Using Cavity Ring Down Spectroscopy to measure greenhouse gas concentrations and estimate flux to the atmosphere using a closed flux chamber

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TITLE

Using Cavity Ring Down Spectroscopy to measure greenhouse gas concentrations and estimate flux to the atmosphere using a closed flux chamber

RUNNING TITLE

Using CRDS to measure greenhouse gas concentrations and flux

ABSTRACT

Atmospheric methane concentrations have risen from 823 ppb in 1841 to 1824ppb in 2013. In that time methane concentrations have risen more rapidly than carbon dioxide levels. Methane also has twenty-one times more global warming potential than carbon dioxide which makes methane an increasingly important greenhouse gas. Demand for potentially cleaner energy sources such as coal seam gas (CSG) has also brought more attention to methane and the need to understand the global methane budget. While the majority of sources and sinks have been identified their individual contributions to the atmosphere are poorly understood. New technology using Cavity Ring Down Spectroscopy (CRDS) allows for parts per billion atmospheric variations in greenhouse gas concentrations to be measured every 2-4 seconds. Methane concentrations were measured at a number of field sites including natural and anthropogenic sources, both as background levels in the atmosphere and inside a closed flux chamber. In the swamps examined in this study methane flux as measured using the flux chamber varied by up to two orders of magnitude for the same wetland. These results suggest that it is difficult to accurately determine the global output of methane from wetlands. The CRDS was also used to measure atmospheric concentrations of methane around cities, farms, coal mines and CSG production areas. CRDS is a useful tool to help understand individual sources and how much methane they could emit.

KEYWORDS

Methane, greenhouse gas, cavity ring down spectroscopy, global methane budget, closed flux chamber

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INTRODUCTION

Methane levels have more than doubled since the beginning of the industrial revolution (Forster, Ramaswamy *et al.*, 2007). Methane trapped in ice cores shows an atmospheric concentration of 722 ppb in 1750 (Stocker, Qin *et al.*, 2013) to 823ppb in 1841at the beginning of the industrial revolution. Following the onset of the industrial revolution methane concentrations increased at a faster rate. In 1978 Etheridge, Pearman et al. stated that the atmospheric background level had risen to 1481ppb (Etheridge, Pearman *et al.*, 2011). By 2013 methane levels has risen to 1824 ppb (WMO, 2014). Since 1750 the global atmospheric concentration of CH_4 has risen by 253% , a far larger increase than the 142% CO_2 increase noted over the same time period (WMO, 2014). For the previous 10,000 years atmospheric levels varied between 580-730 ppb (Forster, Ramaswamy *et al.*, 2007). Ice core data dating back 650,00 years shows methane levels do rise during interglacial warming periods which we are presently in but have not exceeded 900ppb (Forster, Ramaswamy *et al.*, 2007). Additionally methane has twenty-one times more global warming potential (GWP) than carbon dioxide, i.e. it is twenty-one times more effective at trapping heat in the atmosphere (Forster, Ramaswamy *et al.*, 2007, Environmental Protection Agency, 2013). The implication is that methane is becoming more important with time as a greenhouse gas (GHG).

The change in atmospheric levels since the industrial revolution appears to be sourced from increasing anthropogenic activity worldwide; anthropogenic contributions of methane to the atmosphere are now greater than natural emissions (Forster, Ramaswamy *et al.*, 2007, EPA, 2010). Approximately 60% of atmospheric methane

comes from anthropogenic sources while the remaining 40% is from natural sources (EPA, 2010, WMO, 2014). Anthropogenic sources include agriculture, ruminants, biomass burning, fossil fuel exploration and production, manmade wetlands or water catchment areas, and waste management. In 2011 the US Environmental Protection Agency (U.S. EPA) stated that natural gas systems were the largest anthropogenic emitter to the atmosphere, followed closely by enteric fermentation and then landfills (Environmental Protection Agency, 2013). Coal mining, manure management, petroleum systems, waste water treatment were also big contributors. Natural sources include wetlands, lakes, wild animals, wild fires, gas hydrates, terrestrial arthropods and permafrost (EPA, 2010). In natural systems (as well as in landfills and some other anthropogenic systems) methane is produced by methanogenic bacteria in anoxic water logged soils as they decompose organic matter. This is the reason that wetlands are the biggest natural emitter (EPA, 2010).

While most methane sources and sinks have been identified, the amount that they contribution individually are not nearly as well known (Kirschke, Bousquet *et al.*, 2013, Stocker, Qin *et al.*, 2013). Large scale atmospheric concentrations are adequately determined by the use of global monitoring towers situated all around the world which collect air samples daily. Individual source contributions to the atmosphere are not as well understood and quantified. Wetlands have the highest uncertainty range at $\pm 40\%$ for the global methane budget (Kirschke, Bousquet *et al.*, 2013). This is due to the variably for each source and measuring technique. For example wetlands vary in size, temporal location, biodiversity and seasonally. Accurately sampling and characterising these sources can be challenging. Location of sample collection points are critical and

air samples captured and sent to laboratories can be timely and costly. The

contributions from cows is difficult to characterise as well as ruminant diets affect the

methane production (Howden and Reyenga, 1999).

A study by the CSIRO found more than 90% of coal seam gas (CSG) wells tested

positive to fugitive methane emissions (Day, Dell'Amico *et al.*, 2014). They concluded

that the wells with no emissions were ones not in production and that all production

wells produced some fugitive emissions. The mean methane fugitive emission rate for

the tested wells was 3.2 g min^{-1} which is considered low when comparing to the volume

of gas produced by the well (Day, Dell'Amico *et al.*, 2014). The main sources were

equipment leaks, exhausts from gas fuel engines, venting and operation of gas powered

pneumatic devices. Another study located near Camden in New South Whale is based

on a CSG project and its surrounding infrastructure (Pacific Environment Limited,

2014). Over a 12 week period they found that the average methane concentration in the

vicinity of CSG infrastructure was 2.1 ppm, similar to what is found in many urban

areas. They concluded that there was no significant concentration difference within the

project area compared to outside the project area (Pacific Environment Limited, 2014).

A major study in America found depending on methane measuring methods and

individual studies calculated annual natural gas emission vary up to 1.5 to 1.7 times

larger than the U.S. EPA predicted methane emissions (Miller, Wofsy *et al.*, 2013). A

study across Boston found 3356 methane leaks above 2.5ppm. these were linked to

leaking gas pipe lines, as the $\delta^{13}CH_4$ signatures was in the thermogenic range (Phillips,

Ackley *et al.*, 2013). The process of extracting natural gas from the ground and the

infrastructure involved are known to emit methane. It is unclear if the amount of

methane being released to the atmosphere during gas production is significant compared to other sources.

In the past technology has limited the ability to measure methane at normal atmospheric concentrations as analysis was dependant on collecting samples in flasks and analysing them in a laboratory. New technology using cavity ring-down spectroscopy (CRDS), specifically a Picarro G2201-I, is capable of detecting methane and carbon dioxide levels at parts per billion concentrations above background as well as and carbon isotopes levels in real time (Picarro.Inc., 2014). These devices allow for continuous monitoring of methane levels which can be used to detect concentration changes and pin point sources. They can be used in conjunction with older methods to measure other parameters like methane flux. I have developed an improved methodology for determining flux based on previous research but by taking advantage of new technology we can improve the quality of these measurements. In this study I test the use of flux chambers to characterise methane production over an area. Flux is the flow per unit area from a given area and in this study I will be looking at the amount of methane emitted from various anthropogenic and natural sources. I will be reporting on trialling an improved method for flux chamber measurements which is faster, easier, cheaper, and more portable than what has been done in the past. Part of the measurements that were made was of weather conditions and variations throughout the day. Additionally the CRDS analyser can be used to measure GHG levels from a vehicle, in conjunction with a GPS to make maps of GHG concentrations and to trace emission to sources. I will also be reporting on the changes in atmospheric background concentrations around various natural and anthropogenic sources.

To manage methane emissions more effectively and attempt to reduce the output of sources we need to gain a better understanding of individual methane sources and sinks. Using the CRDS the spatial and temporal uncertainties surrounding methane generation by individual sources could be minimised. In this project I will target known methane producing sources such as wetlands, agriculture, compost heaps (EPA, 2010, Kirschke, Bousquet *et al.*, 2013) and water bores to test for their methane generation using the CRDS. The CRDS will also take concentration levels while driving in cities, open country side and in various setting to monitor change in atmospheric levels, detect any unknown sources and gain a better understanding of back ground levels.

METHODS AND THEORIES

The base instrument used for all results shown in this paper is a CRDS-based GHG concentration analyser. CRDS is a time/signal decay based technique which measures the time it takes for the light intensity of a near infra-red laser to decay in an optical cavity filled with gas sample, after the laser is switched off (Picarro.Inc., 2014). Gas concentration is then determind by measuring the strength of the adsorption at the near-infrared spectrum (Busch, 1997).

$$I(t, \lambda) = I_0 e^{-t/\tau(\lambda)}$$

I_0 is the transmitted light at the time when the laser is switched off, $I(t, \lambda)$ is the intensity of the light in the cavity at time t, after laser turn-off. I_0 and $\tau(\lambda)$ is the ring down time constant. Measurements are made at a number of frequencies, corresponding with peaks near-infrared peaks for the C_{12} and C_{13} in CO_2, and the near-infrared peaks for C_{12} and C_{13} in CH_4. These allow total concentrations of CH_4 and CO_2 to be

calculated, as well as the isotopic signatures of both (i.e. $\delta^{13}CH_4$ and $\delta^{13}CO_2$). $\delta^{13}CH_4$ is useful as it may be used to help identify methane sources as the isotope signature can help differentiate between thermogenic and biogenic sources (Schoell, 1980). A sample is taken ever 2-4 seconds with results shown graphically on the instrument screen in nearly real time. After each day instrument air was run through the CRDS analyser to check calibration.

The CRDS analyser is somewhat limited as it can only read gas concentrations over a rather limited range. Picarro guarantees methane concentration accuracy for between 1.8 – 12.0 ppm in HP mode and 10-1000 ppm in HR range. A GPS, weather monitoring device capable of measuring, temperature, pressure, humidity and wind direction was also fitted the vehicle. An external pump was used to increase data recording efficiency and to reduce gas transit time from sampling hose to improve time match up with GPS data. Results are then presented on a computer screen for real time analysis and interpretation.

Two types of measurements were collected during this study. Much of this work concentrated on the development of the flux chamber technique. Additionally spatial data was collected to assist in characterising an area and establishing background atmospheric concentrations.

2. FLUX

Flux is the measurement of the flow of a quantity per unit area per unit time (NASA, 2014). It can be calculated by change in concentration over a period of time in a given area. In this study the closed chamber method was trialled. The basic equation for flux is given by Yver-Kwok (Yver-Kwok, Müller *et al.*, 2013).

$$F = \frac{\Delta C}{\Delta t} \frac{pVM}{RTA}$$

Where F is mass flux (Units). $\frac{\Delta C}{\Delta t}$ is the fitted linear increase of the gas mole fraction in the chamber with time (mol mol^{-1} s^{-1}). p is the pressure in the chamber (atm) (1 atm = 101 325 Pa). T is temperature (K). R is the gas content. Yver-Kwok used 0.0821 L atm K^{-1} mol^{-1}. V is the volume for the chamber (L). A is the surface area enclosed by the chamber (m²). M is the molar mass of the gas being measured (g mol^{-1}) (Yver-Kwok, Müller *et al.*, 2013).

2.1 FLUX CHAMBER DESIGN

When not used in the laboratory the analyser needs to be fitted to a vehicle as it uses a lot of power, which limits the sources that can be targeted for flux measurements. A 124.3L bucket was used for the main chamber. It was fitted with a 14cm computer fan to keep the air in the chamber properly mixed. It was also equipped with a digital thermomotor and barometer to monitor changes in pressure and temperature. The volumes of the additional devices inside the chamber were subtracted from total bucket volume. Sampled air was taken from the top of the chamber in the centre and returned air was released at the base. 6mm internal diameter hoses were used to connect the chamber to analyser and pump. The volume of hoses was added to the overall chamber volume. The final chamber volume with joining hoses was 129.6L. See figure 2 for basic set up of chamber. Flotation rings can also be attached to the base of the chamber to measure flux over water. Additional hoses can be added to measure sources further from the vehicle. Concentration changes can be monitored in real time by the results presented on the computer screen.
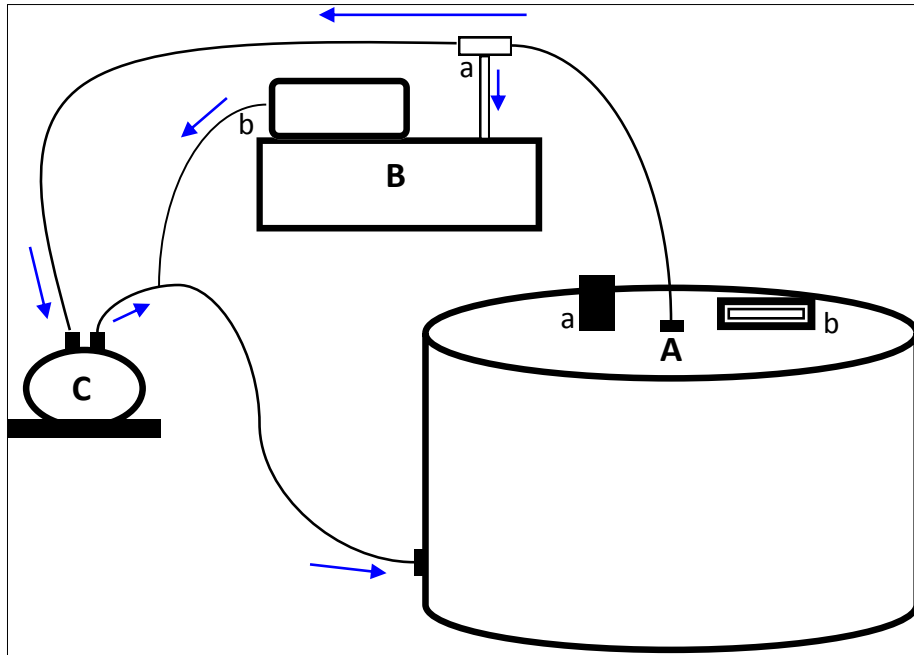
Figure 1: Schematic diagram of the closed chamber in the dry ground testing set up. A – 124.3L closed chamber fitted with internal fan for even gas mixing, thermometer and barometer. a.) External battery attached to top for power. b.) weather logger. B - Picarro Analyser. a.) Chamber air flows past and a sample is taken roughly every 2-4 seconds into the Picarro analyser for CRDS. b) Sample air is returned to the out let hose back and into chamber to maintain pressure and volume. C - External air pump capable of pumping 6 litres per minute to speed up process. Chamber gas flow path. ⟶

The flux chamber was tested in the laboratory using CO_2 gas as it is safer, cheaper and easily available. Test methods were repeated until results were consistent and within a range of the calculated predicated results. A flow rate was maintained at approximately 1mL per minute. This proved to be difficult to maintain as equipment had difficulty both keeping a constant flow and measuring it properly. See table 1 for results from the last two days of lab testing prior to testing the chamber in the field.

Chamber tests start as soon as the chamber is placed over the target source and the base is sealed. Start and finish time is recorded for each test and is then used to process data. Between tests the chamber is lifted off of the sources, trapped gas is released and the chamber is not used again until it reaches background concentrations again.

2.2 BACKGROUND SAMPLING

To gather background and base level concentrations the CRDS is fitted to a GPS equipped vehicle and sampling hose to the roof. The vehicle is then driven around the area of interest and GHG concentration levels are recorded as well as being displayed on the instrument screen. The same track may be driven at various times during the day and year to gather a better understanding of changes to back ground levels. Slower speeds are driven in areas of interest to gather more samples. A weather station can also be attached to the vehicle which can monitor wind speed and direction, temperature, humidity and pressure. This data can help identify the direction the source may be located.

2.3 DATA ANALYSIS

GHG concentrations are graphed against time in seconds to determine concentration change with time. The slope of the linear regression of the GHG concentration data is used to determine the flux of that particular source. Pressure and temperature data for each individual flux chamber tests are entered into the equation. Total volume may also be changed depending on the length of hoses used. Refer to Methods and theories section 2 FLUX for flux equation. The isotopic signatures are also studied to help determine origin of methane.

The GPS data is used in conjunction with GHG concentration data to generate maps of change in concentration relative to location. ArcMap is used to generate these maps. This allows back ground concentrations to be established for that particular location.

OBSERVATIONS AND RESULTS

3.1 FLUX CHAMBER LABORATORY RESULTS

Table 1 shows the final method to be used and the results achieved. Figure 2 is what the corresponding graphs look like. The predicted concentration and the measured concentration were out by an average of 3.31% so the method appeared acceptable to apply to field measurements. The CO_2 flow from the gas cylinder did not stay at a constant rate due to such low concentration being released so an average of start, middle and end flow rates was used.

Test #	Measured flow (ml/min)	Measured flux (kg/m2/min)	Chamber flux	% difference
1	0.96	6.19E-06	6.07E-06	-1.92
2	1.18	6.91E-06	6.90E-06	-0.18
3	1.23	7.11E-06	7.76E-06	8.36
4	1.07	6.21E-06	6.56E-06	5.28
5	1.15	6.68E-06	6.94E-06	3.71
6	1.22	7.06E-06	7.40E-06	4.58
			Average	3.31

Table 1: Laboratory results for flux chamber method using CO_2 gas. Test 1 and 2 conducted on the 9/7/14 and tests 2,4,5, and 6 on the 10/7/14. Measured flow is an average of flow rate taken at the beginning and end of each test.

Changes to the chamber design include tilting the fan, replacing external pump with one that had a net flow, change gas sampling position and return position, placing a rubber matt under the chamber to reduce gas escaping between the base and hard floor surface for laboratory tests only.
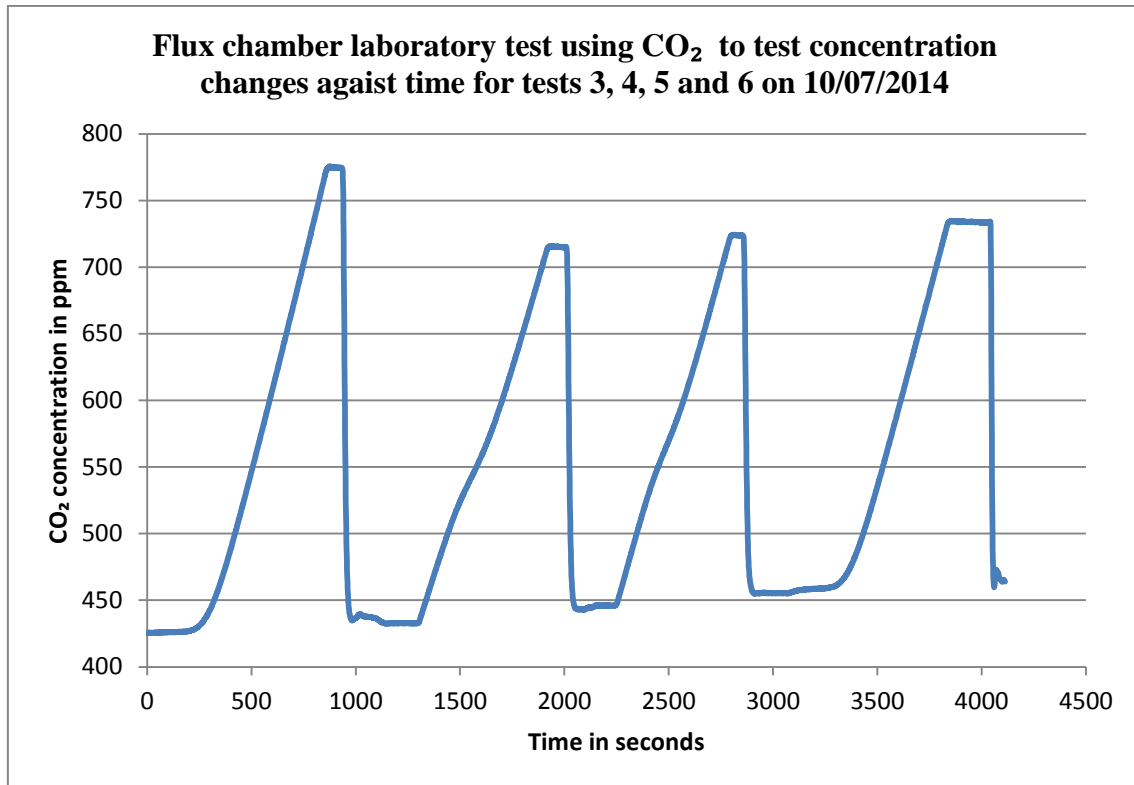
Figure 2: Graph of test 3, 4, 5 and 6 final laboratory tests using CO_2 gas on the 10/07/2014.

3.2 FLUX CHAMBER FIELD RESULTS

Flux chamber tests were primarily run over wetlands of varying water depths. Water less than a few centimetres deep did not require flotation devices attached. Weather data was recorded where possible but due to connection of wires data logging occasionally failed mid-way through tests. Background concentrations are typically the concentration at time zero. CO_2 concentration changes are also graphed against time as they can give a good indication if the test is running well and what other processes may be happening inside the chamber at the same time.

Lake Frome consistently produced methane at all 3 test sites as show in figure 3. The rate at which methane is produced varies. Test 1 produced methane at a slower rate and

was also over shallower water. Test 2 concentration flattens out, the chamber also stared to sink and it is unknown if the sinking chamber had an effect on this. Test 2 and 3 shows methane being released at various rates. CO_2 only decreased in Test 1, this may be due to time of day as test 2 and 3 was conducted later in the afternoon. More sunlight may increase the photosynthesis activity but CO_2 dose appear to rise again towards the end of the experiment. Temperature variation between start and finish of tests is quite low and doesn't appear to be a strong correlation. Isotope data of all 3 test is very similar ranging between -40 and -55 and trending towards -55 the longer the test runs which is just inside the natural wetlands and swamps $\delta^{13}C\text{-}CH_4$ range of -55 ± 3 (Pacific Environment Limited, 2014).

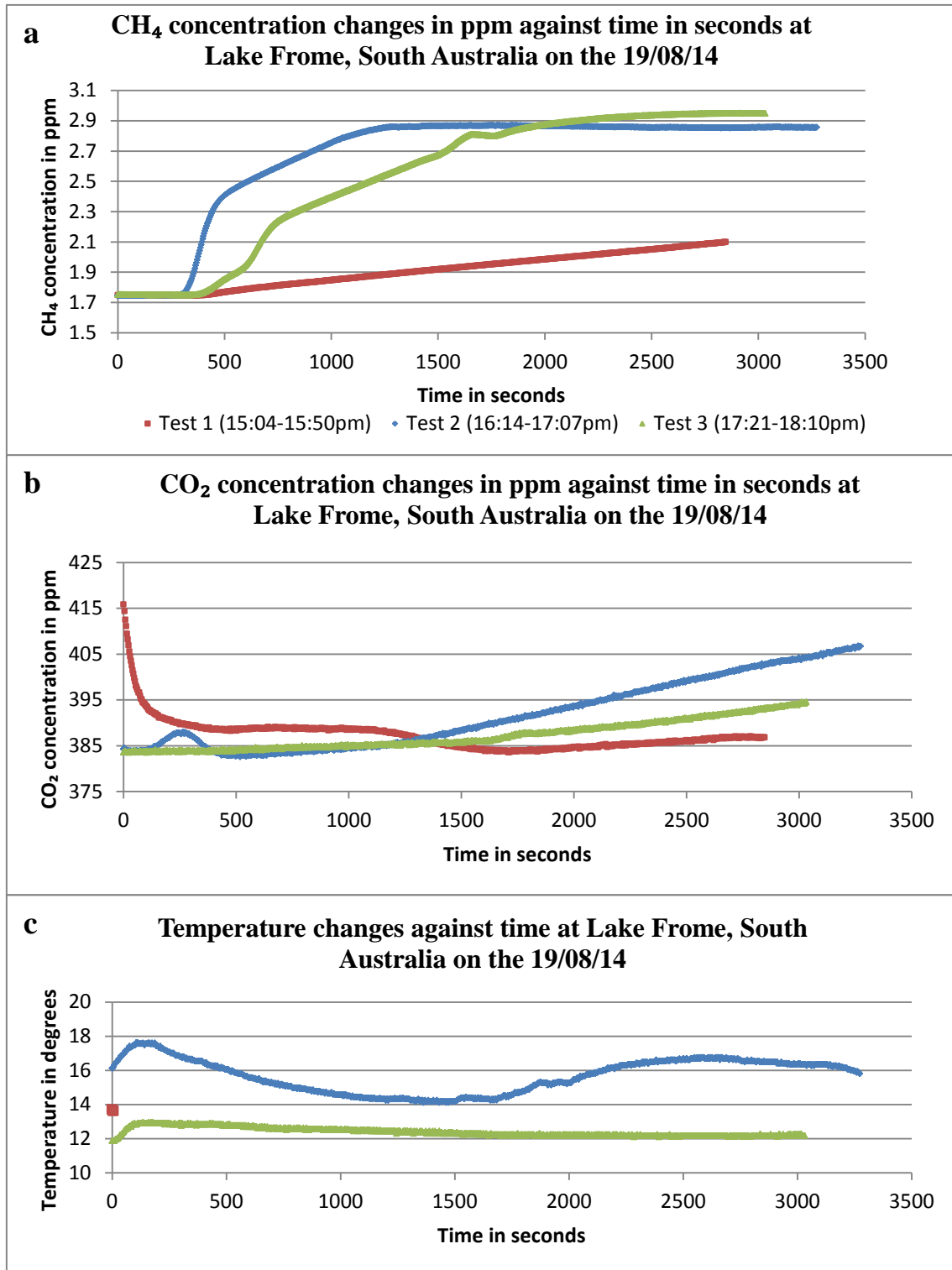**Figure 3: 3a. Flux chamber CH₄ concentration change in ppm against time for all 3 tests on Lake Frome in the South East of South Australia. Test 1 was over shallower water but all 3 tests used the floating flux chamber method. 3b. Flux chamber CO₂ concentration change with time for same 3 tests. 3c. Flux chamber temperature change against time. Test 1 temperature reading failed after first reading represented by red square.**

