final report

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Development of Hydrogen Sulphate Emission Factors

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Overview

Abstract

Due to increased community expectations and reporting requirements, hydrogen sulphide (H_2S) from anaerobic lagoons has been identified as a significant issue for the abattoir industry. Whilst numerous studies have been undertaken overseas (e.g. Clanton and Schmidt (2000), Chen and Parkhurst (1997), Jacobson *et al*. (1997), Bicudo *et al*. (2001) and Zahn *et al*. (2002)) no data is available with respect to the emission of hydrogen sulphide from abattoir treatment lagoons in Australia. This lack of data hampers management of hydrogen sulphide emissions as no information is available on average emissions or how to determine emissions from these sources.

Intensive sampling as undertaken at two Queensland meat processing facilities. Hydrogen sulphide emission rates were derived for the anaerobic treatment lagoons at these sites The emission rates also identified a possible relationship between effluent loading rate and hydrogen sulphide emission rate. This data will assist processor and the community by having:

- Hydrogen sulphide emission rates for anaerobic systems;
- Hydrogen sulphide emission factors for NPI reporting;
- Knowledge which can be translated into the design of processes capturing anaerobic gases from anaerobic ponds; and
- Information that can be used to determine ways to reduce hydrogen sulphide emissions from the meat industry.

Executive summary

Air samples, effluent samples and associated data were collected from two abattoirs within southeast Queensland over a 12-month period. The samples were collected with a view to determining hydrogen sulphide emission rates for abattoir treatment lagoons. Hydrogen sulphide concentrations were measured using a number of techniques, including a wet chemistry method, electrochemical cells, a Jerome meter and Gas Chromatography. Emission rates were determined using either a USEPA flux chamber or a back calculation method to develop industry-specific emission factors.

The rate of emission of hydrogen sulphide per square meter per year determined in this project is shown in Table 1.

Table 1: Hydrogen sulphide emission rate per square meter

Site	Average emission rate (kg/m^2.year)	Standard deviation	Median emission rate (kg/m^2.year)	BOD loading (kg BOD/ha.day)	COD loading (kg COD/ha.day)
Sunland Proteins	0.14	±0.1	0.08	2,500	6,250
Valley Beef	4.3	±2.7	3.6	10,000	20,000

Overall, the highly loaded Valley Beef lagoon had a higher hydrogen sulphide emission rate than the covered ponds at Sunland Proteins, which had a lower effluent loading rate. Additionally, the data indicated a relationship between BOD loading and hydrogen sulphide emission rate as well as the percentage of COD removed by treatment and hydrogen sulphide emission rate. As only two sites were sampled, this relationship could not be fully validated.

Analysis of samples collected at the two sites over a 12-month period revealed:

1) Measurement of hydrogen sulphide concentrations in similar samples using a number of techniques gave different results for similar samples from the same source;
2) There was a significant difference in calculated emission rates between the back calculation method and the USEPA flux chamber, with the chamber providing consistently lower emission rates;
3) The difference in measured concentrations provided by the various analytical methods was insignificant compared to the difference in calculated emission rates provided by flux chamber and back calculation techniques;
4) Rates of hydrogen sulphide emissions from covered lagoons remained relatively constant with time and were much lower than those measured for uncovered lagoons;
5) Rates of hydrogen sulphide emission from uncovered lagoons varied with time;
6) Use of a USEPA flux chamber appeared to inhibit hydrogen sulphide emissions from uncovered lagoons and is therefore unsuitable for determining emission rates;
7) Crusted lagoon surfaces inhibit emissions; and
8) Crusted lagoons with surface cracking emit more hydrogen sulphide than those without cracking.

The emission rates developed for this project will assist processors and the community by quantifying hydrogen sulphide emission rates for anaerobic systems. These emission rates can be used for regulatory reporting, design of capture systems and for developing strategies for reducing hydrogen sulphide emissions in the meat industry.

Background

The emission of hydrogen sulphide (H_2S) from anaerobic lagoons has been identified as a significant issue for the meat industry in Australia due to increased community expectations and reporting requirements. This has lead to the imposition of increasingly stringent regulations regarding air quality. One that has been adopted overseas is 50 parts per billion (ppb) in air (University of Minnesota 2004) for property boundaries in the United States. In Queensland a value of 5 ppb of hydrogen sulphide in air is defined as a "*goal relevant to the aesthetic enjoyment of places and local amenity*" (OQPC 2004).

Numerous studies have examined hydrogen sulphide emissions from lagoons treating animal wastes (e.g. Clanton and Schmidt (2000), Chen and Parkhurst (1997), Jacobson *et al*. (1997), Bicudo *et al*. (2001) and Zahn *et al*. (2002)). However a search of the American Society of Agricultural Engineers online database and the ScienceDirect database (over 1700 journals) did not find any articles relating to hydrogen sulphide emissions from abattoir lagoons. This lack of data hampers management of hydrogen sulphide emissions as no information is available on average emissions or how to determine emissions from these sources.

Project objectives

The aim of this project was to raise understanding of the nature of hydrogen sulphide release from abattoir treatment lagoons and to provide practical information to facilitate future measurement and management of the gas from these sources.

The project objectives were to:

1) Review and identify the most appropriate methodologies for measuring hydrogen sulphide emissions from meat-processing plant anaerobic lagoons;
2) Identify three suitable meat-processing sites for field-testing over a period of up to six months;
3) Conduct a thorough program of research that measures hydrogen sulphide emissions from meat industry anaerobic lagoons; and
4) Develop industry-specific median emission factors (and typical range) for hydrogen sulphide emissions from anaerobic lagoons. It is anticipated that these will be expressed as kg hydrogen sulphide/m^2 lagoon area and kg hydrogen sulphide/tonne hot standard carcass weight (HSCW) (product).

Methodology

This report details the determination of hydrogen sulphide emission rates for two industry sites in Queensland (Valley Beef at Grantham and Sunland Proteins at Landsborough). Only two sites were used, as a third site could not be found prior to commencement of the project.

The methods used to determine the emissions from the sources were based on the USEPA Flux Chamber (Gholson *et al.* 1989; Kienbusch 1986) and the STINK downwind model (Smith 1993; Smith 1995) for the uncovered Valley Beef site and a direct measurement method based on standard source emissions methodology for the Sunland Proteins site (i.e. Standards Australia (1995)).

The project was undertaken in four stages:

1) Preliminary method evaluation – Valley Beef
2) First round of lagoon sampling - Valley Beef and Sunland Proteins
3) Second round of lagoon sampling - Valley Beef and Sunland Proteins
4) Reporting

Site selection

Valley Beef

Valley Beef is an abattoir located at Grantham in Queensland that has a number of anaerobic lagoons. Sampling was undertaken on the newest of the lagoons. This lagoon is shown in Figure 1.

Figure 1: Valley Beef anaerobic lagoon (facing north west)

The lagoon was surveyed using a Trimble Pro XRS GPS unit. A schematic of the lagoon from the survey is shown in Figure 2. The icons on the left hand side of the image show the approximate location of the long term logging points while the icons on the right hand side show the approximate location of the short-term sample points. Downwind sampling locations were changed in response to local meteorology at the time of sampling. The three flux chamber sampling locations are shown at Pt 1, Pt 2 and Pt 3.

