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Characterisation of Regional Fluxes of Methane in the Surat Basin, Queensland

Phase 1: A Review and Analysis of Literature on Methane Detection and Flux Determination

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Report for the Characterising the Regional Fluxes of Methane Seepage in the Surat Basin, Queensland.

A Project undertaken as part of the Gas Industry Social and Environmental Research Alliance (GISERA)

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Executive summary

Methane seepage to the atmosphere is a common phenomenon in sedimentary basins containing coal deposits. Natural connectivity between coal seams and coal bearing aquifers and the atmosphere results the seepage of 'background' emissions of methane to the atmosphere. This project addresses the location and quantity of background methane emissions in the Surat Basin, Queensland, Australia. In particular, this report presents results of Phase 1 of the project '*Characterising the regional fluxes of methane seepage in the Surat Basin, Queensland*' undertaken as part of the Gas Industry Social and Environmental Research Alliance (GISERA) between APLNG and CSIRO. Phase 1 of the project is a '*Survey, Review and Analysis of Literature*' with the aim of tailoring a set of methods to the specific problem of locating and quantifying methane seeps. The testing of these methods is the aim of the Pilot Phase (Phase 2).

The recommendation from this review is that Phase 2 of the project consist of two components, namely:

(1) A field survey combining mobile survey and remote sensing methods to establish the location and approximate magnitude of seeps in the Walloons outcrop/subcrop areas of the Surat Basin, and,
(2) Establish an atmospheric measurement station to measure and source background methane fluxes from seeps.

The mobile survey in (1) is designed to locate the distribution of seeps using existing industry mapping and rapid deployment methods to obtain first estimates of fluxes by combining plume concentrations with atmospheric transport techniques. Remote sensing methods will be combined with the survey to both augment the mobile survey methods and establish whether useful measurements of plume concentrations can be obtained. The atmospheric measurement component in (2) is designed to provide high quality 'baseline' capability to the measurement of fluxes at key locations. In addition, deployment of remote sensing methods at the measurement tower will provide further concentrations constraints on atmospheric transport modelling.

Undertaking both these components will provide a scientifically defensible program for Phase 3 of the project '*Broad scale application of methane detection*'. This approach is designed to deal with the problems of:

(1) Considerable uncertainty associated with the distribution of methane seeps in this region, and,
(2) Diffuse/low methane fluxes from seeps and low atmospheric concentrations/detection difficulty.

The proposed methods are cost effective, scientifically robust, able to resolve fluxes and potentially scalable to large areas. It is recommended that in Phase 2 of the project the research team:

- Liaise with industry personnel to determine an appropriate mobile survey strategy and location of the pilot study for Phase 2
- Implement a mobile survey combined with remote sensing methods to locate seeps in the study region
- Undertake limited methane isotope sampling to establish sources of methane in preparation for potential further sampling in Phase 3.
- Undertake a pilot of atmospheric trace gas concentration measurements and transport modelling at location(s) informed by mobile survey, remote sensing and industry consultation.

1 Introduction

Methane seepage to the atmosphere from sedimentary basins containing coal deposits is commonplace. Methane emissions globally from geological sources are between 60 and 80 million tonnes per year (Mt y^{-1}) with between 13 and 29 Mt y^{-1} originating from seeps and micro-seeps (Etiope et al. 2012). These sources are primarily located along coal basin fringes associated with coal outcrop and subcrop formations. This project addresses these pathways of methane emissions that are considered 'non-anthropogenic' and are here referred to as 'background' methane seeps. Natural connectivity between coal seams and coal bearing aquifers and the atmosphere occurs as a result of cracks and connectivity pathways that connect coal-bearing strata with overlying soils and surface fissures providing conduits for the transport of methane to the atmosphere. This process is separate from anthropogenic pathways associated with coal mines and natural gas extraction. This project will also separate these sources of methane from biogenic sources such as decomposition of organic matter and feed lots. The consideration of the impacts of CSG field development on potential connectivity and preferred pathways of methane to the atmosphere will be part of future studies and are not considered here.

This project consists of three phases. This report documents results obtained for Phase 1 of the project. Appendix 1 of this report provides a workplan for implementation in Phase 2. The three phases are (Fig. 1.1):

- **Phase 1** consisting of a survey, review and analysis of literature on methane detection and measurement. The literature will be assessed on its applicability to develop customised methods for application to the task of quantifying methane sources and fluxes from seeps in the Surat Basin. Methods for remote sensing imaging, spectroscopy, atmospheric concentration, flux and source detection will be reviewed and a best strategy based on these methods will be proposed for deployment in the Surat Basin in Phase 2. This report advises on the best methods for deployment of a pilot study flux and establishment of a broader scale application of methods.
- **Phase 2** which will deploy a pilot study to measure methane sources in the Surat basin. The pilot study will consist of field trial(s) of (a) a remote sensing pilot, and/or (b) a ground based detection and monitoring pilot. The remote sensing approach will test new methodologies (e.g. Differential Absorption Lidar) and imaging methods. Ground based detection will test the use of atmospheric concentration and/or flux measurements as inputs to determine the capability of atmospheric transport modelling to determine fluxes of methane on a defined spatial scale.
- **Phase 3** will apply a broad scale application of methods to assess regional methane sources based on remote sensing methods to develop a survey of regional methane sources within the Surat basin. Ongoing ground based monitoring will provide a 'baseline' of methane seepage fluxes and their seasonal variations as the basis of an ongoing monitoring program.

Phase 1 of the project is entitled 'Survey, review and analysis of literature'. This phase consists of a literature review and analysis of methane detection and measurement methods with the aim of tailoring a set of methods to the specific problem of locating and quantifying methane seeps in the Surat Basin. The review will also consider the sensitivity of methods to the task of detecting and quantifying fluxes. Existing remote measurement methods for methane detection work well for concentrated point sources (e.g. pipeline leaks) but function poorly when used to detect and measure diffuse low concentration fluxes such as seeps. The research task being tackled in this project is to design, tailor, develop and adapt methods to this problem.

The **Phase 1 objective** is:

> *Review and analyse literature on methane detection and measurement. Development of tailored methods for application at pilot sites in the Surat Basin, Queensland.*

The **Phase 1 output** is:

> *A report containing proposals for discrete testing of methods at pilot sites for use in Phase 2 and the design of measurement protocols to quantify variability in background sources and ongoing monitoring at monitoring sites.*

This report utilises existing CSIRO capability to comprehensively review methods and develop an integrated measurement program of methane sources and fluxes for deployment in Phase 2 of this research program within the Surat Basin. The aim is to refine methods of methane detection, locate existing significant seeps, identify sources of methane, characterize the flux of gas and develop a scientifically robust 'baseline' of methane fluxes from seeps. The challenge is to identify methane that has migrated from a coal seam reservoir to the surface *via* seepage and separate these fluxes from other sources (e.g. biogenic methane).

In this report we present the findings of Phase 1 of the project, which involved a detailed review of literature relating to hydrocarbon seeps and the various methods used to characterise them. This report constitutes Phase 1 output of review of methods and workplan for Phase 2. The remainder of this report assesses various methods currently available for detecting seeps and measuring methane emission flux, and, recommends methodologies that are suited for use in the Surat Basin in Phase 2 of the project. The workplan for Phase 2 is provided in Appendix 1.

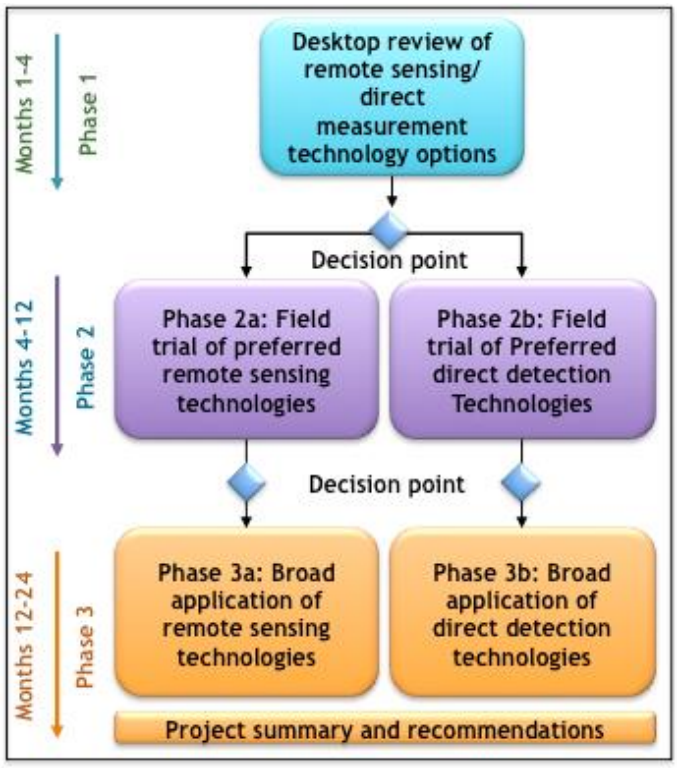

Figure 1.1. Schematic representation of the three phases of the project.

2 Methane Seeps

2.1 Global Methane Seeps

Natural methane seeps occur as a result of gas migration from underlying source rocks, including coal seams, to the surface layers by pathways such as diffusion through porespace, faults, cleavage lines and permeable alluvial sediments. In some cases, seeps may be associated with outcrops of porous shales of coal seams. The porosity and permeability of overlying strata affects the rate of seepage but other aboveground factors such as seasonal variation, atmospheric pressure or the presence of overlying water and ice (Etiope, 2012) can also lead to variation in seep rate or its location. Extraction of oil and gas from source rocks may also affect the rate of seepage (Klusman, 1993; Duffy et al., 2007).

'Thermogenic' methane production associated with coal seams, occurs along with the generation of other hydrocarbons (ethane, propane etc) from organic matter held under high temperature and pressure at depths of thousands of meters for millions of years. In sedimentary basins containing coal, methane is contained within various stratigraphic layers derived through dissolution, adsorption and trapping of migrated gas. Petroleum industry wells drilled into these layers extract gas for energy production. 'Biogenic' methane, on the other hand, is generated as a result of bacterial metabolism of either simple organic molecules (such as acetate) or the reduction of CO_2 in an anaerobic environment. The main sources of methane in the terrestrial environment include soils, wetlands, rice crops, ruminants such as livestock, termites, biomass burning, organic waste, and landfills. Emissions from these biological sources amount to about 224 80 Tg CH_4 per year (Etiope et al. 2012).

As well as natural seeps it is also possible for some mining, petroleum or other activities to induce seepage. Energy derived from combustion of coal seam gas is considered to be less greenhouse intensive than most other fossil fuels; however, the potential for fugitive releases of methane from production activities has recently come under scrutiny, largely as a result of high estimates of fugitive emissions from unconventional gas production in the United States (Howarth et al., 2011). However, the actual extent of fugitive (and background) methane release from the Australian CSG industry is not yet known with high uncertainty (Day et al., 2012). The most obvious example is coal mining which releases methane to the atmosphere through venting of open pit and underground operations. Seeps can also be caused by a geological events such as a tremor or earthquake. The Lusi mud volcano that developed in Java during 2006, for example, was initially attributed to nearby gas exploration drilling; however subsequent investigations showed that it was most likely caused by an earthquake in the region (Sawolo et al., 2009; Lupi et al., 2013).

Natural seeps may occur both on land (terrestrial) and under water (fresh water or marine) and there are many reports in the literature describing and quantifying seeps from around the world including lakes (Oremland et al., 1987), arid land (Klusman and Jakel, 1998), alpine regions (Etiope et al., 2010), tidal flats (Judd et al., 2002), oceans (Washburn et al., 2005) and even urban areas (Baciu et al., 2008). These geological sources of hydrocarbons have been classified as macroseeps and microseeps, but there are various other sources including mud volcanoes and geothermal vents (Etiope, 2012). Macroseeps are generally considered to occur over large surface areas due to migrated hydrocarbons and have been used extensively to explore for oil and gas, particularly in the United States and Middle East (Dickinson and Matthews, 1993). The features of microseeps are usually subtle but nevertheless are important indicators of hydrocarbon reservoirs and are still used for oil and gas exploration.

Worldwide, it has been estimated that there are more than 10,000 documented natural terrestrial seeps, some of which have been catalogued into a commercial database known as GLOGOS (i.e. Global Onshore Gas-Oil Seep), This database includes geographical and geochemical data that are catalogued by country and classification, and contains more than 1,150 seeps from 84 countries (Etiope, 2009). None of these catalogued seeps are located in the Surat Basin.

Global methane emissions from geological sources are significant and have been estimated to contribute between 40 and 80 Tg CH_4 per year, representing 7 to 14 % of current global methane emissions (Etiope, 2012). Of this, microseeps are thought to account for about 10-25 Tg y^{-1}, although these estimates are subject to high uncertainty (Kvenvolden 2004; Etiope; 2012). Another potentially large source of methane to the atmosphere is from agriculture. For example, intensive agricultural activities such as feedlots, can emit quantities of methane greatly in excess of natural gas production (McGinn et al., 2008). Because of the importance of microseeps to oil and gas exploration, there have been many studies worldwide to detect and characterise the seeps and a wide range of methods have been employed for this purpose ranging from direct soil gas analysis to remote sensing and other indirect methods.

2.2 Methane seeps in the Surat Basin, Queensland

The Surat Basin extends from northern NSW to southern Queensland, occupying about 300,000 km^2 (Geoscience Australia, 2013) and is an important coal seam gas production area in Australia. Current production from the basin, all of which is in south-eastern Queensland, is around 139 PJ per year but with proved and probable (2P) reserves of almost 27,000 PJ (Queensland Department of Natural Resources and Mines, 2013).

A potentially large source of background methane is from microseeps, which are frequently indicators of underlying of hydrocarbon reserves (Klusman, 1993). Sometimes seeps may be obvious, such as the case in the Condamine River near Chinchilla where methane is bubbling from the river bed or in dams and lakes where methane may be bubbling from decomposing vegetation or from underlying coal formations. However in most cases, seepage is less obvious but can occur over wide areas nonetheless. The amount of methane released through natural seeps may be substantial.

The Queensland Gasfields Commission recently examined historical records relating to methane seeps throughout Queensland. They found the results of a number of surface soil gas surveys conducted in the region between about 1983 and 1996 where elevated levels of methane and other hydrocarbons were detected not only in the Surat Basin but also the Eromanga, Cooper, Georgina, Bowen and Galilee Basins (Gasfields Commission, 2013). Moreover, there have been reports of methane outbursts associated with artesian water bores drilled in the Chinchilla region that date back to the beginning of last century (Gray, 1967).

Despite the history of natural methane seeps in the Surat region, there have been recent suggestions that drilling and hydraulic fracturing activities associated with CSG operations may generate connectivity pathways and thereby provide a route for methane to leak to the surface (Tait et al., 2013; Santos and Maher, 2012). These claims are based on measurements of ambient concentrations of methane near the ground surface and radon in the vicinity of gas production wells, however, the presence of natural and agricultural methane sources complicates the interpretation of such ambient measurements so these assertions remain unproven.

The establishment of a background monitoring capability is the first step in determining the amount of methane that enters the atmosphere naturally as part of seepage relative to the release of methane from fugitive emissions. Fugitive emissions are those that escape from gas production infrastructure such as gas wells, compressors, pipelines and processing plants. In response to the high uncertainty in fugitive methane emissions, the CSIRO in collaboration with the federal Department of Industry, Innovation, Climate Change, Science, Research and Tertiary Education (DIICCSRTE) is currently engaged in a separate preliminary research programme to directly measure emissions from CSG production wells and other infrastructure across NSW and Queensland. That project is also investigating the use of atmospheric monitoring methods with the view to using these to provide regional monitoring of emissions from CSG activities. Accurately characterising both background seepage and fugitive emissions is important for greenhouse accounting and management of industrial emissions. This project is concentrating on significant sources of methane in CSG production regions other than those concerned directly with CSG production itself.

While there are many such studies reported in the open scientific literature, there are relatively few specific to Australia. In one reported study, Simpson et al. (1991) used airborne remote sensing to survey

the Palm Valley gas field in the Northern Territory. They also conducted various field measurements including soil gas analysis at the site to validate the remote sensing data. In Queensland, soil gas surveys have been performed since at least the early 1980s as part of private oil and gas exploration programmes and recently a number of the reports from these investigations have been made publicly available (GasFields Commission, 2013). These surveys were conducted over much of Queensland including the Surat, Eromanga, Cooper, Georgina, Bowen and Galilee Basins involving measurements made on more than 5000 samples.

There are also several reports of gas seeps in Queensland especially associated with artesian water bores, some of which date back to 1916 (Gray, 1967). More recently, a significant seep in the Condamine River near Chinchilla was investigated by the Queensland Department of Natural Resources and Mines (2012) and is the subject of continuing research (Sherman et al., 2013). Also in Queensland, Day et al. (2013) measured methane emissions from a terrestrial gas seep near Chinchilla while measuring fugitive emissions from CSG wells in the region.

At present, there is very little quantitative information on the magnitude of natural seeps in the Surat Basin, including virtually all other Australian gas producing sedimentary basins, but such data are critical to properly apportion methane emissions. In recognition, this collaborative research program between Australia Pacific Liquefied Natural Gas (APLNG) and CSIRO has been established as part of the Gas Industry Social and Environmental Research Alliance (GISERA) to characterise regional fluxes of methane within the Surat Basin. The overall objective of this project is to provide a comprehensive quantitative estimate of background methane emissions from soils, rivers and agricultural infrastructure for the Surat Basin. In the following sections of this report, methodologies used for identifying and characterising methane seeps is reviewed and discussed.

3 Methane Detection and Flux Determination Methods

Microseeps are almost always indicated by some form of surface expression (Klusman, 1993). Indicators include:

- The presence of gas in the soil – either as free gas contained within the interstitial volume of the soil or as gas adsorbed onto the soil particles.
- Elevated ambient gas concentrations above the surface.
- Changes in the vegetation in affected areas; for instance, plant dieback or different vegetation type.
- Mineralogical or chemical differences between affected and non-affected regions.
- Ocean floor seeps, gases and oil films on the water surface.

All of these effects have been exploited to detect gas seeps but while detection is obviously an essential step in characterising methane seeps, quantifying the flux of methane from a seep (i.e. volume of gas per unit time) is both more important and more difficult.

Many seeps throughout the world have been the subject of investigation using a wide range of methods to detect and in some cases, measure emissions rates of methane and other gases. A summary of those relating to Australian seeps is provided in Table 3.1 which shows the types of methods employed and whether or not emission flux was measured. Also shown is a small selection of studies made in other countries that serves to illustrate the range of methods available studies.

Table 3.1 shows a distinction between those methods that provide concentration measurements of methane contrasted against those methods yielding information on fluxes. For the purposes of this work, it is important to determine both location of seeps and their fluxes. Methods that provide concentration measurements only must be combined with meteorological observation and atmospheric models to yield estimates of fluxes. The following section reviews the methods for both detecting gas seeps and quantifying their emission fluxes in Table 3.1 in detail.

Table 3.1 Summary of some studies of gas seeps in Australia and elsewhere.