Methane production rates are once again inconsistent with test site locations as seen in figure 4. Test 1 and 2 are within 15 meters of each other and start time is only an hour difference but production rate is not the same. Test 2 produced more methane and CO_2 concentration decreased the most as seen in figure 5a. Test 3 methane production was inconsistent and began to decrease, this could be a mass release of methane and then mixing decreased the concentration but this is unlikely due to the time it takes to decrease. Both test 3 and 4 saw CO_2 concentrations increase, both test were conducted later in the afternoon which is consistent with CO_2 data at Lake Frome which saw a rise of CO_2 concentrations instead of a decrease. Test 4 produced the second highest methane production for all wetland tested throughout the project behind the Urrbrae Wetlands in Figure 7. It was within 20m of test site 3 yet results are very different. The stepping pattern of the concentration line suggests the release of methane is not constant. There is also less scatter of the isotopes for test 4 compared to test 1, 2, and 3. Isotopic signature is trending toward -55 which is consistent of wetlands and swamps. There is little to no correlation between temperate data and methane concentration change.
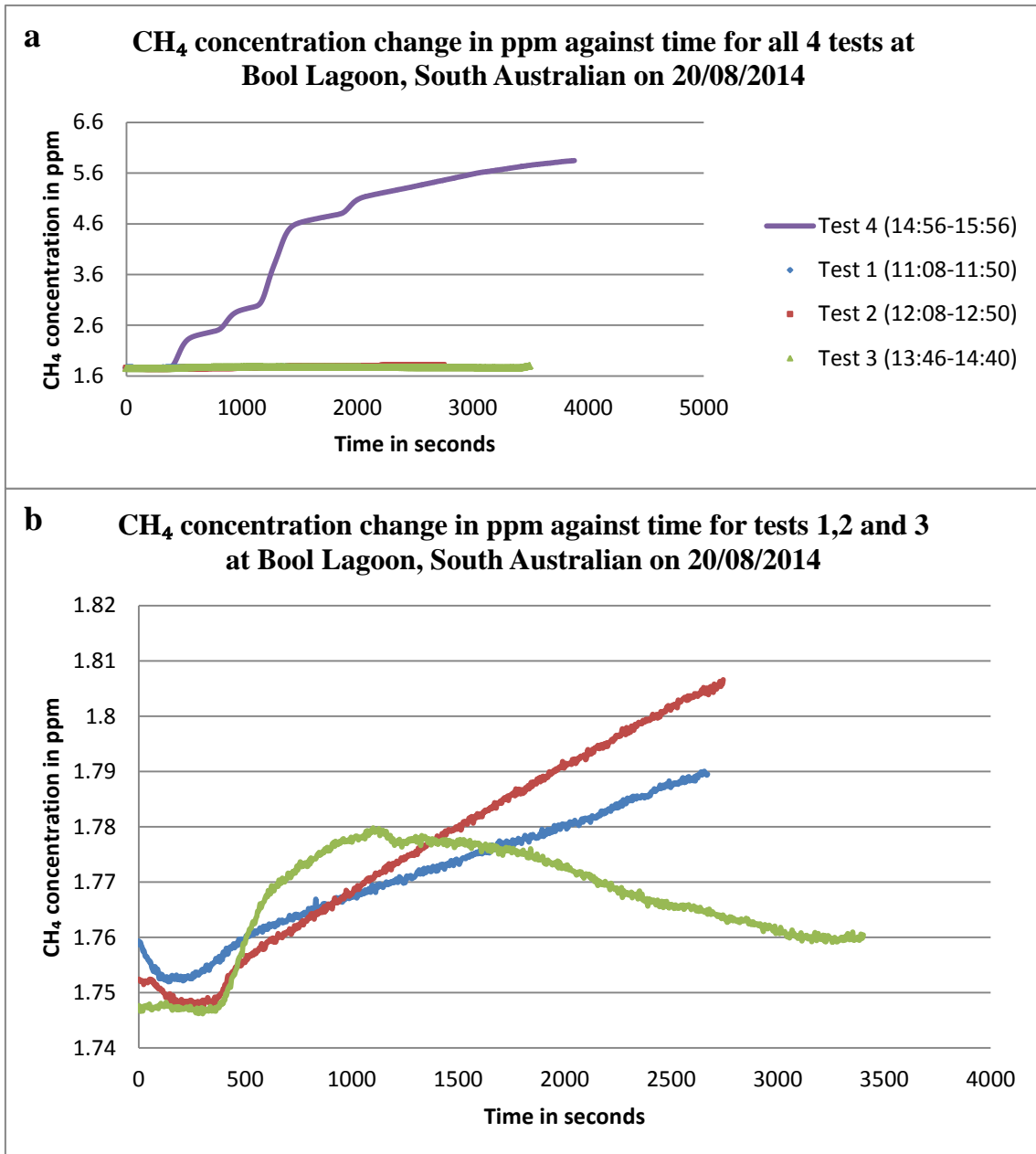
Figure 4: 4a. Flux chamber CH$_4$ concentration change against time for all 4 tests at Bool Lagoon in South Australia. Floating flux chamber method was used for all 4 tests. 4b. Flux chamber tests 1, 2 and 3 are shown to see change in concentration easier as test 4 limits the detail seen in figure 4a.
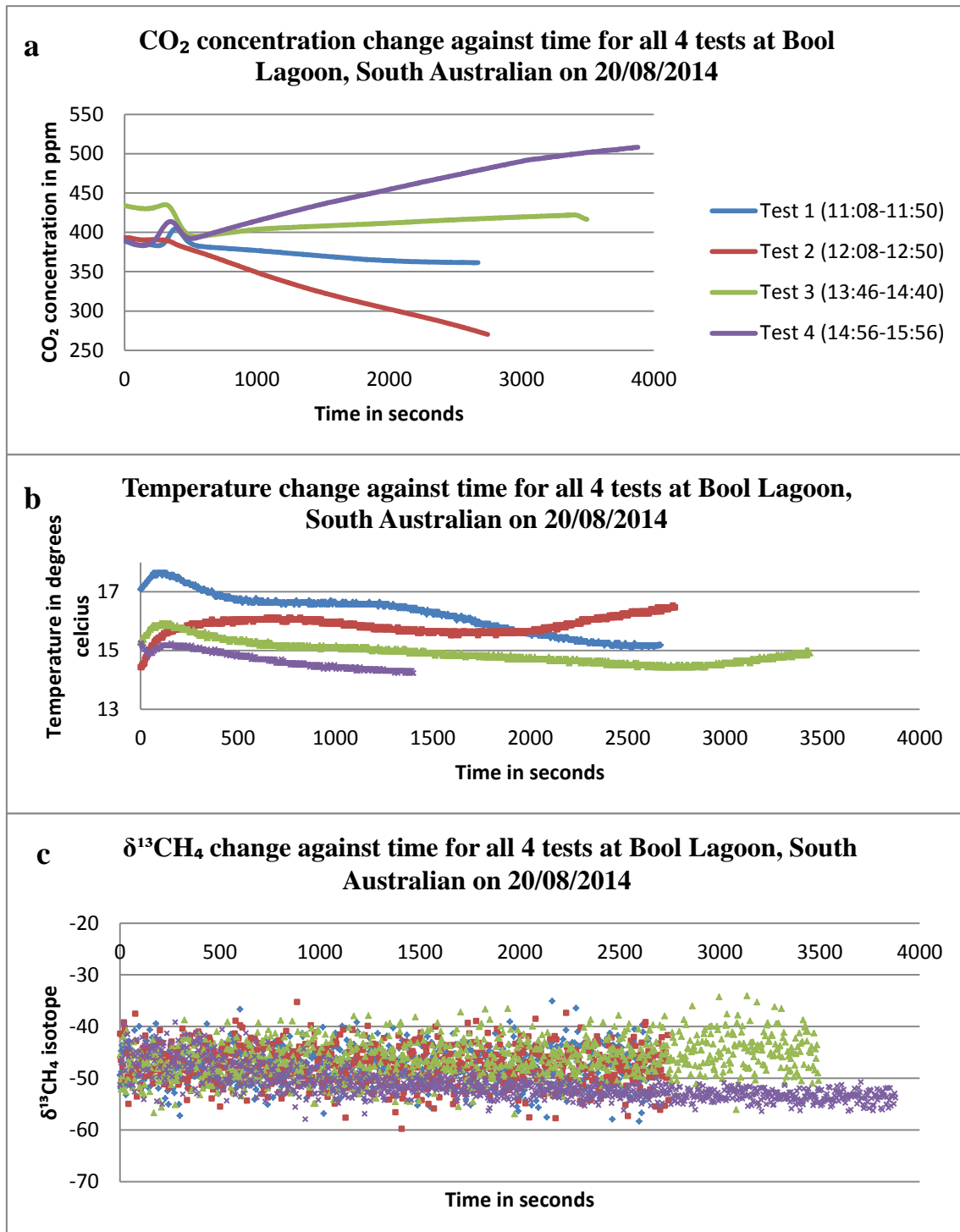
**Figure 5. 5a. Flux chamber CO₂ concentration change against time for all 4 tests at Bool Lagoon.
5b. Flux chamber change in temperate with time for all 4 tests. Test 4 temperature reading failed
mid was through test. 5c Flux chamber δ¹³CH₄ isotopic signature change with time for all 4 tests.**

The Killarney state forest is located in central NSW were several CSG production projects are taking place in the district. The small wetland changes seasonal and was a known methane producing source from preliminary tests conducted in late 2013 where disturbing the water logged mud produced elevated methane concentrations. Test 1 produces methane at approximately ten times the rate of Test 2. Test 1 was conducted at a warmer part of the day and less CO_2 is produced suggesting that the water plants are photosynthesising or the methanogenic bacteria are working at a faster rate. CO_2 production is very minimal compared to tests at other location throughout the project. The rate of methane released is very constant for both tests, this may have something to do with how the methane is trapped wetland. Both Test 1 and 2 have the same isotopic signature ranging between -40 and -55which is consistent with other wetland tests.

A **CH₄ concentration change against time at Killarney state forest wetland, NSW**

$y = 0.0002x + 1.7831$
$R^2 = 0.9977$

$y = 3E\text{-}05x + 1.7788$
$R^2 = 0.9982$

Test 1. (14:54-15:55)   Test 2. (07:25-08:34)

B **CO₂ concentration change against time at Killarney state forest wetland, NSW**

C **Temperature change against time at Killarney state forest wetland, NSW**

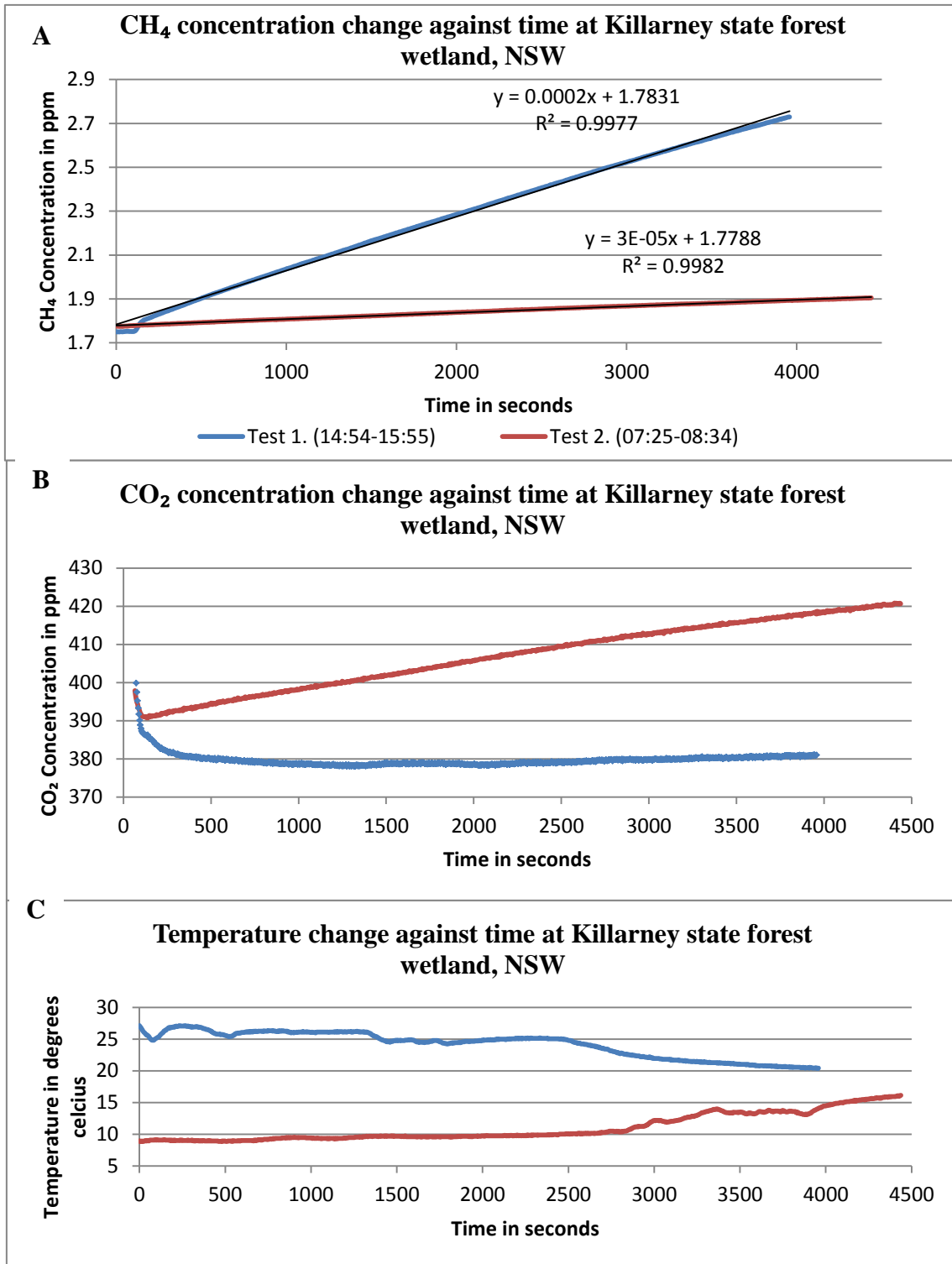**Figure 6: Flux chamber CH₄ concentration change against time in Killarney State Forest as a small wetland. Test 1 is taken on the 14/08/2014 in the afternoon and test 2 is taken on the 15/08/2014 in the morning. Both tests use the chamber over water up to 5cm deep with small water plants cover 50-60% of the ground. 6b. Flux chamber CO₂ concentration change against time for Test 1 and 2. 6c. Change in temperature for both tests.**

Urrbrae Wetlands is located in the outer suburbs of Adelaide next to a major highway. Areas of the wetland have been man made to act as a run off and catchment area. Elevated back ground levels were not detected but a local school catches methane off the wetland by disturbing the bottom and capturing the bubble. Due to its close location to the university it was an easily accessible wetland to test. Test 1 is over the over flow run off area and no water was present during time of test but soils were wet. Test 2 was off the board walk into the first catchment area of the wetlands. In figure 7 test 2 shows a quick release of methane at two periods. Methane concentration begin to decrease after the mass release suggestion possible mixing of gas through chamber, consumption of methane by organisms or diluted by CO_2 as figure 8a shows a steady increase in CO_2. The first mass release of methane could be related to putting the chamber in place and walking through the water logged muds. After test 2 the ground under the chamber was disturbed by applying pressure and bubbles were released. By 14:58 a concentration of 199.3ppm was reached. Without disturbing the soils methane release is much slower. For test 1 CH_4 concentration and temperature closely resemble each other's spikes but overall temperature change is less than one degree.
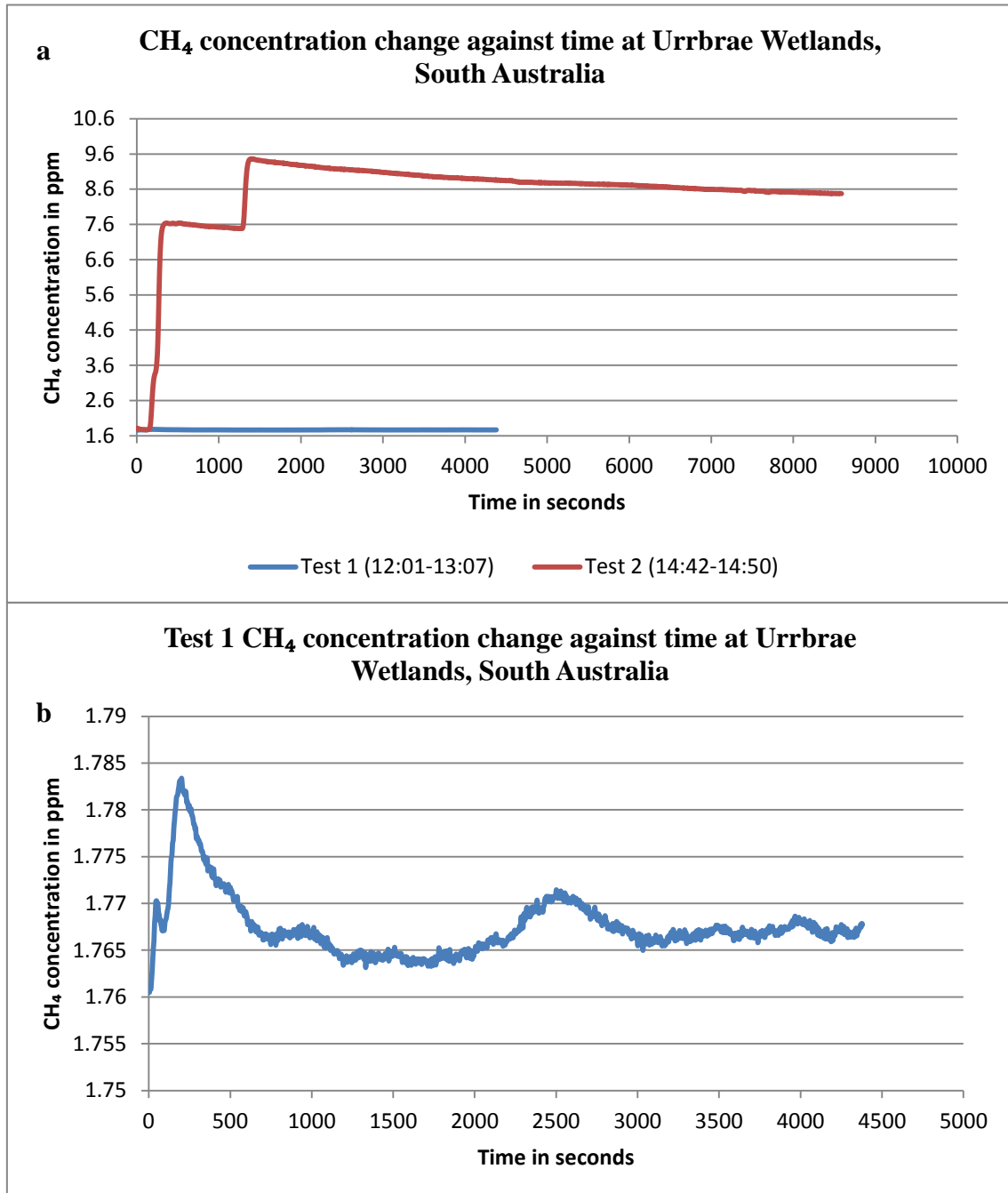
Figure 7: 7a. Flux chamber CH₄ concentration change with time at Urrbrae Wetlands, South Australia. Test 1 on the 15/07/14 and Test 2 on the 22/07/14 and uses floating flux chamber method. 7b.Flux chamber test 1 as test 2 limits the detail of test 1.

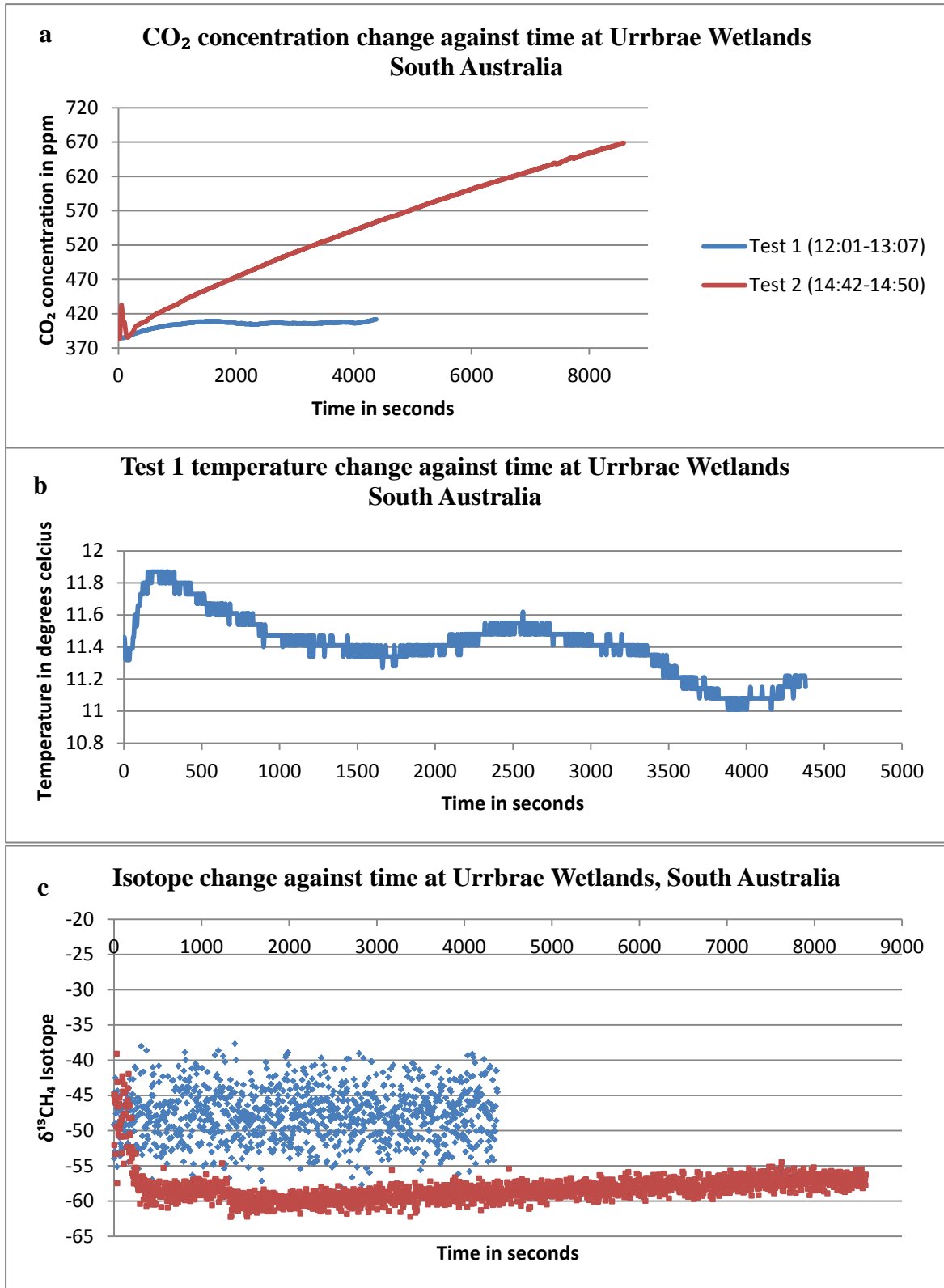**Figure 8: 8a. Flux chamber CO₂ concentration changes for Urrbrae wetlands. Test 1 on the 15/07/14 and Test 2 on the 22/07/14. 8b. Flux chamber temperature change with time for test 1. 8c. δ¹³CH₄ isotope change against time for both tests.**

The Lightning Ridge Bore Bath Tests produced a variety of numbers. It was a known source due to preliminary sniffer tests conducted in late 2013. The water supply for the baths comes from a well over 1000 metres deep that taps into the Great Artesian Basin and cuts through several formations targeted for CSG. The well is cased but well data was unable to be found. The baths are open 24 hours a day and the water flows in at a constant rate so methane released should not vary during the day and only if water flow is changed. Test 1 used the floating chamber over the shallower pool, test 2 used the floating chamber in the larger pool approximately 1.7m deep. Test 3 uses a 33.8L chamber system without a mixing fan or weather logging capabilities as this was over the inlet of water into the bath where bubbles were frequently seen rising to the surface as the larger chamber did not fit properly. The highest concentration recorded from test 3 was 1791ppm which is outside of the Picarro guaranteed range and may have contaminated the machine as test 4 was not as consistent with other tests. Figure 9 shows the concentrations changes for tests 1 and 2 inside the flux chamber. Test 1 and 2 are very similar as shown in figure 9a and fluxes shown in Table 2. High amounts of CO_2 were also released throughout experiment. Longer tests produced stronger isotope signature. Test 1 and 2 becoming more biogenic suggesting the methane source is from microbial activity and not thermogenic methane extracted from coal seams.
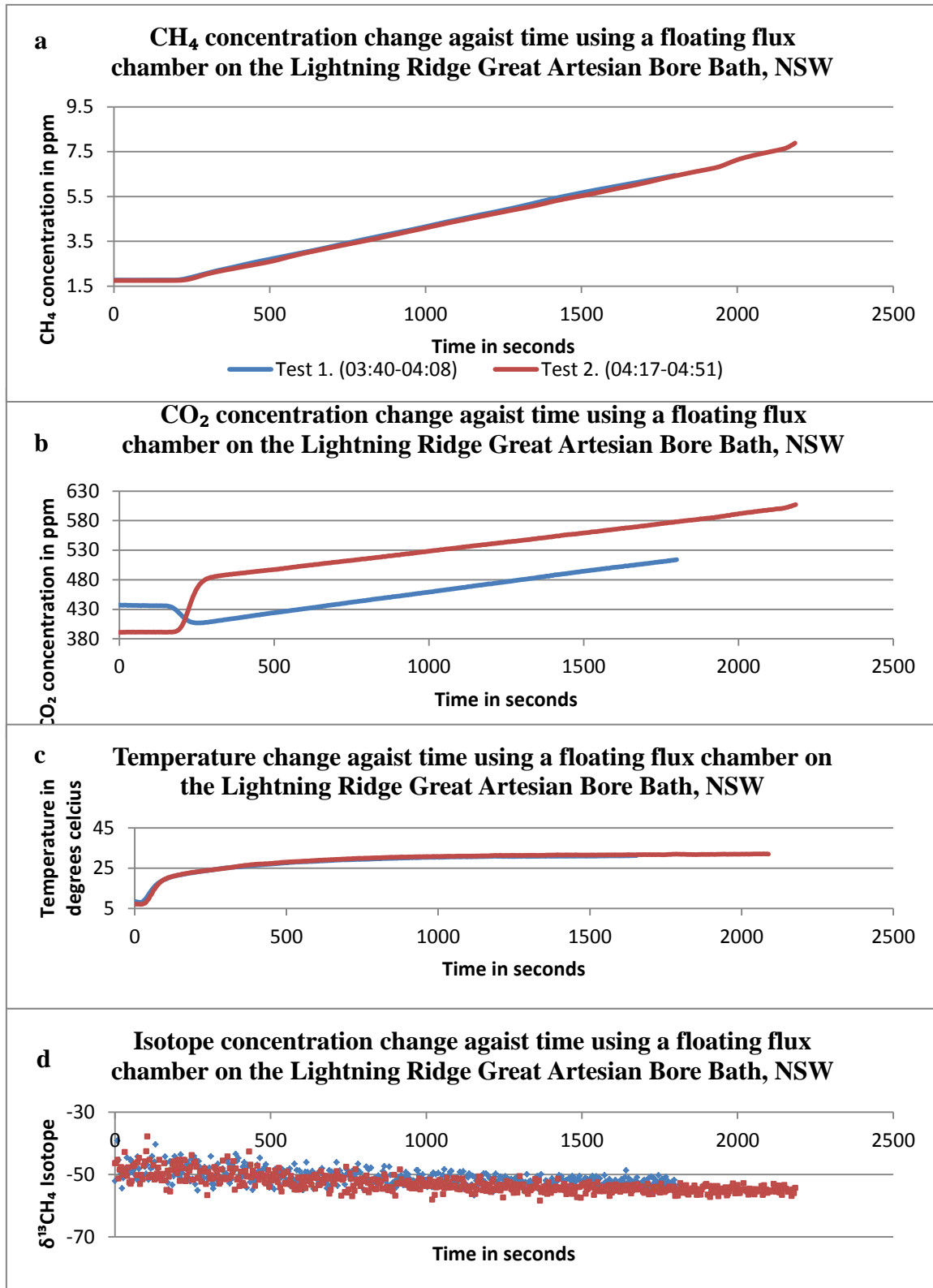
Figure 9: Lightning Ridge Bore Bath flux chamber results for test 1 and 2. Test 3 is not shown due to different sized chamber used. 9a. Flux chamber CH₄ concentration change with time. 9b. Flux chamber CO₂ concentration change with time. 9c. Flux chamber temperature change against time. 9d. δ¹³CH₄ isotope change with time.

Preliminary tests were also conducted at water bore in the South East of South Australia which cuts through several poor quality coal measures. It produced elevated methane concentrations when water was released and the amount of methane released depends on the amount of water flow. Due to lack of equipment a proper test could not be conducted but it should be noted the amount of CO_2 released was significant.