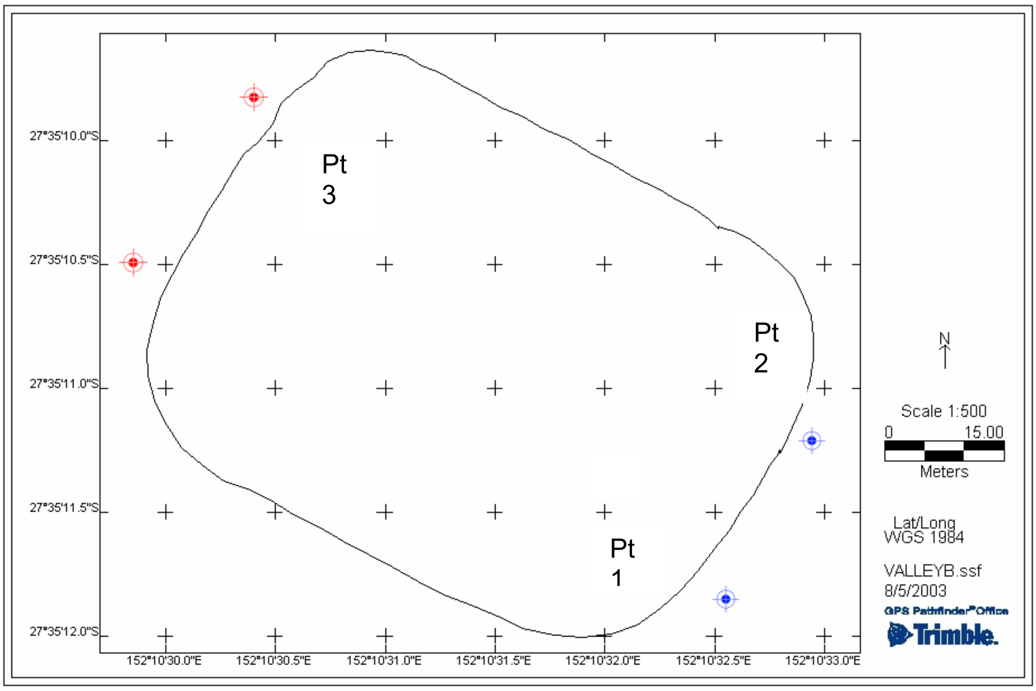

Figure 2: Schematic of Valley Beef lagoon

Sunland Proteins

Sunland Proteins is a rendering facility with two anaerobic lagoons with each taking half of the total effluent loading. The lagoons, shown in Figure 3, have a combined surface area of 600 m^2, all of which is covered with an impermeable synthetic liner. Gaseous emissions from under the covers are drawn through ducting into an on-site biofilter. Hydrogen sulphide samples were collected from the ducting, prior to the biofilter. This sample location is shown in Figure 4.

Figure 3: Lagoons at Sunland Proteins

Figure 4: Sample duct and sampling equipment

Area source emissions measurement

Three methods were used to determine emission rates during this project. These were the USEPA flux chamber (direct method), STINK modelling (indirect method) and stack sampling methodology, which incorporates concentration and mass flow rate through a duct.

USEPA flux chamber

The USEPA flux chamber is widely accepted for sampling of gaseous emissions from solid and liquid surfaces. It is reasonably easy to position and use the device on these surfaces, hence it was considered to be the most suitable sampling device for this project.

To allow easy movement of the chamber on and off the lagoon, an extended boom was constructed for a vehicle-mounted crane from which the chamber was suspended. A schematic of the chamber is shown in Figure 5.

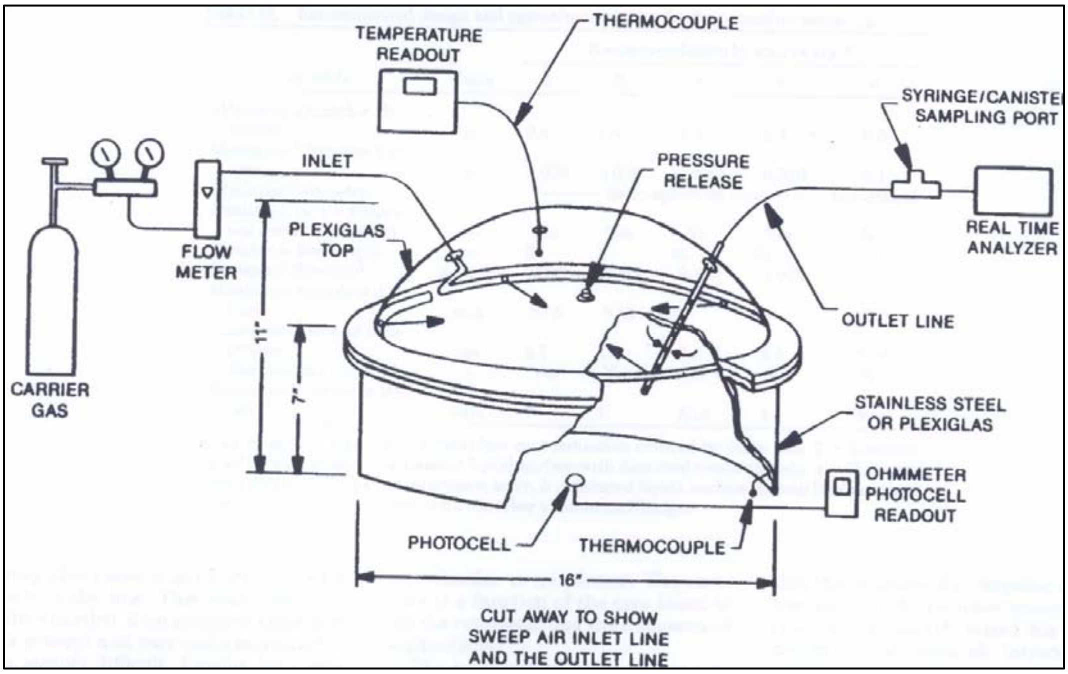

Figure 5: USEPA flux chamber (Kienbusch 1986)

Sampling was undertaken according to standard protocol (Fleer 2002; Kienbusch 1986). Instrument grade air was passed into the flux chamber at a rate of 5 litres per minute. The flow rate was determined using a 0-5 litre per minute rotameter that was precalibrated with a Gillian bubble flow meter. Exhaust air from the flux chamber was drawn through ¼” Teflon tubing using a 12 volt sample pump at a rate not exceeding 2 litres per minute. Excess air was vented through a ¼” vent hole in the roof of the chamber. A Cox Tracer temperature recorder was placed onto the flux chamber to measure the ambient temperature. A second sensor on the temperature logger was used to measure the internal chamber temperature.

STINK modelling

A simple model (STINK), developed by Smith (1993; 1995), was used to determine emission rates for area sources. This method is simpler than other back calculation methods as it uses gas concentrations measured at the downwind edge of a source, along with site-specific meteorological data, to calculate an average hydrogen sulphide emission rate for the source. The model uses the Gaussian equation to calculate a concentration at a downwind location. This Gaussian equation, as detailed by Smith (1995), is shown as Equation 1.

$$C(x,y,z)=\frac{E}{\pi\sigma_y\sigma_z}\exp\left(-\frac{y^2}{2\sigma_y^2}\right)\exp\left(-\frac{z^2}{2\sigma_z^2}\right)$$ **Equation 1**

Where:

- C is the concentration averaged over time t;
- x, y and z are the downwind, cross wind and vertical distances measured from the source;
- σ_z and σ_y are the dispersion coefficients representing the crosswind and vertical spread of the plume respectively and which are increasing functions of x and t; and
- u represents the average wind speed.

Samples were collected downwind of the source using either a Jerome meter or an Odalog low range unit. Concentrations were recorded on a field sheet for the Jerome meter or logged by the Odalog for download at a later date.

The model requires a number of inputs, including the lagoon width (X), lagoon length (Y), wind direction (anti clockwise from vertical axis), longitudinal and lateral distances to receptor from centre of lagoon (x, y), averaging time, surface roughness height and the height for calculation of concentration profile (sampling height). Considering the simplicity of the inputs required by the model and that the sample site was very close to the source, it was decided to use the 1/10th rule of thumb, in which the roughness height for a site is the height of any obstructions divided by 10. The surface roughness of the Valley Beef site was estimated to be 0.15 m.

The STINK model was designed to model sources aligned along the north south axis. Galvin *et al*. (2004) showed that the dimensions input into the model were an important factor when using the model on smaller irregularly shaped or aligned (i.e. not north south) lagoons such as the Valley Beef Lagoon (Figure 2). To overcome this obstacle, each modelling session simply defined the length and width of the source as the model’s X and Y inputs. Then the wind direction was altered by the angle in which the lagoon was different from the North axis (30°). After modelling, the model output provides a table of non-dimensional concentrations for increasing sampling heights according to stability class. A definition sketch of an area source is shown below as Figure 6.

