen gas background and negative carbon isotope values for the carbon dioxide. If the diffuse gas emissions had been able to be collected quantitatively, the nitrogen gas values would have been smaller with the composition being dominated by methane and carbon dioxide gas; similarly the carbon isotope values for carbon dioxide would have been slightly positive (enriched in the ^{13}C isotopes) due to the slight isotopic fractionation produced when anaerobic fermentation of organic matter occurs to produce methane.

[¤] Gas samples were taken in 2013 as part of a CSIRO Innovation Science Fund (ISF) project on fugitive emissions. In the case of the small positive pressure sample able to be taken from the enclosed food digestor tank, the bulk composition is dominated by methane and carbon dioxide with a small nitrogen gas component. A small amount of residual air was present as evident by the low oxygen+argon level. The carbon isotope value for carbon dioxide is positive (enriched in ^{13}C) due to the anaerobic fermentation of food (fruit/vegetables/processed foods/meat) and flowers in the food digestor plant.

[¥] The termite emissions are a composite gas sample of termites, soil, fungal and the microbial community within the mound. Gas samples were taken in 2014 as part of a CSIRO Innovation Science Fund (ISF) project on fugitive emissions.

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