3.3 FLUX CHAMBER CONCENTRATION RESULTS

Table 2 is a summary of fluxes calculated from chamber tests over water bores and wetlands. Flux results are present in three different units; kilograms per metre squared per minute, grams per metre squared per day and standard cubic feet (SCF) per year which is the units used in the petroleum industry. Surface area for main chamber is 0.312 m_2 and volume is 129.6 litres. Flux chamber experiments show over the same wetland that methane production changes and in some cases methane is being consumed. The Urrbrae wetlands changes by 2 orders of magnitude between test 1 and 2. Towards the end of test 2 concentrations start to decrease suggesting some sort of consumption of methane is occurring in the chamber. Test 2b shows the rate at which methane is consumed for the later half of the test. This is also seen at test site 3 at Bool Lagoon. Killarney state forest produced methane at a more constant rate as seen in figure 6a. Test 1 methane flux was an order of magnitude larger than Test 2. Test locations were approximately 100m apart over water less than 5cm deep and which was dry during the summer months. Fluxes calculated at the Lightning Ridge Bore Bath suggest the majority of the water surface of the baths release the same amount of methane except where the water is released into the bath. Test 1 and 2 produced very

similar final flux results. Test 3 produced the higher number but that is due to its position over the water inlet where bubble were frequently seen. The lightning ridge test produced some of the highest isotopic signatures of the project despite the water coming from greater depths. Lake Frome results also vary by an order of magnitude when test locations were only approximately 50m apart. Test 1 was conducted during a warmer part of the day which could be the reason for the higher methane production. Bool Lagoon was the largest wetland tested, Test 4 produced the highest flux which was 2 orders of magnitude larger than test 1 and 2. Test 3 saw consumption of methane in the last half of the test.

Table 2: Flux Calculations for all Chamber tests. NA indicates unavailable data due to equipment failure. An approximate temperature is used and is written in brackets in the appropriate column. 100 kPa is assumed where pressure data us unavailable. *consumption is calculated. **different sized chamber used. * CRDS analyser may not have been performing to adequate standard due to abnormally high reading recorded just prior to test. Extra hose length was used.**

Location and Test number	Date	R^2 value	Average Isotope	Average Temperature (°C)	Average Pressure (kPa)	F (kg m-2 min-1)	F (g m-2 day-1)	F (scf m-2 year-1)
Urrbrae Wetlands Test 1.	15/7/14	0.1893	-47.78	11.34	100.27	1.69E-11	2.43E-05	4.60E-04
Urrbrae Wetlands Test 2a.	22/7/14	0.0984	-58.27	NA (15)	NA	2.83E-09	4.07E-03	7.95E-02
Urrbrae wetlands Test 2b.*	22/7/14	0.9632	-58.53	NA (15)	NA	-2.27E-09	-3.27E-03	-6.39E-02
Killarney Forest 1.	14/8/14	0.9989	-47.74	24.04	99.62	4.17E-09	6.01E-03	1.26E-01
Killarney Forest 2.	15/8/14	0.9985	-48.32	11.13	99.54	5.31E-10	7.65E-04	1.47E-02
Lightning Ridge Bath 1.	17/8/14	0.9996	-51.34	28.14	99.44	4.97E-08	7.16E-02	1.55E+00
Lightning Ridge Bath 2.	17/8/14	0.9991	-53.50	29.99	99.47	5.00E-08	7.20E-02	1.57E+00
Lightning Ridge Bath 3.	17/8/14	0.9948	-81.25	NA (30)	NA	1.57E-04	2.25E+02	4.87E+03
Lightning Ridge Bath 4.	17/8/14	0.9851	-68.83	NA (30)	NA	1.61E-08	2.33E-02	5.03E-01
Lake Frome Test 1.	19/8/14	0.9986	-47.83	NA (15)	NA	1.59E-09	2.28E-03	9.84E-02
Lake Frome Test 2.	19/8/14	0.9891	-49.92	15.11	102.63	1.03E-08	1.48E-02	2.74E-01
Lake Frome Test 3.	19/8/14	0.9263	-50.13	12.41	102.70	1.05E-08	1.52E-02	2.76E-01
Bool lagoon Test 1.	20/8/14	0.9975	-47.42	16.03	102.28	2.54E-10	3.66E-04	6.88E-03
Bool lagoon Test 2.	20/8/14	0.9953	-47.56	15.89	102.23	4.24E-10	6.10E-04	1.15E-02
Bool lagoon Test 3.*	20/8/14	0.0232	-45.99	14.86	NA	-2.49E-11	-3.59E-05	-7.01E-04
Bool lagoon Test 4.*	20/8/14	0.8645	-51.73	14.58	NA	2.09E-08	3.02E-02	5.87E-01

3.4 BACKGROUND LEVEL RESULTS

Back ground levels were measured using the CRDS analyser fitted to the vehicle and sampling air from the top right hand side of the vehicle away from car fumes. Slower speeds were driven around areas of interest.

Figure 10 shows no signs of elevated background concentrations leading up to the lagoon or on its very edges even though flux chamber tests proved the lagoon produces methane. This suggests the rate of methane production is very low or methane is very easily mixed into the atmosphere and measuring its methane generation by driving around the edged is not a suitable method.
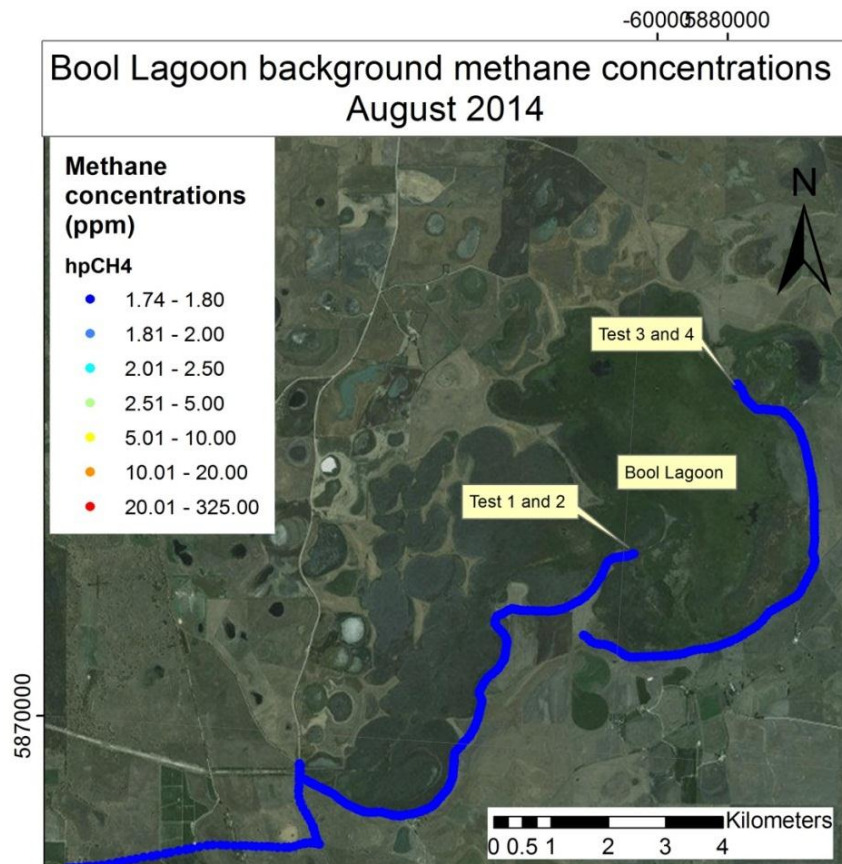
Figure 10: Background atmospheric CH$_4$ concentration around Bool Lagoon, South Australia on the 20/08/2014. Location of flux chamber tests 1, 2, 3 and 4 are situated on the edges of the lagoon.

The figure 11 compares a change in background methane levels in the Riverina rice growing areas at two separate times during the year. Figure 11a is from December 2013 where crop are in the growing phase. Water is left on the rice crops for all or most of the growing season. Permeant water is applied from December. Water was visible on many of the rice crops during the December drive. Figure 11b is from august 2014. July and august is the preparation time for rice crops where the application of nitrogen, phosphate fertilizers and levelling of rice fields occur (RGA, 2014). The highest concentration recoded in December was 5.7ppm while driving on public roads around rice fields. A rise in background CH$_4$ occurs as soon as the first irrigation channel was crossed on the eastern side of the map. Numbers decrease closer to Griffith where there

are less rice fields. Citrus trees, grape vines, swamps and other fruit tree crops were driven past but rice fields produced the highest numbers. The same track was attempted to be driven in August but not all road could be driven on due to wet conditions. Rice crops were in the preparation phase and no water was lying on the fields. Irrigation canals were also emptier. The highest concentration recorded was 1.81ppm which was recorded in the town of Griffith and not associated to rice production. Concentrations were significantly lower during august and lower than the current global atmospheric average. Weather conditions in august were much cooler with some light rain compared to December which was warm and dry although this should not have a significant effect on recorded concentrations.

Other crops such as cotton were targeted because flood irrigation is also a method used. Driving on public roads around cotton farms in December 2013 did not produce any elevated results. Crops were not visible from the road due to high irrigation walls.
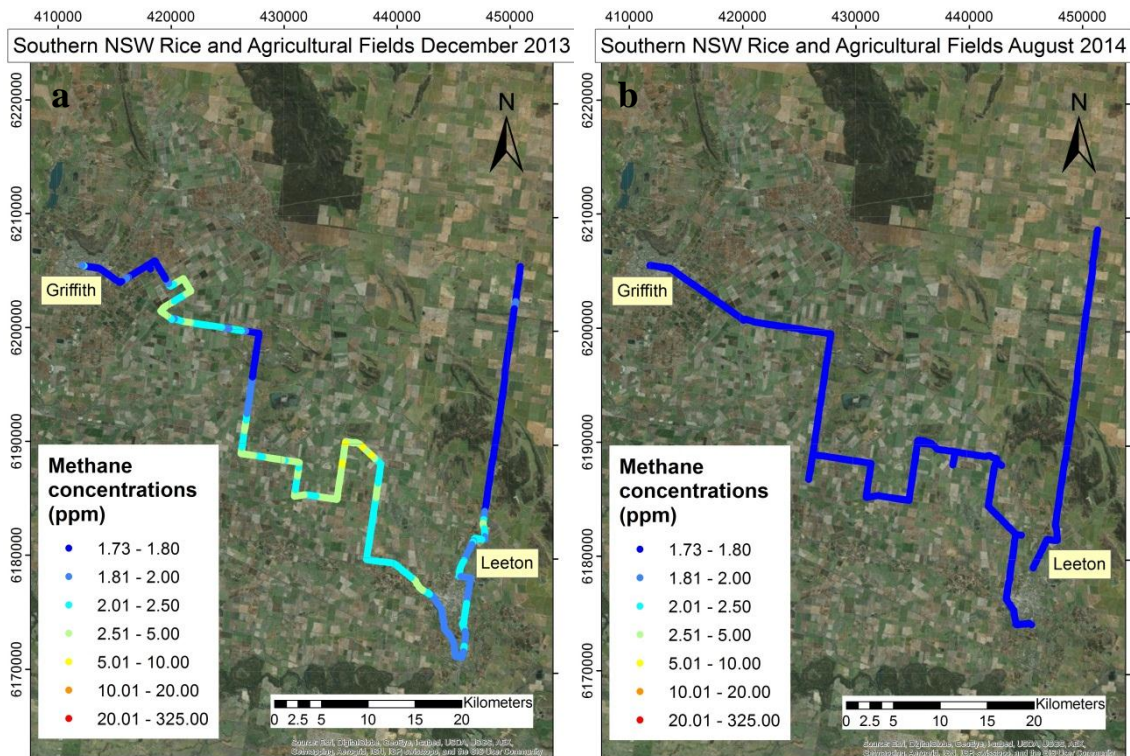
Figure 11: Atmospheric methane concentration in ppm in rice and agricultural fields between Griffith and Leeton, NSW. Right hand image from December 21st 2013 between the hours of 5-8am during the growing season where fields are flooded with water. Left hand images from August 18th 2014 between the hours of 6-9am during the preparation season and fields were dry.

As shown in figure 3 Adelaide city methane concentrations vary greatly throughout the city and suburbs. Isotopic signature also varied greatly. No numbers could be directly associated with the river Torrens, an adjacent small wetland or the Urrbrae wetlands. Spikes in numbers could not always be associated with a source and possible leaks of gas pipes could be a source. Gardner Island landfill site in Port Adelaide which closed in 2000 produced the highest concentration of 321.1ppm. It was unclear if there were any increase in CH_4 concentrations coming off the adjacent Torrens island power plant powered by natural gas as the land fill site was very close. In figure 3b 17.5ppm was the highest concentration recorded with a $\delta^{13}CH_4$ signature of -32. Natural gas is typically

around -36.8%(Phillips, Ackley *et al.*, 2013) and the reason behind elevated number in this area could be due to a gas leak. Numerous other roads have been driven in the city and produced similar results of unknown spikes in concentrations from unidentified sources. The same track can also be driven several times producing different results each time. The average city methane concentration was 2.13ppm for this drive. This number doesn't not include data collected on Garden Island. Including Garden Island the average concentration goes up to 4.67ppm.
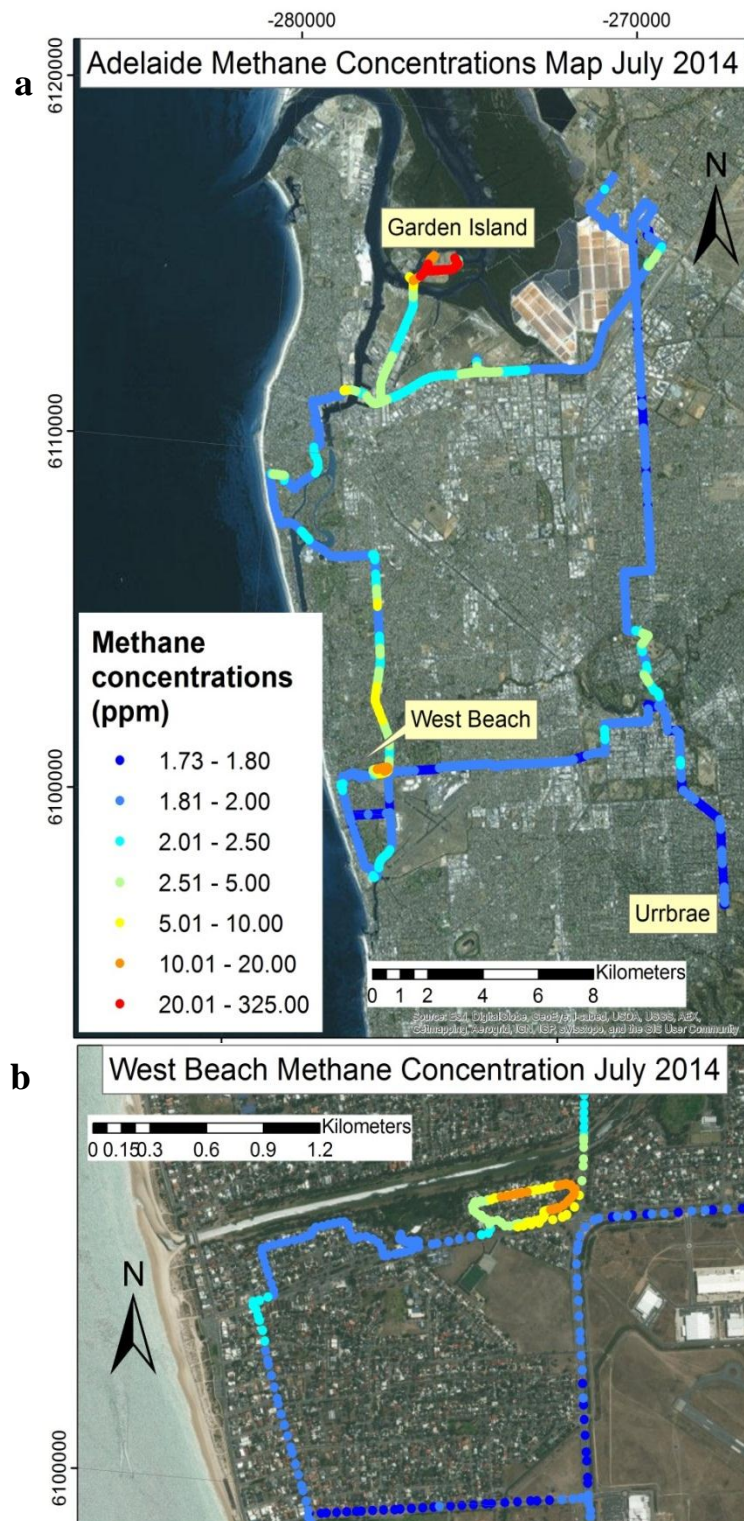
Figure 12. Atmospheric methane concentration in ppm around Adelaide on July 22nd 2014 between the hours of 3pm and 8:30pm. 3a. map of whole area driven. 3b. zoomed in section of map 3a showing increased concentrations in a neighbourhood.

Figure 13 shows the change in methane concentrations while driving on public roads around open cut coal mines in the Upper Hunter Valley region. The highest concentration reaches was 33.7ppm. For concentration above 30ppm the average isotopic signature was -78.15 and concentrations over 5ppm is -77.85 which is well outside the coal extraction range of -35±3 (Pacific Environment Limited, 2014). The average methane concentration was 2.71ppm for the drive.
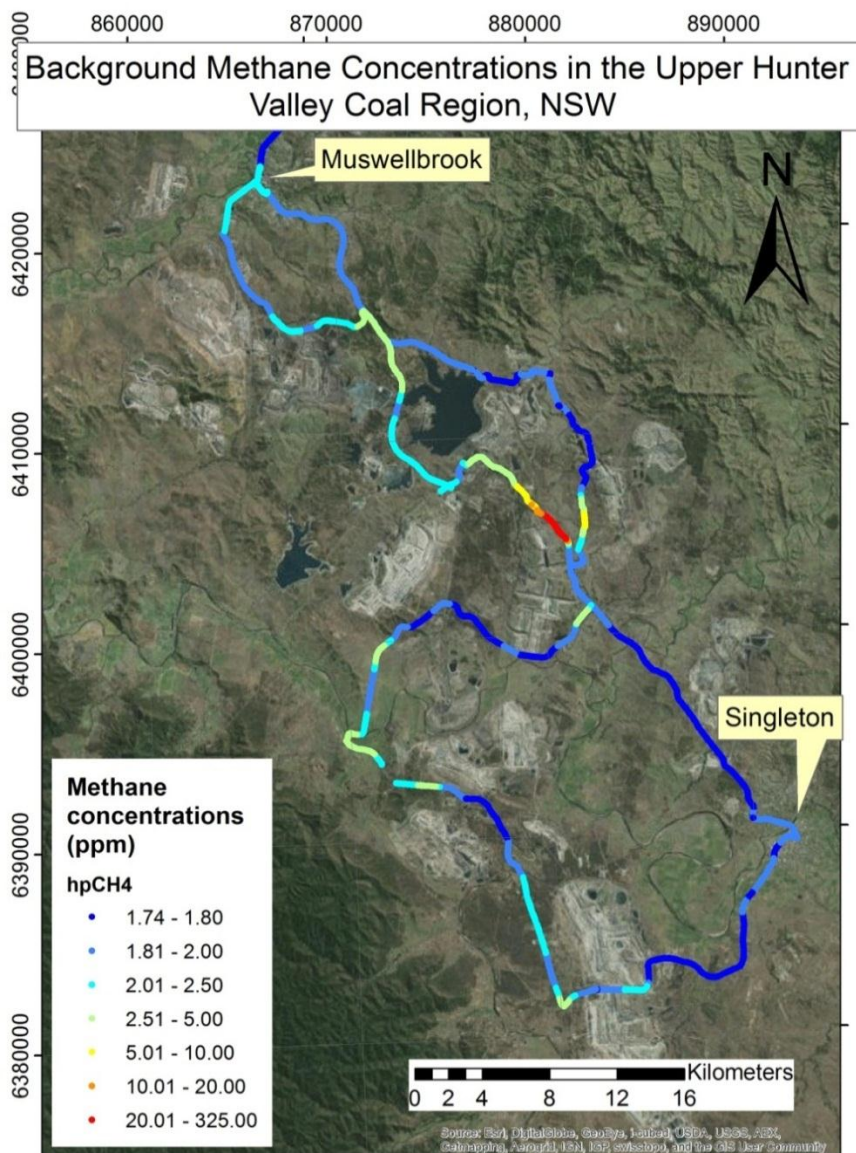
Figure 13: Atmospheric methane concentration in ppm from Muswellbrook to Singleton through open cut coal mines between 5pm and 8pm on the 15th August 2014

Figure 14 and 15 show the background methane concentration while driving on public roads. This is a CSG producing area and infrastructure could be seen at various locations along the drive. It is not known what wells were in production and what were inactive. Elevated levels were record in between Chinchilla and Dably but satellite imagery does not show CSG Infrastructure however satellite imagery is not up to date and may not show recent operations. Figure 15 shows methane concentrations were below background while driving through CSG fields.
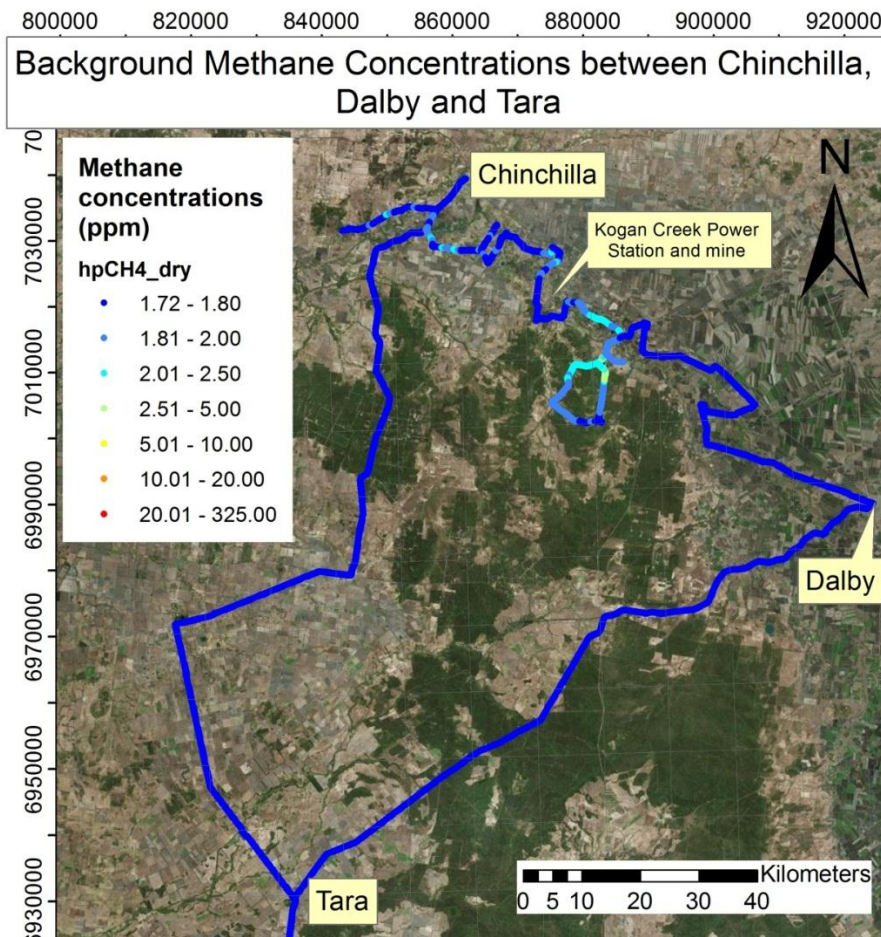
Figure 14: Atmospheric methane concentration in ppm between Chinchilla, Dalby and Tara on the 19th and 20th of December 2014. Track is driven on public roads passing through some CSG fields, past an operating open cut coal mine and across the Condamine River.
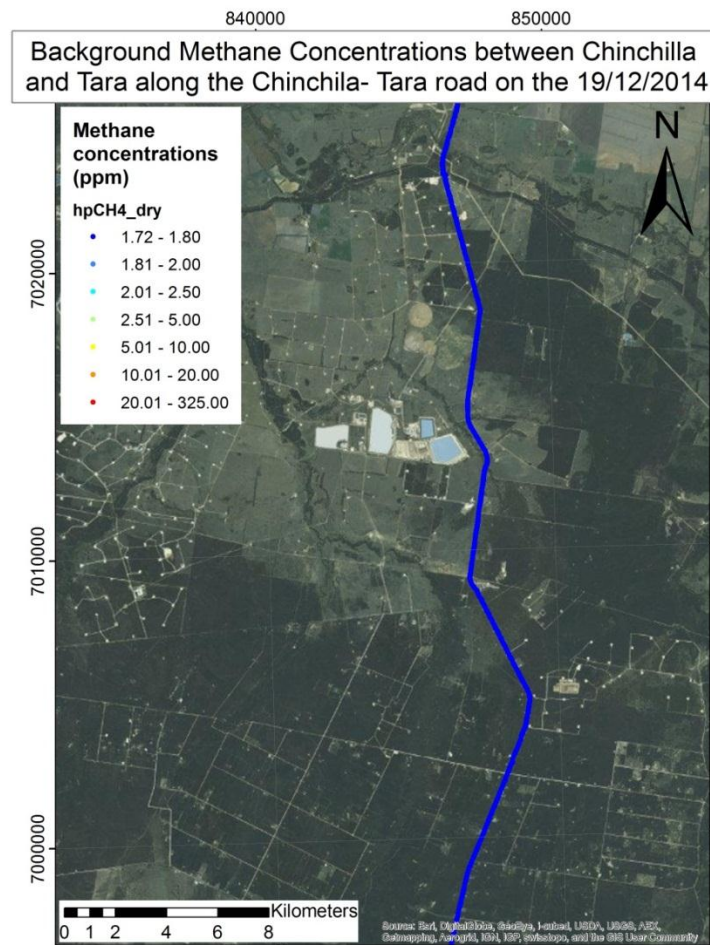
Figure 15: Atmospheric methane concentration in ppm on the road between Chinchilla and Tara through CSG fields.

A method similar to that used to gather back ground levels was used around the Urrbrae agricultural farm. A longer hose was attach so atmospheric level around the farm and in animal pens could be gathered. No chamber or air trapping method was uses. Figure 14 compare methane levels from cow, pigs, sheep and a compost heap. There were nine compost bins setup next to each other varying in levels of decomposition. The spikes from the compost readings are thought to be from another source and carried over by a gust of wind as levels are not consistently high. The first and second bin which has the highest peaks also had minimal decomposition and contained fresh hay, grass clippings and manure. Cows produced the second highest numbers, there were three cows in

separate pens under a shelter with open sides. Levels above 2ppm are consistent with other reading from cows that have been noted when driving past cows on the edge of the road side or passing cattle trucks. The concentration from pigs was lower than expected. The highest number record was 1.95ppm from inside the dry sow which holds male pigs over the age of 6 months. The grower room, farrowing room and dry sow were all enclosed with ventilation fans. The drains were also tested which produced concentrations less than 1.9ppm. The farm has a methane digester which does have methane in it and does have small leaks. Sheep pens under a shelter with open sides were also tested which produced numbers slightly higher than pigs.
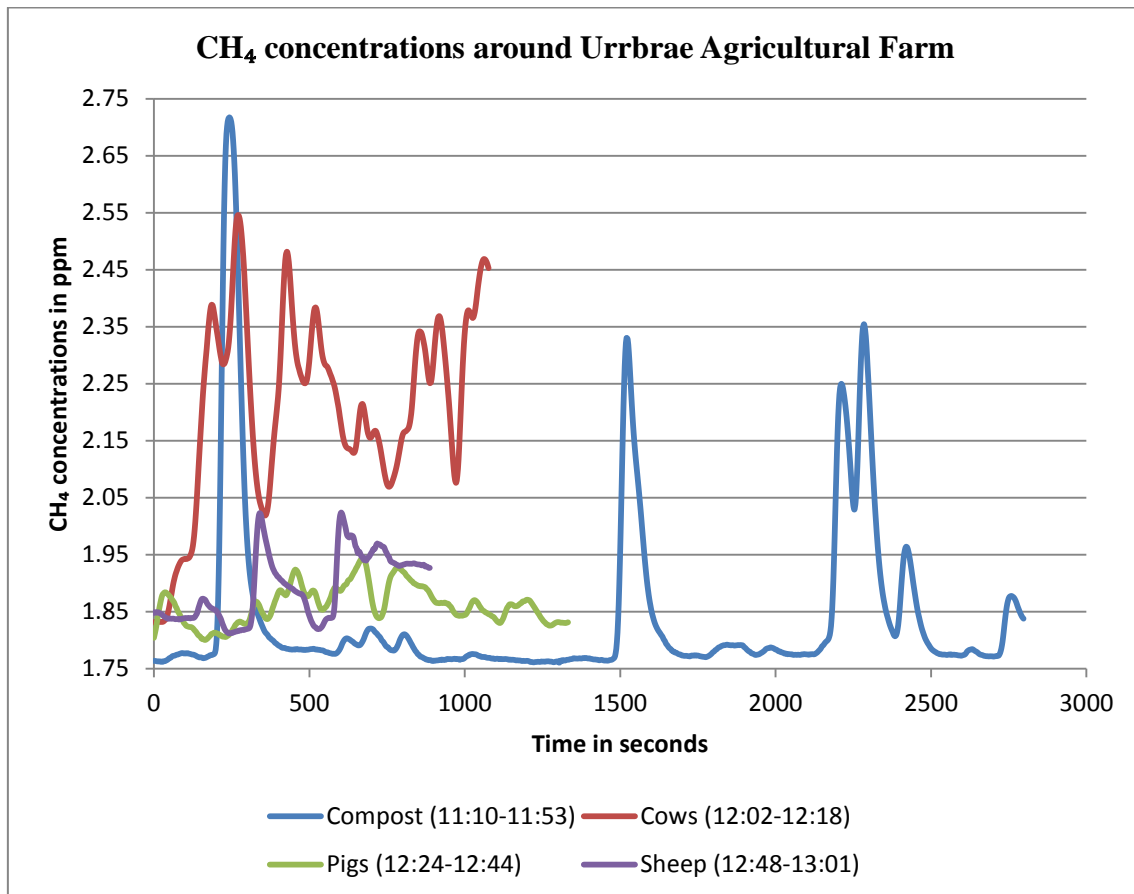
Figure 14: Methane concentrations around Urrbrae Agricultural school using a CDRS background detection method with a longer hose attached to reach animal enclosures and over various sources on the 23rd July 2014.