STUDY	LOCATION	METHODS	FLUX MEASURED?
Simpson et al. (1991)	Palm Valley, NT, Australia	• Multispectral remote sensing to detect a colour anomaly ~1.5 x 6 km • Soil gas analyses and soil pH • Vegetation differences • Mineralogy differences	No
Various 1983 to 1996 (released by Queensland Gasfields Commission)	Queensland, Australia	• Soil gas surveys using probes and GC analyses • Data used for mapping various basins	No
Qld Dept of Natural Resources and Mines (2012)	Condamine River, Queensland, Australia	• Gas analyses and mapping of gas bubbling events	No
Day et al. (2013)	Chinchilla region, Queensland, Australia	• Flux chamber measurements of a localised seep site • Plume traverse of the same site	Yes
Dickinson and Matthews (1993)	Wyoming, USA	• Soil gas surveys using probes and GC analyses • 1890 samples used to develop maps of the region • Total area surveyed ~3300 km^2	No
Klusman and Jaykel (1998)	Denver-Julesburg Basin, Colorado, USA	• Soil gas survey using probes • Flux chambers used to map emission rates	Yes
Duffy et al. (2007)	California, USA	• Emission rates measured by enclosing vents • Gas composition measured with micro GC and isotope IRMS	Yes
LTE (2007)	Raton Basin, Colorado, USA	• Mobile ground surveys • Soil gas surveys using probes • Flux chambers at methane seep sites	Yes
Etiope et al. (2010)	Giswil, Switzerland	• Analyses of gas emanating from gas vent; composition and isotopic ratios • Flux chamber measurements to map emissions on 115 m^2 site • continuous monitoring of gas flows from vent over ~3-week period	Yes
Karion et al. (2013)	Utah, USA	• Large scale plume traverse using aircraft • Study aimed at measuring fugitive emissions from oil and gas production; probably included seep emissions	Yes
Etiope et al. (2013)	New York and Pennsylvania, USA	• Observation of flames associated with macroseeps • Analysis of gas for hydrocarbons and carbon isotopes • Flux chamber measurements of microseeps adjacent to flames and other seeps nearby	Yes

3.1 Static Terrestrial Methods

3.1.1 SOIL GAS PROBES

One of the most common methods for characterising hydrocarbon seeps is to measure soil gas composition and concentration. There are two basic approaches: (1) free gas and (2) adsorbed gas. In the first method a probe is driven into the soil up to a depth of usually less than 1 m and a sample of the interstitial gas collected for analysis. The second method involves collecting soil samples which are then heated or otherwise treated in a laboratory to remove gas physically adsorbed to the soil particles. Adsorbed gas surveys apparently have the advantage of being applicable to core samples from areas overlain by water where there is no free air present, although it appears that most terrestrial surveys are currently based on free gas analysis. It is also unlikely that the adsorbed gas method would be suitable for detecting methane due to the difficulty in quantitatively sorbing methane at low concentrations.

Soil gas surveys are commonly used for assessing and monitoring contaminated sites, especially for volatile organic compounds but also other gases including methane. Consequently, various standard methods for sampling and analysis are available (e.g. ASTM D7648 - 12 Standard Practice for Active Soil Gas Sampling for Direct Push or Manual-Driven Hand-Sampling Equipment). The methodology for soil gas analysis is relatively straightforward and essentially involves driving a metal probe into the soil then extracting a gas sample for analysis either on site or a remote laboratory. A schematic diagram of a sample probe is shown in Figure 3.1.

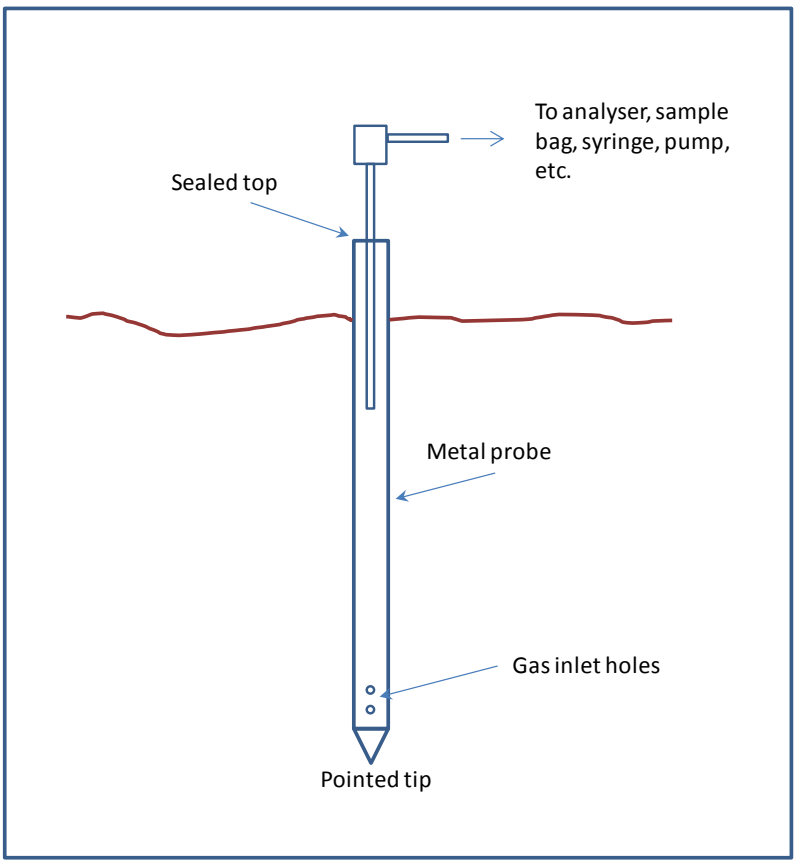

Figure 3.1. Schematic representation of a soil gas sampling probe.

Probes can be manually driven into the soil to the required depth; although for deeper sampling mechanical systems may be used to force the probe into the soil (Klusman, 1993). Alternatively, purpose drilled boreholes may be used for sampling (Hers et al., 2004). Soil gas is drawn from the surrounding soil

into the probe by applying a vacuum at the top of the probe. The vacuum can be applied by a pump or in some cases a syringe. Prior to collecting gas samples, the probe is usually purged by withdrawing some of the soil gas through the probe to ensure a representative sample is collected.

Sample gas extracted through the probe can be analysed directly in the field with a gas analyser attached to the probe system or more often by placing it in a suitable container then performing the analysis in a remote laboratory. Frequently the analyses are performed using a gas chromatograph (GC) but sometimes the isotopic composition of the gas is also measured to determine whether the gas is biogenic or thermogenic in origin. Data from soil gas surveys using probes can be used to produce maps showing the spatial distribution of soil gas concentration within a region but obviously a large number of samples are needed to create accurate maps given the likely spatial heterogeneity in methane fluxes in soil and must be repeated through time to determine temporal variability.

Soil gas surveys have been used extensively to prospect for oil and gas since at least the 1930s (Jones and Drozd, 1983). Klusman and Jaykel (1998) describe a survey undertaken in the Denver-Julesburg Basin in Colorado in the Unites States in which soil probes were used to collect samples of interstitial soil gas. They also used soil gas flux chambers as part of their survey, which are described in more detail in Section 3.1.3. The Klusman and Jaykel study examined a 1 ha test site within a region with known gas seepage. The soil gas samples were collected at 1 m depth and the data used to map the methane emission profile of the site.

Similar techniques have also been used widely in Australia. In Queensland for instance, numerous soil gas surveys were made in the Surat Basin and other potential oil and gas producing regions between the early 1980s to mid 1990s. Most of these surveys were performed by commercial geochemical consultants and were aimed at exploring the region for commercial deposits of oil and gas but many of the reports are now available on the Queensland Gasfields Commission's website (Gasfields Commission, 2013). The surveys involved field visits to sites throughout Queensland to collect soil gas samples using the probe method. Soil gas was generally sampled at depths ranging from about 0.5 to 1 m and analysed by GC for methane but also for a range of other alkanes up to pentane. Analyses were usually performed in the field at a specially set up laboratory.

The results of the Queensland surveys have been plotted on maps to show the distribution of the various hydrocarbons, although it should be noted that the spacing of the sample grids was quite coarse. Generally samples were spaced at intervals of at least 2 km but in some cases the spacing was of the order of 10s of km. The results of the surveys conducted over about 13 years, which included more than 5000 individual soil gas samples, yielded methane concentrations up to about 240 ppm methane in the soil, however, as may be expected, the range of values was highly variable with many of the results less than 10 ppm.

The examples discussed above were aimed at examining natural seeps; however, the methodology can equally be applied to seeps arising from anthropogenic causes. In a very comprehensive study in the Raton coal basin in the United States, soil gas surveys were used (among other techniques) to locate and quantify emissions from seeps both naturally occurring and those associated with coal bed methane (i.e. CSG) activities in the region (LTE, 2007). The method used by this group, however, differed from most other soil probe studies. Firstly, rather than a hollow probe, a rod about 13 mm in diameter was driven into the ground to a depth of around 1 m then withdrawn. A plastic tube was then sealed into the hole and gas extracted and analysed on site with a portable multi-gas analyser. As well, the flow of gas from the tube was measured to yield an emission rate. Like previous studies, the gas surveys were plotted on a map of the area using a GPS unit to locate each point to facilitate mapping.

In general, soil gas surveys do not provide quantitative information on the fluxes of methane from seeps, although high concentrations of gas may be associated with higher emission fluxes.

3.1.2 PASSIVE SAMPLING

Soil gases may be sampled using an adsorbent material placed below the ground surface. Klusman (1993) describes a method where free soil gas is adsorbed onto a suitable material such as activated carbon which is exposed to the soil gas for periods of perhaps several weeks. After exposure, the sample is collected and

the adsorbed gases analysed in a laboratory. The advantage of this method is that it integrates the gas concentrations over the period of the sampling and also tends to average out variability due to atmospheric effects that may be apparent with other methods.

Passive sampling is frequently used for monitoring soil gas at contaminated sites and is also used in some hydrocarbon prospecting surveys. Commercial sampling systems are available for both applications. In one system, samplers comprising an adsorbent material enclosed in a Gore-Tex fabric sleeve designed to exclude moisture, are buried within the soil (Amplified Geochemical Imaging, 2013). The exposed samples are collected and analysed in a specialist laboratory for various target compounds. The use of these samplers has been reported for collecting C_2 to C_4 hydrocarbons in a seep site in the Middle East (Hirst et al., 2004). Although such systems are capable of collecting many different types of compounds, at present there are no adsorbents available suitable for collecting methane. Consequently, the use of passive sampling for detecting methane seeps would necessitate that methane be accompanied by other gases capable of being retained by the adsorbent.

3.1.3 FLUX CHAMBERS

The soil gas surveys discussed above are generally only applied to determine the occurrence and composition of soil gas – measuring emission flux is usually not performed, although probe methods have been used to measure flux in limited applications (LTE, 2007). More commonly flux chambers are used to measure emission rates of soil gases.

There are numerous flux 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 methane (or other gas) within the chamber over time. Flux chamber measurements are mostly made in the 'static' mode in which the gas concentration within the chamber is measured over a period of time. An example of the static mode of operation is shown in Figure 3.2.

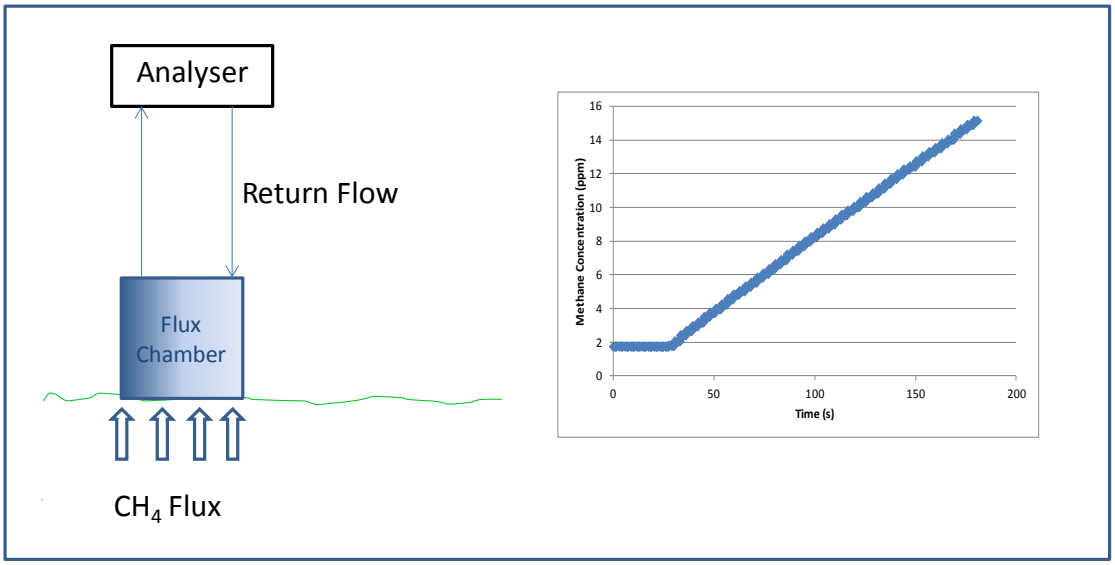

Figure 3.2. Schematic representation of a flux chamber operated in the static mode. The plot to the left shows the methane concentration within the chamber as a function of time.

In the static mode, there is no exchange of air with the outside atmosphere so the concentration of gas increases within the chamber as gas flows from the soil into the chamber during the course of the experiment. By measuring the rate of change of concentration, *dC/dt* (i.e. the slope of the plot shown in Figure 3.2), the gas flux, *F*, can be calculated according to Equation 3.1.

$$F = \frac{dC}{dt} \times \frac{V}{A} \qquad \text{Equation 3.1}$$

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. They are usually readily portable with coverage areas between about 0.1 and 0.5 m^2 (Pihlatie et al., 2013) but larger chambers are occasionally used (Carras et al., 2009).

The gas may be analysed during each experiment with a portable gas analyser in which case, the sample pumped to the analyser is returned to the chamber to prevent ingress of air. Alternatively, small gas samples may be removed with a syringe and analysed off-line (Denmead, 2008).

Flux chambers can also be operated as flow-through systems where diluent air or other gas flows into the chamber at a constant, known rate. In this mode, the steady state concentration of the gas is measured and the flux is given by Equation 3.2.

$$F = (\mathrm{C_{out}} - \mathrm{C_{in}}) \times \frac{f}{A} \qquad \text{Equation 3.2}$$

where *F* is the gas flux (mass per unit area per unit time), C_{out} is the gas concentration in the outlet flow from the chamber, C_{in} is the gas concentration in the inlet flow, f is flow rate of diluent gas and *A* is the area enclosed by the chamber.

It has 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. Static chambers may also be unsuitable in high flux applications since the gas concentration within the chamber can rapidly exceed the dynamic range of the instrument (Carras et al., 2009). However, static chambers have significantly higher sensitivity compared to flow through systems and thus in many soil flux measurements, where the emission flux is usually low, the static method is more practical.

Although flux chambers are a simple and well proven for measuring soil gas flux there are a number of factors that can adversely affect the results if due care is not taken. In particular, even 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 may 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.

Turbulence within the chamber may also affect the measured emission rate (Denmead, 2008). Some static chambers use a small internal fan to ensure that the gas is well mixed within the chamber while others do not. Debate continues as to the optimum design of flux chambers (Pihlatie et al., 2013).

Notwithstanding the potential problems associated with flux chambers, because of the relatively simplicity of method they have been used extensively for measuring soil flux, including from methane seeps. Flux chamber measurements were used in the CSG methane seep study conducted in the Raton Basin in the United States to map methane emissions in locations identified as seepage sites (LTE, 2007). A portable static chamber was used to measure emission fluxes at points adjacent to seeps identified previously in another part of the study. An example of the results is shown in Figure 3.3 where individual flux chamber measurements are indicated as coloured dots on the aerial photograph. Emission flux contours have been interpolated between each measurement point to yield an emission map.

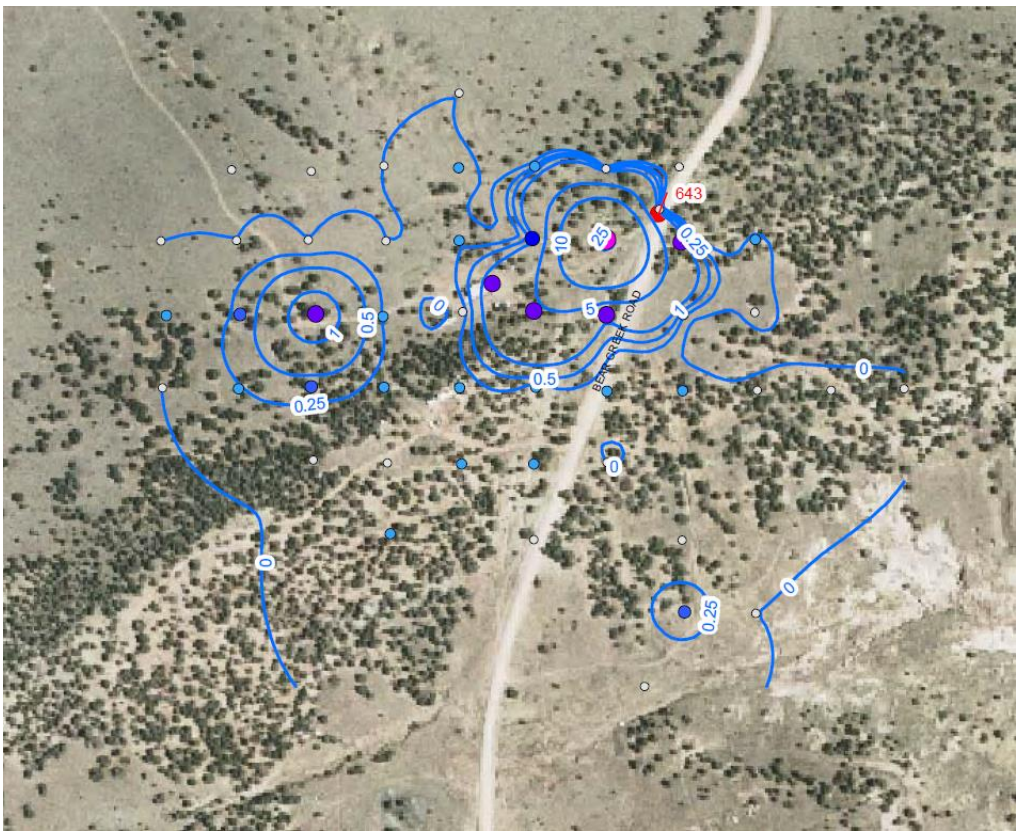

Figure 3.3. Methane emission map of a seep in the Raton Basin USA (from LTE, 2007). Methane contour lines are in units of mol/m^2 day and the horizontal scale along the bottom of the image is 975 m.

Flux chamber measurements have also been used successfully to map small scale methane seeps in Europe (Etiope et al., 2010) and Australia (Day et al., 2013). Etiope et al. (2010) measured emissions at an alpine site in Switzerland using static chambers. Forty three measurements were made within an area of about 8 × 16 m, and the results plotted to produce a contour map showing the emission flux of the several seep points located within the test area. Day et al. (2013) also concentrated on a relatively small area near Chinchilla in Queensland. In this case 50 measurements were made within an area about 40 × 80 m. The results of that study are shown in Figure 3.4 and clearly indicate that there was a strong methane source mostly localised to an area of about 20 m × 20 m square.