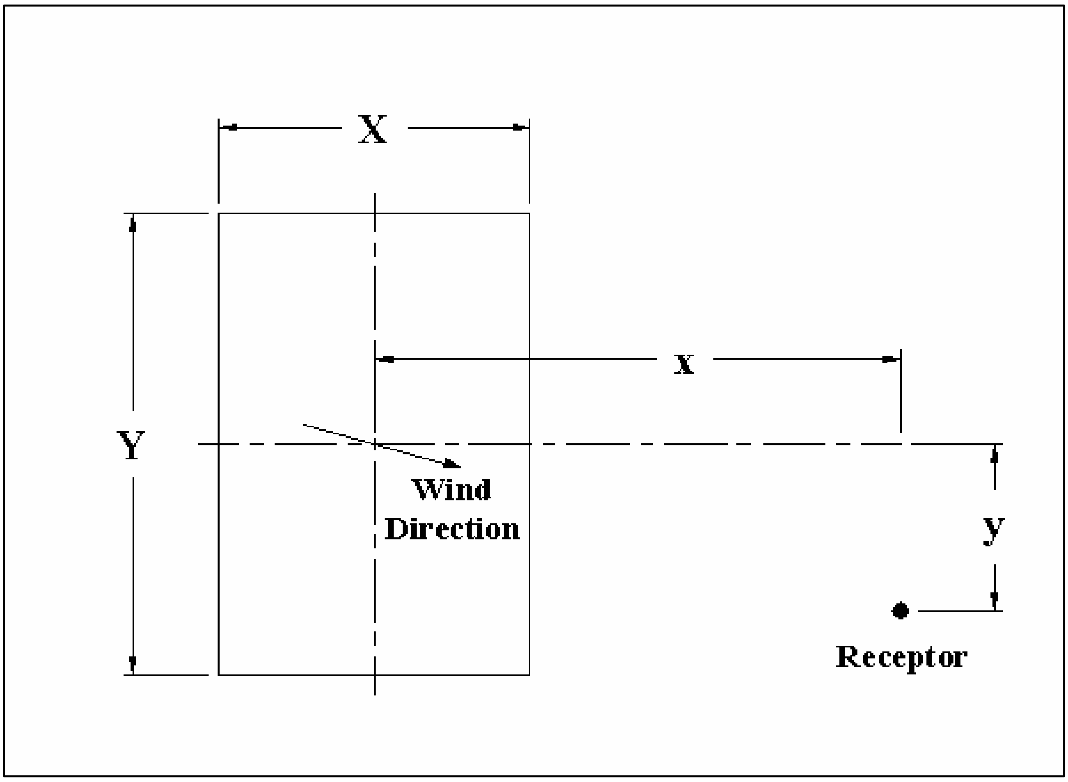

Figure 6: Area source for the STINK model

Ducted sources

The Sunland Proteins lagoons are covered, thus, the flux chamber or back calculation from modelling could not be used to determine emission rates. Emission rates were calculated by measuring the concentration of hydrogen sulphide in the duct and duct velocity. As the sampling location is a duct, stack methodology was employed (AS NZS 4323.1: Stationary Source Emissions Method 1: Selection of sampling positions (Standards Australia 1995). Duct velocity was measured with a TSI model 8346 hotwire anemometer.

Meteorological data collection

Meteorological data was collected using a custom made weather station, which is shown in Figure 7. The station used two sonic anemometers (Gill Instruments 2003) at heights of 1 and 4 metres to measure wind speed and direction, and other associated meteorological data including humidity, temperature, heat flux and solar radiation was also collected. Specifications of the station are shown in Table 2.

Table 2: Automatic weather station specifications

Sensor Type	Model	Height	Range	Details
Vaisala Temperature Probe	Humitter 50Y	4 m and 1 m	-10 to +60 °C	± 0.6 °C at 20 °C
Vaisala Humidity Probe	Humitter 50Y	4 m and 1 m	10 to 90% RH operating range 0-100% RH)	Up to ± 3% at 90% RH
Sonic anemometer	Windsonic (Gill Instruments)	4 m and 1m	0-60 m/s and 0-359°	Wind direction accuracy: ± 3° at 20 m/s Wind Speed accuracy: ± 4% at 20 m/s Wind direction resolution: 1° Wind speed resolution: 0.01 m/s
Li-Cor Radiation Sensor	LI200SZ	4 m		Sensitivity: 21µV/W/m^2 Conductivity: 0.4 W/m. °C Temperature error: 0.2%/°C

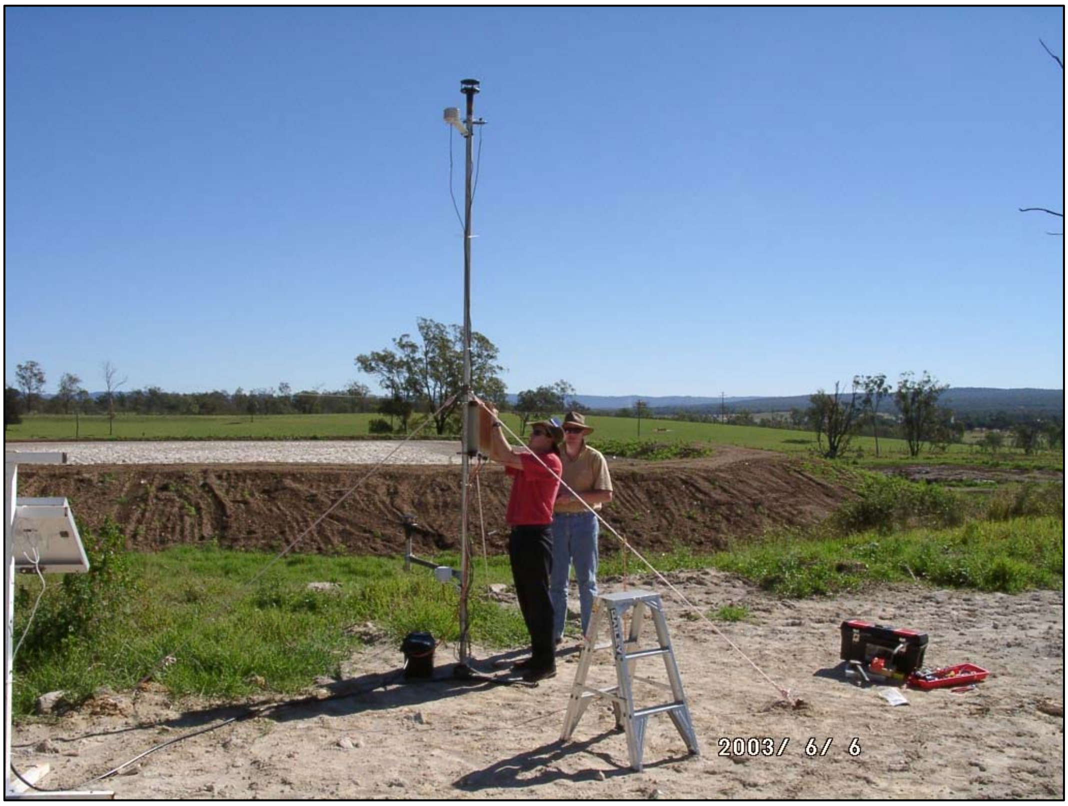

Figure 7: Weather station being installed on site (looking north west)

Stability classes were calculated using the Sigma-A method (USEPA 2000). This method is accepted by the USEPA and has been used extensively (e.g. Tripp *et al*. (2004)). It uses the standard deviation of the wind direction in combination with the scalar mean wind speed to define atmospheric stability (USEPA 2000). Using the STINK model, hydrogen sulphide concentrations were combined with the meteorological data to determine hydrogen sulphide emission rates.

Effluent sampling and analysis

Effluent samples were collected from the inlet and outlet pipes of the lagoons. At the Valley Beef site, samples were taken from the inlet headworks and the lagoon outlet pipe. Samples at the Sunland Proteins site were taken from the inlet of the lagoons and from a capped outlet point on the north-western edge of the lagoons.

All sampling equipment was thoroughly rinsed with effluent immediately prior to sample collection. Once collected, samples were placed on ice and transported to DPI&F's Toowoomba offices, where they were stored in a refrigerator until transported to the Toowoomba City Council laboratory. Samples were analysed using the laboratory methods adopted by Toowoomba City Council for Alkalinity (mg/l), COD (mg/l), Total Iron (mg/l), pH, Sulphate (mg/l), Sulphide (mg/l) and Total Solids (mg/l). Inlet and outlet effluent temperature were measured on site using a Raynger ST thermometer.

Hydrogen sulphide measurement (air)

Odalog

Process

A 0-50 ppm Odalog unit (high range) and a 0-2 ppm Odalog unit (low range) were used to determine hydrogen sulphide concentrations. The units each contain an electrochemical cell. A chemical reaction in the cell causes current flow that is related to the concentration of the gas. Where used, the high and low range units logged data at 1 minute and 10 minute intervals respectively. The Odalog units were only used to measure ambient concentrations or concentrations in the air from the flux chamber exhaust.

Where the Odalog was used in conjunction with the flux chamber a custom housing was used where the air could be drawn past the sensor at a rate of 2 litres per minute. The housing is shown in Figure 8.