DISCUSSION

For the purposes of this study the background atmospheric methane concentration is assumed to be lower than 1.8 ppm. During this work typically low concentrations varied a lot between 1.74 and 1.8ppm. Much of this low concentration variation appeared random and may be related to a combination of minor atmospheric variations and instrument noise. Interestingly this is still lower than the current global average of 1.824ppm(WMO, 2014).

During this study a number of factors that appeared to affect the quality of the data and the performance of the instrument were observed. These will be discussed in the following paragraphs. First I will discuss issues arising from the flux chamber testing, results from the flux chamber tests, then from the background studies. I will also discuss some issues that are pertinent to the use of CRDS equipment overall.

Initial testing of the flux chamber using CO_2 in the laboratory was not quite as good as hoped. This could be due to inadequate mixing of CO_2 in the chamber as CO_2 is significantly heavier than CH_4. It is also likely that the flow rate of the CO_2 was not accurate as the flow used was at the lower limit of the instrument. The valve on the CO_2 tank also did not supply a constant flow at the low levels needed to mimic expected methane flux. The operation of the flux chamber in the field could use improvement in both its temperature and air pressure recording ability as this is crucial for flux calculations and its flotation capabilities.

The methane flux observed in wetlands varies by up to two orders of magnitude, with some tested systems actually consuming methane, i.e. the decrease in concentration produced a negative flux. Flux chamber results showed emissions vary depending on the location of the chamber within the wetland. Wetlands such as Killarney, the first test site at Lake Frome and first two test sites at Bool Lagoon showed relatively steady changes in methane concentration and therefore steady quantities of methane released. Test sites 3 and 4 at Bool Lagoon, test sites 2 and 3 at Lake Frome and the Urrbrae Wetlands all showed uneven methane release rates, that tended to look like bursts of methane activity flowed by extended periods of time with no or lesser methane released. Interestingly despite the uneven methane release rate at many sites, the CO_2 tended to have a more linear relationship. Isotope signatures also change between wetlands but typically represented the normal $\delta^{13}C\text{-}CH_4$ signature of around -55.)

Emissions also vary throughout the day, as seen in the Killarney State Forest wetland results. In this test it was observed that the amount of methane produced in the afternoon was approximately an order of magnitude greater than what was produced in the morning. Flux chamber tests would need to be done overnight the see how methane flux varied from night time conditions to day time. Ideally a test would need to be done for twenty-four hours straight to see how the system changes on a daily basis and then repeated each season to monitor the differences in emission seasonally.

Measuring flux using the CRDS allows concentration to be monitored on a second's basis which gives better insight into the processes occurring in the chamber. For example, this allowed me to see that in some situations methane was being emitted and then consumed. If samples were collected for analysis every 15 minutes (as might have been done for older flux chamber tests, this behaviour would not have been observed.

The CRDS and closed flux chamber method is a better way to understand how methane is released from systems but due to the large localised variations that we observed may not be suitable for estimating total emission for a whole wetland. The variations in flux results for tests at the same wetland were orders of magnitude different indicating that the assumption that methane emissions were uniform over an entire wetland is incorrect and therefore cannot be applied to all wetlands. However the amount of methane released can also depend on disruption of the bottom causing the release of bubbles, as seen at Urrbrae wetlands. Disruptions to these systems or even wind over the water surface could see a mass release of methane into the atmosphere.

While collecting GHG background data around Bool Lagoon, even when within meters of the water's edge methane concentrations did not exceed 1.8 ppm i.e. concentrations were essentially background for this study. However flux chamber tests on the lagoon indicated methane is produced by the wetland. Background levels around Urrbrae, Killarney and Lake Frome also showed concentrations around methane producing wetlands to be at or below background concentrations. This gives a good insight into how methane is dispersed into the atmosphere, showing quick dispersion, mixing and rapid rising. Methane produced in such low concentrations will be very hard or impossible to detect using this preliminary background method.

As rice is grown for human consumption it is classified as an anthropogenic methane source (IPCC, 2014). The results from the August drive through rice fields near Griffith, NSW suggests that methane is not produced or is only produced at very low rates when the fields are not in the production phase for rice, as atmospheric concentrations did not

exceed 1.8ppm. On the other hand, during the December drive when rice was being grown in the area the highest concentration recorded was 5.7ppm, with concentrations consistently above 5 ppm while driving past many rice fields. The average back ground concentration in the area was 2.6 ppm for that day in December, significantly higher than the background observed during our August trip. Interestingly the rice fields were approximately the same distance from the sampling point on the vehicle as the wetlands were but no elevated methane concentrations were observed from the wetlands. This suggests that rice crops in the production phase produce more methane than some wetlands. Closed flux chamber tests need be done over the rice fields during the growing season when the fields are flooded as bacteria prefer the water logged soils. This would provide a better understanding of methane emissions in this setting. Additionally it would be interesting to compare flux data from fields that use different fertilizers to see if that has an effect methane production rates. Flux chamber tests also need to be done on dry soils in the area to see if any methane is produced that cannot be detected by background concentration tests.

Background concentrations can be highly variable and the CRDS analyser is a useful tool to help understand methane sources and their emissions. The issue with this method is it helps to map out variations in methane concentration, but these concentrations are dependent on a number of factors, including e.g. weather conditions and distance from the source. To capture the variation background concentration over the same path would need to be repeated at various times during the day and year. Ultimately other existing methods to measure flux need to be tested and new techniques need to be developed for use over larger study areas.

City methane concentrations vary from standard background levels to 321 ppm. By far the biggest emitter was found to be a landfill. This was followed by what I have interpreted to be leaks in gas pipes as the isotopic signature suggest a thermogenic origin. Gas pipe leaks are a relatively easily managed source (i.e. repairing the leaks) and the CRDS analyser is the ideal tool to identify them. There were numerous spikes in concentration where sources were not able to be determined and this requires further investigation. Excluding the data recorded from the Garden Island Landfill Adelaide's average concentration of 2.13ppm lies within the typical urban range of 1.8-3ppm (Pacific Environment Limited, 2014). However including the data from the landfill brought the average up to 4.67 ppm, well above typical urban levels.

The highest concentration recorded for the Upper Hunter Valley coal region was 33.7ppm while the average concentration for the drive was 2.71ppm. This value is higher than the 2.1ppm average around a CSG project (Pacific Environment Limited, 2014). I concluded that coal mining is a big methane contributor to the atmosphere based on consistently higher methane concentrations recorded around coal mines compared to other background concentrations drives. Further testing needs to be done to narrow down where the methane is coming from and what the exact flux from each source is.

Around CSG fields in Queensland elevated there were few high concentration readings that could be directly associated to CGS activity. It should be noted that it was difficult to get close to CSG infrastructure but it was visible from the vehicle. Permission to access sites is needed to get a better understating of concentration and flux around CSG

wells. During the CSG drive in QLD there were areas with elevated concentrations but it was difficult to determine if it was directly related to CSG activity. It is well known some CSG equipment leaks (Day, Dell'Amico *et al.*, 2014) but the CRDS analyser needs to be within close proximity to detect it and the use of a near-infrared camera would be useful to help pick up leaks. The CRDS could then be used to determine the amount of methane being emitted.

Data collect at Lightning Ridge Great Artesian Bore bath shows that water bores in the Great Artesian Basin are a way that methane is brought to the surface and released into the atmosphere. The bore is also the town's main water supply so any water extracted from that well will contain some methane. It is worth noting that there are other similar bores in the area or it is likely that there are others in similar settings around the world that would also emit methane this way. It is another anthropogenic source that would be very difficult to put an exact methane emission rate on, but would be worth characterising better.

It is well know that cows produce methane and this study has allowed me to see how the CRDS analyser detects methane from cows and how those concentrations compare to other sources. Typically when around one cow or driving past a cattle truck the CRDS analyser detect concentrations above 2ppm. Pigs also produce some elevated concentrations but not as high as expected, while sheep also produce higher than expected results. Concentrations around the farm were consistently higher than back ground numbers recorded around wetlands.

CONCLUSIONS

Looking at the change in atmospheric methane concentrations around wetlands, coal mines, CSG fields, rice fields, cities and country areas has given me a preliminary insight into the potential amount of methane that can be generated by each source. Each site needs further investigation to accurately determine their outputs and their controls. This may require a combination of various testing methods. The variability within a wetland and its dependence on time of day makes it significantly more difficult to accurately measure the amount of methane produced by an entire wetland system. To globally define an amount of methane released into the atmosphere by wetlands would then be even more difficult to estimate. Atmospheric back ground concentration tests still do not pick up slow or low emitting sources such as the wetlands that were studied. The way that methane mixes in the atmosphere limits our ability to detect it from a distance. Similarly it is difficult to determine if the amount of methane emitted by anthropogenic sources like CSG operations is significant in comparison with other natural and anthropogenic sources. It is notable that the highest methane concentrations that were recorded during this study could generally be traced back to anthropogenic sources. The number of different sources and how each source releases methane is unique and possibly unable to be measured and build into the global methane budget accurately.

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- Martin Kennedy my supervisor for your help though out the year and all other staff at the Sprigg Geobiology centre
- Joshua Gilroy, Santos and staff at the Santos Narrabri operations centre for making our data collection trips possible.
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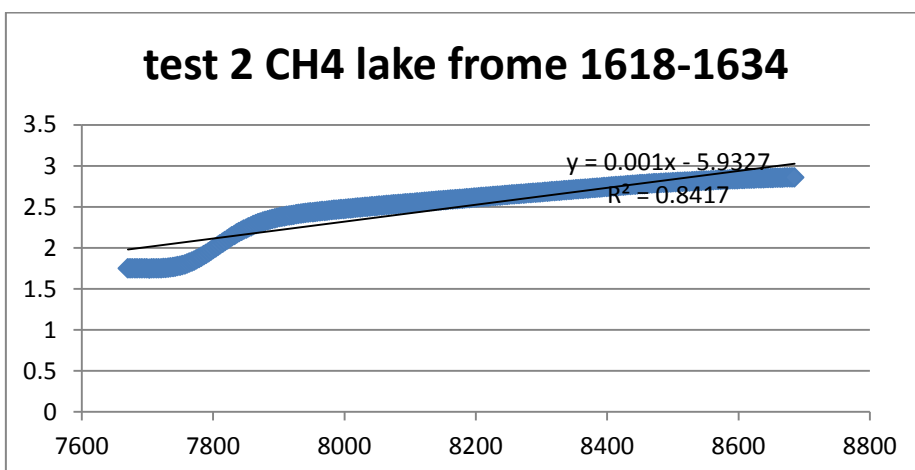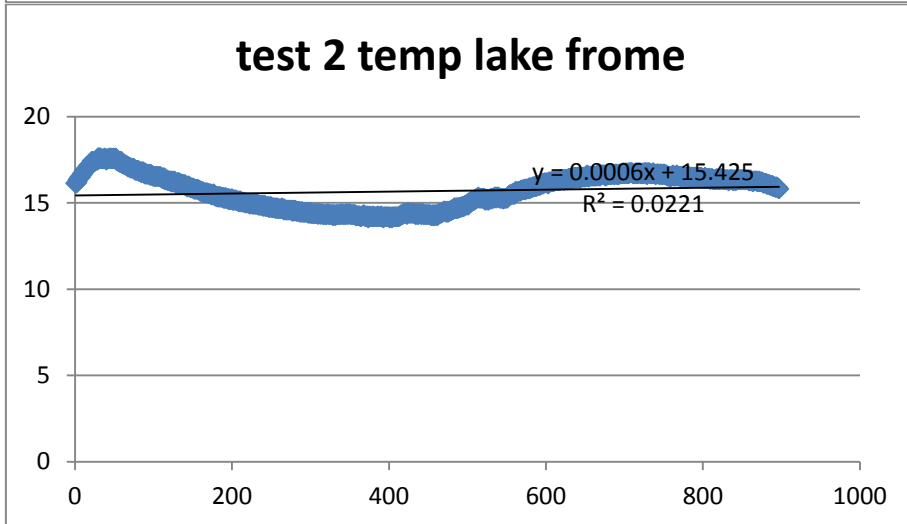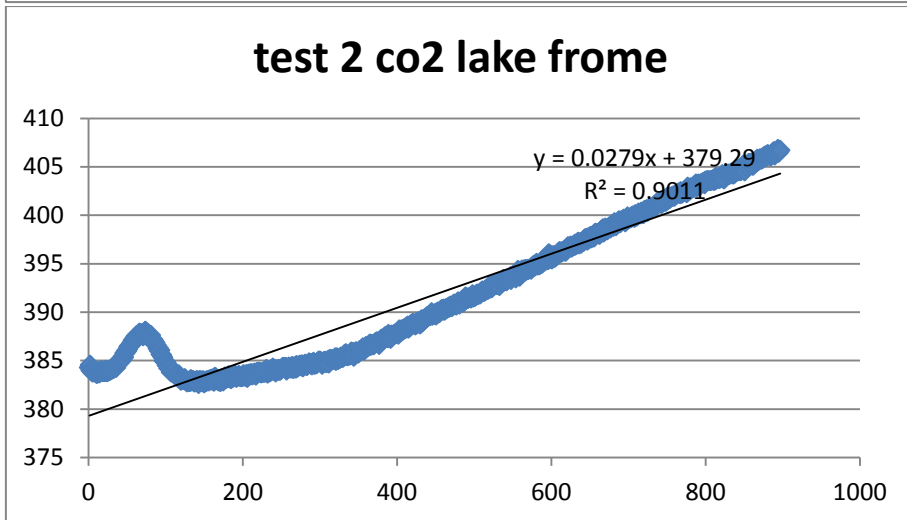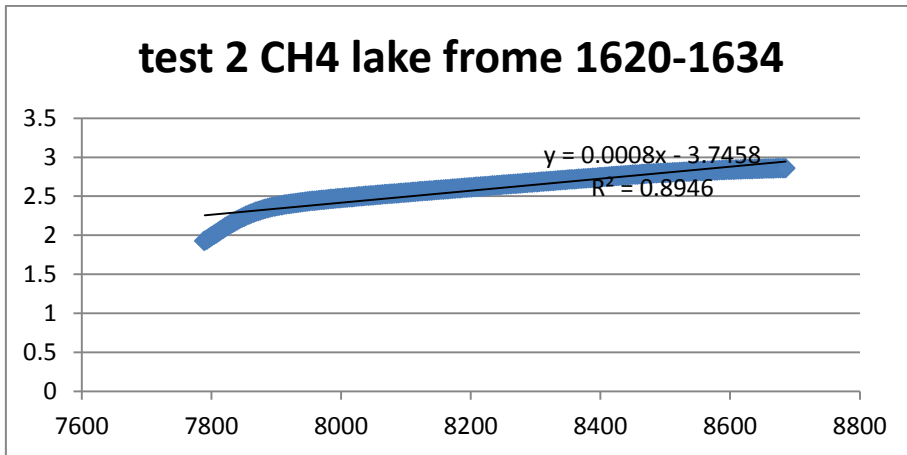## APPENDIX A: LAKE FROME TEST RESULTS
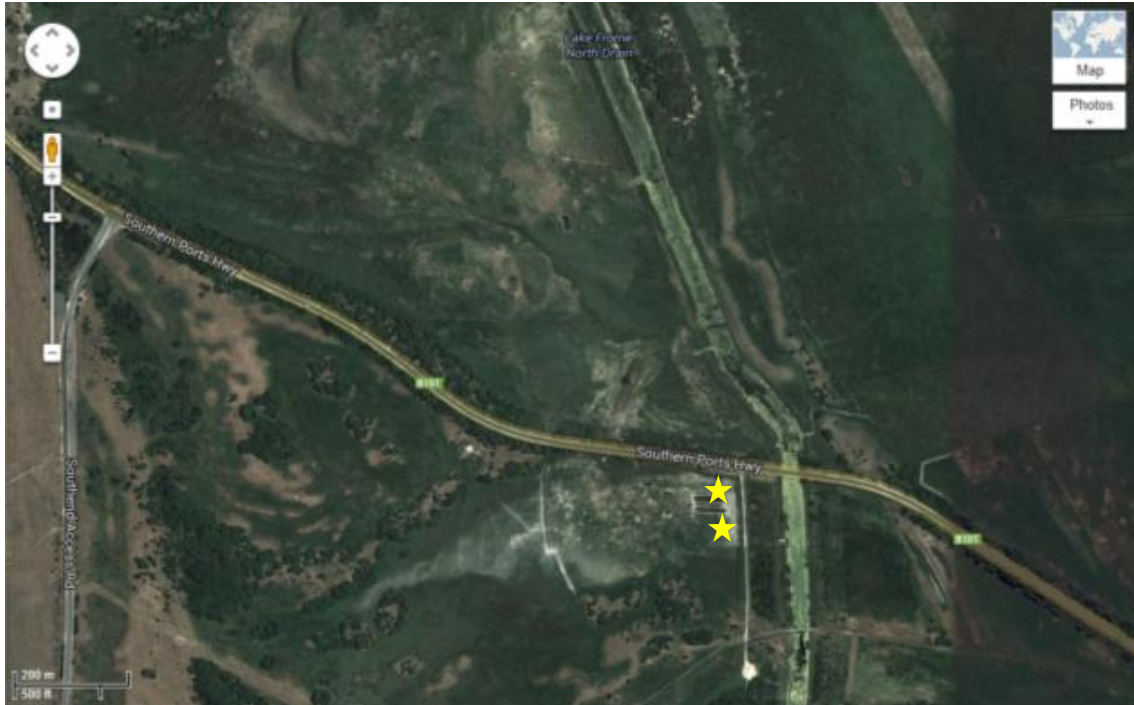
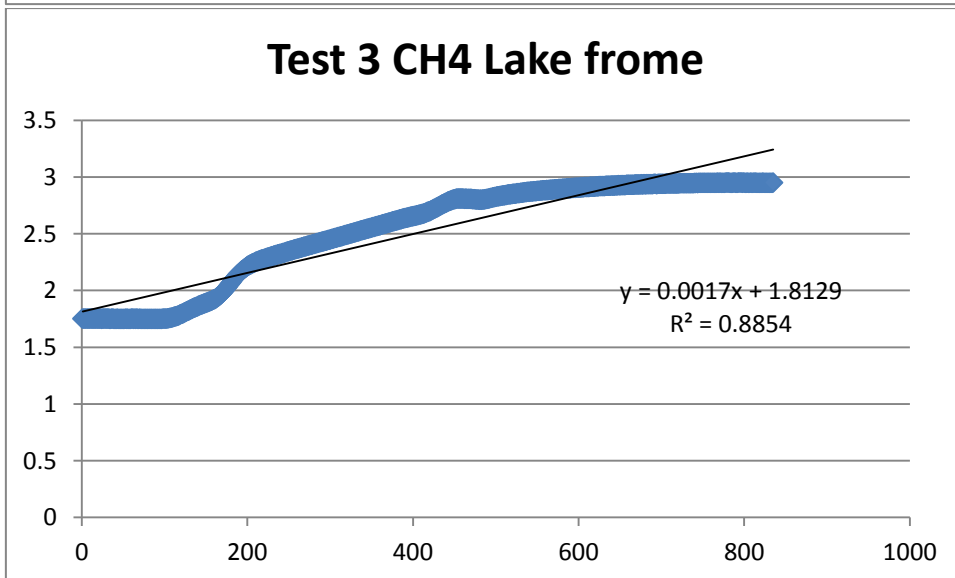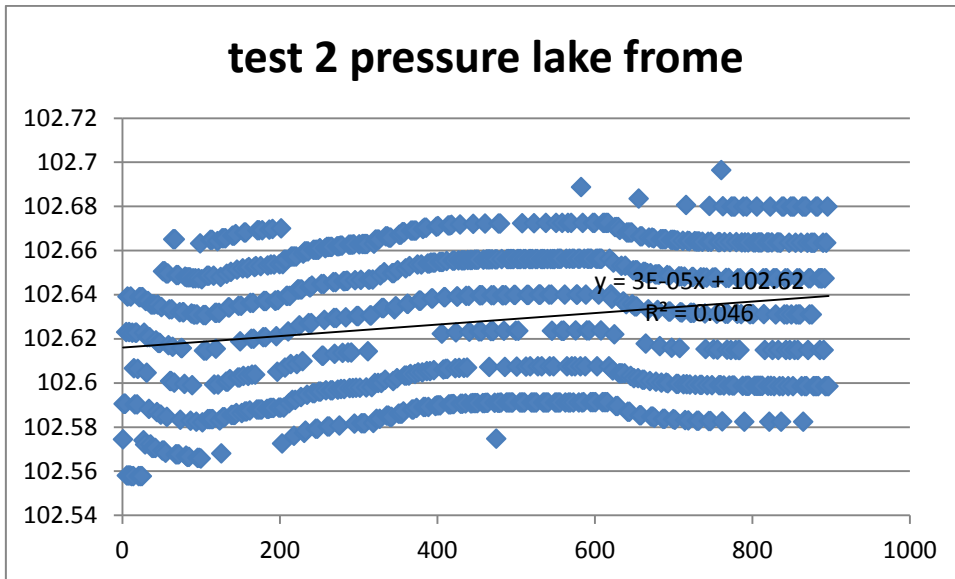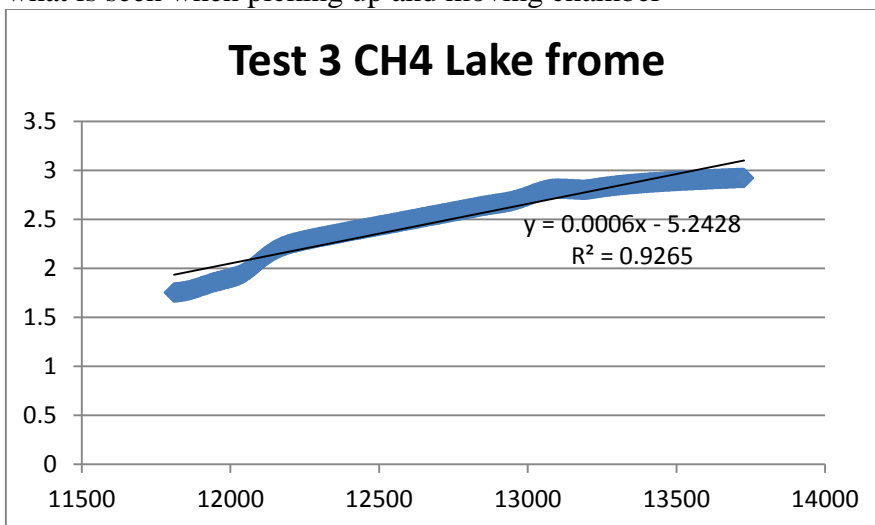|	Start Time	Finish Time	Coordinated	Comments
1st	15:04	15:50		Just over the rivoli farm fence into lake frome. Close to highway and track corner
2nd	16:14	17:07		Aprx 120m down track away from main road. Chamber sank considerably, chamber also took a long time to clear gasses out, may be an issue with the pump
3rd	17:21	18:10		Aprox 5 m back toward main road

Test 1 CH4 Lake frome

$y = 0.0005x + 1.7138$
$R^2 = 0.9952$

Test 1b CH4 Lake frome

$y = 0.0001x + 1.2531$
$R^2 = 0.9986$
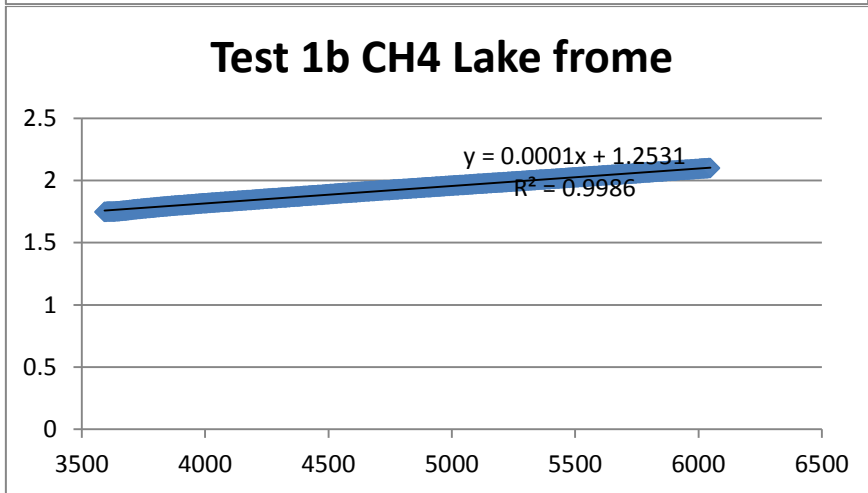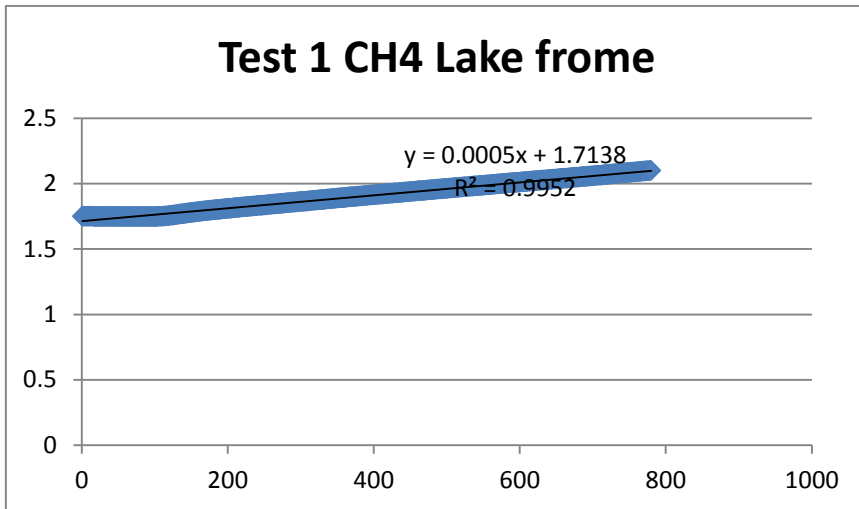
Test 1b taken from 15:10 to 15:50 when concentration rate became consistent
*temp and pressure failed for this test

test 2 CH4 lake frome 1618-1634

$y = 0.001x - 5.9327$
$R^2 = 0.8417$

test 2 CH4 lake frome 1620-1634

$y = 0.0008x - 3.7458$
$R^2 = 0.8946$

test 2 co2 lake frome

$y = 0.0279x + 379.29$
$R^2 = 0.9011$

test 2 temp lake frome

$y = 0.0006x + 15.425$
$R^2 = 0.0221$

test 2 pressure lake frome

$y = 3E\text{-}05x + 102.62$
$R^2 = 0.046$

Test 3 CH4 Lake frome

$y = 0.0017x + 1.8129$
$R^2 = 0.8854$

Finish time changed to 18:11. Looking at data, unrealistic spike occurs after. Typical of what is seen when picking up and moving chamber