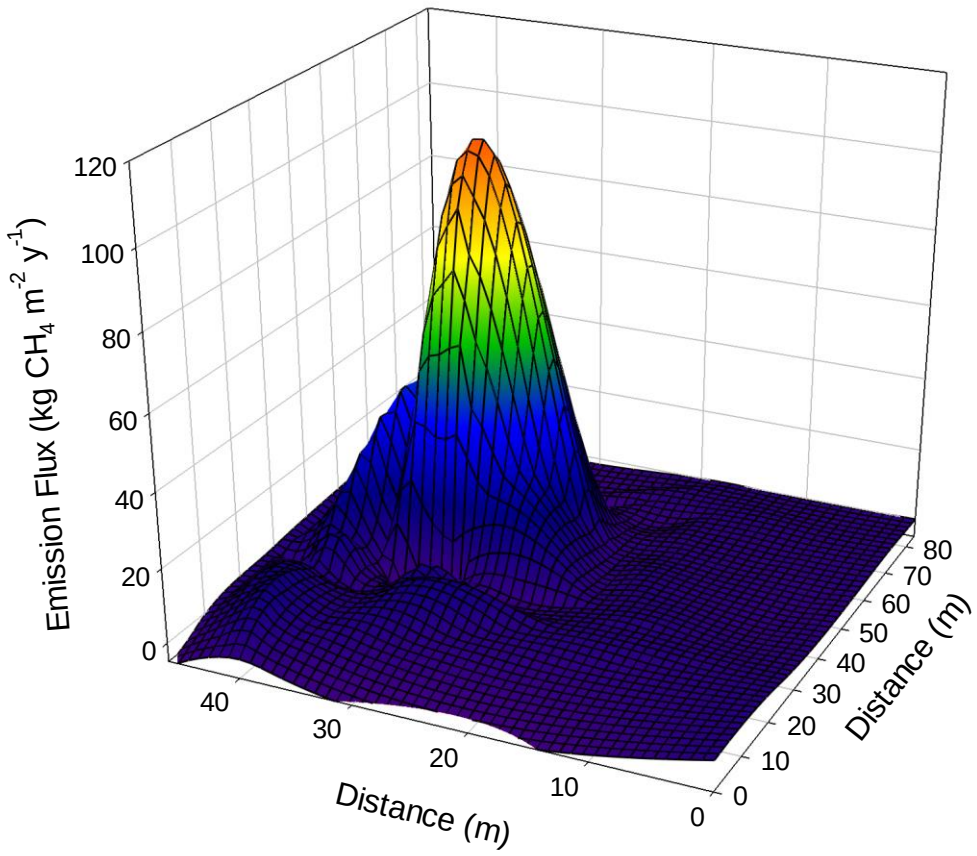

Figure 3.4. Methane emission flux profile of a methane seepage site in Queensland (from Day et al., 2013)

In another study by Etiope et al. (2013), two sites in New York State and Pennsylvania in the United States were investigated. At both of these sites, gas is seeping from the ground at a rate sufficient to sustain a flame. The New York site is a natural occurrence discovered in the 1600s whereas the Pennsylvanian site is within a disused gas producing region and the authors concluded that the gas seep may be due to a leaking abandoned well. At both sites methane and other gas emission rates were measured using a portable flux chamber and the data again used to map the emission profiles in the vicinity of the principal vent associated with the flame. The areas surveyed were localised up to about 600 m^2. At the New York site, the authors also discovered two other microseeps without obvious physical signs by measuring ambient methane levels and were able to measure the emission rates of these using the flux chamber.

A variation on flux chamber measurements was used by Duffy et al. (2007). Instead of measuring rate of change of the gas composition within the chamber, they attached gas sampling bags to the chambers and collected the gas evolved over a 15-day period. The volume of the collected gas was measured in an offsite laboratory. A similar approach was used by Etiope et al. (2010) to measure the emission flux from a source in the Swiss Alps over about a three-week period. In this case, a vent about 2 m^2 in area was covered with a plastic sheet that was sealed at the edges by covering with earth and rock. A flow meter was connected to the plastic 'tent' and the flow measured continuously over the test period. This method yielded an average flow rate from the seep of around 50-60 mL min^{-1}, however there were strong diurnal variations in flow. This highlights the point that spot measurements may not be representative of the long term average emissions rate from methane seeps.

Flux chamber measurements such as those discussed above are very useful for accurately showing the emission profile of the seep site provided that the seeps are confined to a relatively small area <1km^2. Contour maps produced using this technique also allow the total emission flux from the study area to be estimated. On the down side, flux chamber yield only point samples and hence a large number of

measurements must be made determine the actual flux from an area. For instance, in the Etiope et al. (2010) study in Switzerland the average sampling density at the site was about one flux chamber measurement every 3 m^2. Moreover, the small area covered by individual chambers means that there may be significant variability between measurements even within close proximity, thus requiring many replicate measurements for high levels of accuracy (Denmead, 2008).

Because of the large number of individual measurements required it is generally not practical to produce high resolution emission maps at a regional scale. Although regional scale measurements have been reported in the past (e.g. Klusman and Jaykel, 1998; Griffiths et al., 2010), the measurements were made at very wide spacing so that any seeps between the sample points were missed. Consequently, flux chambers are not considered to be suitable for locating and detecting seeps over large areas such as the Surat Basin unless seeps are clustered into groups over small areas. Instead, other more rapid methodologies such as mobile surveys using instrumented vehicles or remote sensing would be more suited for initial detection ahead of more detailed flux chamber surveys. These methods are considered in the following sections.

3.2 Mobile Terrestrial Methods

3.2.1 METHANE SURVEYS

Methane seeps may be distributed over very large areas of covering thousands of square kilometres and consequently some method of surveying a region is required for detecting the presence of individual seeps. In many cases, gas sampling over a grid pattern can provide an indication of the spatial distribution of microseeps. This approach was adopted for the Queensland surveys discussed previously. In each of these cases soil gas samples were collected over the region of interest and the results used to plot a concentration map for the survey area. Similarly, Klusman and Jaykel (1998) measured flux chambers to determine microseep flux distribution in the Denver Julesburg basin in Colorado. In principle, surveys based on spot measurements made at point locations can be applied to very large areas. In one example a group interested in radon flux used flux chambers to map the emission distribution across the entire Australian continent (Griffiths et al., 2010). However, such surveys are time consuming and often the measurement locations are widely spaced so that some emission sources are not detected. It is clearly of benefit to have a method for comprehensively and efficiently identifying emission sources against ambient levels.

One method is to use a vehicle fitted with a methane analyser to detect elevated ambient concentrations of methane. When higher levels of methane are found, the source can be traced and other methods such as soil gas analyses and flux chambers used to characterise the seep. Vehicle surveys have been used for many years and the CSIRO used this approach during the early 1990s to detect fugitive emissions from open-cut coal mining in NSW and Queensland (Williams et al., 1993). They used a flame ionisation detector (FID) methane analyser mounted in a vehicle to track methane plumes emitted from coal mines. While FID instruments have high sensitivity to methane and other hydrocarbons, they require a supply of high purity hydrogen to operate, which complicates mobile surveys.

Since then significant advances in instrumentation have been made and high sensitivity methane analysers such as cavity ringdown spectrometers (CRDS) that do not require external gas supplies are now commercially available. The response time of these instruments is often sufficiently fast so that surveys can be made while the vehicle is driven at normal speeds. As a result, it is feasible to survey large areas reasonably quickly. The instruments are frequently coupled with global positioning system (GPS) receivers so that spatial maps of methane concentration and be readily produced using GIS software. These systems are becoming more common and have been used for mapping leaks in urban gas reticulation systems, for instance (Phillips et al., 2013).

Mobile surveys have also been used to identify gas seeps. One of the most detailed was undertaken in the Raton Basin in Colorado during 2007 (LTE, 2007). The purpose of this investigation was to locate methane gas seeps and asses their potential as safety hazards. Although the focus of that study was to identify potential safety hazards, the methodology is the same as that required for assessing greenhouse gas emissions.

A ground survey was conducted of public, lease (private) roads and trails using a 4WD vehicle which fitted an Apogee leak detection system (which was based on an infrared spectrometer), GPS and meteorological instruments. The total distance covered during the two-month survey period was more than 5000 km. Any increase in methane concentration above background was investigated to locate the source. Once the source was located, more detailed characterisation of the site was performed, including soil gas analysis and flux chambers at multiple locations within the seep locality.

Vehicle-based measurements of ethane concentration and wind speed and direction were inverted with the use of Gaussian plume dispersion modelling to infer source distributions in a region of hydrocarbon seeps (Hirst et al., 2004). This study benefited from the barren desert environment where ethane likely had a very low background and negligible other sources.

Recently, mobile surveys have been used in Australia to investigate fugitive emissions from CSG operations. In one instance ambient methane concentration and ^{13}C isotope measurements were made around the Tara region during 2012 (Santos and Maher, 2012), however, they did not attempt to locate the sources of methane detected.

Figure 3.5 shows an example of a plot of methane concentration as measured by CSIRO during a survey in NSW and clearly shows the presence of high methane concentrations adjacent to a commercial composting facility against background levels.

Figure 3.5. An example of a mobile survey of methane concentration close to an emission source. Scales needed for concentration and distance

In a study by Day et al. (2013) mobile surveys located a number of sites around Chinchilla in Queensland where elevated levels of methane were apparent. In one case, the methane was due to cattle grazing along the side of the road. Several other instances were apparently due to methane emissions from nearby CSG production wells and in one case, a gas processing plant. In addition to these sites, one other location was examined where methane was seeping from the ground. This site had been previously located as a result of a mobile survey by one of the authors. There were no obvious signs of CSG production activity within at least 2 km of this site. The methane seep was quite localised to a land area less than about 20 m square. Once the site was identified, flux chamber measurements were made to map the extent of the source and quantify the emissions rate along with plume traverses (Section 3.2.2).

Surveys may also be conducted by taking grab samples at various locations rather than using a continuous analyser. This method was used in a study of emissions from the Denver-Julesburg basin in Colorado (Pétron et al., 2012). An advantage of this is that the air samples can be analysed for a much wider range of compounds specific to coal associated methane; the Pétron group measured concentrations of various hydrocarbons as well as methane. However, the sampling locations are much more widely spaced compared to continuous measurements.

Mobile surveys are generally conducted using by measuring methane concentration but observation of other phenomena may provide evidence of gas seepage. For example, changes in vegetation may be associated with seep sites and these variations may therefore provide an indication of seeping gas. This has been observed at a site south of Sydney where methane leaking from underlying strata was causing dieback of local vegetation, thus proving a clear indication of seepage sites (Williams et al., 1997). The Raton Basin study (LTE, 2007) also observed vegetation dieback in areas of gas seepage. Vegetation anomalies apart from dieback associated methane seepage have also been reported. Klusman (1993) cites data from Texas in the United States where the dominant oak species of the region were replaced by maples in areas with high levels of gas seepage. Other features such as mineralogy may be examined by mobile surveys, although at ground level these may be difficult to observe. Some forms of remote sensing may be more suitable for discerning small changes in vegetation type or mineralogy between gas affected regions and surrounding land.

Mobile surveys are likely to be an important aspect of any study to characterise methane seeps because they offer a relatively fast and cost-effective method to detect methane seepage. However, there are important considerations. These methods are subject to prevailing weather conditions. In windy conditions, detection will occur only if the vehicle is travelling downwind of the plume; sources may be missed if the survey route is upwind. As well, the concentrations measured are highly dependent on the atmospheric conditions. For example, under cool stable conditions (e.g. night time) concentrations are likely to be higher than under well mixed conditions (i.e. in daytime conditions in full sun), even though the emissions rate is the same. Finally, surveys generally only measure concentration. On their own, surveys of this type do not yield emission fluxes. However, with some additional measurements of meteorological conditions it is possible to derive fluxes from measurements of the methane concentration in plumes. This methodology is discussed below.

3.2.2 MOBILE GROUND BASED PLUME TRAVERSES

By mapping the methane concentration across the plume as a function of crosswind distance and height above the ground, and multiplying by wind speed, it is possible to calculate the methane source emission flux. Figure 3.6 represents the idealised downwind geometry of a plume formed as methane seeps from a ground level source.

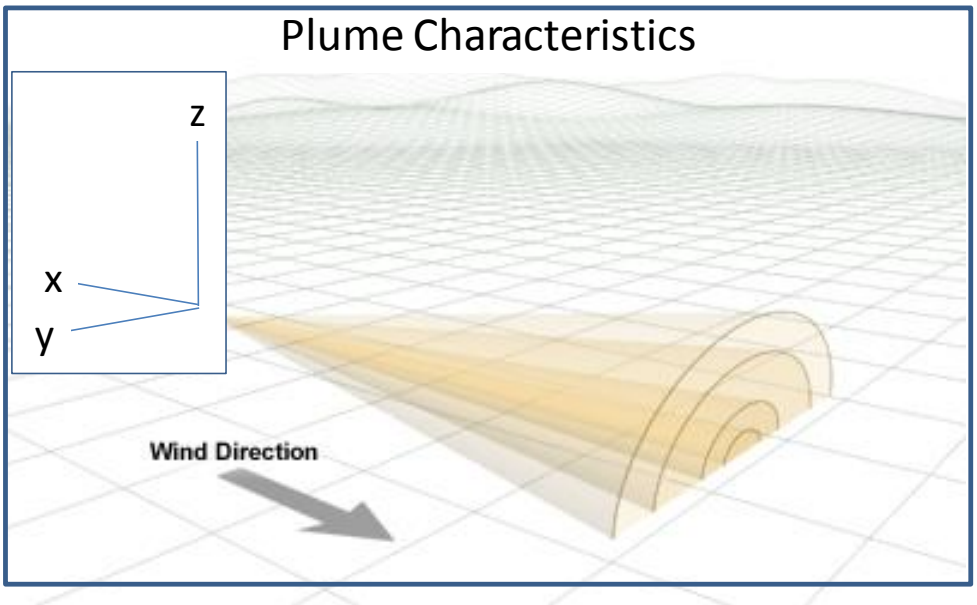

Figure 3.6. Geometry of a plume derived from a ground level source such as a methane seep.

The technique is represented in Equation 3.3:

$$Q = u \int_{-y}^{y} \int_{0}^{z} c(y,z) dy dz \qquad \text{Equation 3.3}$$

where *Q* is the emission flux, *c* is the concentration of methane, *y* and *z* are the crosswind and vertical distance, respectively, and *u* is the wind speed.

This method has been widely used both in Australia and worldwide for measuring emission fluxes of methane and other gases. Carras et al. (1991) used an aircraft to transect plumes at a regional scale to measure methane fluxes from Sydney and Brisbane during the early 1990s. One of the advantages of using aircraft is that methane concentrations can be measured in both the horizontal and vertical planes thus enabling the full extent of the plume to be defined. Airborne plume traverses were also used recently in the United States to estimate the methane flux from the Uintah Basin oil and gas field in Utah (Karion et al., 2013). This study was aimed at measuring fugitive emissions from shale gas operations in the basin but the method measures the flux from all sources. Consequently it is likely that the results included some contribution from natural seeps, decomposing organic matter in soils, methane from wetlands, lakes and weirs, and fugitive emissions.

While airborne surveys have certain advantages, especially with regard to measuring the height of the plume, there are some limitations. Firstly studies involving aircraft are usually expensive. They are also generally suited to large scale or regional studies where the plumes are many kilometres in width. More importantly, however, ground level sources such as methane seeps may require low level traverses, which may not be practical with aircraft due to the proximity to terrain and civil aviation restrictions. Some of these problems may be overcome to some extent by the use of unmanned aerial vehicles (UAVs); however, the endurance and payload limitations of these systems would need to be considered.

Plume traverses can also be conducted in many applications using a vehicle fitted with a methane analyser. Here the vehicle is driven through the plume to measure ground level concentrations. However, it is usually not practical to measure the methane concentration in the vertical direction. Instead, atmospheric observations are used estimate the plume height and the concentration profile assumed to follow a Gaussian distribution. Since the plume height is estimated rather than measured, it is generally the largest source of uncertainty associated with ground based plume traversing (Lilley et al., 2012). To reduce this uncertainty, traverses are best made when the atmospheric mixing height is lowest, e.g. cool, early morning conditions.

Notwithstanding the uncertainty associated with ground traverses, the method has been used successfully for estimating methane emissions from open-cut coal mines in NSW and Queensland (Williams et al., 1993). Surveys were made using a 4WD vehicle over distances of up to about 50 km. Measurements were made during early morning when that mixing heights were low and ground level concentrations were enhanced. Wind speeds under the conditions of the experiments were usually too low to be measured accurately with a conventional anemometer available at the time so instead, wind speed was measured by tracking helium filled balloons. An example of the results obtained by Williams et al. (1993) is shown in Figure 3.7.

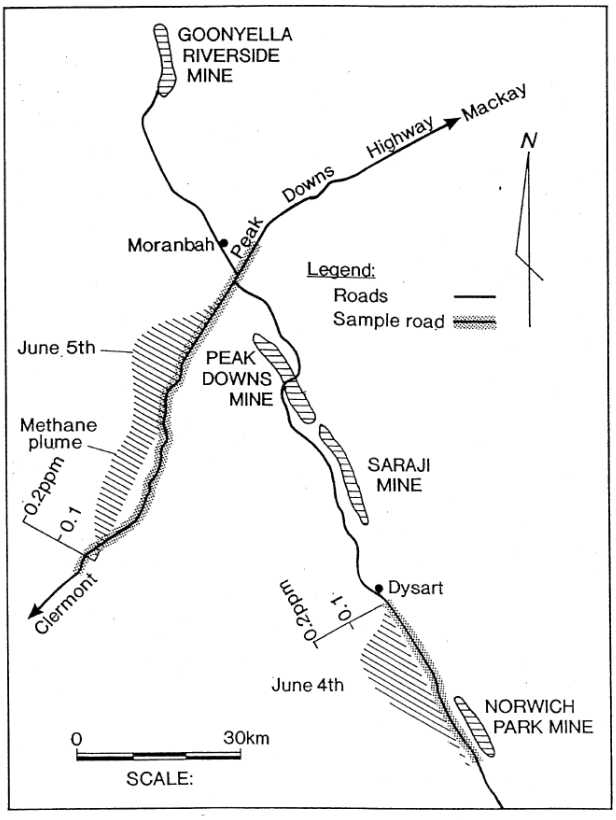

Figure 3.7. Methane concentration profiles measured in plumes emanating from open-cut coal mines in Queensland (from Williams et al., 1993)

Figure 3.7 shows the methane concentration above background as a function of distance, relative to several large open-cut coal mines in the Bowen Basin in Queensland. The results show that the methane enhancement within the plume compared to background may be quite low. In this example the maximum methane peak was only 0.2 ppm against a background of about 1.8 ppm. This illustrates the importance of using stable high-resolution instrumentation if accurate results are to be obtained. Vehicle traverses have also been employed more recently for measuring coal mining greenhouse emissions. Lilley et al. (2012) used the technique to measure CO_2 emissions from spontaneous combustion at an open-cut coal mine in NSW.