Figure 8: Odalog and housing in use

Jerome meter

Process

The Jerome meter was used to determine hydrogen sulphide concentrations downwind of the source, in the flux chamber exhaust and in the ducting at Sunland Proteins. The internal pump was used to draw samples from the various sources. Responses from the instrument were recorded on field sheets at the time of sampling.

Collection from sources

Flux chamber

The sensor on the unit was regenerated prior to use according to the manufacturers instructions. A custom housing was designed to enable a sub-sample of gas to be drawn from flux chamber exhaust stream. The instrument and housing is shown in Figure 9. One reading per minute was taken using the Jerome meter and a value in ppb was recorded.

Figure 9: Jerome meter and housing in use

Downwind

Downwind samples were taken at heights of 1, 2 and 3 metres. Samples were taken when wind was blowing across the lagoon towards the sample location. Care was taken not to sample when the wind was blowing from the direction of the abattoir buildings, as other sources of hydrogen sulphide may have been present.

Ducting

Samples were drawn directly from the air stream using the internal pump.

Gas chromatography

Gas samples were collected by drawing a sample from the air stream into Tedlar sample bags using a hand pump. For the flux chamber samples, air was drawn from the custom made chamber shown in Figure 9. For the ducted samples, air was drawn directly from the air stream using the hand pump.

Prior to the sample being taken, the sample bag was primed and purged to minimise any possible adsorption of the gas to the bag. Time was also spent pumping air through the hand pump to ensure that if the gas was going to be absorbed by the pump, it was fully saturated prior to sampling.

Samples were analysed by the Safety in Mines Testing and Research Station (SIMTARS) at Redbank, Queensland, using SIMTARS laboratory procedure LP0037- “Procedure for analysis of sulfur gases by GS-FPD”. The detection limit of this method was 0.2 ppm (200 ppb) for each of the analytes (hydrogen sulphide, carbonyl sulphide, methyl mercaptan and ethyl mercaptan).

Wet chemistry

Process

Hydrogen sulphide concentrations in air were determined using a modified version of the South Australian Environmental Protection Agency Test Method 03.05, “*Determination of Hydrogen Sulphide*” (SAEPA 1995). The South Australian method uses cadmium sulphate, which has safety and stability issues. The cadmium was replaced by the safer and more stable compound, zinc acetate, which acts in a similar manner to cadmium sulphate by causing the sulphide to form insoluble zinc sulphide.

A 12-volt diaphragm pump in series with an Email Gas (Model 610) meter was used to draw the air from the source at a controlled rate. The first impinger contained 3% hydrogen peroxide solution (approximately 100 ml), while the second impinger was left empty. The third and fourth impingers contained the zinc acetate solution (100 ml). Samples were taken over a period of 30 minutes. During the trapping process the impingers were immersed in ice water to facilitate adsorption.

Once sampling was complete, the volume of gas that had passed through the solutions was recorded from the gas meter. Atmospheric pressure during the period of sample collection was also recorded with an electronic barometer. The contents of the first and second impingers (if present) were discarded, while the contents of the third and fourth impingers were transferred into labelled containers and placed on ice. The sample weight was recorded at the laboratory to determine the volume of solution in the containers. All samples were then freighted to Leeder Consulting in Melbourne for analysis. The sampling solutions in the third and fourth impingers were analysed separately to ensure no breakthrough had occurred. Breakthrough refers to the front impinger becoming saturated by the gas being trapped and the gas therefore, travels directly into the second impinger. Significant concentrations of the product being trapped in the second impinger generally indicate breakthrough.

Collection from sources

Samples were drawn from the flux chamber at Valley Beef and the ducted source at Sunland Proteins. Where samples were collected from the flux chamber they were drawn from the chamber at a rate of 2 litres per minute. Where samples were collected from the Sunland Proteins site, air was draw through the impingers at a rate of 1 litre per minute (owing to concerns regarding breakthrough due to the high hydrogen sulphide concentrations).

Jerome meter and Odalog comparison

The performance of the Jerome meter and low range Odalog units were compared by measuring a range of hydrogen sulphide concentrations sourced from a bottle of standard gas and diluted using a dynamic mixing system. A 16-ppm hydrogen sulphide standard was diluted in a range from 0.1 to 2 ppm. The Jerome meter was also compared against the standard at 16 ppm as an additional test. To ensure accurate results the Jerome meter was regenerated and zeroed twice during this period.

Emission rate calculation

Flux chamber

During operation, airflow (m^3/s) and gas concentrations (mg/m^3) were recorded. The emission rate was then calculated using Equation 2.

$$E = \frac{C \times Q}{A}$$ **Equation 2**

Where: *E* is the emission rate (mass of hydrogen sulphide emitted / m^2 / s);

C is the hydrogen sulphide concentration (mg/m^3);

Q is the chamber flow rate (m^3/s); and

A is the area covered by the chamber (m^2).

STINK modelling

After running the model, a non-dimensional concentration (Ψ) for the stability class at the sampling height was obtained. The velocity at the sampling height was calculated using the power law, Equation 3.

$$U_z = U_{ref}\left(\frac{Z}{Z_{ref}}\right)^a$$ **Equation 3**

Where: U_z is the wind speed (m/s) at a height of Z (m) above the ground;

U_{ref} is the wind speed (m/s);

Z_{ref}; is the anemometer height at which U_{ref} was measured; and

a is the Irwin Rural wind profile exponent, which is a function of the stability class.

Irwin Rural coefficients were selected for this research as the areas studied included rolling grazing areas, as detailed in USEPA (2000).

The emission rate was then calculated using Equation 4 (Smith 1995).

$$E_v = \frac{C(z)\hat{u}}{\Psi(z)}$$ **Equation 4**

Where: E_v is the calculated emission rate (mg/m^2.s);
$C(z)$ is the measured hydrogen sulphide concentration (mg/m^3);
$\hat{u}$ is the velocity measured on site at the sampling height (m/s); and
$\Psi(z)$ is the non-dimensional concentration at the sampling height.

The calculated downwind emission rate was then standardised, using Equation 5 (Smith and Watts 1994b), to a standard wind speed of 1 m/s based on similar work with a wind tunnel (for more information see Galvin *et al*. (2004).

$$\frac{E_v}{E_1} \approx V_t^{0.63}$$ **Equation 5**

Where: E_1 is the emission rate at 1 m/s;
V_t is the theoretical wind velocity at half the wind tunnel height as determined using the power law (Equation 4).

The exponent of 0.63 was changed to 0.5 to reflect the use of the formula on lagoon surfaces as described by Pollock (1997) and used successfully by Galvin *et al*. (2004).

Ducted sources

The volume of air passing the sampling point was calculated using Equation 6.

$$Q = \frac{V}{A}$$ **Equation 6**

Where: Q is the flow rate (m^3/s);

V is the measured velocity (m/s); and

A is area inside of the duct (m^2).

The mass emission over time was calculated using Equation 7.

$$MER = Q \times C$$ **Equation 7**

Where: MER is the mass emission rate (mg/s); and

C is the measured concentration (mg/m^3).

The emission rate per square meter of lagoon was then calculated using Equation 8.

$$AER = \frac{MER}{A_P}$$ **Equation 8**

Where: AER is the areal emission rate (mg/m^2.s); and

A_P is the total surface area of the lagoons (m^2).

Results and discussion

Lagoon loading

Processing data (HSCW) for the Valley Beef site was supplied by Mr Paul Lynch and is shown in Figure 10. The average HSCW was 3043 tons per month with a standard deviation of 646 tons. The total HSCW for the period from January 2003 until April 2004 was 48700 tons.