Test 3 CH4 Lake frome

$y = 0.0006x - 5.2428$
$R^2 = 0.9265$

Test 3 CO2 Lake frome

$y = 0.0128x + 381.92$
$R^2 = 0.9253$

Test 3 temp Lake frome

$y = -0.0009x + 12.759$
$R^2 = 0.7032$

Test 3 pressure Lake frome

$y = 8E\text{-}05x + 102.66$
$R^2 = 0.2566$
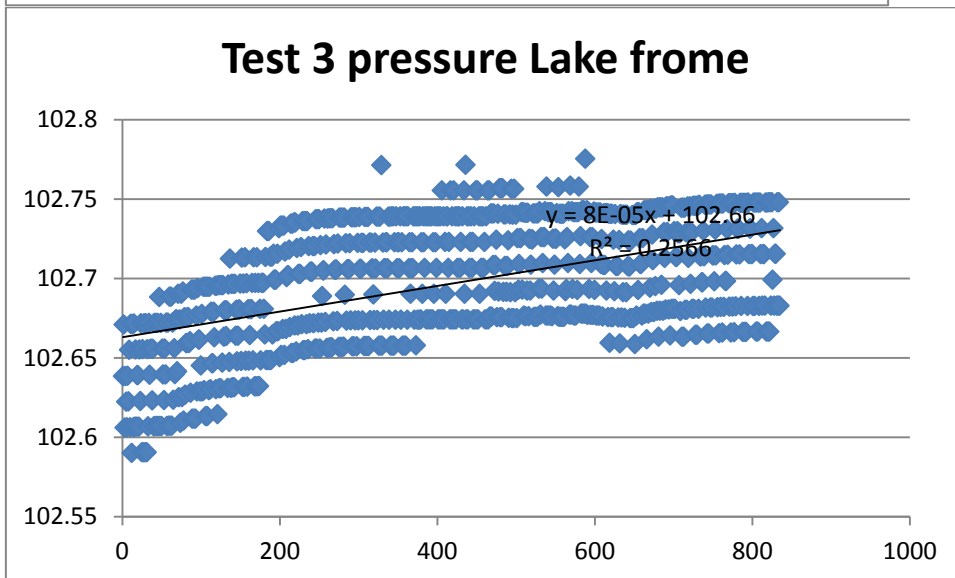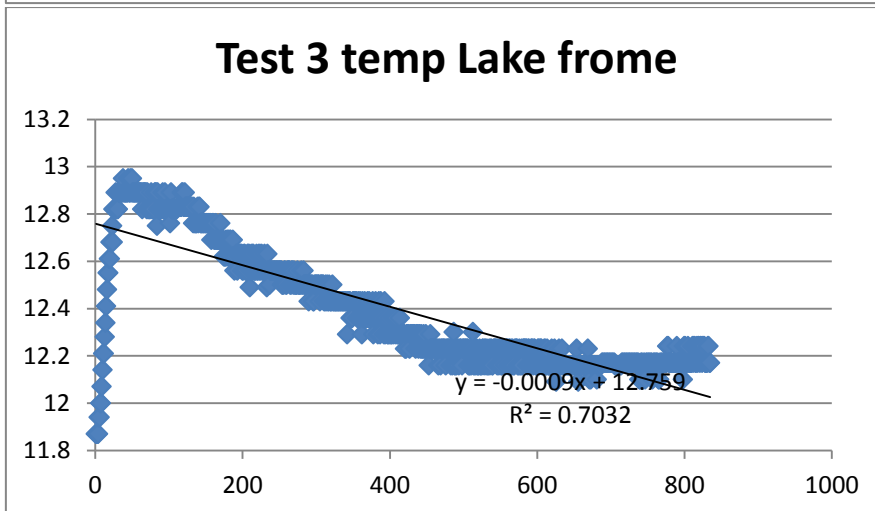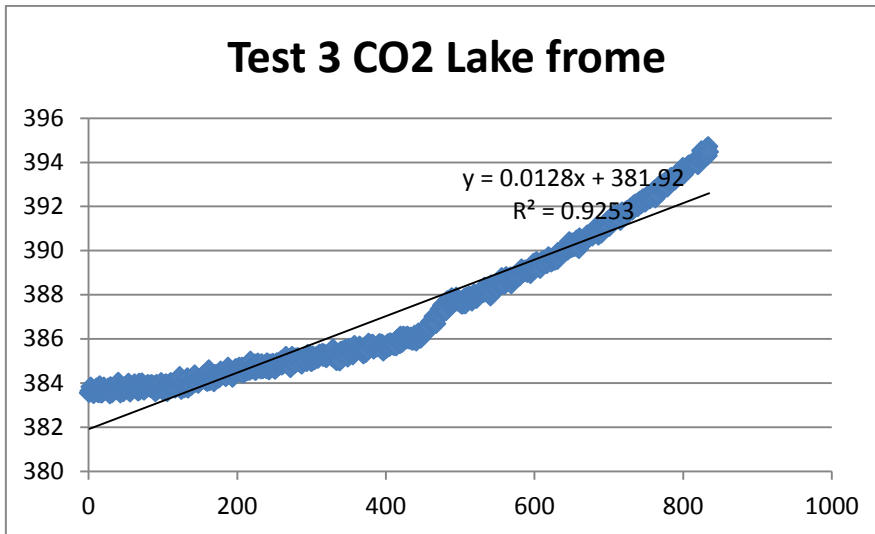
	Y equation	R² value	Start Ch4 level ppm	Finish CH4 level ppm	Difference
1	0.0005x +	0.9952	1.7489	2.09941	

	1.7138				
1b	0.0005x + 1.7568	0.9986	1.74675	2.09941	
2	0.001x + 2.2077	0.5469	1.74482	2.85608	
3	0.0017x + 1.8129	0.8854	1.75217	2.949	

APPENDIX B: BOOL LAGOON TEST RESULTS

First Stop
Past Big hill look out to narrow land strip stretching into Bool lagoon.
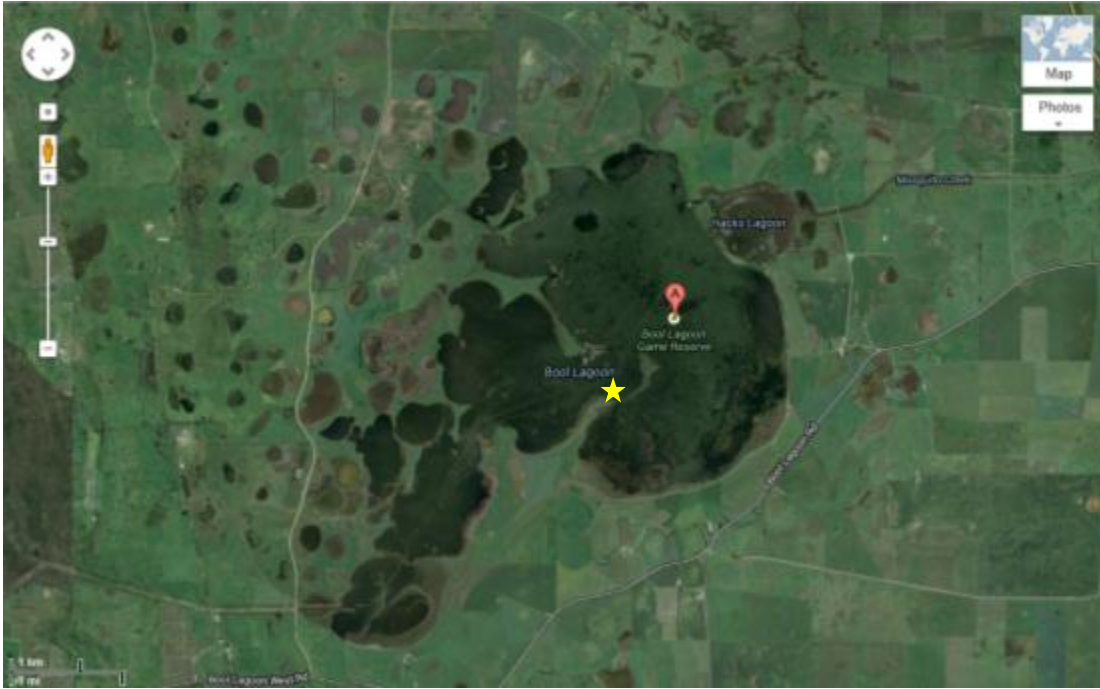
	Start Time	Finish Time	Coordinated	Comments
1st Test	11:08	11:50	473430E, 5891390N (15)	
2nd Test	12:08	12:50	473428, 5891390N (16)	Moved closer to reeds, away from car and slightly deeper water.

- All graphs are methane in parts per Million against time unless otherwise stated

First test location. Note plant life and water depth

Test 1 bool lagoon

$y = 5E\text{-}05x + 1.7526$
$R^2 = 0.9693$
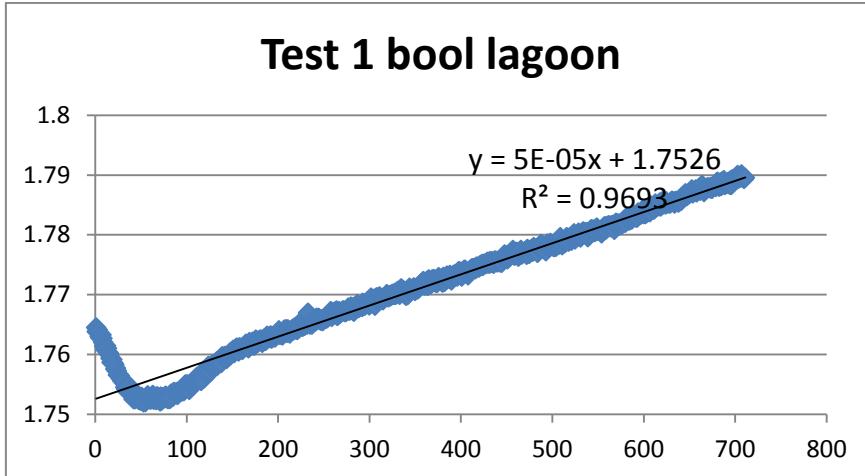
It appears that something in the water or mud is consuming the methane in the initial stages

Test 1b Bool Lagoon

$y = 5E\text{-}05x + 1.7607$
$R^2 = 0.9975$
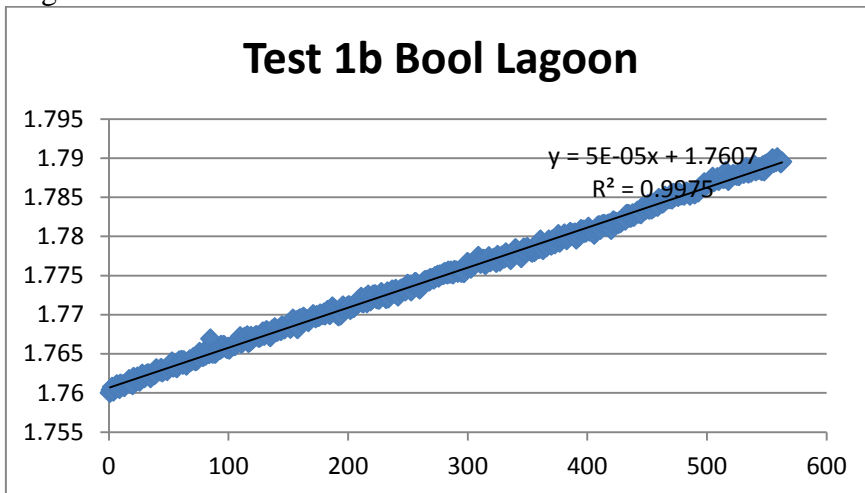
Graph from 11:17am after initial drop in CH4 levels and constant production rate is seen. Better R^2 value

Test 1 Pressure Bool lagoon

pressure

time
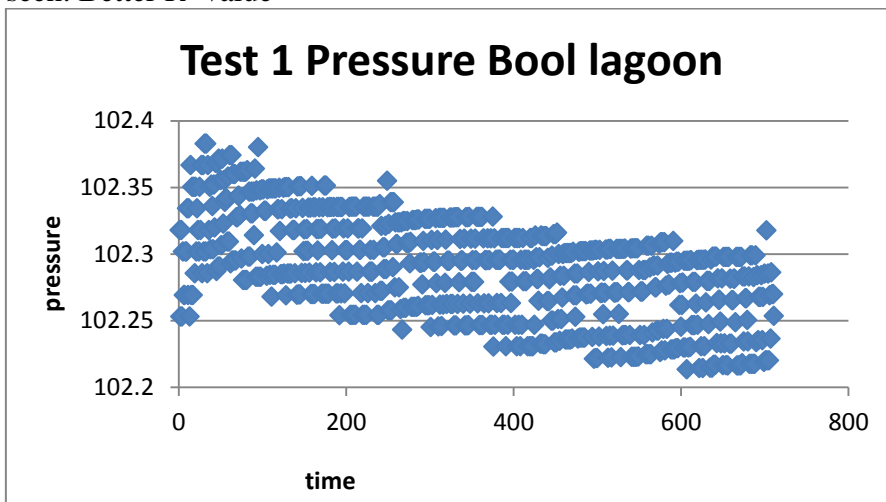
Overall trend of drop in pressure but very minimal

Test 1 temp. Bool Lagoon

Test 2 Bool lagoon

$y = 9E-05x + 1.7453$
$R^2 = 0.9918$

Test 2b Bool Lagoon

$y = 9E-05x + 1.7588$
$R^2 = 0.9984$
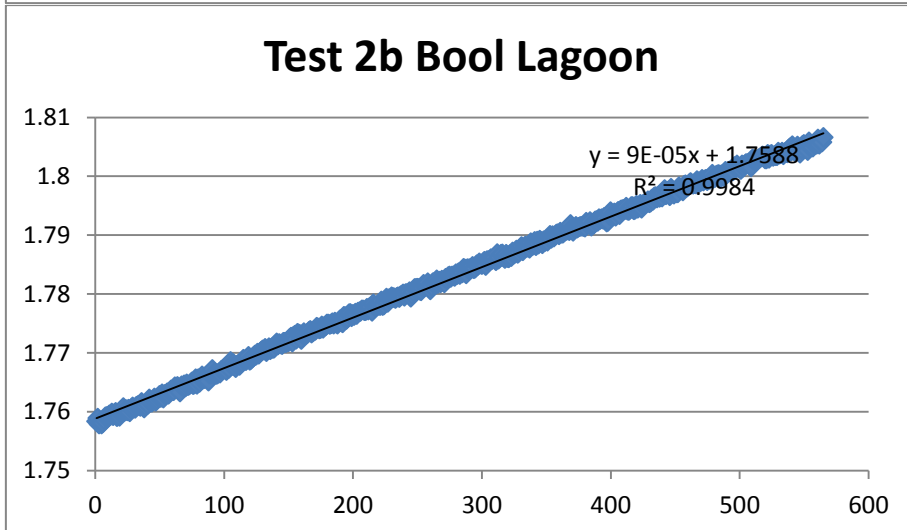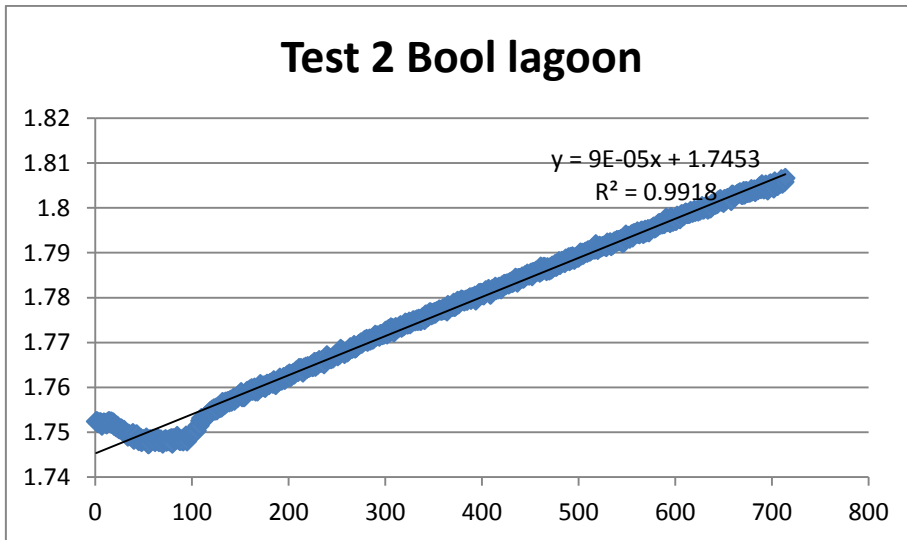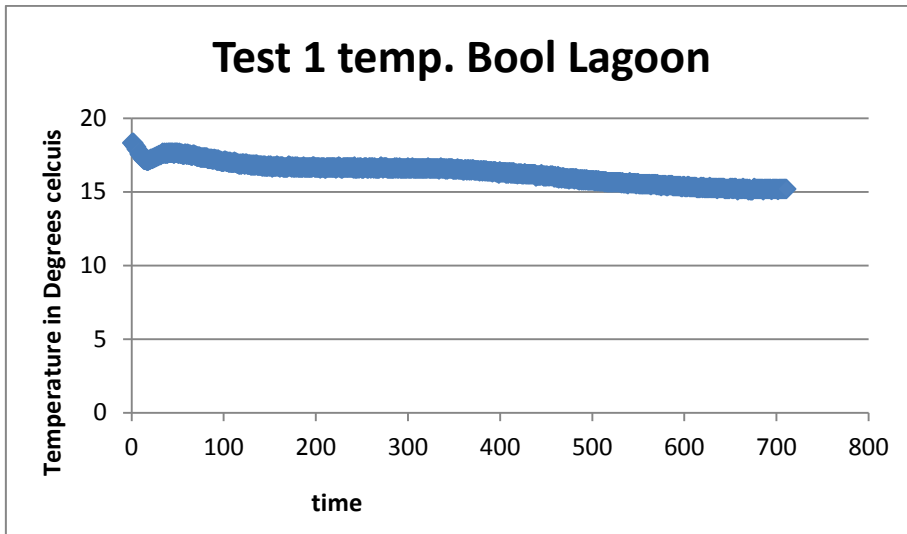
From 12:17pm when methane was no longer being consumed

Test 2 pressure Bool Lagoon

Test 2 Temp. Bool Lagoon
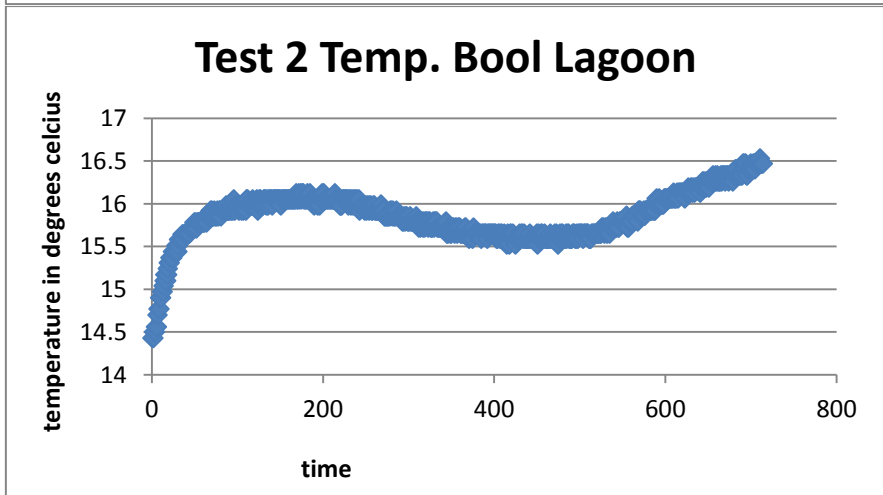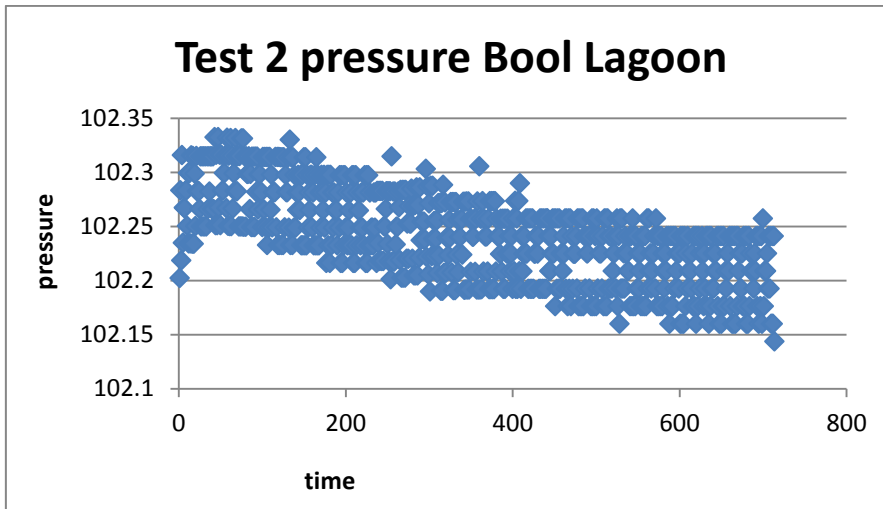
	Y equation	R² value	Start Ch4 level ppm	Finish CH4 level ppm	Difference
1st test	5E-05x + 1.7526	0.9693	1.76447	1.78952	0.02505
1b test	5E-05x + 1.7607	0.9975	1.75999	1.78952	0.02953
2nd test	9E-05x + 1.7453	0.9918	1.75244	1.8066	0.05416
2b test	9E-05x + 1.7588	0.9984	1.75836	1.8066	0.04824

Summary
Both test 1 and 2 had similar pattern of methane levels dropping in the first 5-10 minutes but then being produced at a constant rate following. Pressure drops slightly in both but temperature pattern is very different. Temp in test 1 more closely matches the methane levels. Overall the change in concentration is very small compared to other locations and sources.

Second Stop

Mosquito Catchment area between Bool and Hacks Lagoon.
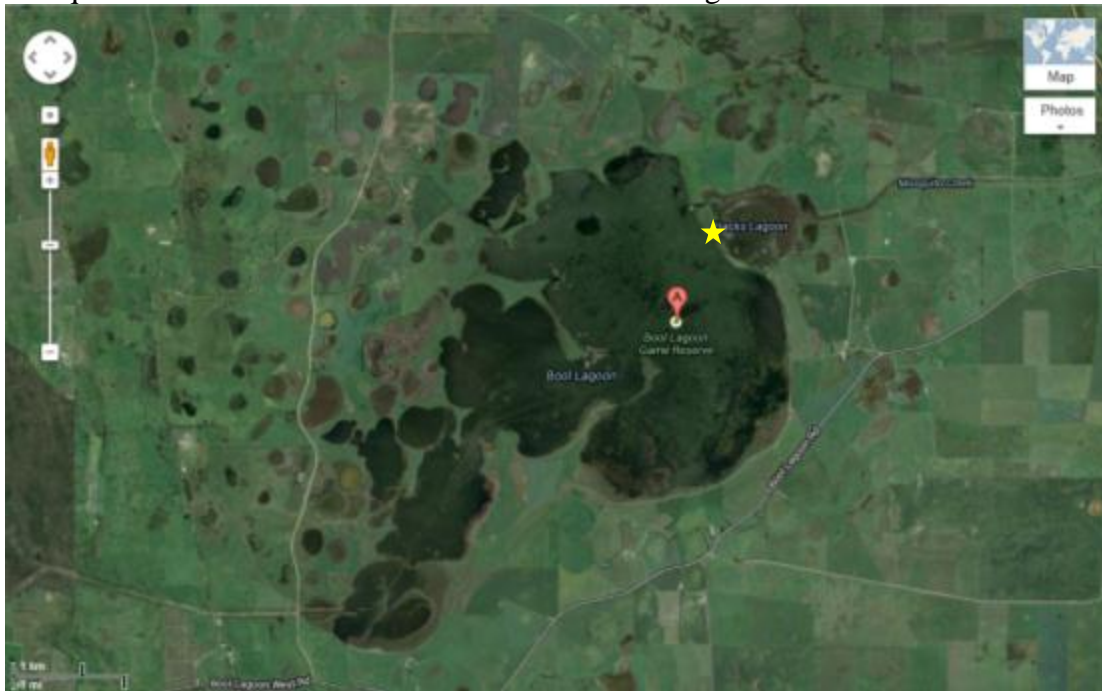
	Start Time	Finish Time	Coordinated	Comments
3rd Test	13:46	14.40	474867E, 5893729N (17)	Bool lagoon side of road bridge
4th Test	14:56	15:56	478476E, 5893739N (18)	Moved closer to hacks lagoon side or road bridge

Typical Bool and Hacks lagoon vegetation

3rd test location, muddier surface

Test 4 location

Test 4 location. Note deeper water, mud was not visible
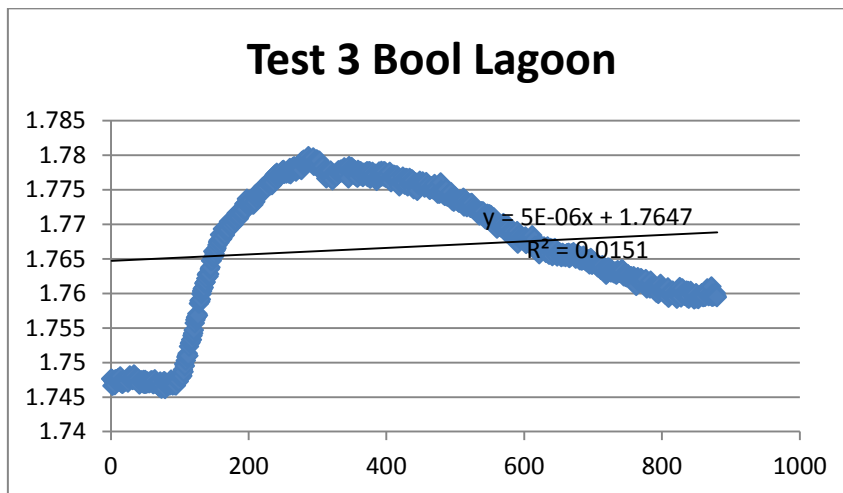
*pressure device failed and no long works in chamber from 13:46pm 20th august on ward.