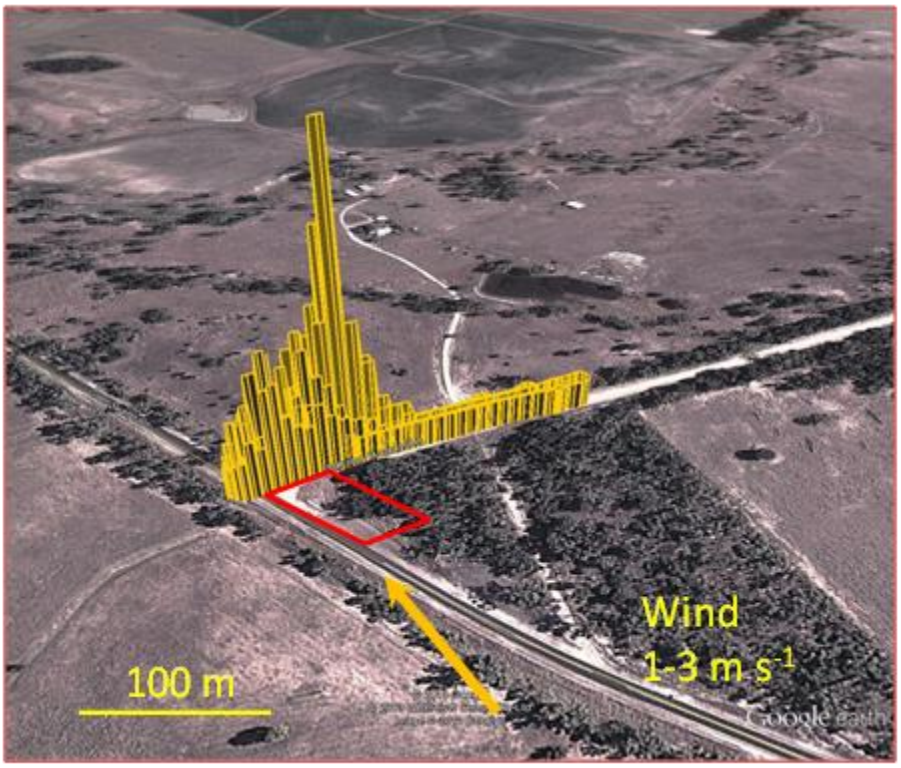

Figure 3.8. Methane concentration profile within a plume derived from a methane seep in Queensland (Day et al., 2013)

Plume traverses provide a versatile method for estimating emission flux over scales ranging from less than 20 m up to tens of km and it is likely that the technique can be successfully applied in the Surat Basin. One of the main disadvantages of this method is that the height of the plume cannot be measured which therefore introduces a significant level of uncertainty to the flux estimates. Traverses are also dependent upon favourable meteorological conditions. Another significant disadvantage of plume traverses, along with most of the methods discussed so far, is that they are essentially an 'instantaneous' measurement. It is possible that emission rates from seeps are subject to seasonal or even diurnal variation so continuous monitoring would be preferable. Using instantaneous methods, such as traverses or flux chambers would require many frequent measurements over extended periods that may not be practical. Instead continuous methods would offer a significant advantage. Continuous top-down atmospheric monitoring is possible using measurements of atmospheric composition and meteorology. These methods can be used in inverse modelling to infer the location and emission rate of sources and are considered in the next section.

3.3 Atmospheric Methods

3.3.1 STATIONARY GROUND BASED PLUME MEASUREMENTS

By combining plume traverse measurements with stationary tower or network based measurements of plume methane concentrations as a function of height, the uncertainties in quantifying methane plumes, discussed in the previous section, can be reduced considerably. All of the examples of measuring plumes by traverses, discussed above, involved large plumes (up to tens of kilometres wide). However, the technique is readily applied at the sub-kilometre scale. For example, Loh et al., (2009) used plume dispersion modelling to assess the applicability of this method to monitoring for leakage at CO_2 sequestration sites. In that study, plume concentrations were measured up to 30 m downwind of controlled releases of methane and CO_2. The concentration and meteorological data were used with a backward Lagrangian stochastic (bLS) dispersion model to estimate fluxes. The authors found that the model accurately estimated fluxes ($\langle Q_{bLS}/Q \rangle = 0.99$, $\sigma_{Q/Q} = 0.29$) when the concentration enrichment exceeded 1% of the background value. Since background concentrations of methane were less than 1.8 ppm compared to background CO_2

concentrations in excess of 390 ppm this technique was found to be particularly sensitive for methane. This study also found that an array of point measurements would be more powerful at leak detection than the open path (line-of-sight) instruments originally used. Further work (Humphries et al., 2012) used such an array of point measurements to perform 'tomography' using a Bayesian inversion technique to locate as well as quantify a source from a set of concentration measurements, to better than 3% accuracy.

3.3.2 ATMOSPHERIC CONCENTRATION MEASUREMENT AND TRANSPORT MODELLING

Continuous measurements of atmospheric composition from one or more stationary locations characterise the background variations that are the result of gas sources and sinks over a wide area. A regional monitoring record can be used to quantify the range of atmospheric variations due to such sources (natural and human-related) before any activities such as CSG production begin. The measurements can also be used as a background reference for establishing fine scale monitoring at point locations, by mobile surveys or mass balance methods over small areas, where the elevation of concentrations above the background level can be accurately quantified to reliably detect and quantify sources.

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Measurements of atmospheric composition from one or more locations record the changes that result from the gas sources and sinks upwind of the measurement. When combined with information on the wind fields, the measurements can be used to infer the location and emission rate of the sources. These are broadly know as inverse, or top down atmospheric methods.

Top down atmospheric monitoring can apply to a range of geographical scales, typically from tens of metres to many kilometres and can involve measurements from fixed or mobile platforms. This lends itself to monitoring geological seeps and links well with the smaller scale monitoring such as flux chambers. A large number of flux chamber measurements can be required to detect an anomaly within an area or to quantify the mean flux of an area (Oldenburg et al., 2003). Because they integrate across areas, atmospheric techniques average out the inherent spatial and temporal variability that affects point soil gas composition or flux measurements. Monitoring with atmospheric techniques can be done continuously, which allows for the composition variations caused by wind variations and the changing emissions rates from seeps and other sources. It can run over periods of many years to characterise seasonal and inter-annual variations and the changes in background levels that may occur as an industry is introduced to a region.

A two year record of regional background methane concentrations is shown in Figure xx. When high methane values caused by light winds and stable night time conditions are removed, the record more closely follows the lower range of concentrations representative of the free troposphere. Many of the remaining elevated values in the filtered record can then be traced to emissions from sources such as the controlled releases at gas handling facilities (Etheridge et al., 2011; 2013).

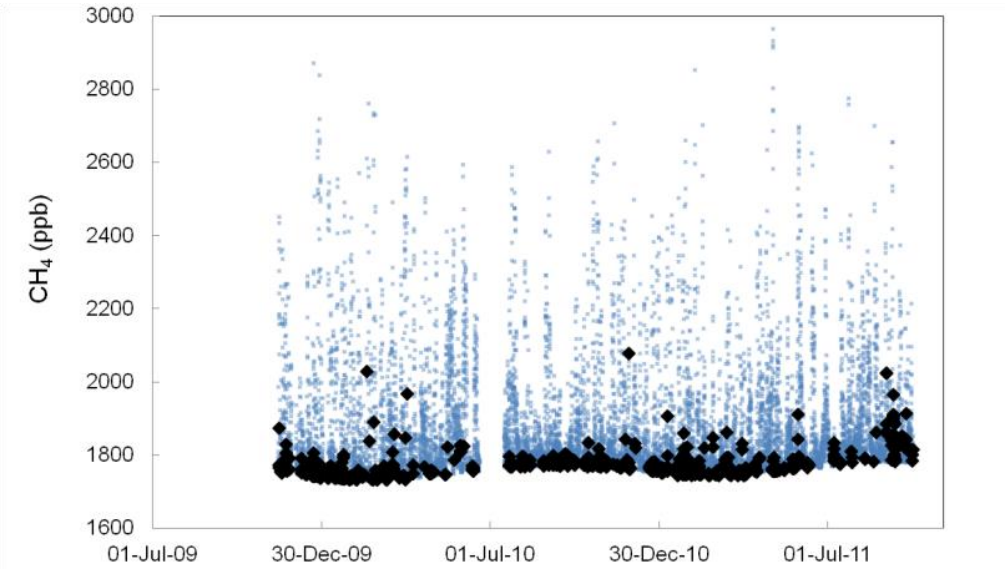

Figure 3.9. Hour mean methane concentrations from the atmospheric monitoring station at the CO2CRC Otway Project (Loh et al., 2011; Etheridge et al., in preparation). Blue crosses are all data, black triangles are filtered data (see text).

A similar regional continuous atmospheric monitoring station has been established at Arcturus, near Emerald in Queensland (Berko et al., 2012). The methane record shows a smaller range of concentrations (200-300 ppb), as would be expected from the more arid conditions of that region. Occasional elevated methane levels of about 100 ppb in the Arcturus record have been traced through transport modelling to emissions from coal mines tens of kilometres (Etheridge et al., 2010).

Seeps could potentially be detected by similar background monitoring used at the Arcturus and Otway stations, depending on their emission rate and proximity to the station. A monitoring network could be devised from estimates of seep locations and strengths, using atmospheric dispersion modelling, to optimise the detection and quantification of continuous monitoring. Targeted, smaller scale monitoring campaigns described earlier could then be deployed in areas where the continuous monitoring infers likely sources to be.

At Cape Otway, Victoria, the CSIRO and CO2CRC undertook continuous monitoring at two points nad an inverse modelling system using backward Lagrangian transport modelling to infer the source location and emission rate of a controlled gas release at the CO2CRC Otway project (Luhar et al., 2013). The predicted emissions compared favourably with the measured values (Table 1), though the result is better for methane because of its lower background concentration and variability and thus a higher signal to noise ratio. This test provides improved confidence in using atmospheric concentration measurements to measure methane fluxes from point source emissions.

	CH_4		CO_2	
Source parameter	Actual	Predicted	Actual	Predicted
q (g s^{-1})	8.4	7.8 ± 1.5	96.2	180.6 ± 57.2
x_s (m)	- 49	-59.9 ± 7.3	- 49	- 49.3 ± 12.7
y_s (m)	-136	-172.2 ± 9.1	-136	- 87.5 ± 37.0
z_s (m)	2.5	14.2 ± 1.7	2.5	10.2 ± 7.3

Table 3.2. Source strength and location derived from the Bayesian inverse modelling (Luhar et al., 2013).

3.3.3 EDDY COVARIANCE

The eddy covariance (EC) method calculates the flux from the land surface to the atmosphere from high frequency measurements of the fluctuations in wind speed and concentrations. It is widely used in micrometeorology and ecosystem studies to measure continuous fluxes of CO_2, water vapour and heat exchange between ecosystems and the atmosphere. EC measurements are usually made from a short stationary tower (Figure N.N).

High frequency analysers have recently been become available enabling methane fluxes to be measured by the EC technique, such as the Li-7700 (Li-Corr, Nebraska, USA) and the Picarro G2311-f analyser (http://www.picarro.com/products_solutions/gas_analyzers/fast_co2_ch4_h2o_for_ec_flux). An example of a period of CH_4 EC flux measurements is given in fig xx. The "footprint" of EC is of the order hundreds of metres which would be suitable for monitoring the emission rate of a seep if the location is known. An emission due to geological seep would need to be detected and quantified above the natural methane flux, which can vary significantly over hour, diurnal and longer timescales due to production and loss within the soil and exchange with the atmosphere.

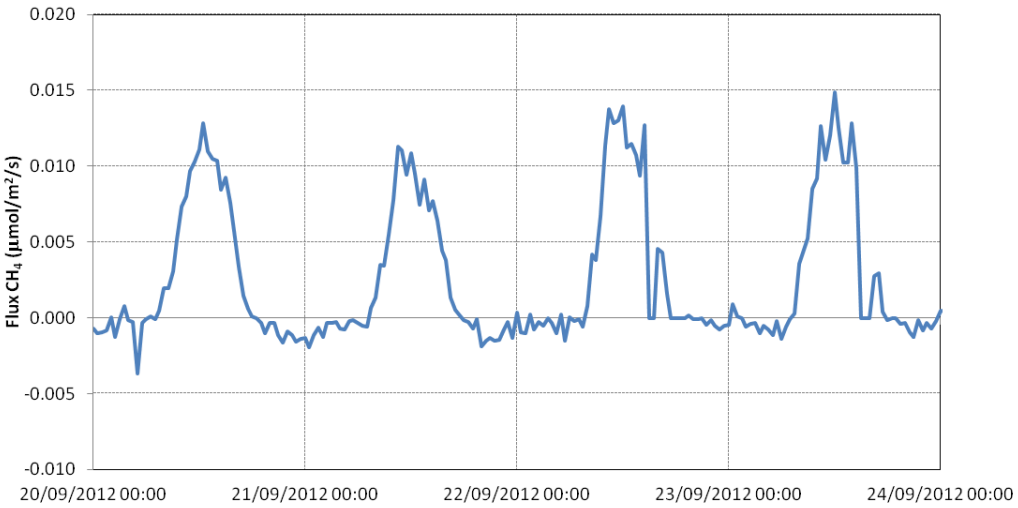

Figure 3.10. Methane fluxes measured from an eddy covariance tower at Arcturus, Queensland. Positive values are emissions to the atmosphere. (Unpublished data of CSIRO and Geoscience Australia).

3.4 Aquatic Methods

Gas transfer across the air-water interface has been studied for decades because of its importance to both chemical process engineering (Danckwerts 1951) and the ecological functioning of aquatic environments such as the ability of rivers to assimilate organic loading (O'Connor & Dobbins 1958). Much of the research in the past few decades has focussed on improving our understanding of carbon fluxes through aquatic ecosystems (Cole and Caraco 1998) and since the late 1990's new impetus has been given to measuring GHG fluxes from reservoirs arising from a concern about the greenhouse gas impact of hydropower reservoirs (Fearnside 2002). In this section we review methods used to measure gas fluxes across the air-water interface that are most relevant for the quantification of gas seeping from below into rivers, lakes and other bodies with a free surface.

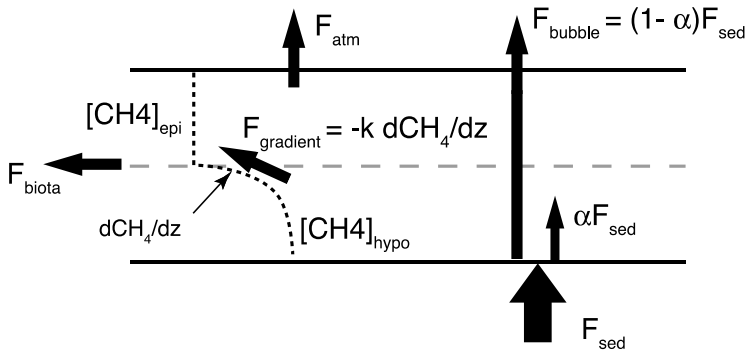

Figure 3.11. Conceptual diagram of methane flux pathways in a water column. F_{sed} is the flux entering the bottom of the system of which αF_{sed} is dissolved into the water column during the passage of the bubbles from the sediment to the atmosphere.

Determining the flux of gas from a seep that enters the bottom of an aquatic system requires consideration of both bubbles and the dissolved gas. Of the gas entering the bottom of the water column (Figure) a proportion of the total gas flux is dissolved into the water as bubbles pass through the water column while the remainder escapes to the atmosphere. In stratified systems the dissolution of gas produces a

concentration gradient with higher dissolved gas concentrations at the bottom of the water column but in well-mixed systems, such as a flowing river, we generally expect a uniform concentration with depth. The proportion of the initial gas flux that dissolves increases with the depth of the water column, i.e. the contact time between the bubble and the water increases, and bubble dissolution becomes less efficient as bubble diameter increases. Using the model of bubble dynamics of McGinnis et al. (2006) we have estimated the percentage of CH_4 dissolving into a 2 m-deep water column (typical of the Condamine River) to fall in the range 1-15% for bubble diameters ranging from 3 to 25 mm.

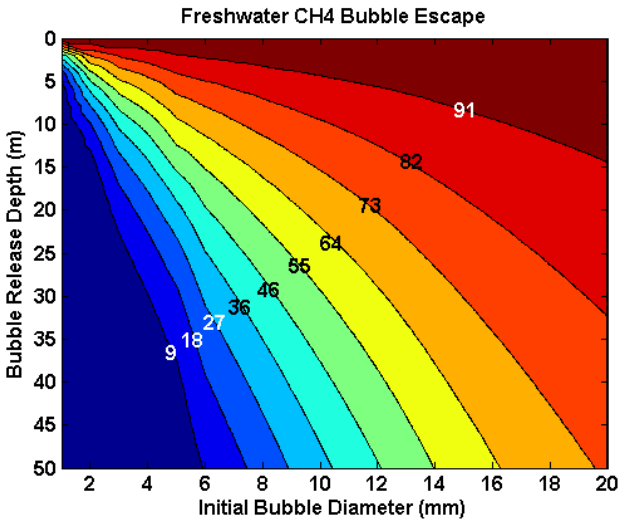

Figure 3.12 Fraction of bubbles escaping to the atmosphere as a function of depth of release and bubble diameter as computed using the model of McGinnis et al. (2006). *Figure courtesy of Tonya DelSontro.*

The dissolved methane leaves the system in three ways: dissolved CH_4 is advected 'out' of the system by river flow; some CH_4 is oxidised *in situ* by methanotrophic bacteria; and the remainder outgasses to the atmosphere *via* the diffusive and bubble pathways. The total flux of gas from a seep within a river reach will be the sum of the diffusive flux, the bubble flux, the *in situ* oxidation flux, and the advective flux. Ultimately, the advected CH_4 will either be oxidised to CO_2 or outgassed as CH_4. The efficiency of oxidation of dissolved CH4 varies widely (by more than 10x) between systems (e.g. Bastviken et al. 2003; Guérin & Abril, 2007) and should probably be determined on a case by case basis. When considering the GWP impacts of the seep flux, the portion of the CH_4 flux that is oxidised to $CO2_{\text{i}}$s only 4% as effective as a GHG (in terms of warming potential) had it been emitted to the atmosphere as CH_4.

The diffusive gas exchange with the atmosphere is driven by the concentration difference between the gas dissolved in the water near the surface and the concentration of gas that is in equilibrium with the atmosphere. Aquatic systems are virtually always supersaturated with methane with respect to atmospheric equilibrium and this concentration difference drives a flux across the entire surface area of a water body. Bubble fluxes have much greater rates than diffusive fluxes but only occur over very small areas. In order to measure the seepage flux it is necessary to determine both the bubble flux and the diffusive flux.

CSIRO research on emissions from reservoirs shows very high and persistent spatial variability in fluxes from systems receiving fresh organic matter from the catchment. In such systems, emissions at the upstream ends of reservoirs (deposition zones for terrestrial organic matter) are often 100 x greater than emissions near the dam wall with the consequence that 80-90% of total reservoir emissions are emitted from about 10% of the surface area (Sherman et al. 2012). The accuracy of estimates of system-wide emissions is greatly improved by accurate resolution of the spatial variability in emissions.

Most direct measurements of gas fluxes across the air-water interface are made using the following techniques:

- Floating chambers (Lambert and Fréchette, 2005)
    - recirculating
    - once-through
- Hydroacoustic techniques (DelSontro et al 2007)
- Bubble traps
    - autonomous continuously recording (Varadharajan and Hemmond, 2012)
    - short term manual sampling

In addition to these direct measurement techniques, it has been common practice to employ the 'Thin Boundary Layer' (TBL) model of gas transfer (Liss and Slater 1974) to indirectly estimate fluxes over large areas using wind speed and measurements of dissolved gas concentration

3.4.1 FLOATING CHAMBERS

Floating chambers (FC) can be used to measure both diffusive and bubble fluxes whereas hydroacoustic and bubble trap techniques are suitable for systems dominated by bubble emissions (Figures 13 and 14).

Floating chambers are deployed on the water surface and the change in gas concentration in the chamber headspace is recorded as done in terrestrial flux chambers; Section 3.1.3) periodically during the duration of the chamber deployment (Lambert and Fréchette, 2005). Early applications of this approach relied on periodic withdrawal of gas samples from chamber for subsequent analysis by GC in a laboratory and did not include a recirculating loop. As field portable gas analysers became available the periodic sampling approach was replaced with a continuously recirculating system. For many lakes and reservoirs, the FC approach was useful for CO_2 but not for CH_4 because of the relatively high limit of detection and coarse resolution of field gas analysers (Tremblay, pers. comm.). The relatively recent advances in online gas analysers such as the cavity ringdown spectrometer (CRDS, e.g. Picarro 1301) have allowed very accurate measurement of the low concentrations of CH_4 (0.7 ppb resolution) typically encountered in freshwater environments. CRDS instruments have also simplified the logistics by eliminating the need for sample dessication prior to measurement. CRDS-based FC systems were first adapted for field use on lakes by CSIRO and are now routinely used for measuring FC headspace gas concentration by many organisations around the world.