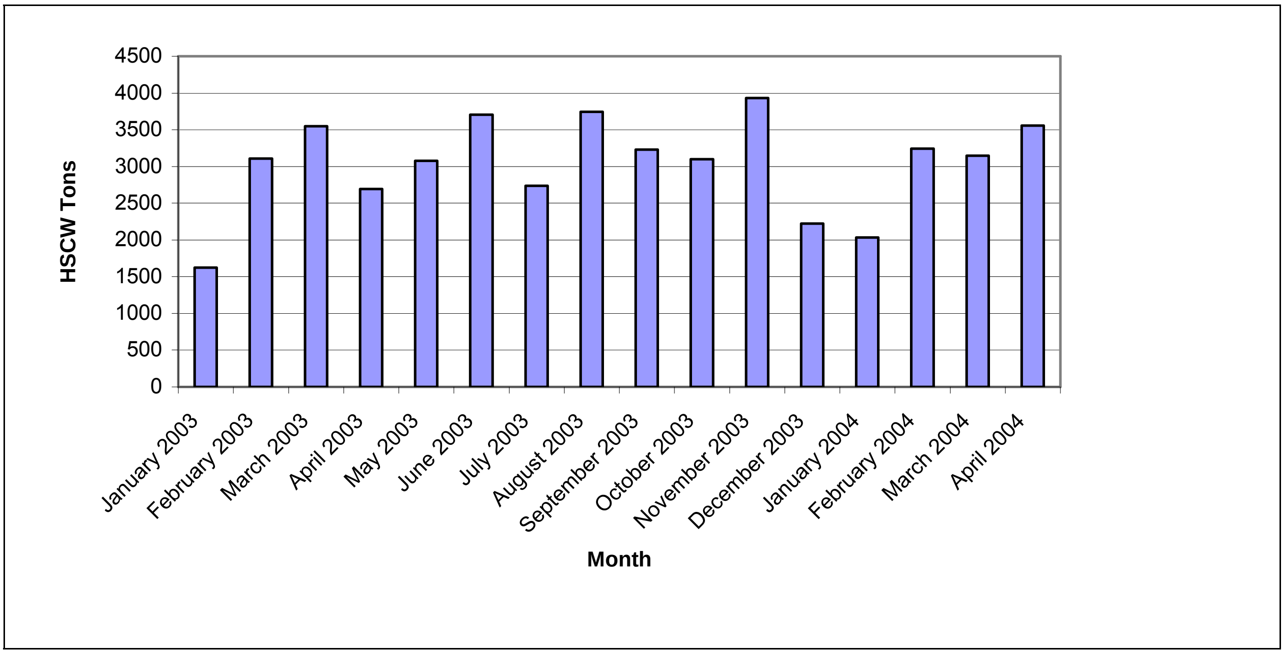

Figure 10: Valley Beef HSCW values for 2003-2004

Jerome meter and Odalog comparison

The Jerome meter has been used extensively at or near intensive livestock operations (e.g. Wood *et al*. (2001) and Rhoades *et al*. (2003)). As there is some conjecture over the responses from techniques used to measure hydrogen sulphide concentrations (See Table 4 below), it was decided to compare the low range Odalog unit against the Jerome meter. The Jerome meter is designed for low range measurement, whereas the Odalog unit has only recently been released and has not been extensively trialled. The results of the comparison, which was undertaken under laboratory conditions, are shown in Figure 11.

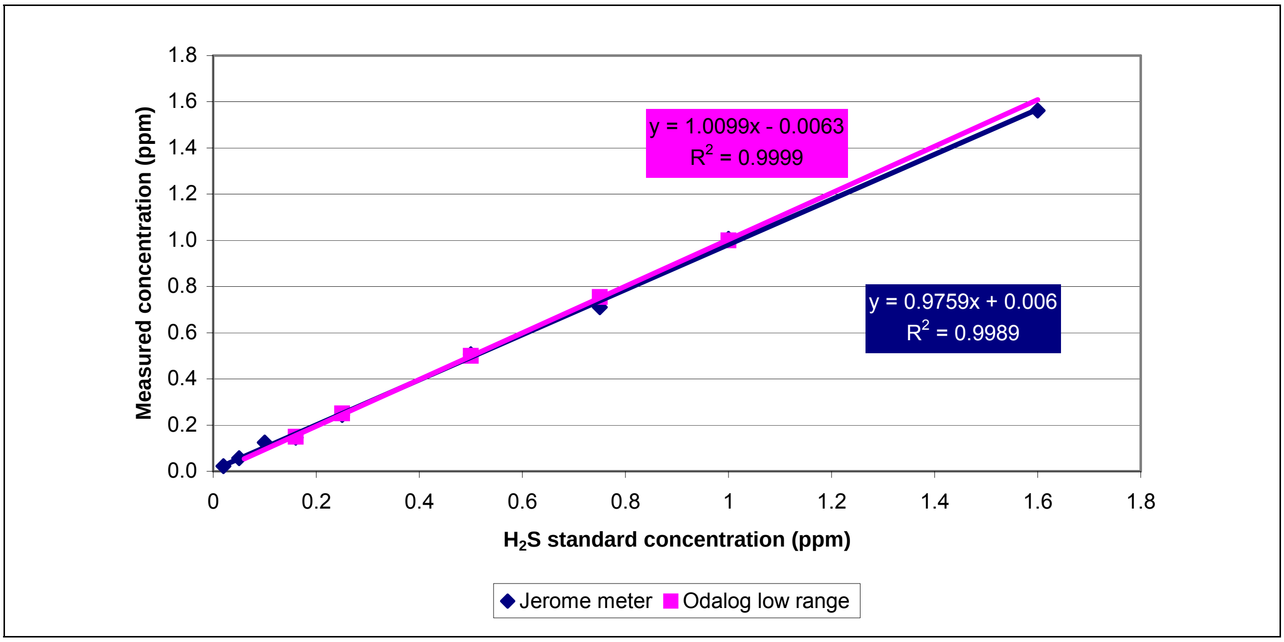

Figure 11: Comparison of Odalog and Jerome meter

Figure 11 shows that for gas concentrations up to 1.6 ppm (1600 ppb) both the Jerome meter and the low-range Odalog provided reliable measurement of the hydrogen sulphide standard.

A further comparison was undertaken on the bottled standard using only the Jerome meter at a higher concentration of 16 ppm. The results are shown in Table 3.

Table 3: Comparison of Jerome meter with bottled standard

Standard concentration of hydrogen sulphide (ppm)	Measured concentration of hydrogen sulphide (ppm)
16	15
	16
	16

Figure 11 and Table 3 indicate that when undertaking ambient monitoring near abattoir lagoons, both the Odalog and the Jerome meter would give similar results up to 1.6 ppm of hydrogen sulphide. In addition, the Jerome meter can measure hydrogen sulphide at concentrations up to 16 ppm accurately. From this it is concluded that either unit is suitable for measuring ambient hydrogen sulphide concentrations near anaerobic lagoons.

Stage 1

Stage 1 sampling was undertaken on 24 July 2003 at the Valley Beef facility. The aim of Stage 1 was to identify the most suitable method or methods for determining hydrogen sulphide emission rates for anaerobic abattoir lagoons. This included:

- measuring downwind concentrations with a Jerome meter and back calculating emissions using the STINK model;
- placing the flux chamber on at least one point on a lagoon to collect samples for hydrogen sulphide analysis from which an emission rate can be calculated; and
- trialling a number of analysis methods to identify the most suitable technique for measuring hydrogen sulphide concentrations in air samples derived from abattoir lagoon emissions, including:

- Impinger sampling of the flux chamber exhaust air;
- GC analysis of the flux chamber exhaust air;
- Use of an Odalog to measure hydrogen sulphide in the flux chamber exhaust air; and
- Use of a Jerome meter to measure hydrogen sulphide in the flux chamber exhaust air and ambient air.

Flux chamber sampling

Surface cracking was observed in the lagoons crust. In an attempt to control leaking between the flux chamber and the surface, a square sheet of Perspex was attached to the base of the chamber. Figure 12 shows the flux chamber in use on the lagoon surface while Figure 13 shows a close up of the lagoon. The surface cracking became more extensive closer to the centre of the lagoon and, therefore, the flux chamber was placed within 1-2 metres of the bank.

Figure 12: USEPA flux chamber at point 2 on the primary lagoon

Figure 13: Close-up of flux chamber at point 2.

Concentrations measured in the exhaust of the flux chamber at a single point (sample point 2) are summarised in Table 4.

Table 4: Comparison of analytical techniques (Point 2)

	Analysis technique			
	High range Odalog	Jerome meter	Gas chromatography	Wet chemistry
Number of analyses	20	10	2	1
Minimum	Did not detect[1]	13 ppb	<200 ppb	N/A
Average		**39 ppb**	**600 ppb**	**178 ppb**
Maximum		92 ppb	1000 ppb	N/A
Standard deviation		25 ppb	565 ppb	N/A

For a single point measured over a short time period, Table 4 shows:

- the three techniques gave concentrations that were different by at least a factor of four;
- the gas chromatography technique overestimated concentrations compared to the other techniques; and
- the data from the Jerome meter indicated temporal variation.

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[1] The limit of detection for the high level Odalog was 100ppb.