Test 4 Bool Lagoon

$y = 0.0047x + 1.9584$
$R^2 = 0.8888$

Test 4 temp Bool Lagoon
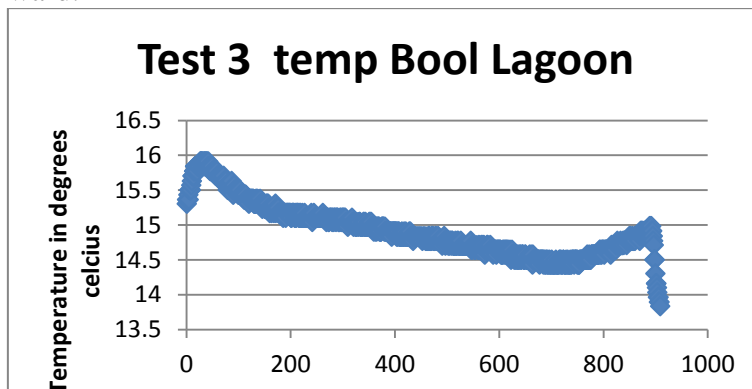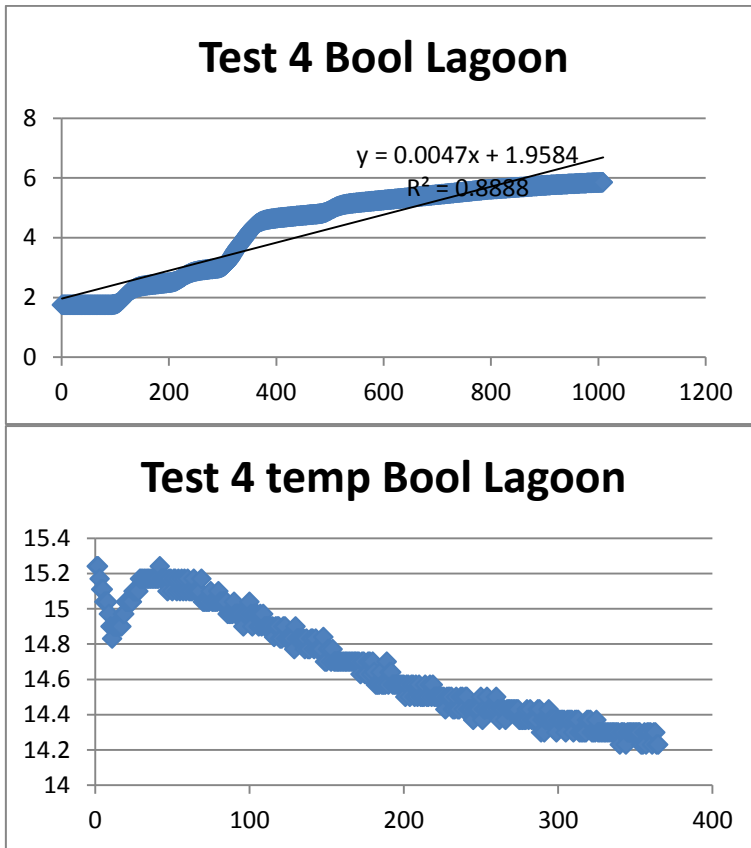
Temperature device fails at 15:18 and no longer collect data after this time. Can assume a trend of decreeing pressure. This is probably directly related to the sun setting and cooler temperature in the later afternoon.

	Y equation	R^2 value	Start Ch4 level ppm	Finish CH4 level ppm	Difference
3rd test	6E-06x + 1.7644	0.023	1.74765	1.79543	0.04778
4th test	0.0047x + 1.9584	0.8888	1.74922	5.84648	4.09726

Summary
The 4th test saw the most interesting and highest methane levels reached. Stepping in the methane levels I think are related to the varying rate at which methane can escape and it comes and goes in phases instead of at a constant and continuous rate. Test 3 is very confusing.

APPENDIX C: KILLARNEY STATE FOREST TEST RESULTS

	Start Time	Finish Time	Coordinated	Comments
1st Test (14/8/14)	14:54	15:56	773392E, 6650225N 84	Chamber sank a little into muddy water. Closer to oginal spot visited in dec 2013.
2nd Test	07:25	08:34	773450E, 6650248N Zone 55J	Closer to the road. Average background 1.776/4 On average 30ppb higher than yesterday. 4degreees

test 1 CH4 killarney NSW

$y = 0.0009x + 1.7822$
$R^2 = 0.9977$

test 1 temp killarney NSW

$y = -0.0063x + 27.449$
$R^2 = 0.8595$

test 1 pressure killarney NSW

$y = -0.0003x + 99.785$
$R^2 = 0.7843$

test 2 CH4 Killarney NSW

$y = 0.0001x + 1.7787$
$R^2 = 0.9982$
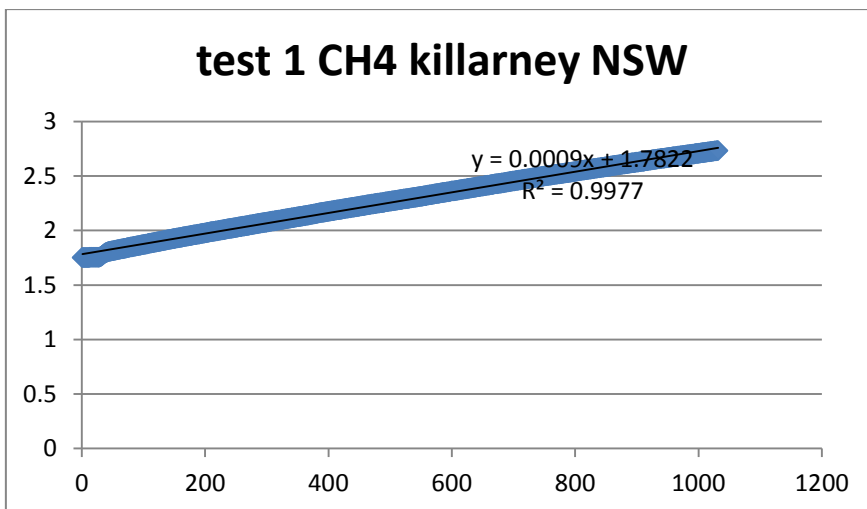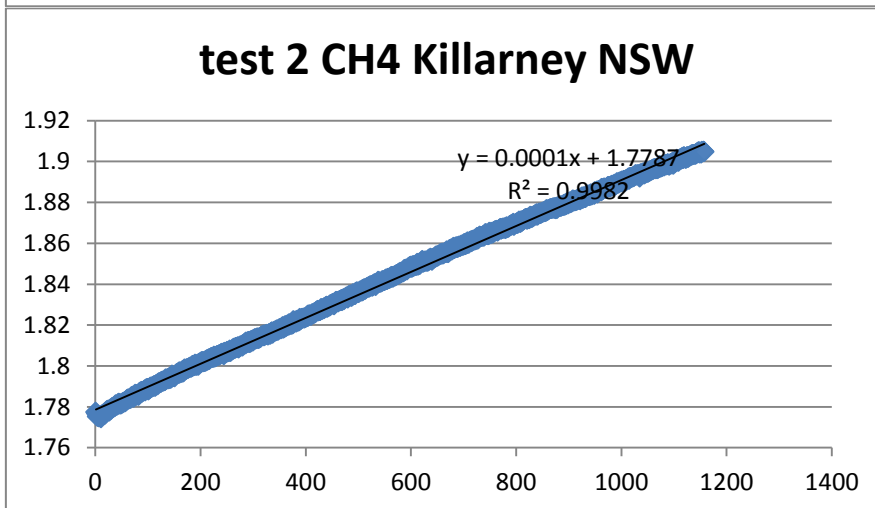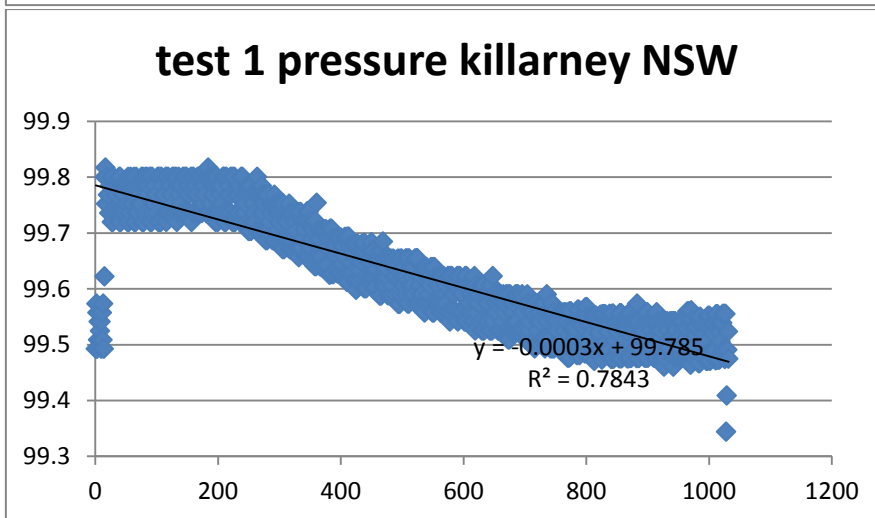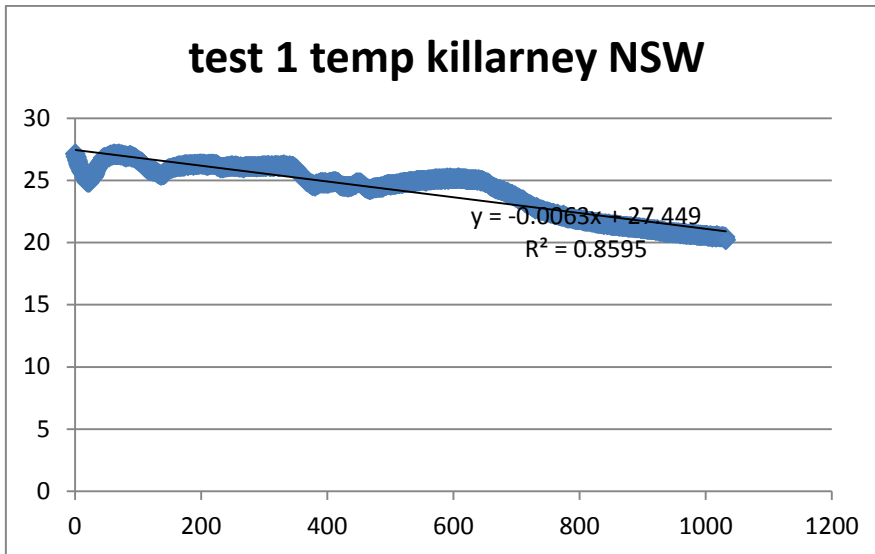
CH4 rate increasing prox 3ppb per 2 min compared to 30ppb per 2 min yesterday afternoon. Maybe temp factor affecting microbes
May be a spike at end of test due to disruption of ground surface when picking chamber up.

test 2 temp Killarney NSW

$y = 0.0059x + 7.5995$
$R^2 = 0.8297$

test 2 pressure Killarney NSW

$y = -9E\text{-}05x + 99.599$
$R^2 = 0.3278$

$y = 0.0002x + 1.7939$
$R^2 = 0.9989$

$y = 3E\text{-}05x + 1.7796$
$R^2 = 0.9985$

- test 1
- test 2
- Linear (test 1)
- Linear (test 2)
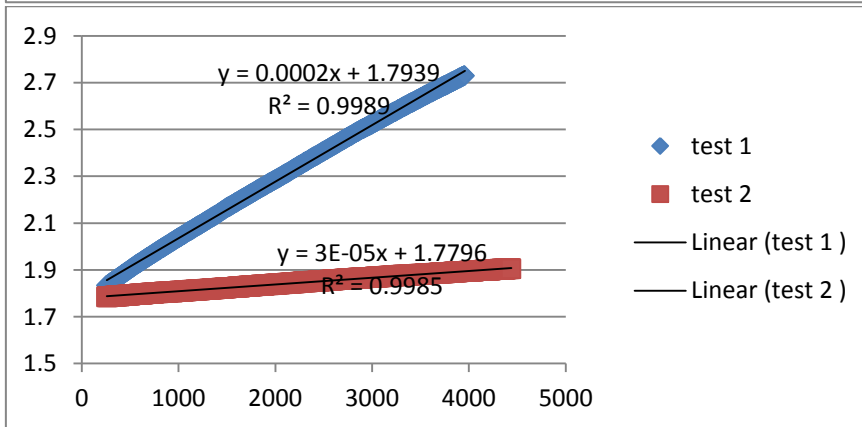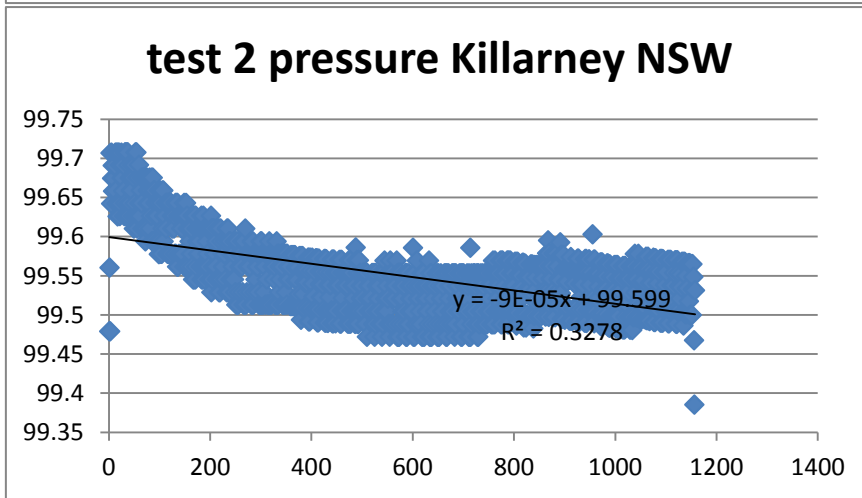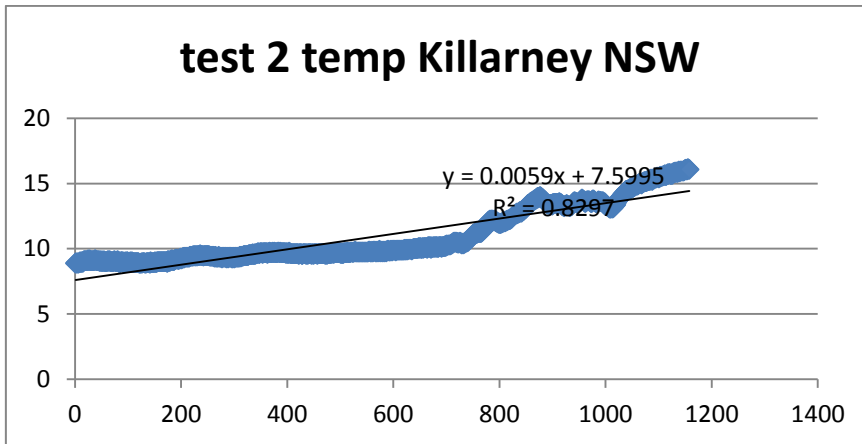
	Y equation	R² value	Start Ch4 level ppm	Finish CH4 level ppm	Difference
1st	0.0009x + 1.7822	0.9977	1.75015	2.73031	0.98016
2nd	0.0001x + 1.7787	0.8297	1.77737	1.90469	0.12732

Summary
Very slow CH4 producing wetlands. Both product a constant rate but amount varies
with time of day

APPENDIX D: URRBRAE WETLANDS TEST RESULTS

Catchment area for run off,
Know to produce methane, local school has a science project running and collect
methane via wading in wetlands and capturing bubbles. Then faring them off.
*must disturb ground to catch the methane bubbles

Date	Time	Comments
15th july	12:01-13:08	On over flow area, water logged soils but not over water. Only floods during perios of very high rainfall and for short periods of time. Minimal ground disturbance 282654E 612867 N. wiggled chamber in soil 5min prior to ending test. No change. Test drive around wetlands. Lower than normal city background. Temp 11.6, humid 88.4, pressure 100.34
22nd july	12:42-14:50	

15th July
On over flow area

hpdelCH4 (12:01-13:08pm)

CO2 (12:01-13:08pm)
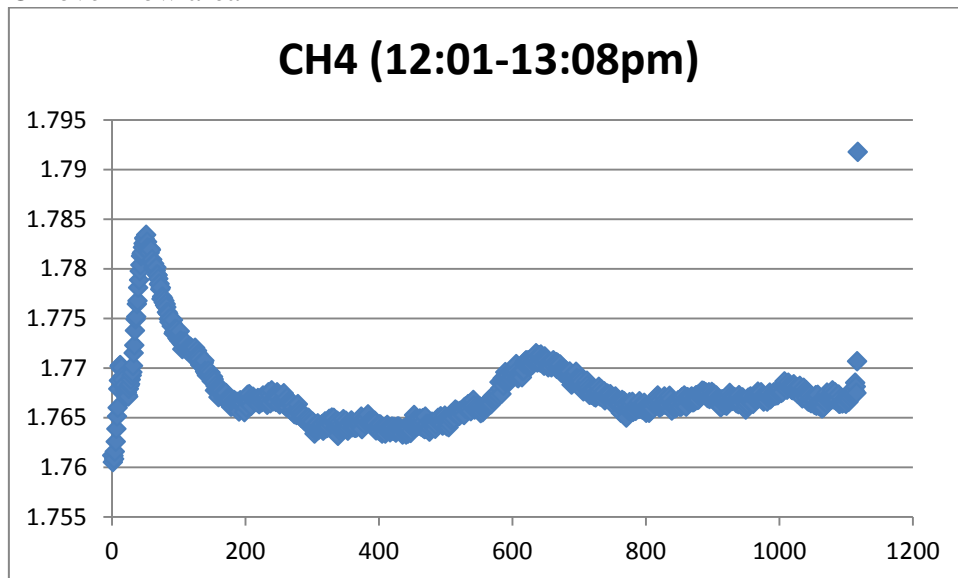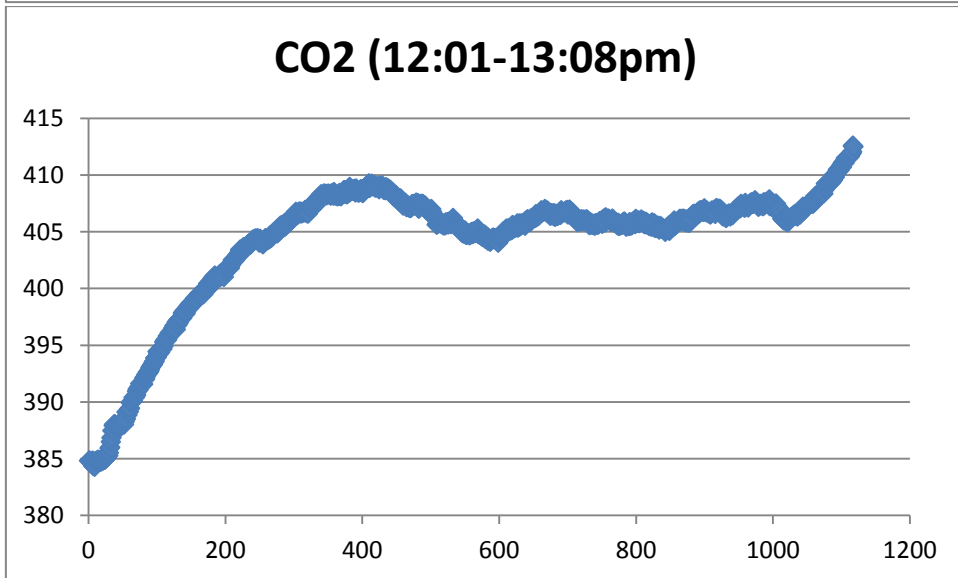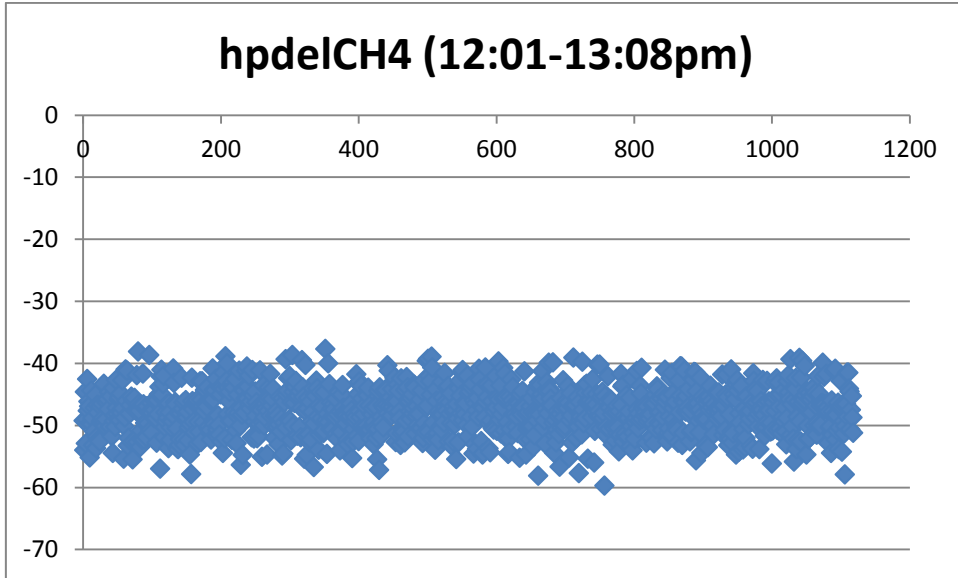
July 22nd
Floating chamber test

hrCH4dry

hrCH4del (12:42-15:21pm)