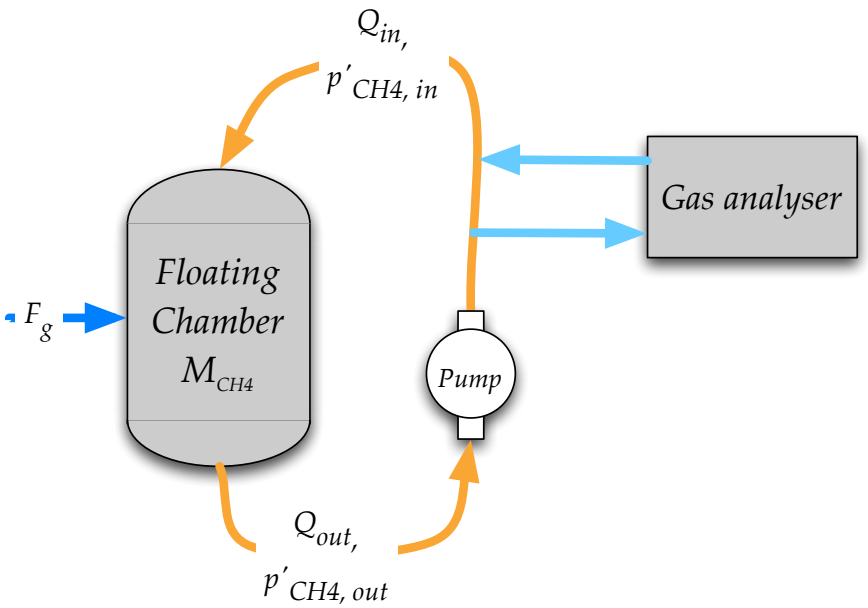

Figure 3.13 Recirculating floating chamber system. Gas is circulated continuously through the yellow circuit and the gas analyser draws a small subsample of this gas stream through its measurement cavity before returning the gas to the recirculation loop.

An example of a FC measurement with both diffusive and bubble fluxes is shown in Figure 9. Diffusive fluxes are indicated by the yellow bands and are characterised by an effectively linear change in concentration with time. Bubble fluxes are shown in the blue ovals and are characterised by rapid increases in concentration that produce a 'step' in the concentration time series.

To calculate a diffusive flux, a linear regression is fitted to the gas analyser data to give the rate of change in partial pressure of CH_4 in the air stream out of the FC, $d/dt\ p'_{CH4,out}$, and the resulting slope is used to determine the flux, F_g, as,

$$F_g = 0.0121866 \frac{V_c p_{atm}}{(A_c T_c)} \frac{d}{dt} p\text{¢}_{CH4,\ out}$$

where V_c is the chamber volume (m^3), A_c is the surface area of the water captured by the chamber (m^2), T_c is the temperature (°K), and p_{atm} is the ambient atmospheric pressure (mb). When bubbles enter the chamber, the flux is computed as the difference in concentration divided by the duration of the deployment (red dashed line in Figure 9).

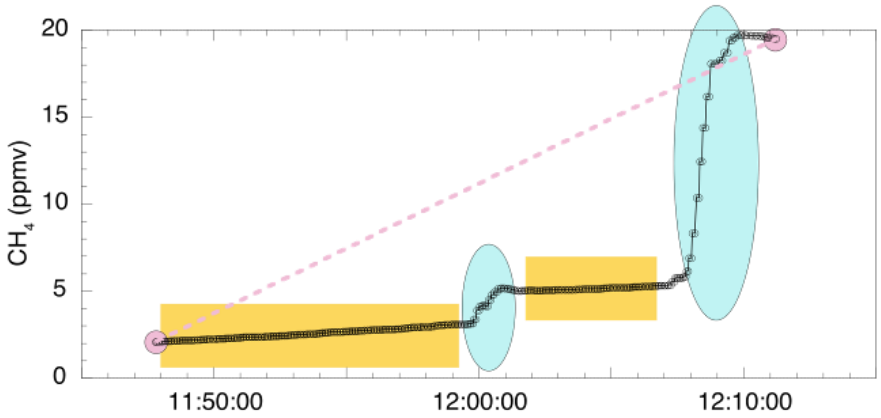

Figure 9 Example of bubbles in a flux chamber measurement. Gold shaded rectangles denote periods of diffusive flux only; blue shaded ellipses show entry of methane containing bubbles into flux chamber. Dashed line links end points used to compute net flux of methane.

Measurement accuracy and repeatability for CH_4 fluxes is best when purely diffusive conditions prevail. The correlation coefficient for the linear regression of a single deployment is typically $r^2 > 0.95$. CSIRO experience in 3 different reservoirs has yielded a typical standard error of replicate measurements (std dev / mean value) of ± 5-10% for diffusive sites (this includes variability associated with changing wind speed between replicate measurements) and ± 50-100% for sites with significant, but intermittent, bubbling.

It is also possible to use a floating chamber in 'once-through' mode (Figure). In this case atmospheric air enters the chamber through an orifice while chamber air is pumped through a gas analyser. Typically, the chamber contains an internal fan to facilitate mixing within the chamber. The 'once-through' mode of operation is conceptually similar to dye-dilution methods used quantify discharge in hydraulic structures. There is an assumption that the gas entering the chamber enters at a constant rate and has a constant composition during the course of the measurement. By varying the flow rate through the chamber, it is possible to dilute the chamber gas concentration and extend the range of fluxes that can be measured by a specific gas analyser should the analyser's maximum limit of detection be exceeded. This method requires measurement of the chamber gas flow rate (Q_{out}) as well as the atmospheric gas concentration. The method may not be suited for use under conditions of variable atmospheric gas concentration.

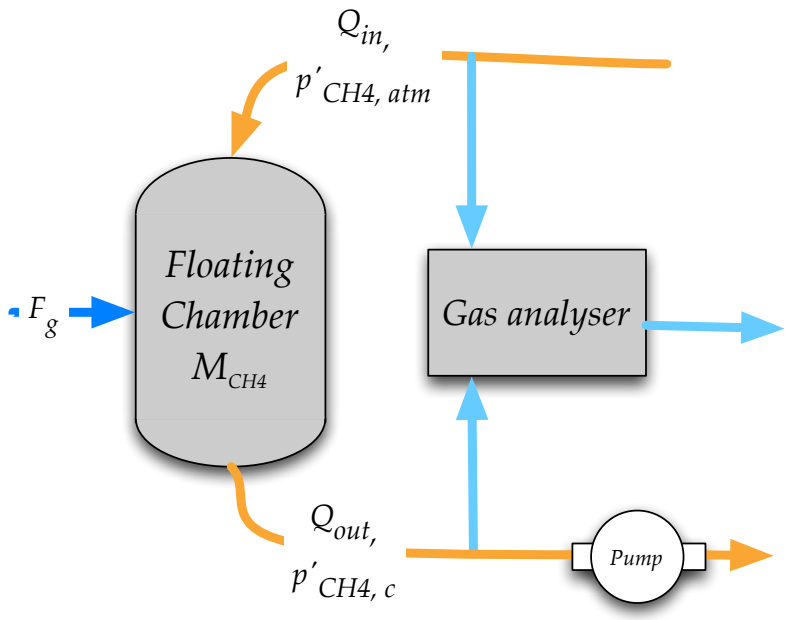

Figure 3.15 Once-through floating chamber system.

Figure 3.16 Floating chambers deployed for diffusive flux measurement in the Condamine River.

Figure 3.17 Picarro gas analyser system used for Condamine FC measurements.

3.4.2 HYDROACOUSTIC TECHNIQUES

Hydroacoustics have proven very useful for the identification and quantification of bubble fluxes in reservoirs (DelSontro et al. 2011). These measurements confirm the very high spatial variability of

individual seeps both in terms of their spatial location and their intensity. They are able to survey large areas quite quickly (Figure 16). To date these systems have been used in a downwards-facing mode which limits their suitability for shallow water columns. Their suitability for use in a horizontal deployment has not been demonstrated but may be possible.

The equipment required for these measurements is quite portable but the analysis of the data requires highly specialised knowledge. Because they measure bubble size and velocity only, they provide a direct estimate of volume flux. It is necessary to collect samples of gas for analysis in order to compute mass fluxes.

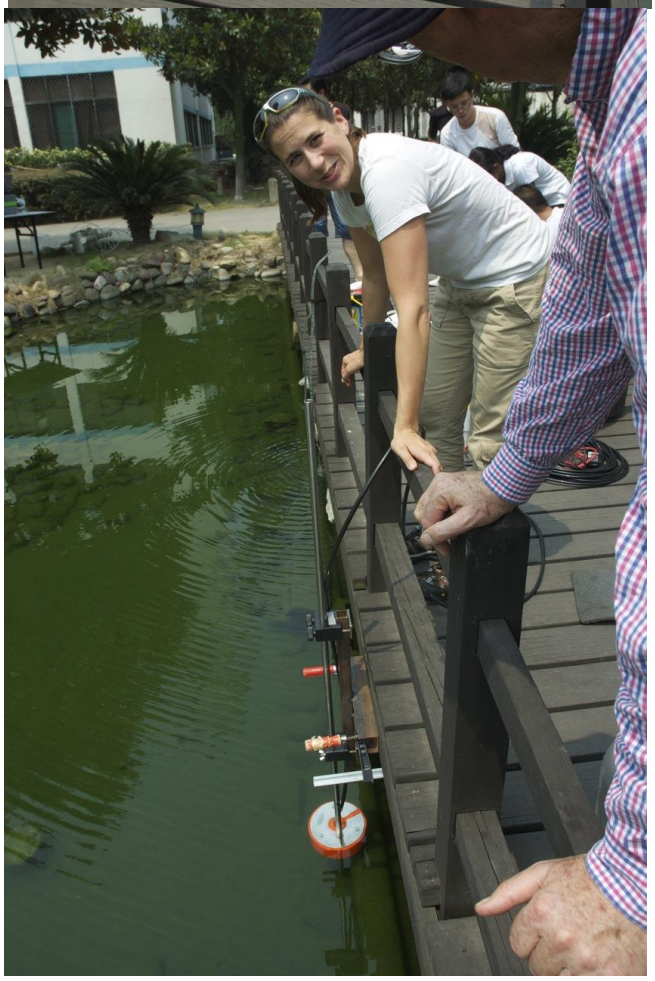

Figure 3.18 Hydroacoustic system for measuring bubble fluxes used by eawag. Left) ancillary computers and power supplies. Right) transducer assembly.

3.4.3 BUBBLE TRAPS

Bubble traps are best suited to measurement of smaller individual bubble plumes. They consist typically of a funnel which collects the gas and delivers it to a chamber (Figure). Initially the system is purged completely with water. As gas accumulates it displaces water from the trap and the volumetric gas flux can be directly determined. By increasing the capture area of the funnel relative to the area of the chamber, a bubble trap can 'amplify' the flux thereby making it easier and quicker to quantify fluxes from weaker sources. Bubble traps often have a spigot and/or rubber septum on the top to allow collection of gas from the chamber headspace for subsequent analysis in the lab by GC.

Figure 3.19 Bubble traps used in the Condamine River. Top) Ready for deployment. Bottom) Checking the traps. Note the trap at the bottom left has collected sufficient gas to rise up out of the water.

A bubble trap provides volumetric flux measurement over a small capture area. This information can provide useful insight into the fine scale spatial variability of individual bubble seeps which is relevant to the design of a sampling protocol to estimate fluxes from an entire reach.

In most natural waters, bubbles are emitted periodically and the accuracy of the volumetric flux rate will be affected by the duration of the deployment. Synchronous bubble emission events from numerous sites throughout Mystic Lake have been observed using long-term deployments of sophisticated bubble traps with embedded pressure sensors and data loggers (Varadharajan & Hemmond 2012). Such bubble events have been correlated with changes in barometric pressure and can reasonably be expected to respond to other causes of pressure drops such as sudden changes in water velocity at the sediment interface. If one assumes that bacterial production of methane in sediments occurs at a continuous rate, bubbles of methane will form and grow in size steadily within the sediment matrix until they become so large that their buoyancy causes them to detach from the sediment and enter the water column. Changes in the ambient pressure due to weather patterns, changing water levels, etc can alter the volume of the bubbles rapidly as well as influence the rate of bubble growth, potentially contributing to the variability in the timing of emission events. To adequately capture the temporal variability of a bubble seep, bubble traps need to be deployed for at least several bubble event periods. The Condamine River is unusual in the sense that the visibly obvious (but still small) bubble plumes emit at a much steadier rate than is typically observed in other systems. Measurement of very large bubble fluxes requires large floating chambers to allow adequate time to observe the change in headspace volume in the chamber.

The gas emission captured by a bubble trap or chamber (mols s^{-1}), is derived from the Ideal Gas Law as

$$\frac{dn}{dt} = \frac{d}{dt}\frac{P\,V}{R\,T} = \frac{V}{R\,T}\frac{d}{dt}P - \frac{P\,V}{R\,T^2}\frac{d}{dt}T + \frac{P}{R\,T}\frac{d}{dt}V$$

where n is the number of mols of gas in a chamber of volume, V, at temperature T (°K) and pressure P (atm) and R is the universal gas constant (R = 8.205746 x 10^{-2} L atm K^{-1} mol^{-1}). Neglecting the pressure and temperature change terms introduces a measurement uncertainty of ≤ 5% for gas flows ≥ 3 L min^{-1} for conditions experienced in the field near Chinchilla.

Deployment of two 1 sq m chambers over the large seeps in the Condamine River have shown very consistent volumetric gas fluxes with a standard error of ≤ 5% in the mean measured flux when quadruplicate measurements are performed.

3.4.4 GAS FLOW METERS

It is possible to directly measure the gas flow rate from a seep by capturing the gas in a hood (e.g. the floating chamber) and routing the gas through a flow meter. This has been done in the United States (Oldaker, pers. comm.). Measuring gas flows accurately at atmospheric pressure with small pressure drops of a few mb is technically challenging. The feasibility of this method depends upon the gas flow rate and the pressure drop available across the flow meter. If a hood can be weighted sufficiently then measurement of arbitrarily high flows is possible.

In the Condamine River, variable bathymetry and the need to conduct measurements over a variety of seeps prevents anchoring the hood to the bottom. In this case the pressure drop available is limited to the additional mass of the chamber supported by the headspace gas as the chamber rises out of the water. In practice this amounts to no more than 3.5 mb.

Using mass flow meters we have found that we can measure up to 7-10 L min^{-1} with some confidence. As the flow rate increases, so too does the pressure drop across the flow meter and eventually this pressure drop exceeds that available in the chamber and gas escapes under the edge of the chamber into the water. Conversion of the volumetric gas flux to a mass flux requires collection of gas samples for laboratory analysis or direct measurement in the field using a gas analyser.

One further consideration is that it may take some time for the system to equilibrate, i.e. for the chamber to fill with gas to the extent that the pressure change in the chamber exactly matches the pressure drop through the flow meter and associated tubing.

The Bronkhorst mass flow controllers used in the Condamine River project have a specified accuracy of ± 0.5% of reading + 0.1% full scale.

3.4.5 THIN BOUNDARY LAYER ESTIMATION

The 'Thin Boundary Layer' (TBL) model (Liss and Slater, 1974) represents gas transfer as occurring by molecular diffusion across thin boundary layers of thicknesses δ_{atm}, δ_{water} characterised by linear concentration gradients on the air and water sides of the interface, respectively (Figure 10). For most gases, including methane, diffusion across the water side boundary layer is the rate limiting step and we neglect as inconsequential the transport across the boundary layer on the atmosphere side of the interface in the remaining analysis.

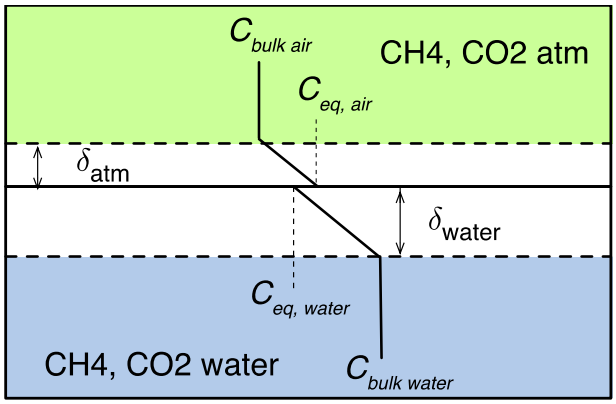

Figure 10 Schematic representation of gas concentrations in the Thin Boundary Layer model. *Figure adapted from Liss and Slater (1974).*

Following Liss and Slater (1974) the flux, F_g (mol m^{-2} s^{-1}), across the interface is given by,

$$F_g = k(C_{bulk\ water} - C_{eq,\ water})$$

where

$$C_{eq,water} = k_H\, p'_{bulk\ air}$$

$C_{eq,water}$ = concentration of dissolved gas at equilibrium with the atmosphere (mol m^{-3})

$p'_{bulk\ air}$ = partial pressure of the gas in the mixed atmosphere (atm)

k_H = Henry's constant (= 1.4×10^{-6} mol m^{-3} atm^{-1} for CH_4 @ 25 °C)

k = gas transfer velocity (m s^{-1})

The solubility of methane in water is strongly temperature dependent and can be reasonably estimated as

$$k_H\,(T) = 3.3 \times 10^{-3} - 1.36 \times 10^{-3} \log(T)$$

where T is the water temperature (°C) and log denotes the base-10 logarithm.

The gas transfer velocity, k, depends upon turbulence in the water column (Vachon et al. 2010) and increases as the turbulent velocity scale increases in response to: wind, penetrative convection driven by surface cooling, and flow-induced turbulence generated by shear stress on the bottom of the river channel.

Application of the TBL to estimate gas fluxes requires an estimate of water column turbulence and data for the dissolved gas concentration. It's application to large lakes and the oceans has traditionally assumed k to be a function of wind speed only (Wanninkhof et al. 2009) whereas its use for rivers assumes that k varies with mean river velocity (O'Connor and Dobbins 1958).

3.5 Isotope Methods

3.5.1 ISOTOPES OF TERRESTRIAL METHANE FLUXES

A potentially powerful tracer to identify methane sources and aid in the quantification of their emission rate is the isotopic composition of the CH_4. Methane from different sources carries distinctive carbon (^{13}C: expressed as $\delta^{13}C$) and hydrogen (^{2}H: expressed as $\delta^{2}H$ or δD) stable isotopic composition.

Measurements of $\delta^{13}C$ in methane in air were used to identify the source of the gas released during the field trials of Loh et al., (2009) and in mobile surveys to quantify the relative contribution of fugitive natural gas emissions to total emissions in basins in Utah and Colorado (Rella et al., 2013). Both of these studies benefited from large methane concentration enhancements and, importantly, significant differences between the isotopic composition of the source methane being assessed and the other methane sources in the area.

Given an atmospheric CH_4 concentration of 1800 ppb with a $\delta^{13}C$ value of -47 ‰, an enhancement of 100 ppb of CH_4 with a $\delta^{13}C$ value of -70 ‰ (such as from a biogenic source) will change the $\delta^{13}C$ value to -48.2 ‰. If the same enhancement of CH_4 was due to a source with a $\delta^{13}C$ signature of -30 ‰ (for example, thermogenic gas), the $\delta^{13}C$ of the atmospheric CH_4 would be -46.1 ‰. In order to discriminate between these two sources, a measurement precision of better than 1 ‰ is required. Larger concentration enhancements would lead to larger isotopic changes. Differences between the methane isotopic composition of the sources that are smaller than these examples reduces the ability of isotopic methds to discriminate between the sources, for example, biogenic natural gas which has $\delta^{13}C$ values closer to many biological methane sources. Methane from coal seams in the Surat Basin has $\delta^{13}C$ values typical of biogenic natural gas (Golding et al., 2013; S. Sestak, CSIRO, personal communication) which suggests there are limited opportunities to use this isotope to distinguish from biological sources. However its $\delta^{2}H$ value is significantly different from biological sources and might allow stronger discrimination, especially in combination with $\delta^{13}C$.