Gas chromatography is generally not used for low concentrations of hydrogen sulphide (i.e. sub 1 ppm) due to a high detection limit (≈200 ppb). A concentration of 200 ppb is well above the concentrations measured by the two other techniques. Thus, the GC analysis is not adequate for analysis of samples from abattoir lagoons. Whilst the GC data in Table 4 had a large standard deviation, this can be explained by the fact that there were only two data points. The results of the GC analysis are shown in Table 5.

Table 5: Results from GC analysis

Sampling location	Analyte concentration (ppm)			
	H_2S	Carbonyl Sulphide	Methyl Mercaptan	Ethyl Mercaptan
Site 2	2.0	<0.2	<0.2	<0.2
Site 3 #1	1.0	<0.2	<0.2	<0.2
Site 3 # 2	<0.2	<0.2	<0.2	<0.2
Limit of reporting	0.2	0.2	0.2	0.2

The data shown in Table 5 is valuable as it shows that at concentrations ranging from less than 0.2 ppm up to 2 ppm, no other sulfur compounds were detected. Gay *et al.* (2003) reported that interference by reduced sulfur compounds may occur when using a Jerome meter. This finding is not supported by Winegar and Schmidt (1998). Clanton and Schmidt (2000) reported that when comparing concentration of hydrogen sulphide measured with a Jerome meter and those measured using GC analysis, a good correlation between the two methods was observed. The GC results indicated that the potential interferents are < 1/10th of the concentration of hydrogen sulphide. We, therefore, conclude that the Jerome meter provides credible estimates of hydrogen sulphide concentration.

The concentrations recorded over time at the three flux chamber samples points are shown in Figure 14.

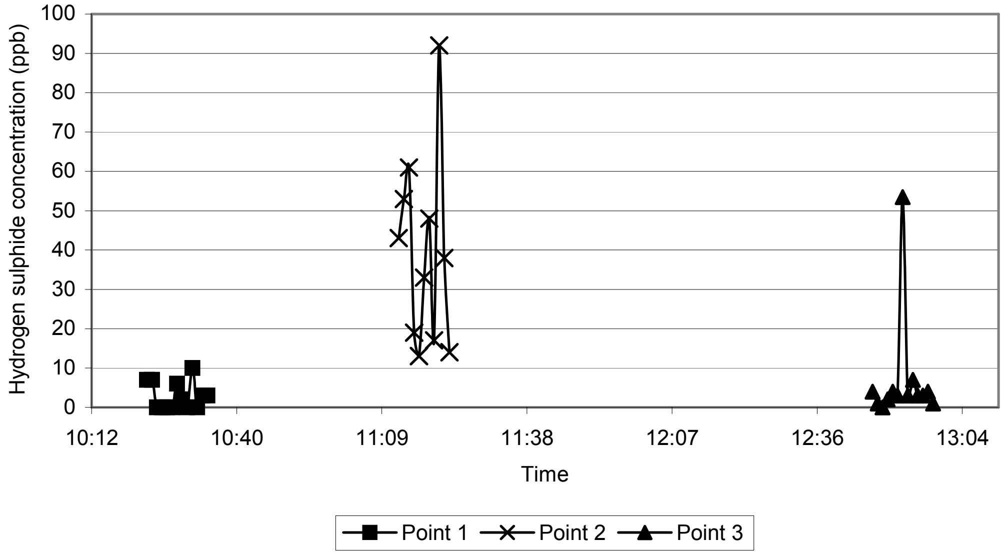

Figure 14: Concentrations measured in flux chamber samples using Jerome meter

Figure 14 shows that:

- Spatial variation of hydrogen sulphide could be a issue for abattoir lagoons as the three points have different concentrations; and

- Measured concentration varied with time, and therefore, variation in emission rate (e.g. Point 2) is an important factor.

The average hydrogen sulphide emission rate for points 1 to 3 measured using the Jerome meter are shown in Table 6. The minimum emission rate that can be measured using the Jerome meter was approximately 0.01 mg/m^2.hr, based on a detection limit of 3 ppb.

Table 6: Average emission rates determined using the Jerome Meter.

Point	Average Emission Rate (H_2S mg/m^2.hr)
1	0.010
2	0.128
3	0.022

Figure 14 indicates that temporal variation and spatial variation may be issues. For short term monitoring these issues could cause over or under estimation.

The emission rates calculated for each of the three points were significantly different ($p<0.0001$, 95%). This variation could be linked to the use of the flux chamber. On the sampling day it was more difficult to place and seal the chamber on points 1 and 3, and therefore, it was concluded that these points might not have been adequately sealed.

Temporal variation is also potentially important. Again, it could lead to under or over estimation of hydrogen sulphide emission rates. It can be seen in Figure 14 that by taking a single sample at any of the points at any time could result in over or underestimation of concentration.

Potentially, spatial and temporal factors may affect measured emission rates. It was not possible however, to quantify the influence of either of these factors, although, these results do indicate that either or both of the factors may influence measured emission rates.

Back calculation

Two sampling sites were used for downwind sampling and were shown in Figure 2. The sites were located on the downwind edge of the lagoon. The actual sample location selection had regard for local weather patterns shown in Figure 15.

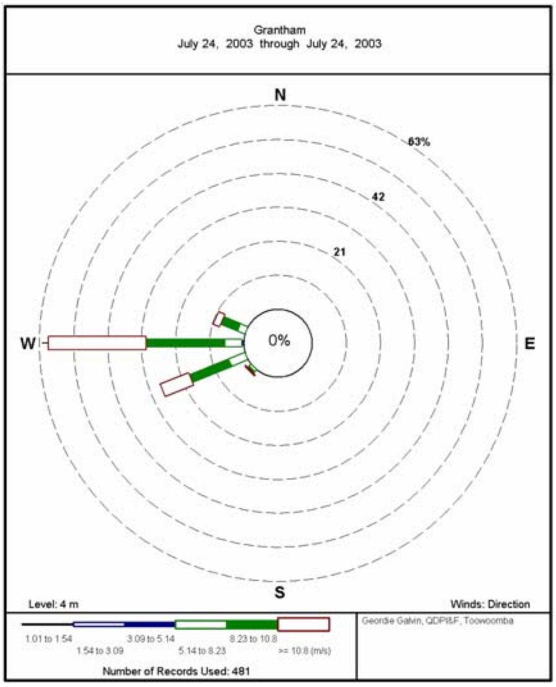

Figure 15: Windrose for July 24, 2003

Figure 15 shows that:

- the wind was predominantly from the west; and
- wind speeds exceeded 8 m/s at the measurement height of 4 metres for much of the day.

Hydrogen sulphide concentrations were measured using the Jerome meter on a number of occasions during the day and the emission rates calculated from these samples are shown in Table 7.

Table 7: Hydrogen sulphide emission rates derived from back calculation

Sample location (on sample day)	Time	Sample height (m)	Wind speed	Measured concentration (ppb)	H_2S emission rate ($mg/m^2.s$)	H_2S emission rate ($mg/m^2.hr$)
1	9:49	1	7.53	12	0.0121	43.56
1	9:49	2	7.53	8	0.0092	33.12
1	11:35	1	8.43	112	0.1241	446.76
1	11:36	2	9.91	114	0.1612	580.32
2	9:47	1	7.23	109	0.1049	377.64
2	9:47	2	7.23	54	0.0604	217.44
2	9:50	1	7.50	77	0.0814	293.04
2	9:50	2	7.50	43	0.0530	190.8
2	9:51	3	7.71	26	0.0456	164.16
2	9:51	0.5	7.71	92	0.1312	472.32
2	11:27	1	9.48	13	0.0164	59.04
2	11:27	2	9.48	14	0.0205	73.80
2	11:28	3	9.32	3	0.0062	22.32
				Average	0.0636	228.79

Table 7 shows that:

- emission rates varied between the two sample sites (Point 1 and 2 average emission rates 276 and 208 $mg/m^2.hr$ respectively); and
- emission rates varied with time;

As expected, the emissions varied with time, most likely due to changing meteorological conditions. The results from the back calculation method showed emission rates ranging from 22.3 to 580 $mg/m^2.hr$. In their work, Zahn *et al*. (2002) used the theoretical profile shape (TPS) method described by Wilson *et al.* (1983) to determine hydrogen sulphide emission rates at an anaerobic piggery lagoon in Missouri. Their results (shown in Figure 16) indicate variation (≈1.8 $mg/m^2.hr$ to ≈ 300 $mg/m^2.hr$) with time and an average emission rate of 38 $mg/m^2.hr$ (1$\mu g/cm^2.s$ ≈ 36000 $mg/m^2.hr$).