CO2 (12:42-15:21pm)
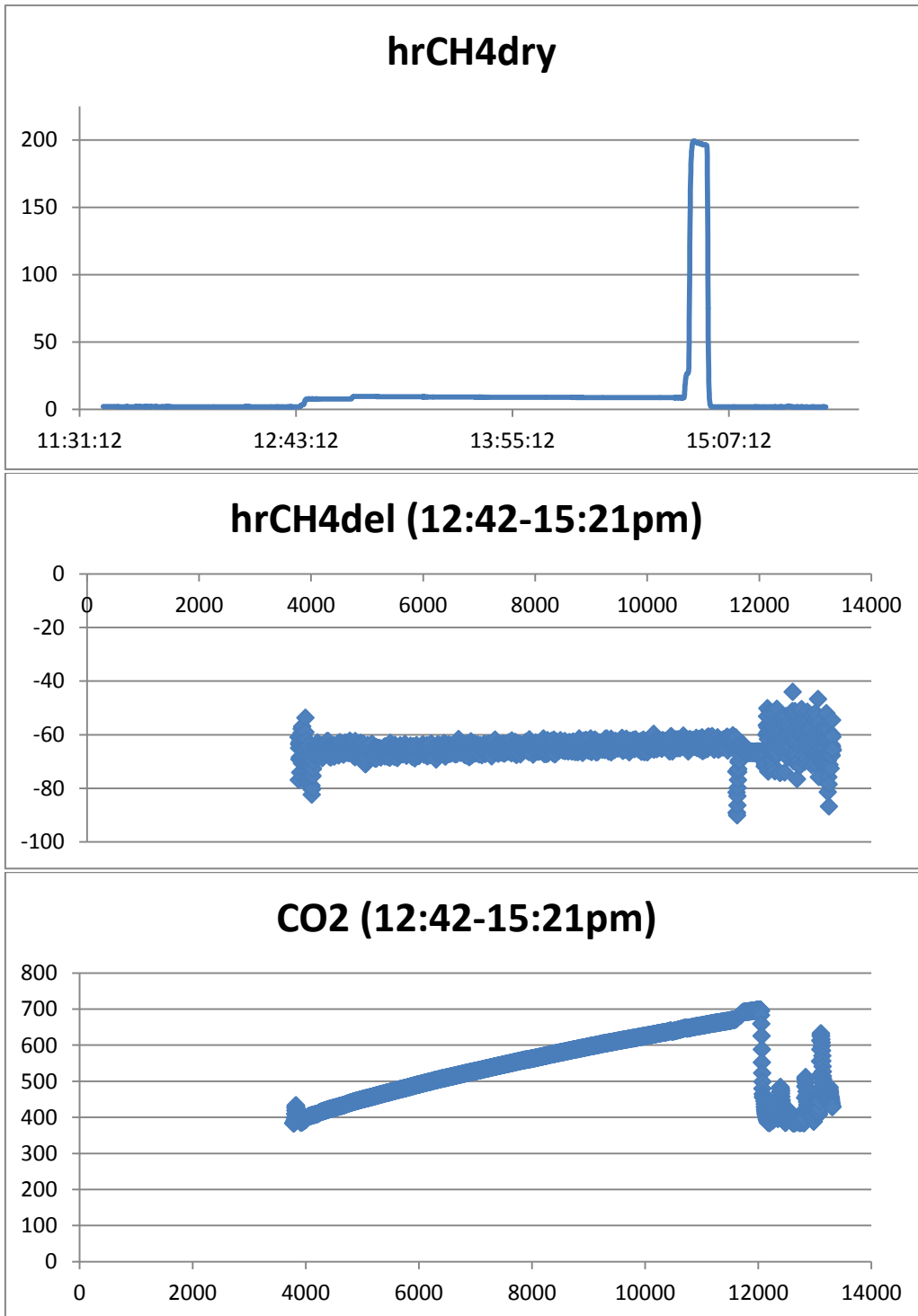
Experiment finished at 14:50 then ground was disturbed by stepping on ground under chamber. Aprox 35cm deep in water. Could visibly see bubbles coming up
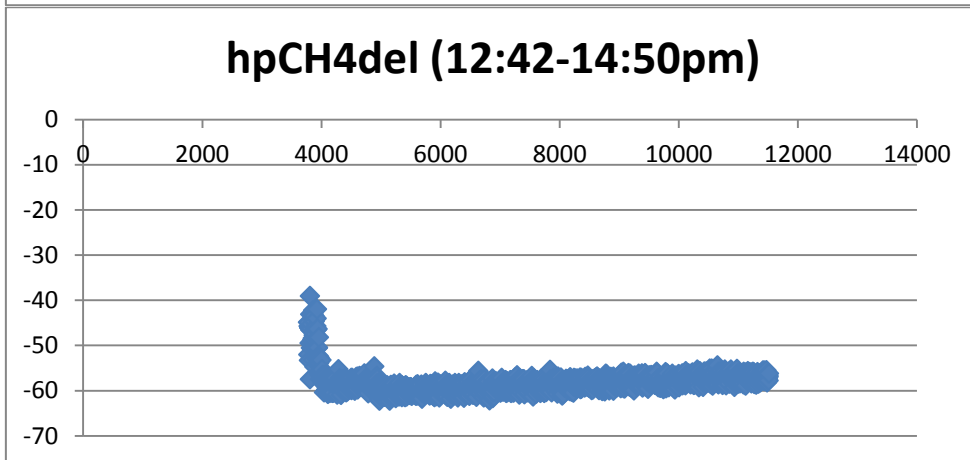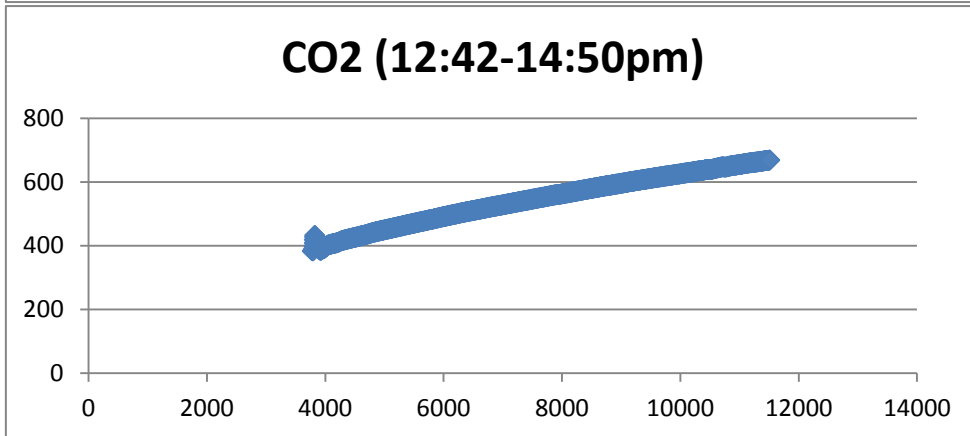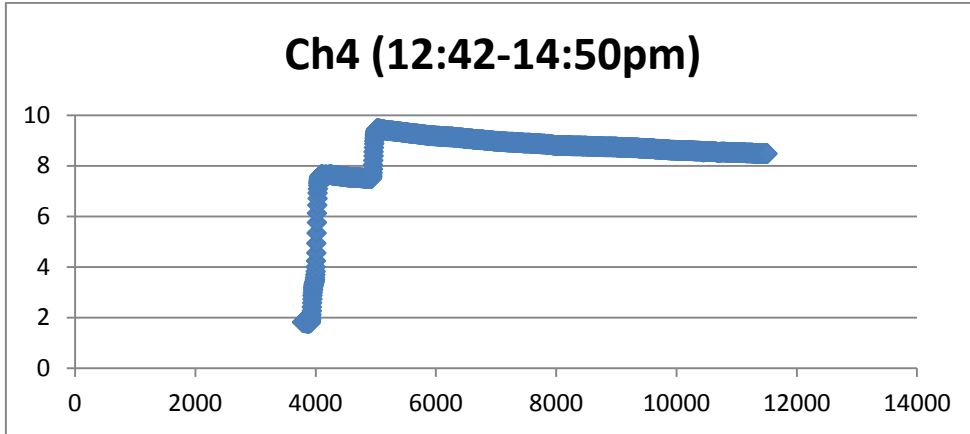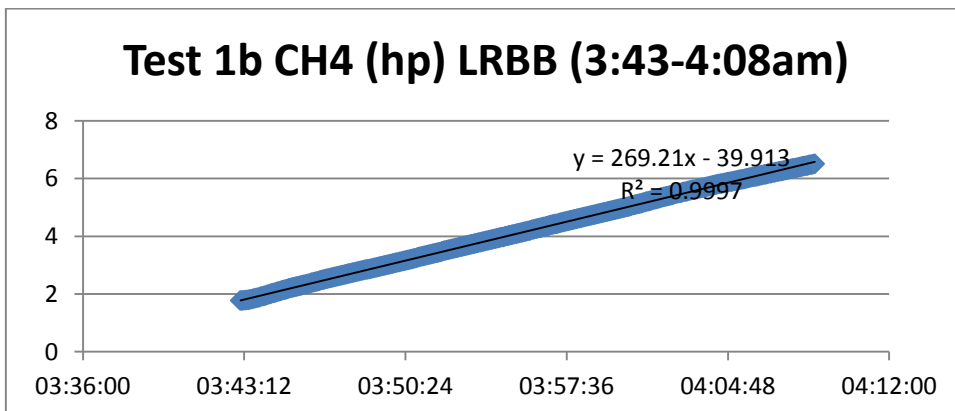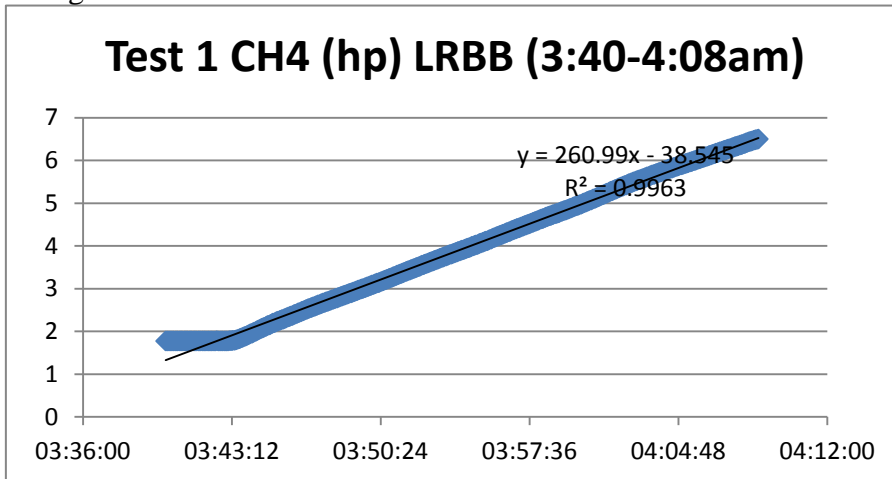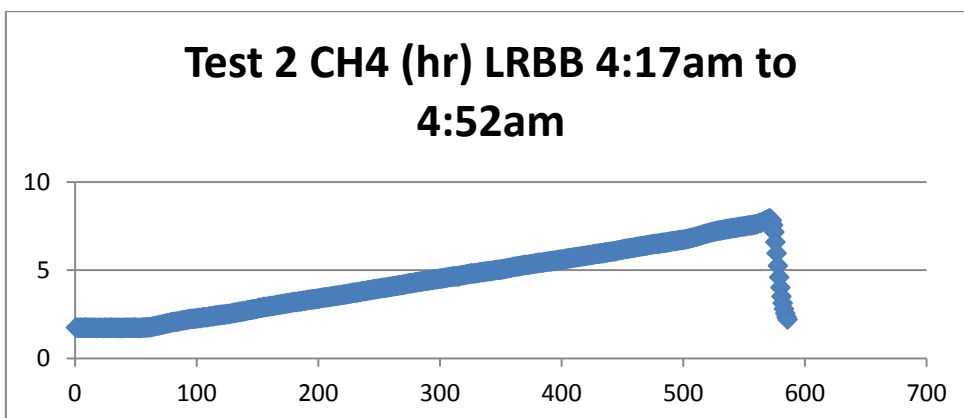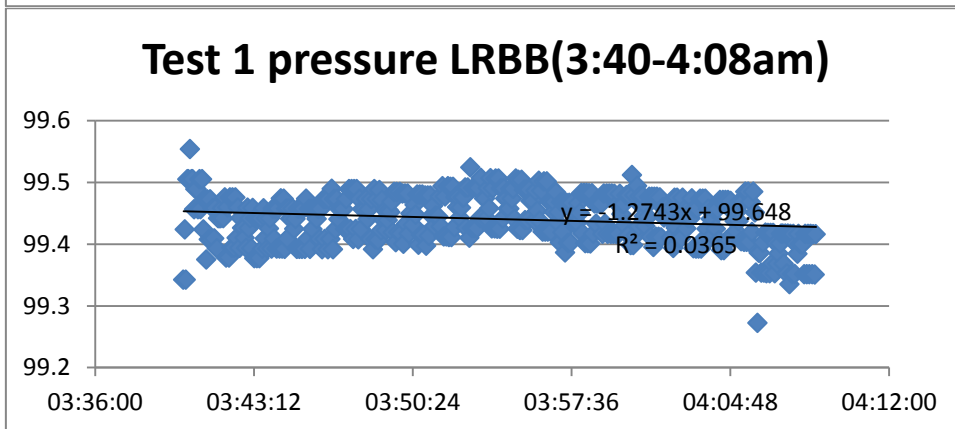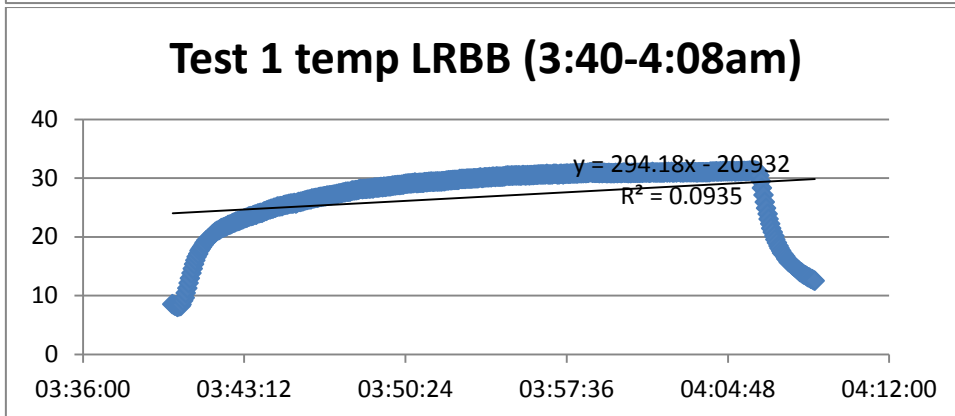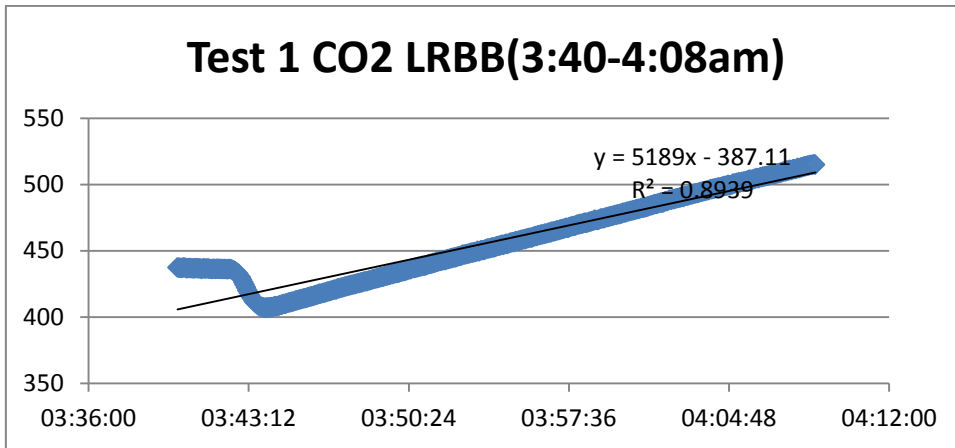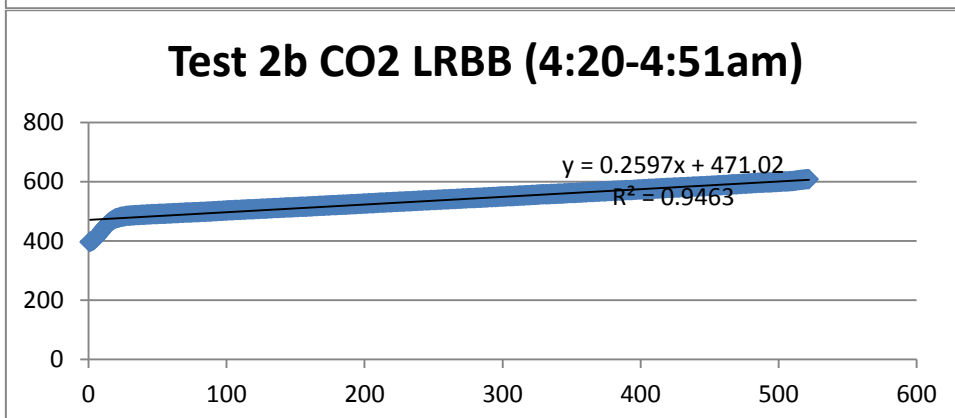
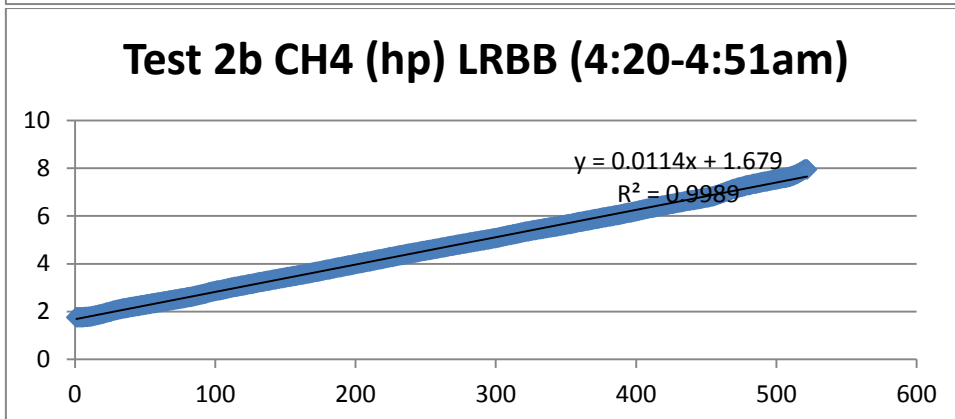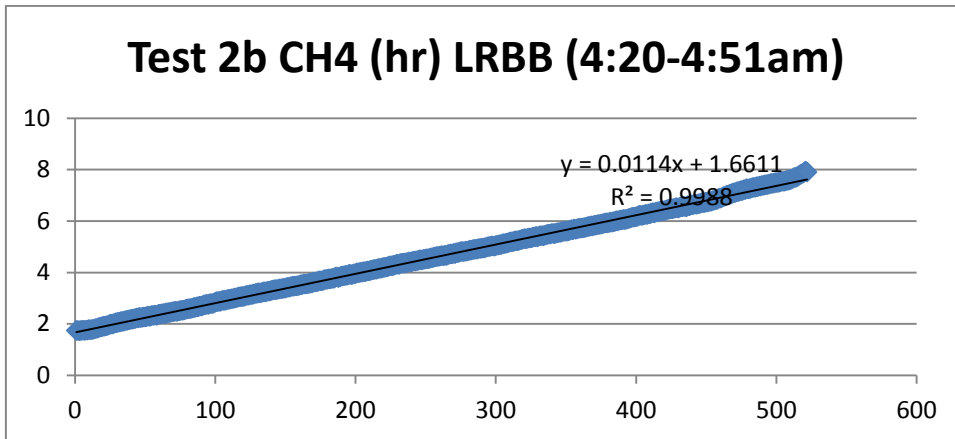**APPENDIX E: LIGHTNING RIDGE TEST RESULTS**
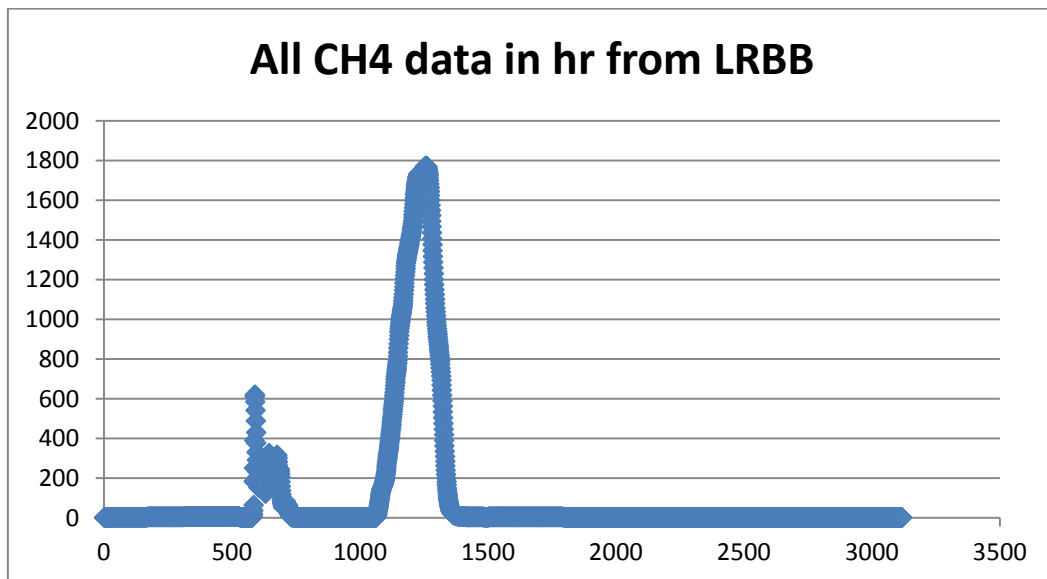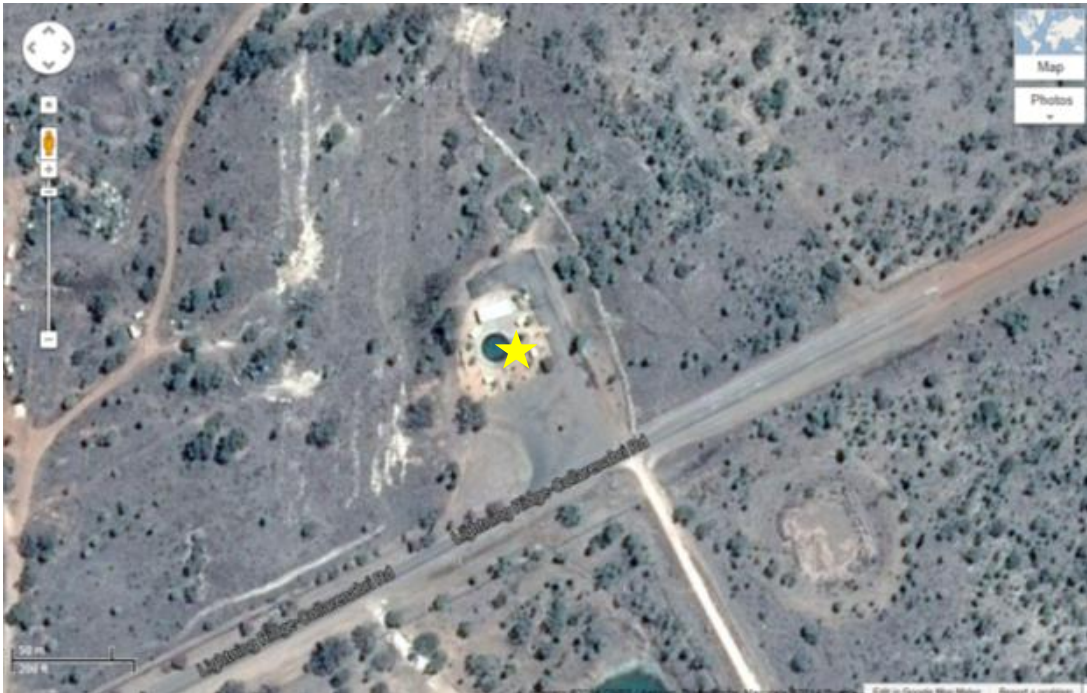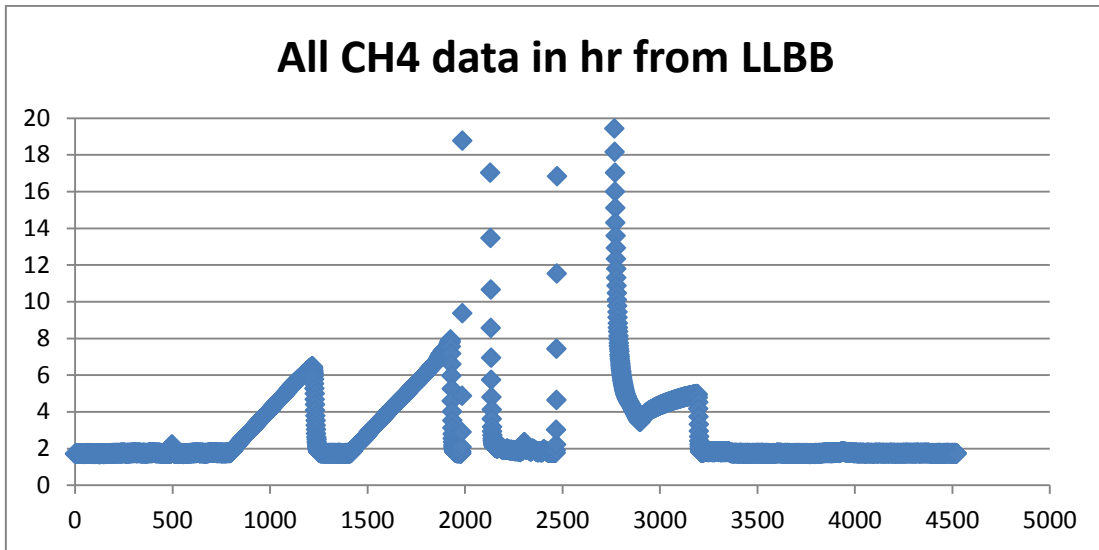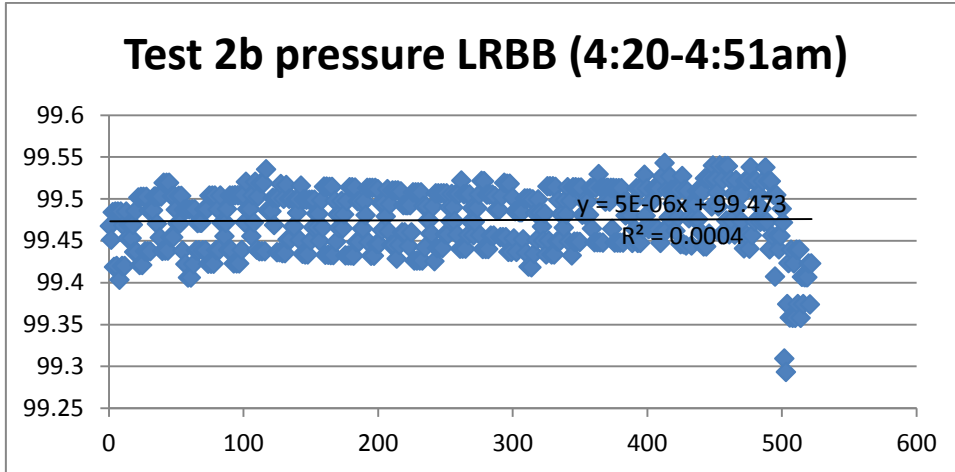
First test done in kiddies pool near drain/exit point for water. Spike up to 620ppm after lifting chamber off water

Test 1 CO2 LRBB(3:40-4:08am)

$y = 5189x - 387.11$
$R^2 = 0.8939$

Test 1 temp LRBB (3:40-4:08am)

$y = 294.18x - 20.932$
$R^2 = 0.0935$

Test 1 pressure LRBB(3:40-4:08am)

$y = -1.2743x + 99.648$
$R^2 = 0.0365$

Test 2 CH4 (hr) LRBB 4:17am to 4:52am

Test 2b CH4 (hr) LRBB (4:20-4:51am)

$y = 0.0114x + 1.6611$
$R^2 = 0.9988$

Test 2b CH4 (hp) LRBB (4:20-4:51am)

$y = 0.0114x + 1.679$
$R^2 = 0.9989$

Test 2b CO2 LRBB (4:20-4:51am)

$y = 0.2597x + 471.02$
$R^2 = 0.9463$

Test 2b temp LRBB (4:20-4:51am)

$y = 0.0094x + 27.516$
$R^2 = 0.3018$

Test 2b pressure LRBB (4:20-4:51am)

$y = 5E\text{-}06x + 99.473$
$R^2 = 0.0004$

	Y equation	R² value	Start Ch4 level ppm	Finish CH4 level ppm	Difference
1b (hp)	269.21x - 39.913	0.9997			
2b (hr)	0.0114x + 1.6611	0.9988	1.73132	7.89447	
2b (hp)	0.0114x + 1.679	0.9989	1.73132	7.89447	

3rd test done with 20L buchet over water entrance where bubbles were visible. Hard to hold bucket in place and opften bubbles would escape nber bucket, assuping due to pressure build up.

22L bucket 5:23-5:36

◆ 20L bucket
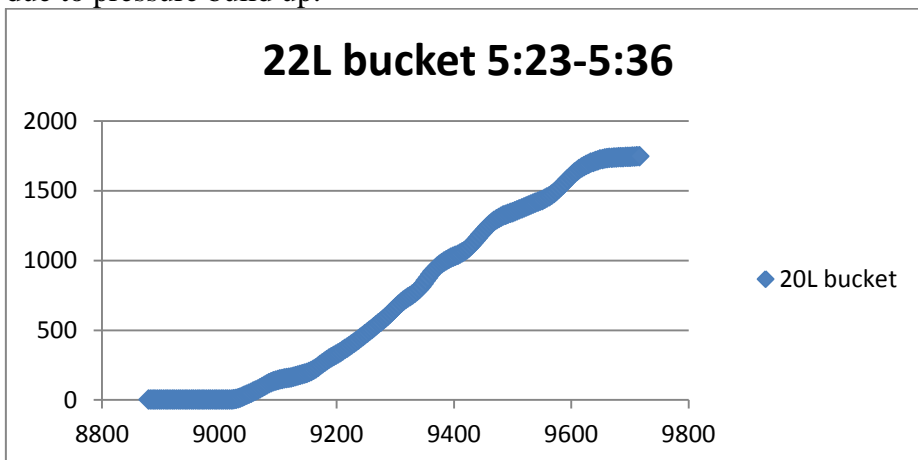
**APPENDIX F: URRBRAE FARM ATMOSPHERIC RESULTS**
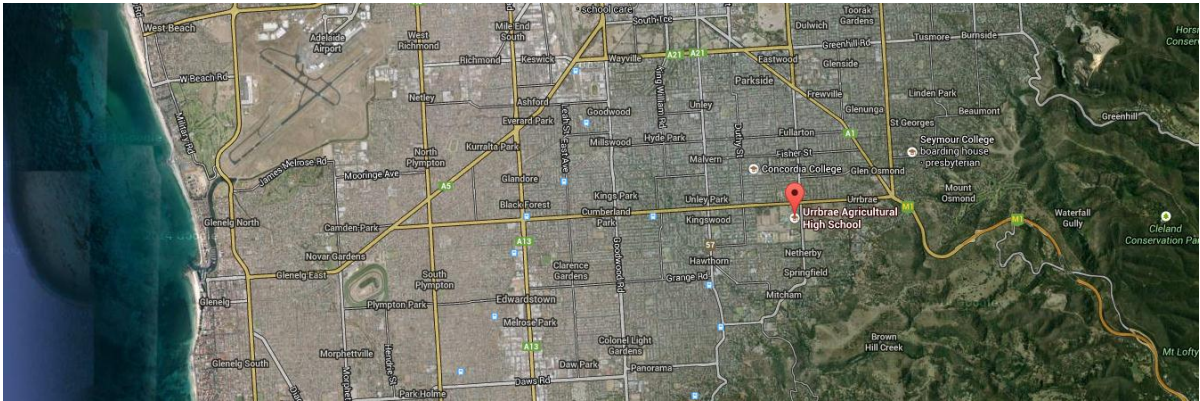
Morning visit to Urrbrae agricultural school. Over cast day with scattered showers and slight breeze.

All data including initial test to find leak in methane digester.

Day plan

| Time	Source	Comments
9:05am-10:46am	Testing leaks on methane digester	
11:10am-11:53	Compost bins x9	
12:02pm-12:18	Cows	
12:24pm-12:44	Pigs	
12:49pm- 12:59?? 13:01pm	sheep	
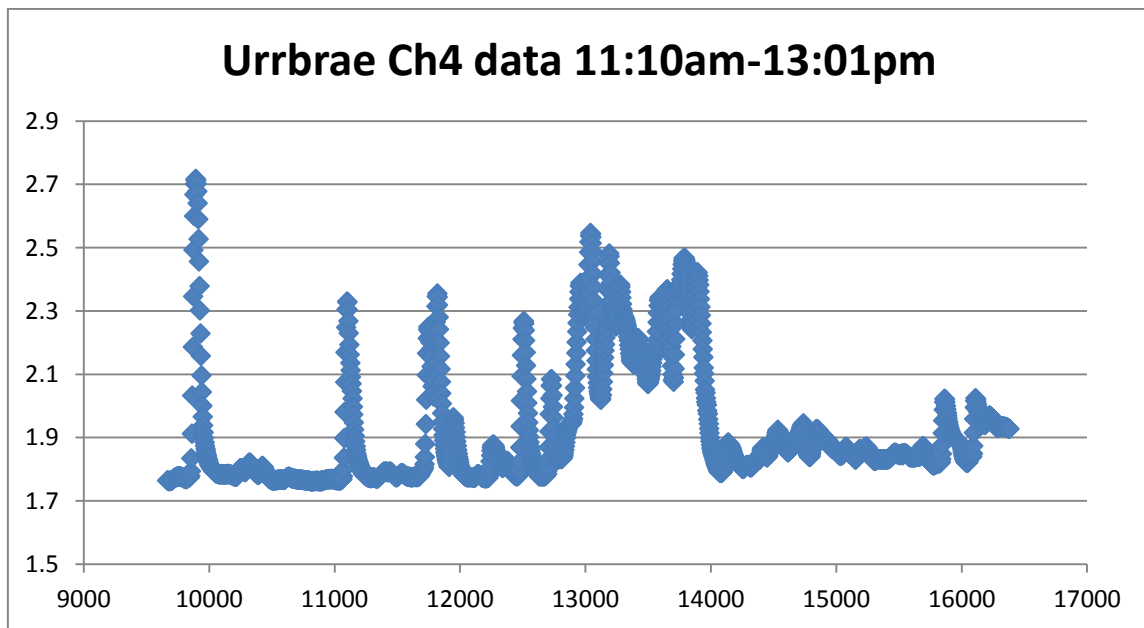
Compost bins

Bins number 1 to 9. 1 freshest to 9 which has been there the longest. Contains horse manure, hay, lawn clipping, minimal food scraps and eggs. Ideally would need to put chamber on compost heaps but poor weather conditions did not allow for it. Raining.