The current state of the art for the measurement of $\delta^{13}C$ and $\delta^{2}H$ of CH_4 is stable isotope ratio mass spectrometry (SIRMS; Rice et al., 2001; Miller et al., 2002). This technique is presently not suitable for continuous operation at field locations and requires samples to be collected from a site and returned to a central laboratory for analysis. Current measurement precisions for SIRMS are ±0.04 ‰ for $\delta^{13}C$ and ±1.5 ‰ for $\delta^{2}H$ of CH_4 on a 1 litre air sample and both these precisions would be suitable for discriminating sources in the cases described above. A suitable sample collection strategy using both manually collected samples and automated sample collection could be used for source identification and quantification but risks missing many episodes as plumes from sources reaching measurement sites. Continuous measurement of CH_4 concentration and stable isotopic composition offers the best opportunity to detect emissions and to identify and quantify the source.

Currently available technology for the continuous measurement of the $\delta^{13}C$ of CH_4 is capable of delivering precision better than 1 ‰ for a 5 minute average (Picarro G2132-i Analyzer datasheet; downloaded from http://www.picarro.com/products_solutions/isotope_analyzers/13c_for_ch4). While details are not yet available, another continuous instrument (Aerodyne Research: QC Laser Trace Gas Monitor) that offers simultaneous measurement of $\delta^{13}C$ and $\delta^{2}H$ is being developed that could be deployed in a (remote) field situation.

A further opportunity for identifying and quantifying CH_4 sources exists in measuring the ^{14}C composition of CH_4. This allows the discrimination of "modern" (mainly biogenic) and "fossil" (geological) CH_4 sources, as modern CH_4 contains the signature of the modern source material while fossil sourced CH_4 contains no ^{14}C. ^{14}C analysis of CH_4 would require large air volume sample collection, separation of the CH_4 and conversion to graphite and then ^{14}C analysis by accelerator mass spectrometry, and is not suitable for field deployment and continuous operation.

3.5.2 ISOTOPES OF AQUATIC METHANE FLUXES

It has become increasingly common to employ analysis of carbon 13 ($\delta^{13}C$-CH_4) and deuterium (δD-H_2O) isotopes in attempts to attribute methane to different potential sources. Using simple mixing models for which there is adequate separation of $\delta^{13}C$ values for the endpoints, it is possible to deduce the relative contribution of the different sources of C as it moves up the food chain. Here we consider a typical thermally stratified freshwater lake or reservoir with anoxic conditions in the bottom waters separated by a strong chemical and thermal gradients from an oxic surface layer.

Bacterial production of methane in anaerobic lake sediments produces very depleted CH_4 in the bottom waters with $\delta^{13}C$-CH_4 for dissolved methane typically ~ -70 to -80 $^{o}/_{oo}$ {Peterson, 1999, #37844; Bastviken et al., 2003, #48540; Schubert et al., 2010, #86542}. In the aerobic surface layer, dissolved CH_4 $\delta^{13}C$-CH_4 tends to be in the range -60 to -50 ppt as oxidation by methanotrophic bacteria preferentially utilises the lighter carbon isotope leaving the heavier isotope to diffuse towards the surface waters. Sediment and particulate organic matter generally have $\delta^{13}C$-CH_4 around -30 ppt (-35 to -19 ppt range, Bastviken et al 2003).

In a thorough study of $\delta^{13}C$ in three SE-Australian billabongs by Bunn and Boon {%Bunn and Boon, 1993, #46191}, the amount of $\delta^{13}C$ in the primary food sources (vegetation, phytoplankton, etc) ranged from -30 to -25 ppt whereas a substantial fraction of primary and secondary consumers (e.g. zooplankton, mussels, fish, etc) had signatures in the range -35 to -30 and suggested that methane, being relatively depleted in ^{13}C compared to other food sources, was likely to provide an important source of C to the food chain.

Because Surat Basin coal seam gas has an $\delta^{13}C$-CH_4 in the range -60 to -50 ppt, i.e. quite similar to $\delta^{13}C$-CH_4 of dissolved CH_4 in natural oxic waters, ^{13}C data is unlikely to shed much light on the source of CH_4 in gas emitted from the Condamine River. Gas samples collected in the Condamine River have $\delta^{13}C$-CH_4 of -59.3 to -63.4 (DNRM 2012) and -54.8 to -58.8 (CSIRO, in prep).

The use of noble gas isotopes, ^{20}Ne, ^{36}Ar and ^{84}Kr, ^{4}He, ^{21}Ne and ^{40}Ar and ^{136}Xe has proven very useful in identifying the relative contributions of methane desorbed from coal seams and that exsolved from groundwater (Zhou et al., 2005; Lollar and Ballentine, 2009).

3.6 Remote Sensing Methods

Attempts to identify gaseous emissions using remote sensing platforms have a long history. A large part of the earlier works were aimed at identifying emissions from volcanic venting and ranged from laser based approaches (Hobbs et al., 1991) to Fourier transform infrared (FTIR) methodologies (Mori et al., 1993). In these studies SO_2 and HCl were of interest, but the common theme of such methodologies, and those that came after them is the targeting of specific absorption features within the electromagnetic spectrum for differing gases.

This section summarises the instrumentation types that have been deployed for the detection of CH_4. The strengths and weaknesses of different instrument types, their respective platforms, and examples of how they were used in the detection of the gases will be presented.

3.6.1 HYPERSPECTRAL SENSORS (4-20 NM SPECTRAL RESOLUTION)

Hyperspectral remote sensing imagers (HSI) that cover the 400-2500 nm spectral region are generally used to estimate surface reflectance spectra which in turn are used to produce ground based products. Such sensors include the Airborne Visible Infrared Imaging Spectrometer (AVIRIS) (Vane et al., 1993), the HyMap sensor (Kruse et al., 2000) and the Airborne Prism EXPeriment (APEX) (Itten et al., 1997).

HSI instruments usually comprise hundreds of spectral bands within the 400-2500 nm spectral region with spectral resolutions that range from approximately 4-20 nm (Figure 9). Imagers fall into two different scan mode configurations:

1. pushbroom and
2. whiskbroom.

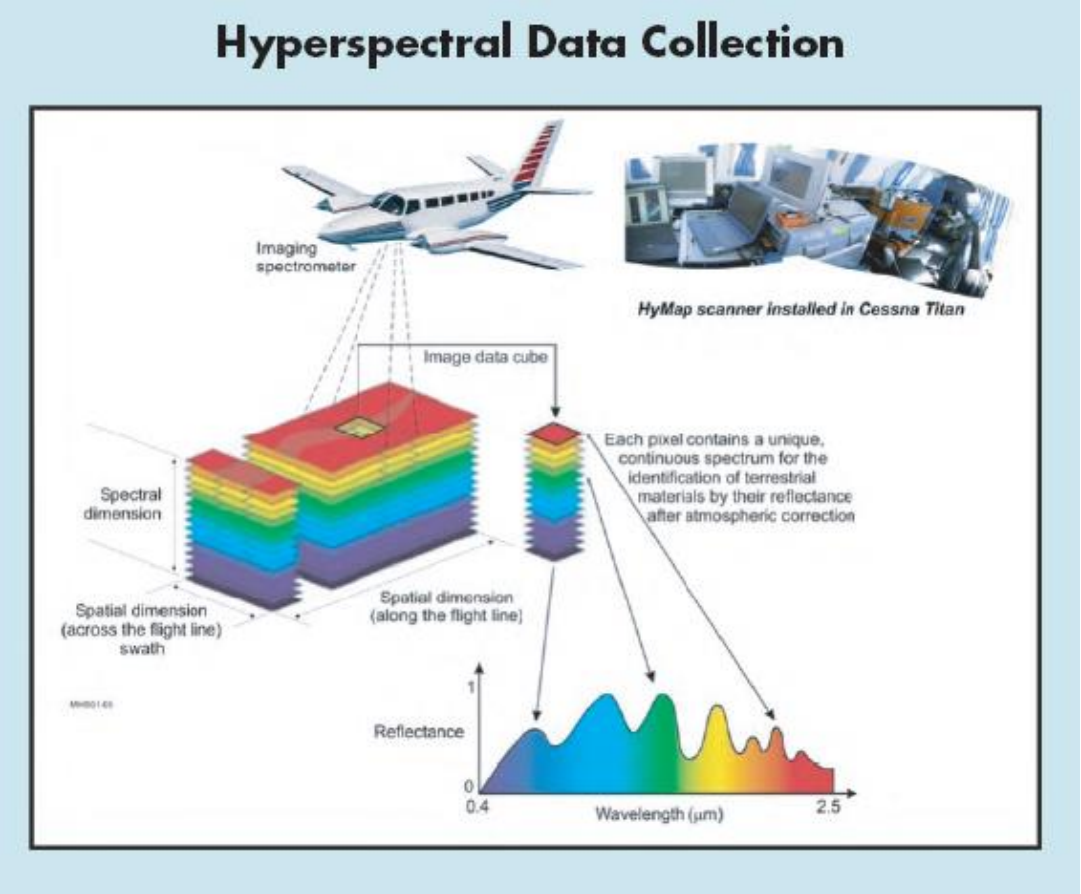

Figure 3.21: Hyperspectral concept.

While both configurations collect across-track data in a different manner HSI's build up a 2-dimensional image by combining the across-track data with the along-track data as the sensor moves, thus creating a raster array of the scene.

The HSI's that encompass the 400-2500 nm spectral region overlap at least two CH_4 absorption features. The features of interest are located at approximately 1650 and 2300 nm (Figure 10). Of the two spectral features, the 1650 nm is the least affected by overlap with other atmospheric constituents (Riris et al., 2010). The 2350 nm spectral feature on the other hand has an overlap with both atmospheric water vapour and surface mineralogical features that occur at 2350 nm such as carbonates (Figure 11).

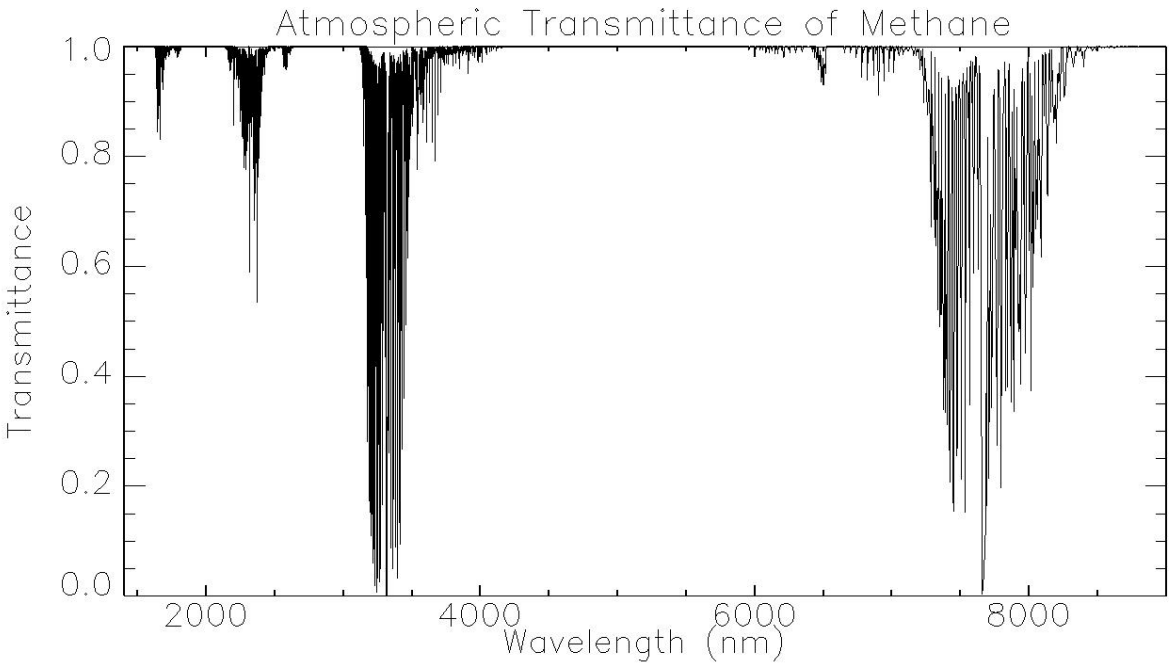

Figure 3.22. Atmospheric transmittance of methane in the 1400-9000 nm spectral range

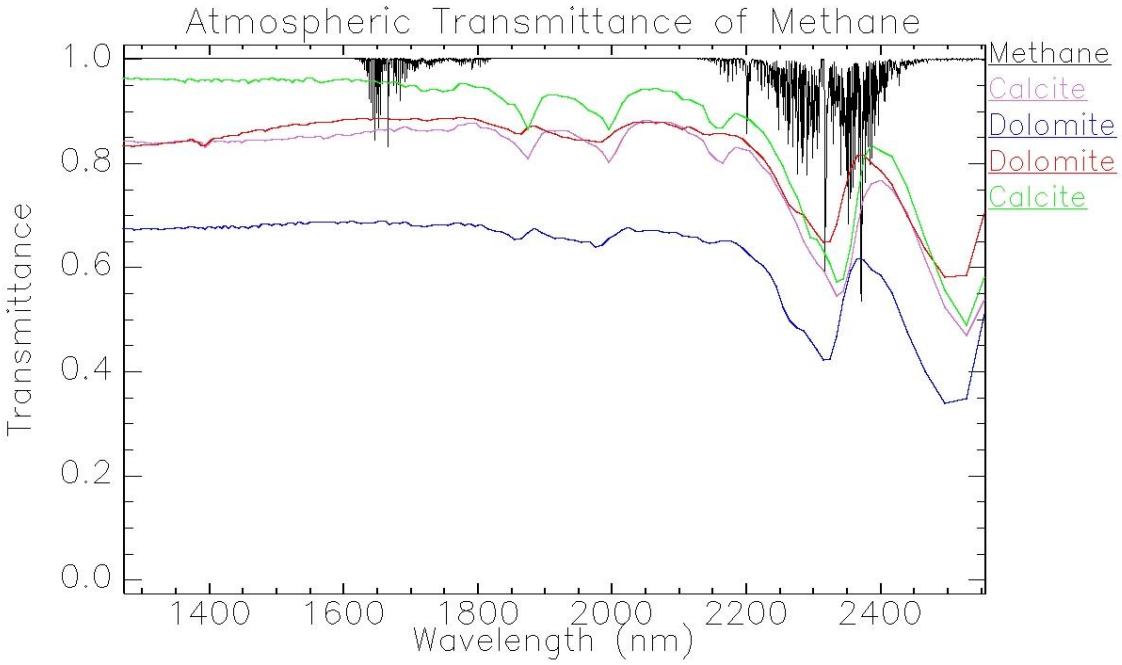

Figure 3.23. The overlap between the 2350 nm methane feature and surface absorption features of minerals. In this case the minerals are the carbonates calcite and dolomite

The AVIRIS has been used in previous studies to estimate CH_4 occurring in natural marine seeps (Bradley et al., 2011; Thorpe et al., 2013) by using a ratio technique between CO_2 and CH_4 spectral bands (Figure 12).

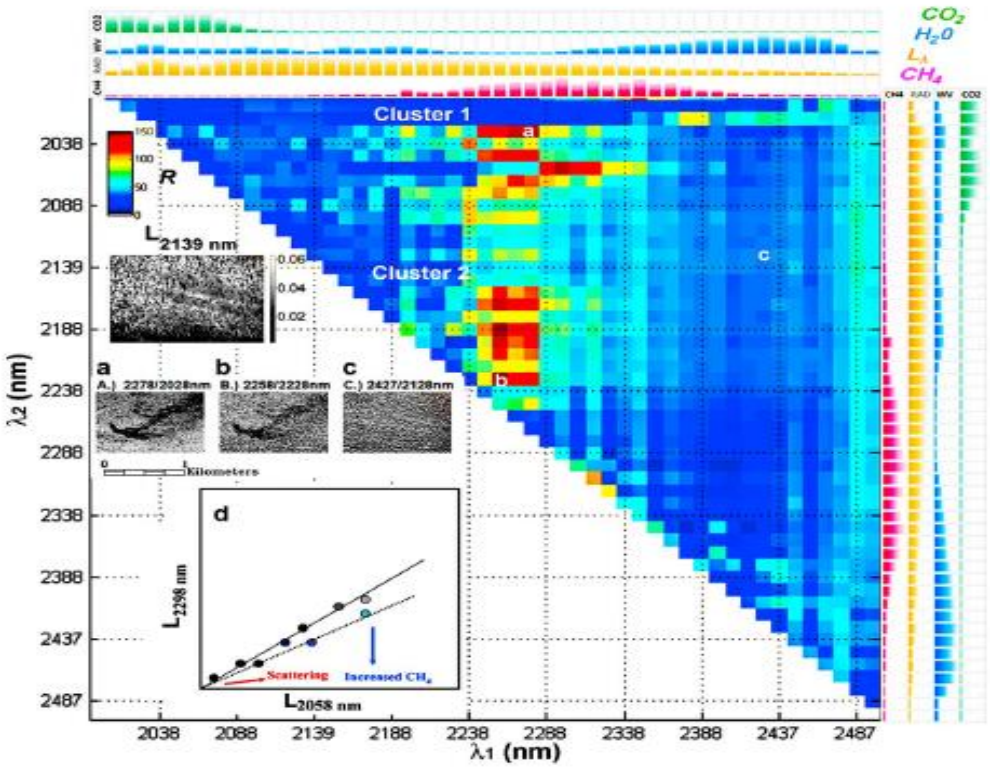

Figure 3.24. Normalized range values, R, from ratio image Trilogy Seep transects as a function of numerator wavelength (λ1) and denominator (λ2). Normalized scale bars of atmospheric absorption (CO2, H2O, and CH4) and radiance are shown to the top and right. (a–c) Pixels labelled a, b, and c on the matrix refers to ratio images. (d) Schematic of radiance L2298 nm versus L2058 nm, lighter colours represents higher albedo and points along the lower line are for increased CH_4 (from Bradley et al., 2011).

Thorpe et al., 2013 also investigated the use of a Cluster-Tuned Matched Filter technique to define CH_4 over terrestrial surfaces. The latter portion of that work has more relevance to this investigation and demonstrated that while it may be possible to detect CH_4 emissions from such instrumentation the method was prone to extensive noise and many cases of false positives due to surface absorptions that naturally occur at 2350 nm (Thorpe et al., 2013).

A sensitivity study of the ability of APEX to detect atmospheric gases (Kaiser, J. W., et al., 2004) concluded that "The retrieval of CH_4 with 3 m ground resolution shows a precision of 50 %, which may facilitate the qualitative detection of strong CH_4 sources". They also note that these are maximum precisions and that the task would be challenging. In this case, as with the AVIRIS studies the 2350 nm CH_4 absorption was used.

The 1650 nm CH_4 absorption feature is generally free from overlaps of other atmospheric constituents and relatively free from surface absorptions. However, in the context of the type of HSIs being discussed, it is more suited towards a limited range of higher spectral resolution sensors (better than 10 nm) for the detection of CH_4. Although the feature is approximately 100 nm wide, commercially available HSIs typically having bandwidths >10 nm will not be able to provide the necessary accuracy required. The transmittance of the 1650 nm CH_4 is approximately 85% but when convolved to typical HSI spectral response functions the absorption of this feature decreases to less than 2 % for CH_4 backgrounds of 1.7 ppm (Figure 13). This tends to place natural variation within the feature well within the instrument noise levels.