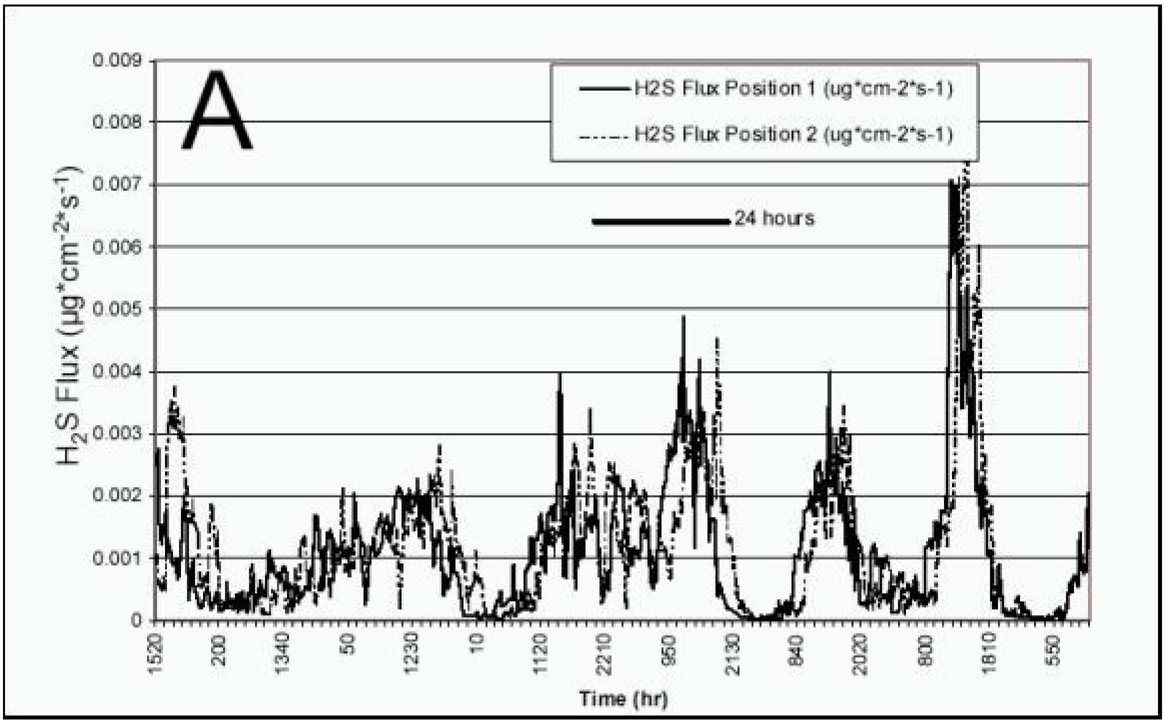

Figure 16: Results published by Zahn *et al.* (2002)

The results detailed in Table 7 are shown in Figure 17.

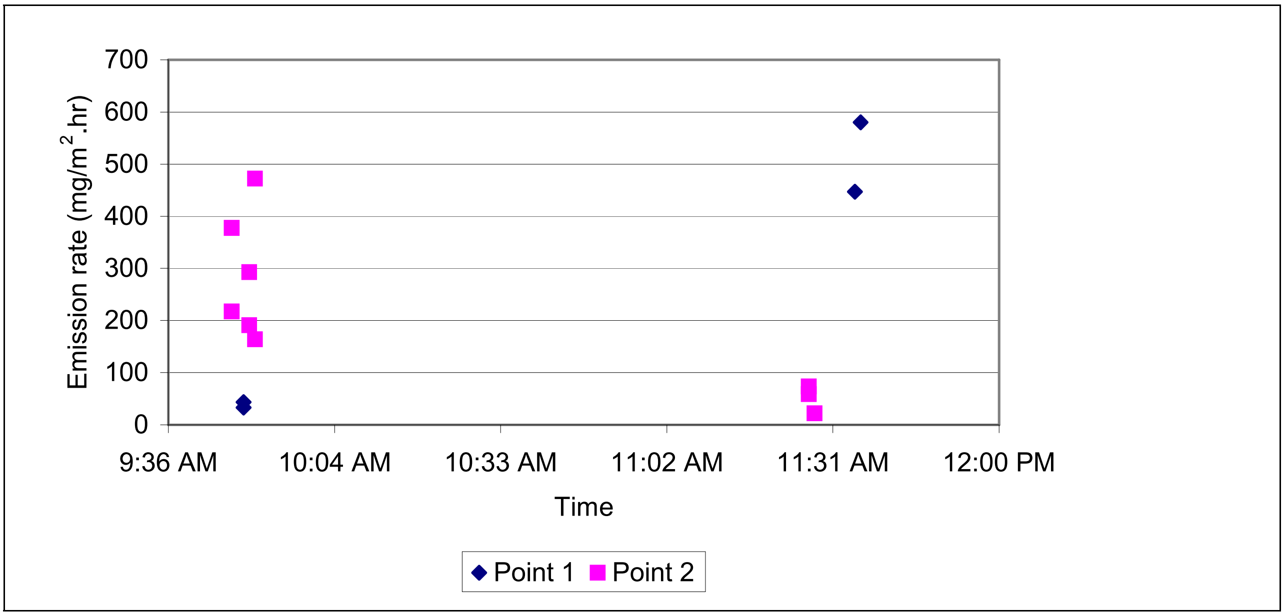

Figure 17: Back calculated emission rates

The results from Stage 1 of this project (Figure 17) were generally lower than the values published by Zahn *et al*. (2002).

Sattler *et al.* examined the emission of hydrogen sulphide from wastewater treatment systems. They concluded that hydrogen sulphide emission was linked to a number of factors, such as surface area (increasing surface area increases the amount of hydrogen sulphide emitted), liquid phase concentrations (Sattler and McDonald 2002) and liquor temperature (Sattler and Devanathan 2004). Generally, higher concentrations of hydrogen sulphide in the effluent and lower concentrations in the gas phase will increase the emission process from effluent to gas (Sattler and McDonald 2002).

Zahn *et al*. (2002) and Bicudo *et al*. (2003) have both reported variation in emission rate with time for area source emissions. For uncovered lagoons, variation in local meteorology would cause variations in emission. Unfortunately, differences in waste treated and local weather conditions between the overseas and Australian sites make a comparison of this project with other work difficult.

Effluent analysis

The effluent analysis results for the Valley Beef site are shown in Table 8.

Table 8: Effluent analysis results Valley Beef

Characteristic	Inlet	Outlet
Alkalinity (mg/L)	309	1030
COD (mg/L)	7900	2970
Total Iron (mg/L)	1.36	2.33
pH	6.5	7.0
Sulphate (mg/L)	38	16
Sulphide (mg/L)	<0.050	7.45
Total Solids (mg/L)	5050	2550
Temperature (° C)	43	36

Comparisons of downwind and direct methods

The aim of Stage 1 was to ascertain the best method for hydrogen sulphide emissions analysis at an abattoir lagoon. While the extensive surface cracking on the lagoons made the use of the flux chamber method impractical, the different analysis methods that were used have been compared in Table 9

Table 9: Summary of calculated emission rates

	Back calculation ($mg/m^2.hr$)	Flux chamber			
		Odalog ($mg/m^2.hr$)	Jerome meter ($mg/m^2.hr$)	Gas chromatography ($mg/m^2.hr$)	Wet chemistry ($mg/m^2.hr$)
Average	229	N/D	0.03	3.48	0.28
Std Dev.	189		0.04	2.94	0.06

The key finding in Table 9 is that the average back calculated emission rates were significantly different ($P<0.001$, 95%) to the emission rates derived using the flux chamber.

This difference was expected, due to the inherent differences between the back calculation and flux chamber techniques as described in Table 2 of the proposal for this project. The flux chamber has a low sweep rate that is, on most occasions, lower than the ambient wind speeds. It has previously been shown that dynamic devices with higher flushing rates (e.g. UNSW wind tunnel) and dynamic devices with low flushing rates (eg. USEPA flux chamber) do not compare well as dynamic devices tend to produce higher emission rates (Cooper *et al.* 1992; Jiang and Kaye 1996). Jiang and Kaye (1996) found that the UNSW wind tunnel and a USEPA flux chamber provided different estimations of emission rates of up to 85% for a range of chemicals. Emission rates derived using back calculation techniques generally predict emission rates that are similar to those derived using wind tunnels (Galvin *et al.* 2004; Sarkar and Hobbs, 2003). Sommer *et al.* (2004) reported that two back calculation models compared well with each other but poorly when compared to a flux chamber. In general, dynamic chambers with high flow rates or back calculation methods have been shown to be the more desirable method for estimating area source emissions (Gao *et al.* 1998a; Gao *et al.* 1998b; Smith and Watts 1994a). Unfortunately due to its elongated shape and higher volume requirement for odour free air, the operation of a UNSW wind tunnel on an abattoir lagoon would be much more difficult than using a USEPA flux chamber.