Bin no.	time	time	CH4 concentration	Comments
1	11:10	11:14	1.770	11:15 a higher number believed to be from another source and wind has carried it over.
2	11:17	11:19	1.778	Photo
3	11:20	11:23	1.808	
4	11:24	11:27	1.776	
5	11:27	11:30	1.762	
6	11:31	11:38	1.772	Possible spike from unknown source
7	11:39	11:42	1.777	
8	11:44	11:50	1.788	
9	11:52	11:56	1.783	

Urrbrae Ch4 data 11:10am-11:53am
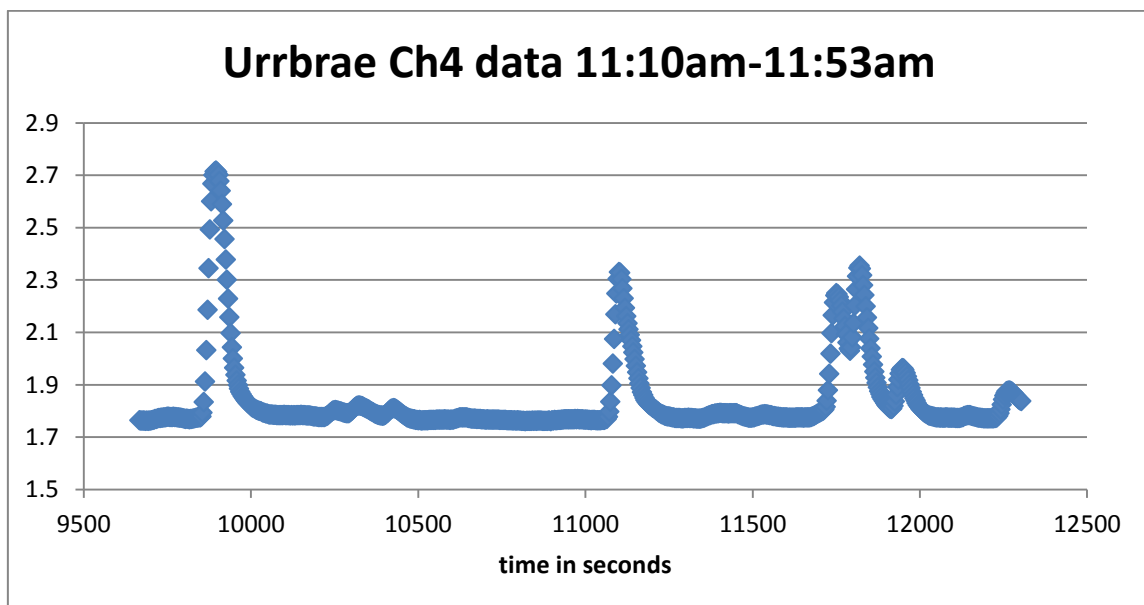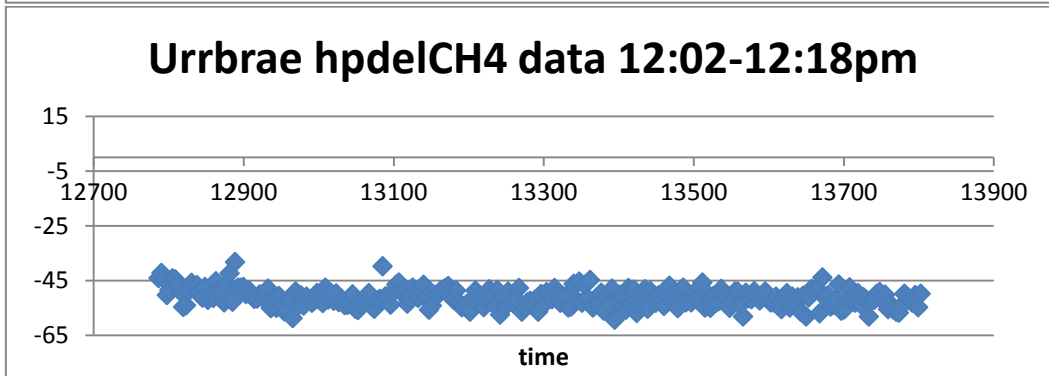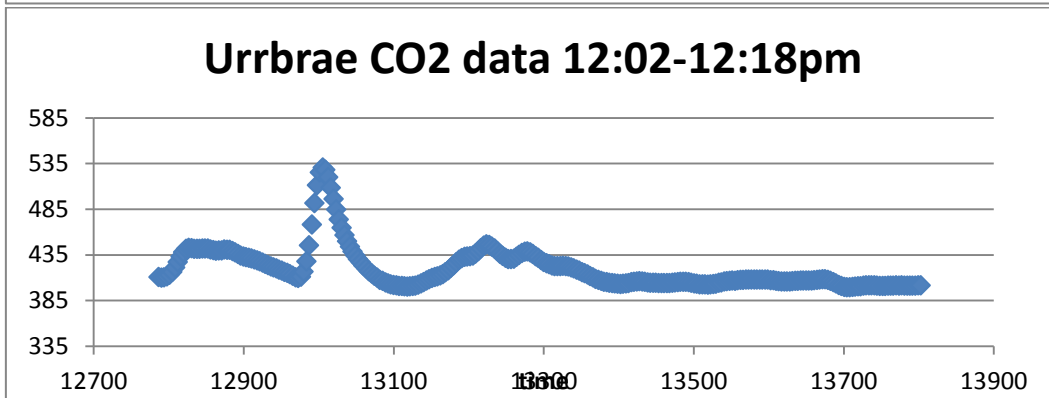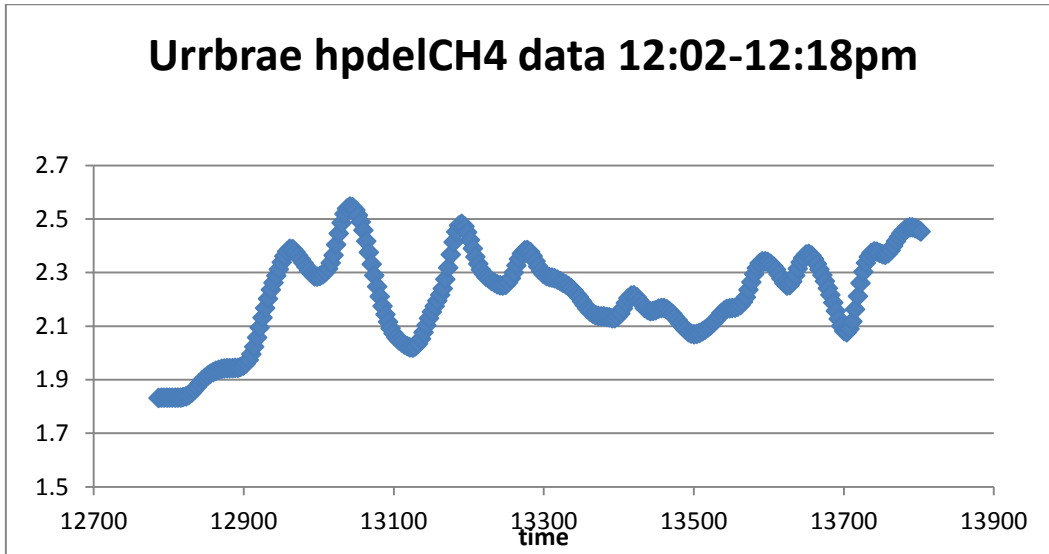
Not a consistently high number so spikes could be from other sources or essentially bubble sof gas escaping at various times

Urrbrae CO2 data 11:10am-11:53am

Urrbrae hpdelCH4 data 11:10am-11:53am
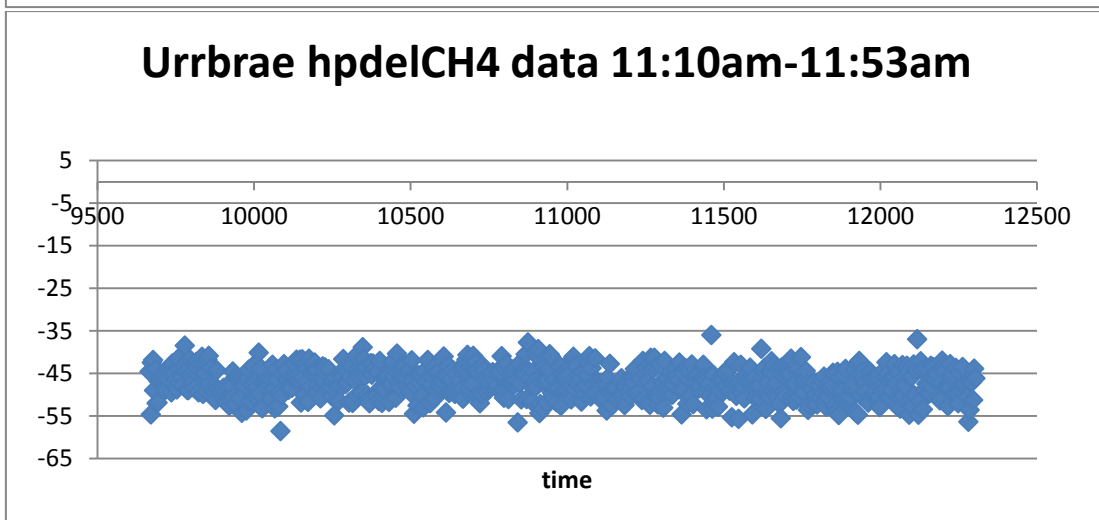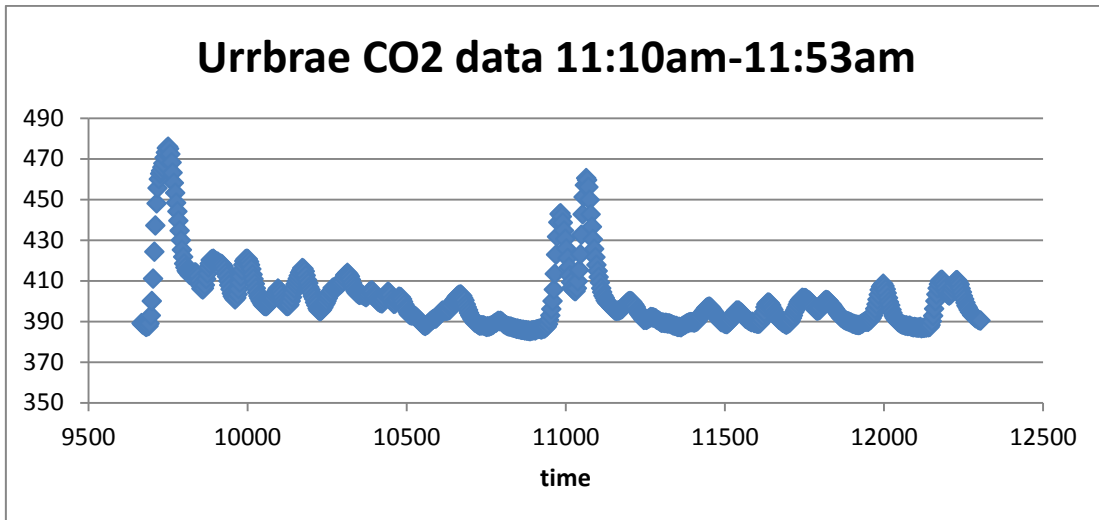
Cows

Open pens, well ventilated. 3 cows, each in individual pens

12:02pm-12:18	Cows

Pigs

12:24pm-12:44	Pigs

3 main enclosed rooms for the pigs. 30m hose used. Very smelly

Area	Time	CH4 concentration	Comments
Grower room up to (6months old)	12:24-12:26	1.888	
Farrowing room (pregnant pigs and piglets)	12:27-12:30	1.809	
Dry sow (males 6 months and over)	12:31-12:34	1.808	
Baby pigs in out side pen	12:35	1.881	
Pig barn drain	12:38	<1.9	
Last drain pipe vent before methane digester	12:43	<1.9	Pipe from sludge to methane digester

Hose was moved through out each area from within arm's reach off floor to the base of pens and closer to pigs mouths

Urrbrae CH4 data 12:24-12:44pm

Urrbrae hpdelCH4 data 12:24-12:44pm

Urrbrae CO2 data 12:24-12:44pm
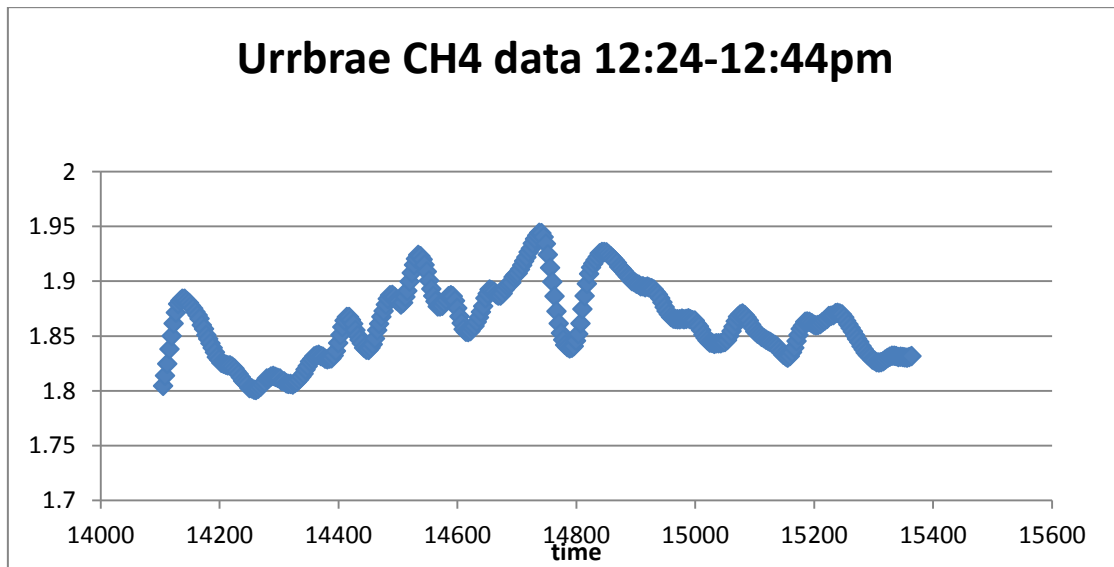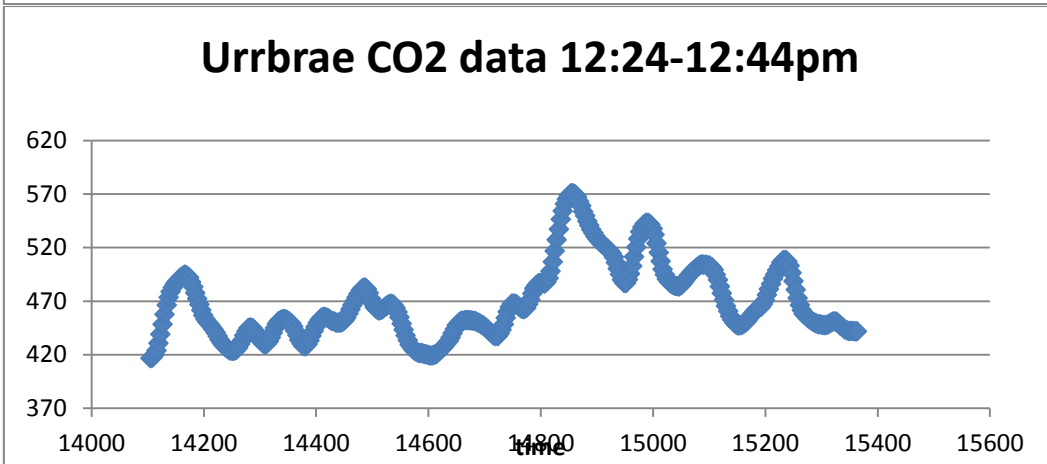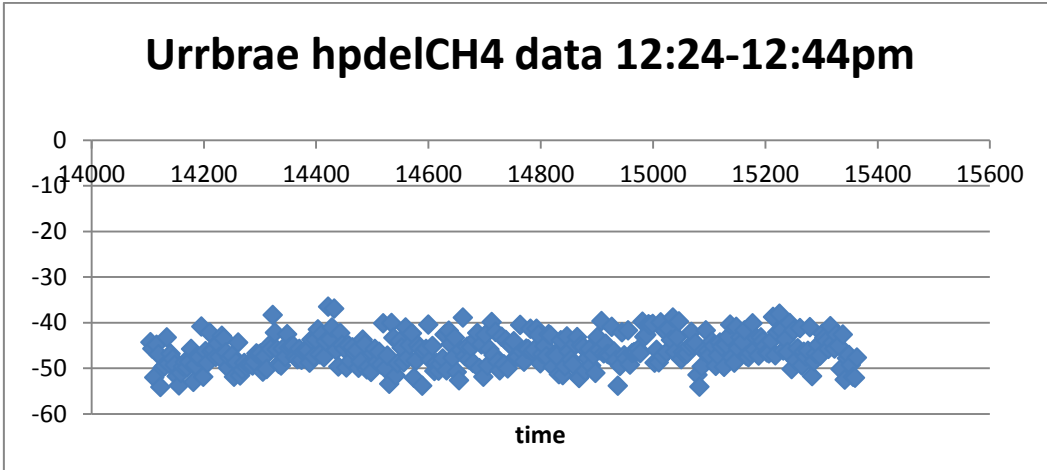
CO2 values are considerably higher but some areas were fully enclosed

Grow room

Farrowing room

Farrowing room

Dry sow room

Baby pigs out side

Baby pigs out side
Sheep

Bad weather cut test short. Chem detect also came on. Possible ammonia??

12:49pm- 12:59?? 13:01pm 12:48-13:01pm	sheep	Chem detect on at 12:51pm

Urrbrae CO2 data 12:48-13:01pm

Urrbrae hpdelCH4 data 12:48-12:55pm
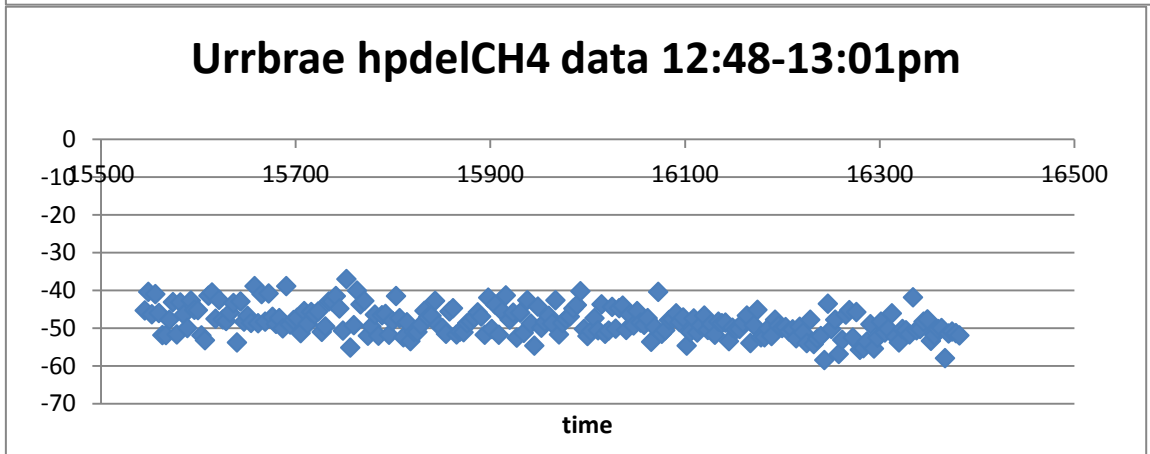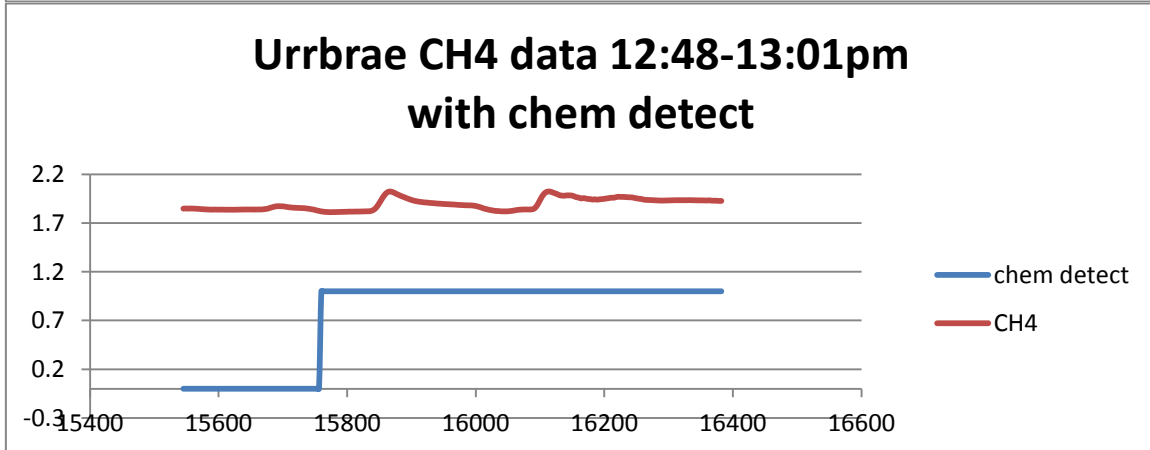
Average from 11:110am-12:55pm	1.919672	
Lowest value	1.76065	
Highest value	2.71741	

APPENDIX G: RESEARCHERS FLUX TABLE

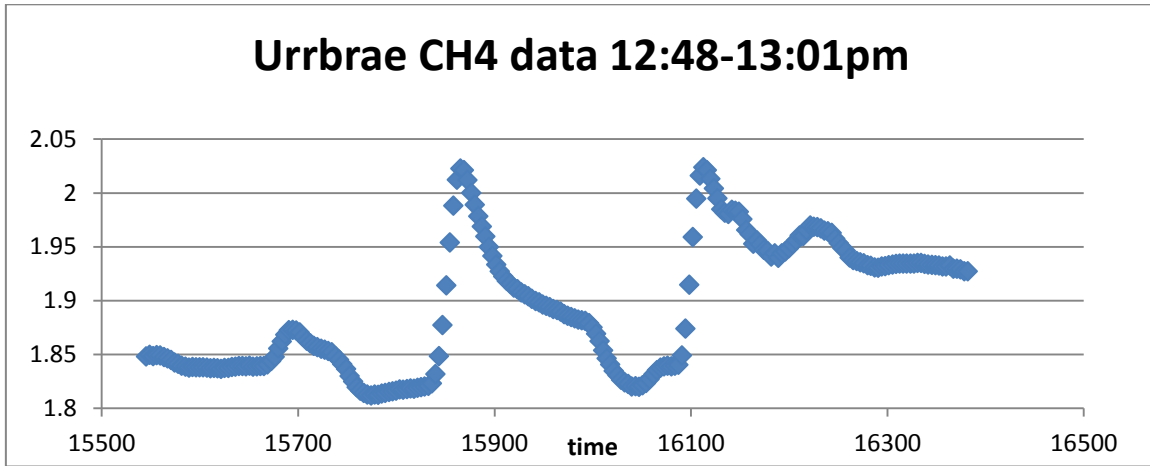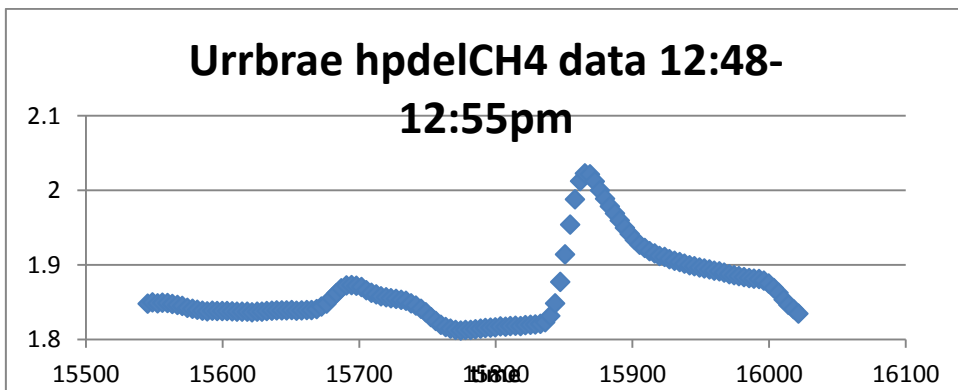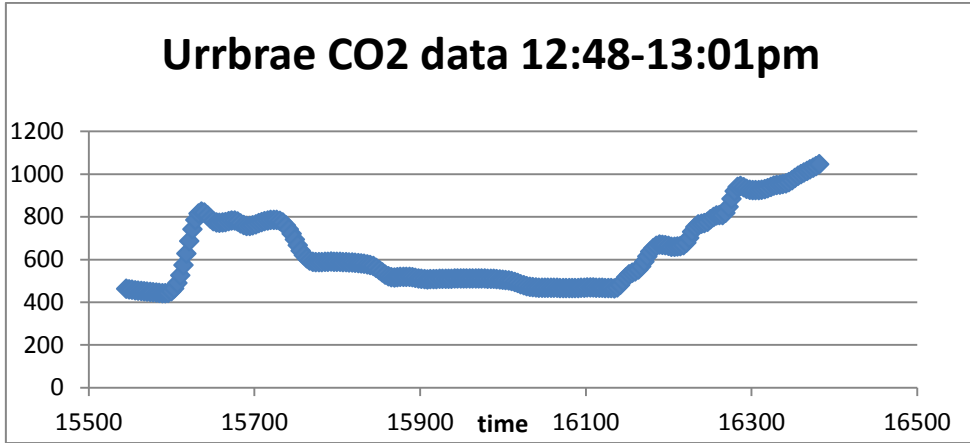|	kg m-2 min-1	temp (20c)	pressure (atm)	A (m2)	V (l)	del c/min (mol mol-1 min-1)	from 1.8 ppm 1min	1 hour	2 hour	4 hour	10 hour
czepiel											
10mg m-2 day -1	6.94E-09	293	1	0.05	9.3	5.71E-08	1.86	5.23	8.65	15.51	36.07
yver-kwok											
same using yk chamber	6.94E-09	293	1	0.25	100	2.60E-08	1.83	3.36	4.92	8.05	17.42
teh's low	9.62E-10	293	1	0.25	100	3.61E-09	1.80	2.02	2.23	2.67	3.96
teh's high	4.48E-07	293	1	0.25	100	1.68E-06	3.48	102.69	203.58	405.35	1010.68
rice usa low	8.33E-09	293	1	0.25	100	3.12E-08	1.83	3.67	5.55	9.30	20.55
rice usa high	1.65E-06	293	1	0.25	100	6.19E-06	7.99	372.98	744.15	####	3713.57
rice griffith	4.67E-08	293	1	0.25	100	1.75E-07	1.97	12.30	22.80	43.79	106.78
bool - low	4.18E-08	293	1	0.25	100	1.57E-07	1.96	11.21	20.61	39.43	95.87
bool - high	5.50E-07	293	1	0.25	100	2.06E-06	3.86	125.43	249.06	496.33	1238.12

APPENDIX H: LAB FLUX TABLE TESTS

delc/delt in ppm/sec	delc mol mol-1 min-1	vol l	surface area m2	pressure kPa	p atm	T K	F kg m-2 min-1
0.1366	8.20E-06	123.1707	0.312318575	100.65	0.993338	295.9	5.82E-06
flow CO2 1 ml/min	flow CO2 2	flow CO2	avg flow ml/min	F kg m-2 min-1		ratio	
1.3	1.4	1.6	1.433333333	8.26E-06	avg	0.70	
				7.49E-06	min	0.78	
				8.07E-06		0.72	
				9.22E-06	max	0.63	
delc/delt in ppm/sec	delc mol mol-1 min-1	vol l	surface area m2	pressure kPa	p atm	T K	F kg m-2 min-1
0.1607	9.64E-06	123.1707	0.312318575	100.65	0.993338	295.9	6.84E-06
flow CO2 1 ml/min	flow CO2 2	flow CO2	avg flow ml/min	F kg m-2 min-1		ratio	
1.3	1.4	1.6	1.433333333	8.26E-06	avg	0.83	
				7.49E-06	min	0.91	
				8.07E-06		0.85	
				9.22E-06	max	0.74	
delc/delt in ppm/sec	delc mol mol-1 min-1	vol l	surface area m2	pressure kPa	p atm	T K	F kg m-2 min-1
0.0872	5.23E-06	123.1707	0.312318575	100.65	0.993338	295.9	3.71E-06
flow CO2 1 ml/min	flow CO2 2	flow CO2	avg flow ml/min	F kg m-2 min-1		ratio	
1.3	1.4	1.6	1.433333333	8.26E-06	avg	0.45	
				7.49E-06	min	0.50	
				8.07E-06		0.46	
				9.22E-06	max	0.40	

APPENDIX I: KILLARNEY STATE FOREST ATMOSPHERIC RESULTS