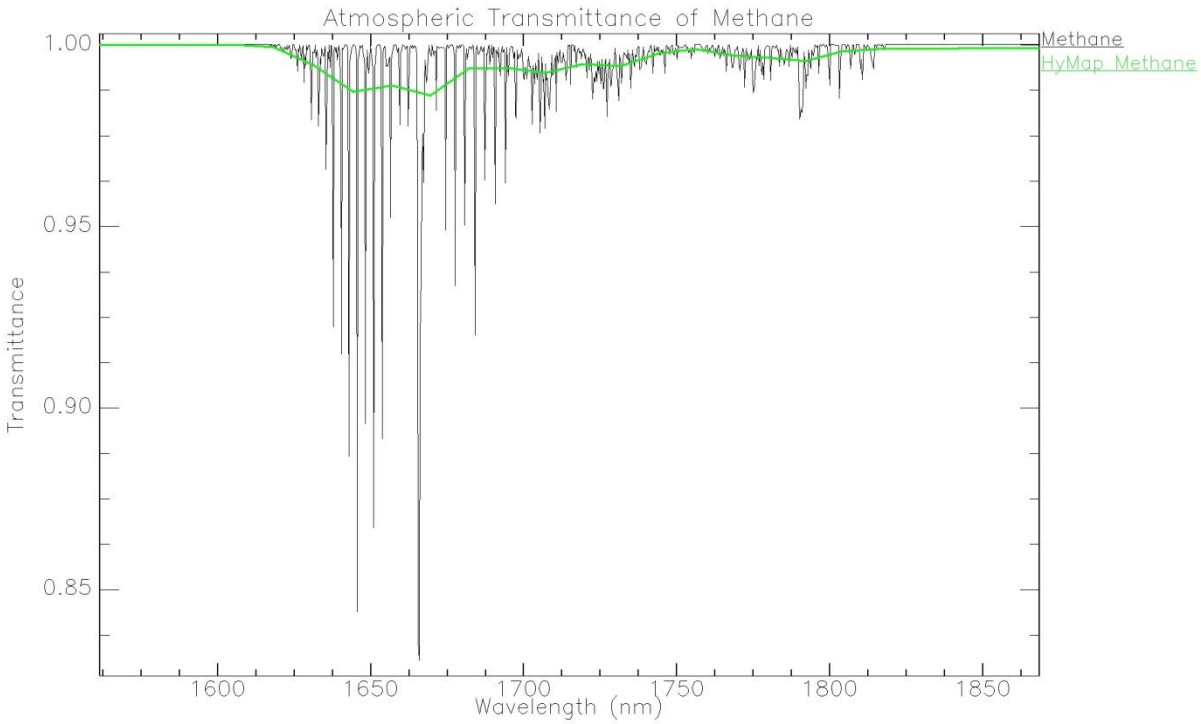

Figure 3.25. Apparent increase in the atmospheric transmittance of methane for a typical HSI which in this case is the HyMap

3.6.2 HYPERSPECTRAL SENSORS (<1NM SPECTRAL RESOLUTION)

While the 1650 and 2350 nm CH_4 features may not be well suited to HSIs, primarily due to spectral resolution and surface absorption feature overlaps, the 1650nm is well suited to several other sensor types. The first is still a hyperspectral instrument but one with a much higher spectral resolution. Such an instrument is the Methane Airborne MAPper (MAMAP) (Gerilowski et al., 2011; Krings, et al.,2013).

This MAMAP instrument measures reflected and scattered solar radiation in the NIR and SWIR. The SWIR yields measurements of atmospheric absorption bands of CH_4 and CO_2 in the spectral range between 1590 and 1690 nm at a spectral resolution of 0.82 nm. MAMAP has been designed for flexible operation aboard a variety of airborne platforms. The signal-to-noise ratio (SNR) of the SWIR channel is approximately 1000 for integration times in the range of 0.6–0.8 s for scenes with surface spectral reflectance values of approximately 0.18. These integration times produce a ground scene size of about 23×33 m^2 for an aircraft altitude of 1 km and a ground speed of 200 km h^{-1}. The CH_4 and CO_2 column retrieval precisions are reported to be typically about 1 %.

The MAMAP is not an imaging system and as such does not produce a raster image like the HSIs described earlier. Rather a collection of point measurements directly under the aircraft. Shown in Figure 14 from Gerilowski et al. (2011) is a series of data collected by the MAMAP. It is noted that the data has been filtered to discount data that does not receive a large enough digital count and to ensure that a high signal-to-noise ratio is maintained.

In the Krings et al. (2013) study MAMAP was used to assess CH_4 emission rates from coal mine ventilation shafts. They found that with respect to the total emissions of the mine, and at the time of the over-flight, the inferred emission rate had a difference of less than 1 % compared to officially reported values by the mine operators, while the uncertainty, which reflects variability of the sources and conditions as well as random and systematic errors, is about ±13.5 %. The bulk of the uncertainty lies with uncertainty in the wind information, primarily wind speed and direction.

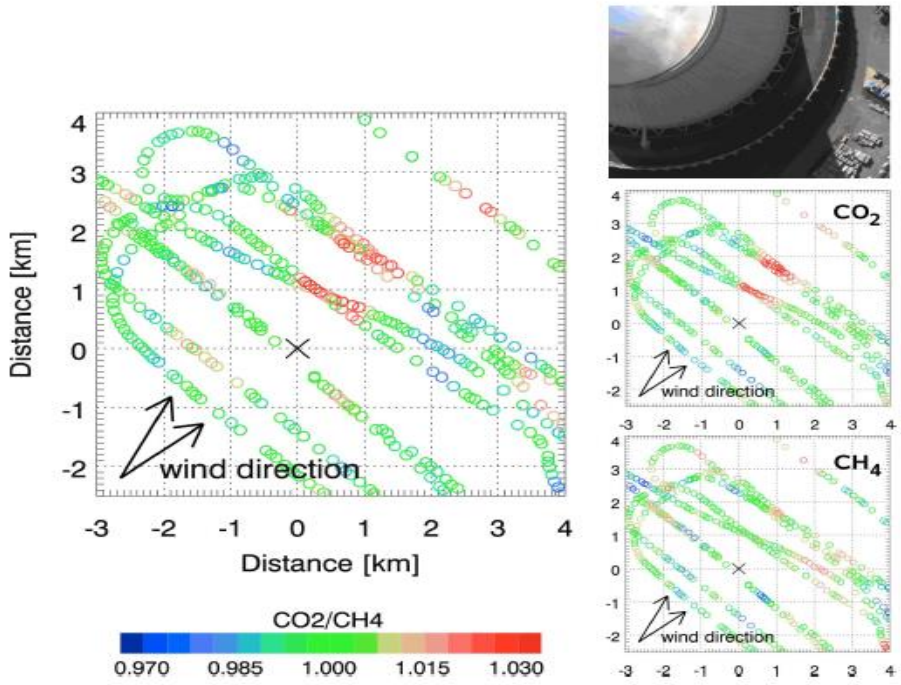

Figure 3.26. Data collected by the MAMAP instrument highlighting CO_2 and CH_4 concentrations and detection (from Gerilowski, et al., 2011)

3.6.3 TUNEABLE LASER: DIFFERENTIAL ABSORPTION LIDAR (DIAL)

Differential Absorption LIDAR (DIAL) provides another means of measuring CH_4. DIAL is a laser based method that allows the concentration of a species to be measured at a remote point in the atmosphere (Chambers et al., 2006; Riris et al., 2010) and uses a pulsed laser operating at two wavelengths, one strongly absorbed by the gas species of interest (on-line) and one weakly absorbed (off-line). The differential absorption between the two wavelengths is a measure of the concentration of the gas as a function of range.

For ground based DIAL units with a scanning telescope/mirror system, an area downwind of a facility or location can be quickly scanned. However, measurement of emissions with a ground based DIAL unit relies on wind to carry the plume through a vertical plane downwind of the area of interest, or alternatively the instrument beam must intercept the plume (Chambers et al., 2006). Assuming that the interception occurs DIAL can be used to scan through the plume and measure a two dimensional profile (height versus horizontal distance) of the gas concentration of interest that, when combined with wind speed measurement, enables the calculation of the mass rate of the species moving through the vertical plane. An example of a plume distribution and concentrations are shown in Figure 15 with an active venting occurring at approximately 10 m.

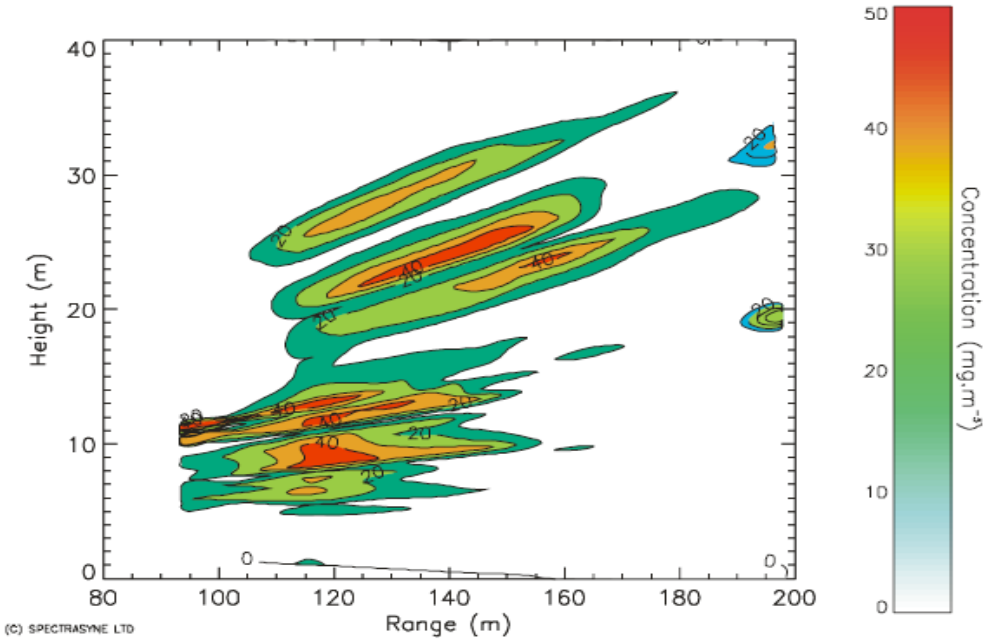

Figure 3.27. CH4 distribution and concentration (From Chambers et al, 2006)

Ground based DIAL systems are generally housed in vehicles and hence to extend the coverage of the detection requires that the vehicle is moved. The plume can disperse in this period of time, or the wind directions may change which would necessitate another location change, and if unaccounted for will lead to incorrect concentration calculations.

An interesting alternative laser based system for the detection of CH_4 is the CHARM® system (CH_4 Airborne Remote Monitoring) (Zirnig, et al., 2004; Zirnig and Ulbricht, 2006). While it is being used to identify leaks in Germany's natural gas pipelines it also used to detect leaks from those pipelines that are located underground. This is analogous to quantifying natural seepages from underground sources. Zirnig et al. (2004) note that any remote detection system capable of performing this task must be capable of detecting flows of as little as 150 L h^{-1}

The CHARM® is a DIAL system that uses the strong CH_4 absorption feature located around 3200nm (Figure 16). While the laser system collects point measurements it does so in a helix pattern as the platform (helicopter) moves along track (Figure 17). This gives a scanned corridor of approximately 18 m. The CHARM® system was flown to test the ability of the system to detect leaks from an underground pipeline was buried at a depth of 0.8 m. Zirnig et al. (2004) demonstrated that in this experimental setup a leak detection corresponding to 100 L h^{-1} was achieved. However, they noted that, as with other DIAL studies that the detection limits will be somewhat dependent on the prevailing wind speed (Figure 18). The effect of wind and its ability to disperse a CH_4 leak/seep will of course play a part in any system that is used to detect such phenomena. To further highlight the ability of this system they note that in 2006 10,000 km of the ER.ON Rhurgas pipeline network was successfully monitored with CHARM.

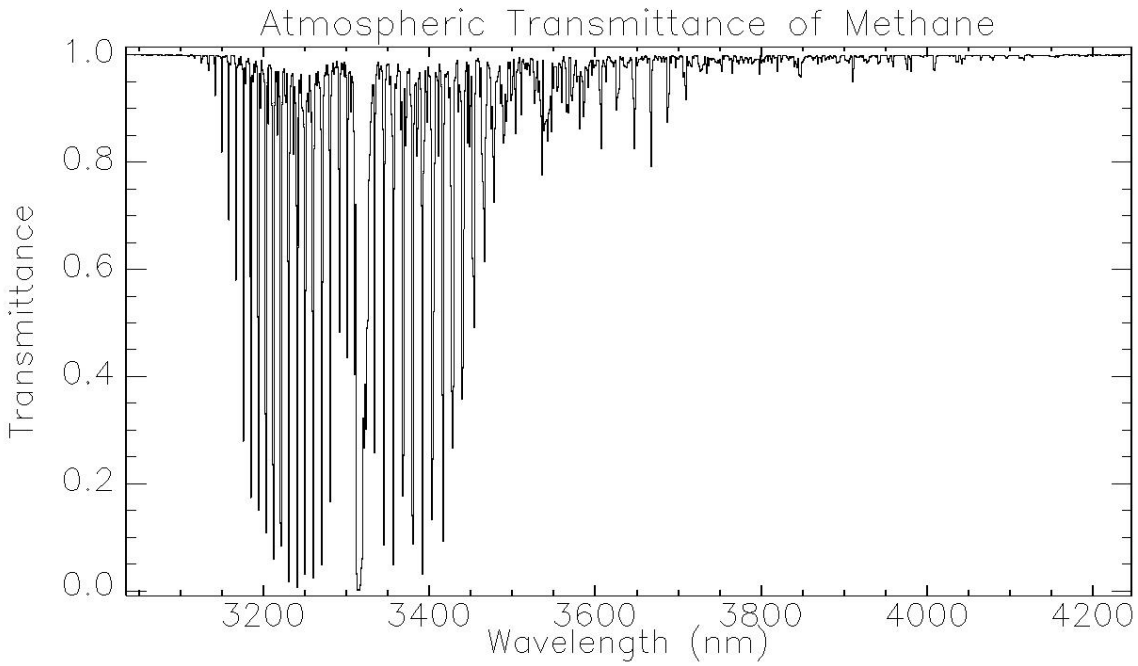

Figure 11. Atmospheric methane in the Mid-Wave Infrared. This region is used by the CHARM DIAL system.

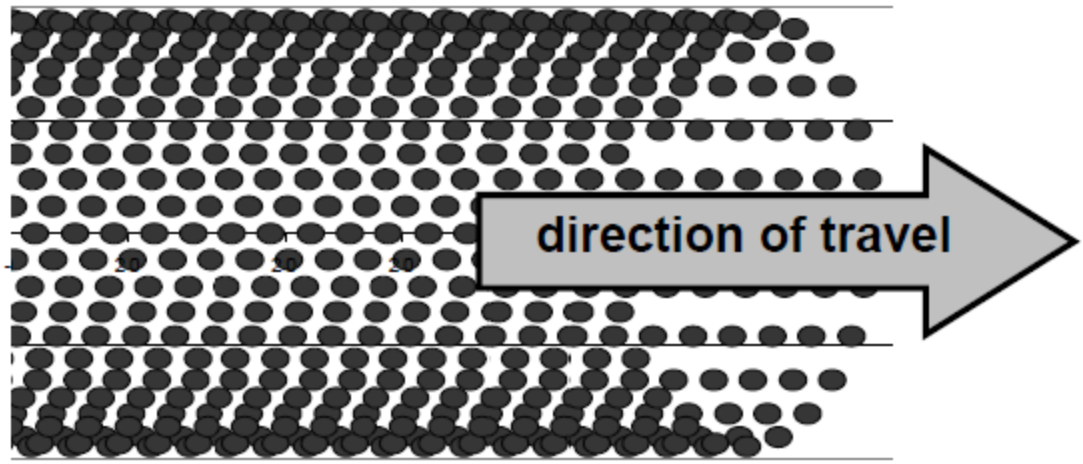

Figure 3.29. Scanning pattern of the CHARM system. The size of the area examined in this manner is 18 m from an altitude of 150m. From Zirnig et al. (2004).

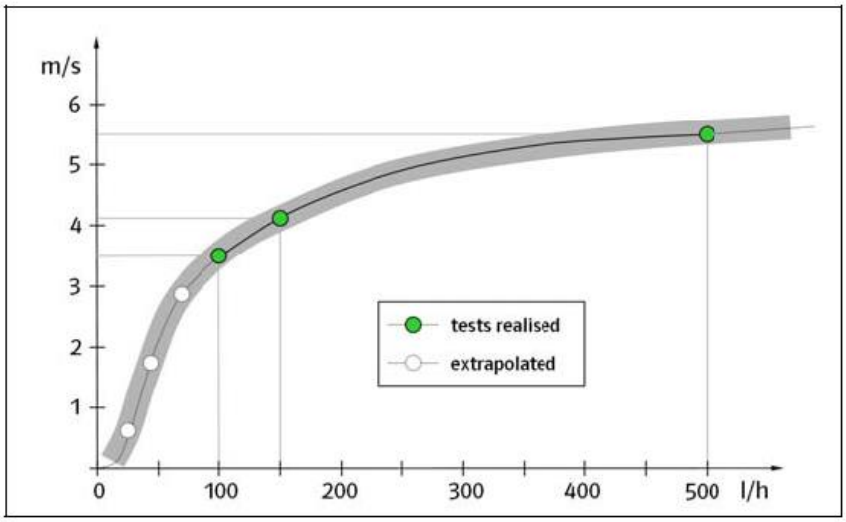

Figure 3.30. The effect of wind speed on the detection ability of the CHARM system. From Zirnig et al. (2008)

Gross et al. (2010) note that active sensing techniques, such as DIAL are well suited to detecting and quantifying specific molecules or atoms at concentrations as low as one part per billion volume but are typically limited to interrogation of one or two species due to the limited bandwidth of the laser source. Additionally, active systems can have a larger spatial footprint and are often more costly and time-consuming to deploy when compared to current passive sensing techniques.

3.6.4 FOURIER TRANSFORM INFRARED (FTIR)

Fourier transform infrared (FTIR) spectroscopy has been long established as a system for the estimation of gases. Previous works have included open-path FTIR spectroscopy (Kirchgessner et al., 1993) and more recently FTIR imagers (Gross et al., 2010). Kirchgessner et al. (1993) noted several areas where improvements could be made and included the establishment of detection limits and the reliability of the measurement methodology under partial plume capture conditions and under source conditions where the emissions release is strongly heterogeneous. They noted that the variability in the background CH_4 can be the same order as the CH_4 contribution from the surrounding study area. In future field investigations, more background measurements are needed to reduce this uncertainty. Alternatively, simultaneous mine plume and background sampling could be conducted. And as noted previously, changes in the wind direction complicate measurement activities and invalidate some measurements due to only a small portion of the plume passing through the sensor. Although the Kirchgessner et al. (1993) study is an older study it does highlight the problems that are inherent when using open-path point measurements. While the study combined the measurements with a Gaussian plume dispersion model they concluded that the estimates of CH_4 concentrations based on the proposed technique may be as low as 20-75 %, and the study could not be used alone to assess the accuracy of overall mine emissions.

Harig et al. (2004) used an imaging spectrometer to assess the feasibility of detecting methane with an imaging spectrometer. Shown in Table 2 are a summary of the SIGIS and RAPID FTIR systems developed by the company Bruker (From Harig, R., et al, 2004).

Table 3.3. SIGIS and RAPID characteristics (From Harig et al., 2004)

	SIGIS	RAPID-BASED SYSTEM
Interferometer	Bruker OPAG	Bruker RAPID
Spectral range	680-1500 cm^{-1} (600-6000 cm^{-1} max)	680-1500 cm^{-1} (600-6000 cm^{-1} max)
Maximum spectral resolution (nominal, $\Delta\sigma = 1/D$)	0.6 cm^{-1} (D = 1.8 cm)	1.1 cm^{-1} (D = 0.9 cm)
Spectral resolution (this work)	4 cm^{-1}	2 cm^{-1} and 3 cm^{-1}
Field of view	7.5 mrad	30 mrad
Field of regard	285 ° x 80 °	360 ° x 60 °
Maximum spectral rate	7 spectra/s ($\Delta\sigma$ = 4 cm^{-1})	32 spectra/s ($\Delta\sigma$ = 3 cm^{-1} single sided interferograms)
NEΔT (triangular apodization, 1000 cm^{-1})	20 mK ($\Delta\sigma$ = 4 cm^{-1}, t = 0.1 s)	40 mK ($\Delta\sigma$ = 3 cm^{-1}, t = 0.05 s, 16 spectra/s)

The study concluded that they were able to detect methane release rates in the 0.05-1.3 $m^3\ h^{-1}$ at a range of 92 m. It should be noted though that while the methane release rates quoted previously were detected they were quantified by other means within the experimental setup. In other words the two systems, SIGIS and RAPID, required the use of other more quantitative calibration/validation data to ascertain its accuracy. Figure 19, from Harig et al. (2004) shows the results of a methane release of 0.14 L s^{-1} (0.5 $m^3\ h^{-1}$) from a 100m distance. While Figure 20 shows the detection of methane released from 1m below the ground at a rate of 0.4 L s^{-1} (1.4 $m^3\ h^{-1}$).

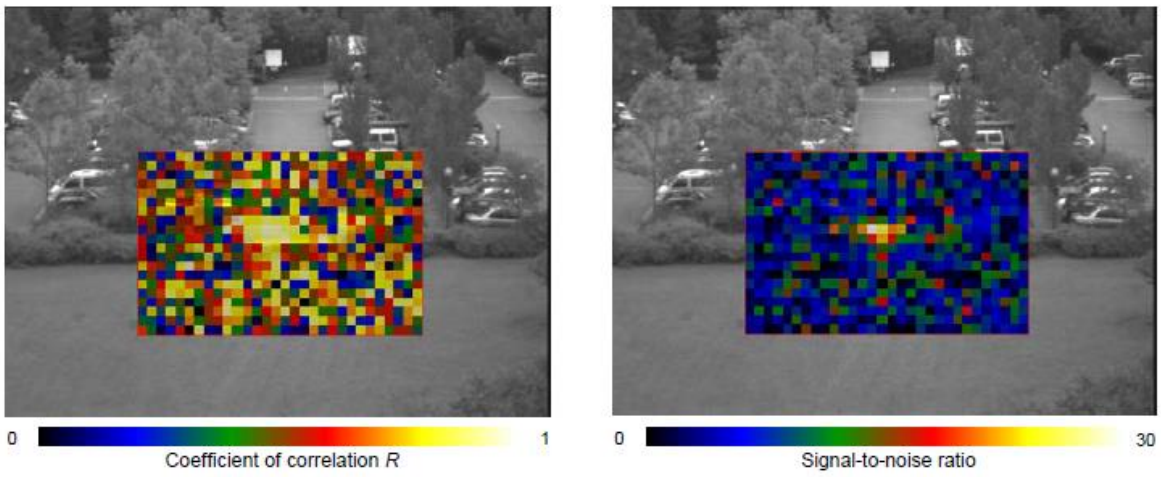

Figure 3.31. Left: False colour image of the coefficient of correlation. Right: False colour image of the signal-to-noise ratio. The release rate of methane was 0.14 L s^{-1} (0.5 $m^3\ h^{-1}$). From Harig et al. (2004).

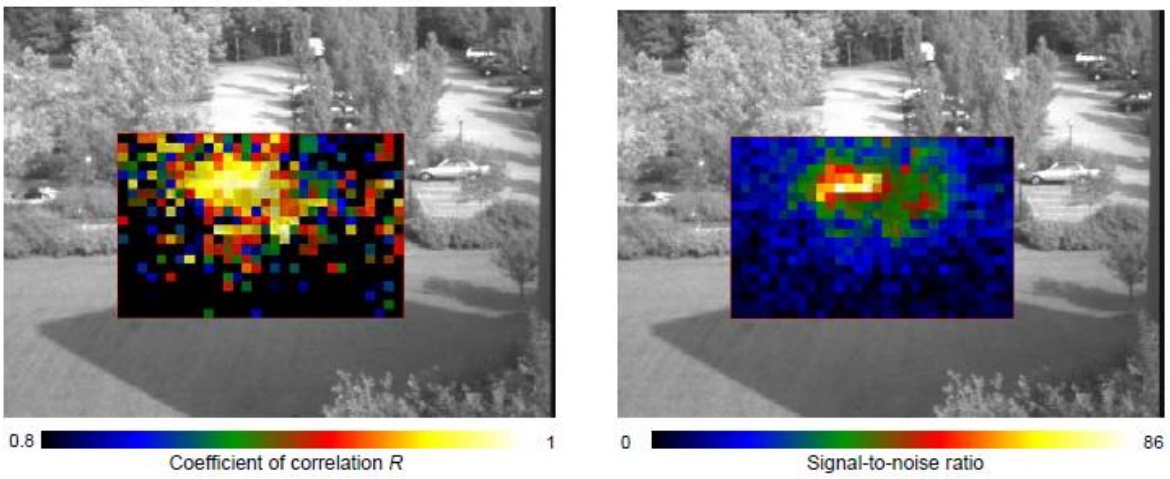

Figure 3.32. Left: False colour image of the coefficient of correlation. Right: False colour image of the signal-to-noise ratio. The release rate of methane was 0.4 L s^{-1} (1.3 m_3 h^{-1}). From Harig et al. (2004)

Like many of the studies mentioned previously, the probability of detection is strongly dependent on the weather conditions, in particular the wind and the difference between the temperature of the methane plume and the brightness temperature of the background (Harig, et al., 2004).

3.6.5 SPACE-BORNE SENSORS

Several space-borne sensors are available for measuring the atmospheric concentration of CH_4. This includes the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) (Bergamaschi et al., 2007), a spectrometer operating in the ultraviolet, visible, and near-infrared wavelength region (240–2380 nm) at spectral resolution between 0.2–1.6 nm (Figure N.N). The dry air column averaged mixing ratios XCH_4 was obtained by normalising the retrieved CH_4 column (based on a band between 1629–1671 nm) with the CO_2 column reference retrieved at 1600 nm. The spatial footprint of this sensor is typically 60 km and was operational between 2002 to April 2012.

The Thermal and Near Infrared Sensor for Carbon Observations (TANSO) Fourier Transform Spectrometer (FTS) on board the Greenhouse Gases Observing Satellite (GOSAT) provides global estimates of the column average dry air mole fractions of CH_4 and CO_2 (Muskett, 2013). The sensor operates with four spectral bands the visible and thermal infrared (see Table 3.xx below) at spectral resolution of 0.3 cm^{-1} and the spatial footprint radius is about 5 km. Although sensors, such as GOSAT, provide accuracy sufficient for global monitoring (Butz et al., 2011), they are limited by the spatial resolution to be applicable for seepage monitoring in coal seam gas fields. In addition, diffusion and advection of methane in the atmosphere from seeps leads to column average concentrations not significantly different from background.

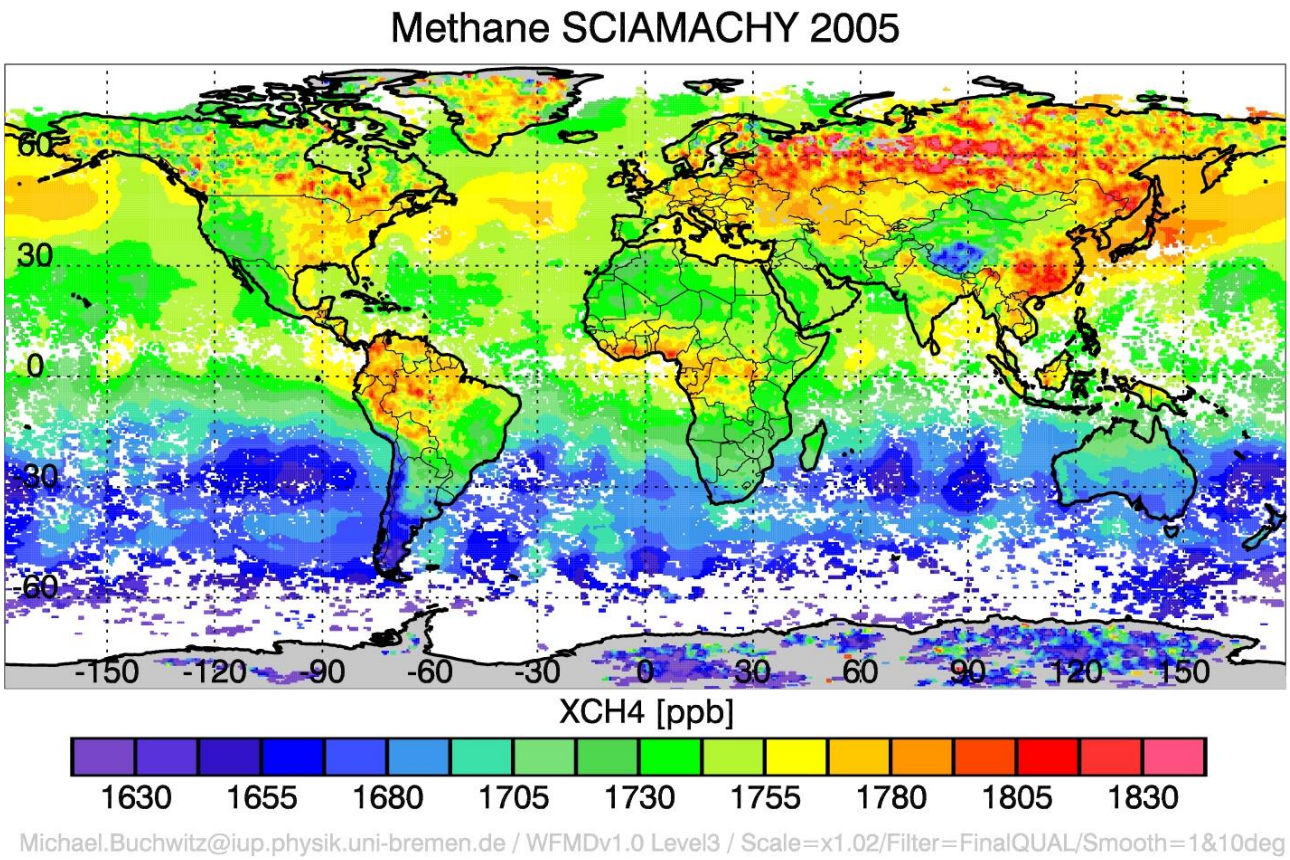

Figure 3.33. An example of atmospheric column average methane concentrations from the SCIAMACHY sensor for 2005.

Table 3.4. Spectral Configuration of TANSO

SPECTRAL BAND NUMBER	1	2	3	4
Spectral range	Vis	SWIR	SWIR	MWIR/TIR
Coverage (μm)	0.75-0.78	1.56-1.72	1.92-2.08	5.5-14.3

4 Recommendations and workplan for phase 2

4.1.1 SUMMARY AND RECOMMENDATIONS

This report has provided a review of all methods available for detecting, measuring and quantifying concentrations and fluxes of methane from background seeps. The distribution and flux of methane from seeps in the Surat Basin, Queensland, is highly uncertain. The recommendation from this review is that Phase 2 of the project consist of two components, namely:

(3) A field survey combining mobile survey and remote sensing methods, and,
(4) Establish an atmospheric measurement station to measure methane concentrations.

The mobile survey in (1) is designed to locate the distribution of seeps throughout the Surat basin outcrop/subcrop region using existing industry mapping and obtain first estimates of fluxes by combining plume concentrations with atmospheric transport methods. The scale of this work is of the order of hundreds of square kilometres and will be bounded by the Walloons Coal Measures and Springbok outcrop/subcrop region as mapped by Bradford (2013). The mobile survey will commence in the region near Dalby and Chinchilla and extend westwards to the extent of the mapping region. Final definition of the area covered will be decided in consultation with industry representatives. Remote sensing techniques (DIAL and FITR) are to be combined with the mobile survey to both augment the mobile survey methods and establish whether useful measurements of plume concentrations can be obtained using these methods. Two technologies recommended for further development are the SIGIS-FTIR and CHARM®-DIAL technologies. The SIGIS has been demonstrated to be able to detect methane leakages from 1m underground (Harig, R., et al, 2004) while the CHARM® has been shown capable of detecting methane from 0.8m underground in both soil coverings and concrete coverings, with the latter detecting methane escaping from cracks within the concrete pad (Zirnig, W., et al., 2004; Zirnig, W., & Ulbricht, 2006). In the pilot phase, the effectiveness and accuracy of these systems to quantify the methane amounts is to be determined noting that their prior use has shown effective methane leak detection in the extensive gas pipeline system of Germany.

The atmospheric measurement component in (2) builds on the mobile survey in (1) and is designed to provide high quality 'baseline' capability to the measurement of fluxes at key locations. In addition, redeployment of remote sensing methods at the measurement tower will provide further concentrations constraints on the atmospheric transport modelling.

Undertaking both these components will provide a scientifically defensible program for Phase 3 'Broad scale application of methane detection'. Furthermore, on the basis of cost, resolution, sensitivity and extension to large scales this approach is the most suitable because it balances the need for wide coverage with the requirement to measure fluxes in detail to determine their quantity and source. The proposed method above also takes into account two specific problems associated with locating and quantifying methane fluxes in the Surat Basin. These are:

(3) The considerable uncertainty associated with the distribution of methane seeps in this region, and,
(4) The diffuse/low flux of methane from seeps leading to low atmospheric concentrations and detection difficulty.

The proposed method is optimal in terms of its capability to overcome these problems. In summary, this review has generated the following findings based on a range of methods and information sources. Additional details are provided in Appendix 1 and a summary of the findings of this report is given in Table 4.1:

- A considerable body of knowledge exists within the various CSG companies operating in the Surat Basin. The research team must consult with industry personnel to determine an appropriate mobile survey strategy and location of atmospheric measurements for Phase 2

- Mobile survey combined with remote sensing methods provides the best chance of locating seeps in the study region given their diffuse distribution and low fluxes.
- Methane isotopes provide an important capability to distinguish sources of methane and a limited number of samples should be collected and analysed in Phase 2 to inform potential further sampling in Phase 3.
- Atmospheric trace gas concentration measurements and transport modelling provide a robust, proven and cost effective means of developing a monitoring capability for methane seeps and it is recommended that this method be trialled in Phase 2 at locations informed by mobile survey, remote sensing and industry consultation.

The following points refer to other methods that, while not recommended for the pilot study in Phase 2, may provide additional useful information in the future:

- The Queensland Gasfields Commission has recently released a number of exploration reports that contain a substantial amount of information on the soil gas composition from wide areas of Queensland, including the Surat Basin. It is recommended that these data be consulted in the development of the finale report for this study.
- Flux chambers are readily portable and relatively straightforward to use so measurements can be made virtually anywhere, including in aquatic environments. The method is also well suited to producing detailed maps of the emission profiles of seep sites; although, depending on the size of the site, many measurements may be required. It is recommended that, if the distribution of seeps is clustered and confined to a small total area, flux chambers be deployed, as these will be the most suitable for mapping seeps.

Table 4.1 Summary of suitability of reviewed measurement methods for detection of methane seeps in Surat Basin to determine flux and source of CH_4.

Method	Remarks	Suitability
Soil Survey	Simple, cheap method to deploy locally. Expensive and difficult to deploy on large scale. May identify diffuse CH_4 seeps. Does not provide flux estimates. May be combined with isotopic measurements to distinguish source.	Too expensive and difficult to deploy at large scale. However, existing data should be exploited.
Flux chamber (terrestrial)	Established and proven method. Straightforward to deploy. Can provide accurate flux estimates over limited areas. Requires intensive field campaigns of limited duration.	Suitable for estimation of CH_4 flux from localised high flow seeps.
Mobile survey	Simple and cheap method to measure CH_4 concentration near ground surface at large scales. Useful to locate sources that can be measured using flux chamber or atmospheric concentration techniques. Cannot estimate CH_4 fluxes based on concentrations alone. Can be combined with isotope tracers to determine CH_4 source.	Suitable for survey of CH_4 seep locations.
Vegetation	Has potential to locate high flux CH_4 seeps. Not suitable for diffuse large scale and low flux seeps.	Not suitable due to absence of vegetation impacts.
Mineralogy	Has potential to locate coal resource where outcropping occurs or from geomorphological features in remote regions.	Not suitable due to high level of stratigraphic knowledge for this region already.
Air-borne concentration	Expensive and complex method for accurately measuring plume CH_4 concentrations which, when combined with boundary layer meteorology data.	Not suitable within timeframe of this study. May be useful during monitoring phase to confirm atmospheric concentration observations.
Atmospheric trace gas concentration and transport modelling	Cost effective method of accurate CH4 concentration measurement. Requires careful positioning of sample point with respect to seeps and prevailing wind direction. Has significant sunk costs at start which yields benefits in long term monitoring. When combined with atmospheric transport modelling can provide information on spatial location and flux of CH4 in landscape. Isotope sampling may yield information on CH4 source.	Suitable for deployment subject to locating seeps via survey methods. Requires access to power and location.
Isotopes	Potentially important information to estimate CH_4 source. Simple and cheap measurements for some isotopes ($\delta^{13}C$). Expensive and complicated for other isotopes (e.g. ^{14}C).	Suitable for strategic sampling in pilot stage
Flux chambers (aquatic)/Bubble traps/Flow meters	Established and proven method. Straightforward to deploy. Can provide accurate flux estimates over limited areas. Requires intensive field campaigns of limited duration.	Suitable for estimation of CH_4 flux from localised high flow seeps.
Hydroacoustic	Relatively new techniques with potential for quantifying distribution function of bubble size.	Not suitable as insufficiently developed for application in Surat Basin.
Thin Boundary Layer estimation	Established method for application in lakes and ocean.	Not suitable as peripheral to task.
Hyperspectral imaging and	Established theoretical basis. Satellite and air-borne hyperspectral imagers too coarse spectral resolution to locate low flux diffuse CH_4	Potentially suitable

Method	Remarks	Suitability
spectroscopy	seeps. Spectroscopic sensors (high spectral resolution) potentially useful and may provide ability to differentiate CH4 flux from a heterogeneous background.	spectroscopy methods. Requires proof of application.
DIAL	Air-borne systems are new technology in methane survey, expensive, limited duration and not widely available. Needs to be developed/proven for low flux diffuse seeps with heterogeneous background. Ground based systems can be combined with mobile survey methods to yield accurate concentrations of plumes. Can be combined with micrometeorology techniques to yield fluxes. Limited duration and dependent on wind direction.	Potentially most suitable technology for survey of CH_4 seeps. Requires proof of application.
FTIR	Mature methodology and potentially useful. Needs development and proof of application for low flux and diffuse seeps as potentially close to detection limit.	Potentially suitable. Requires proof of application.
Space-borne sensor	Spectral and spatial resolution too coarse for this task.	Not suitable.

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Glossary

APPEA	Australian Petroleum Production and Exploration Association
CBM	Coal Bed Methane
CRDS	Cavity Ring Down Spectrometer
CSG	Coal Seam Gas
GISERA	Gas Industry Social and Environmental research Alliance
LAS	Laser Absorption Spectroscopy
TDLS	Tuneable Diode Laser Spectroscopy (Spectrometer)
NDIR	Non Dispersive Infrared

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