The other possible reason for the difference is that the methods have different footprints. Source footprint refers to the area in which the method/device can measure or determine emission rates. For example, the flux chamber can only measure an area equivalent to the surface area of its base. The back calculation method, if used correctly, can encompass the entire source. It is possible that the smoother edges where the flux chamber samples were taken (Figure 13) do not emit as much hydrogen sulphide as the cracked inner area of the lagoon, thus, the downwind method predicts a much higher emission rate. The practical limitations of the flux chamber mean that a representative emission rate was unable to be determined using the chamber.

The recommendation of the NSWEPA that the USEPA flux chamber was their approved measurement device (NSWEPA 2001) and ease of use were the driving factors for using the flux chamber in this project. The data gathered during this research has shown that it is likely that hydrogen sulphide emissions are suppressed by covering the emitting surface using either a flux hood or impermeable cover. This indicates that the downwind method would provide a better estimate of hydrogen sulphide emissions from uncovered ponds.

Emission per HSCW per year

Wet chemistry

Based on a throughput of 38712 tonnes per year HSCW, a lagoon area of 4207.5 m^2 and an emission rate from the wet chemistry methods of 1.4 mg/m^2.hr (Point 2), the calculated emission rate per tonne HSCW is 0.0013kg of hydrogen sulphide (0.0013kg).

Downwind

Based on a throughput of 38712 tonnes per year HSCW, a lagoon area of 4207.5m^2, and an average emission rate from the downwind methods of 228 mg/m^2.hr, the calculated emission rate per tonne HSCW is 0.22kg of hydrogen sulphide.

As discussed previously, the flux chamber method is not suitable for determining emission rates, thus alternatives such as wind tunnels or downwind methods are preferable for determining emission rates from areal sources.

Conclusion

Information derived from Stage 1 measurements allow the following conclusions:

1) Emission rates derived from the back calculation method were significantly higher than those calculated using the data derived from the flux chamber;
2) Differences between methods used to measure hydrogen sulphide concentrations are insignificant compared to the difference between emission rates derived from the downwind and flux chamber methods; and
3) The flux chamber is unsuitable for measurement of hydrogen sulphide emissions from abattoir lagoons where dynamic meteorological processes dominate the emissions process.

Stage 2

The results shown in Stage 1 identified that changes needed to be made to the methodology, including:

- discontinuing use of the flux chamber; and
- to make use of the STINK model to determine emission rates from uncovered lagoons.

Valley Beef

Hydrogen sulphide emissions

The Valley Beef site was revisited during Stage 2 and the use of the STINK model was continued.

A Jerome meter and a low range Odalog unit were used to measure ambient hydrogen sulphide concentrations. The comparison shown previously in Figure 11 suggested that the low range Odalog unit and the Jerome meter compared well at concentrations that were similar to ambient concentrations. Short-term sampling with the Jerome meter was undertaken on 11 November 2003.

The back calculated emission rates derived from the Jerome meter concentrations are shown in Figure 18. The data is for the Jerome unit for the 11th only. The average emission rate was found to be 1067 mg/m^2.hr.

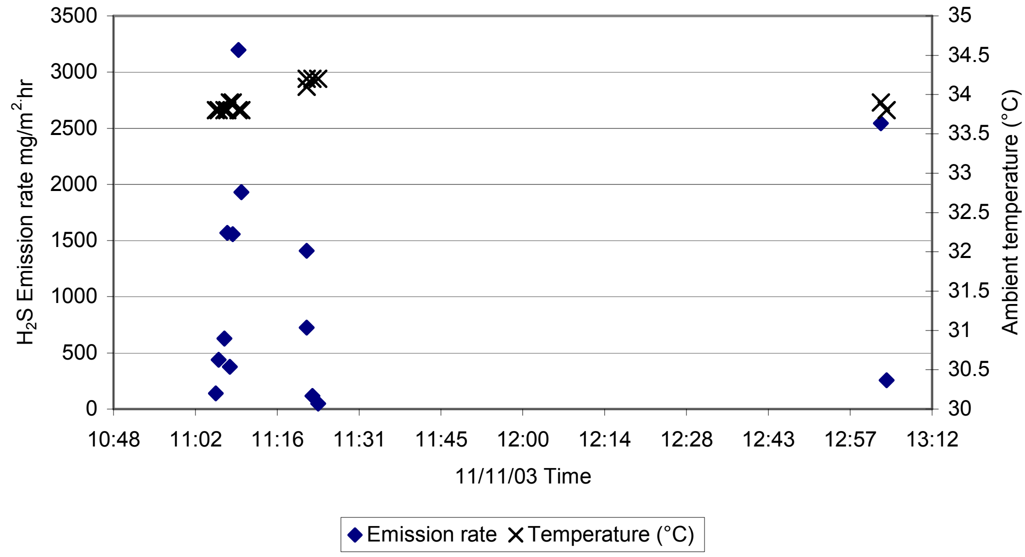

Figure 18: Summary of back calculated emission rates using the Jerome meter

Hydrogen sulphide concentrations were logged with the low range Odalog unit between 11 and 16 November 2003 every 10 minutes. The STINK model was used in conjunction with downwind hydrogen sulphide concentrations. The emission rates calculated using the long term logging data are shown in Figure 19. The average emission rate over the logging period was 522 mg/m^2/hour.

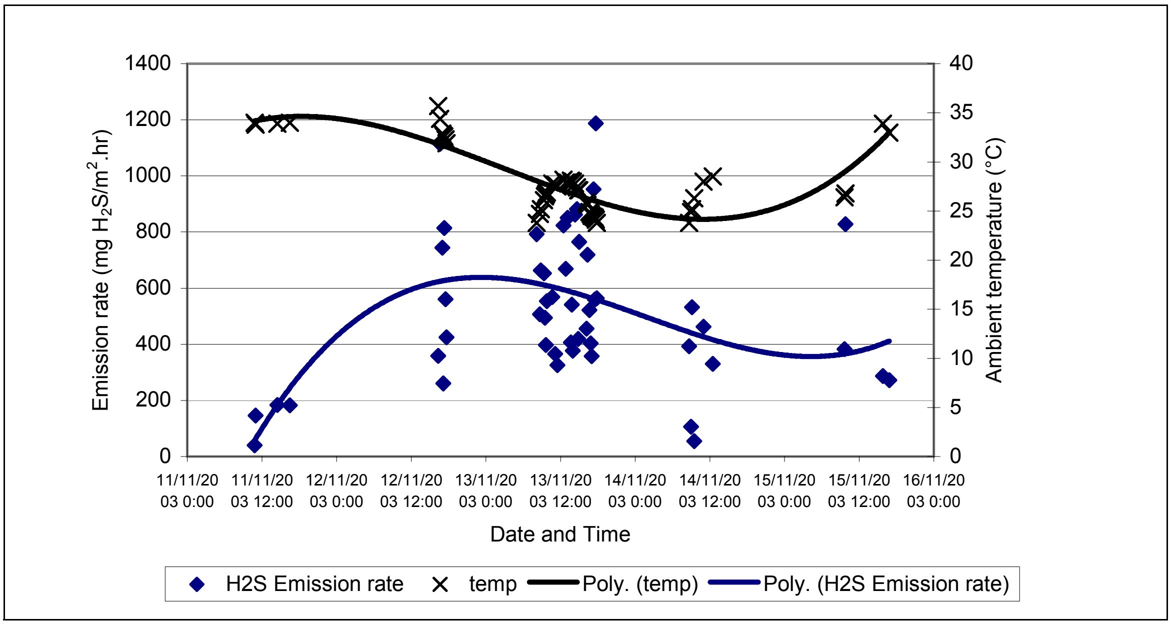

Figure 19: Ambient temperature and emission rates derived using the STINK model

The calculated emission rate over time is compared with wind speed, wind direction and stability class in Figure 20 to Figure 22.

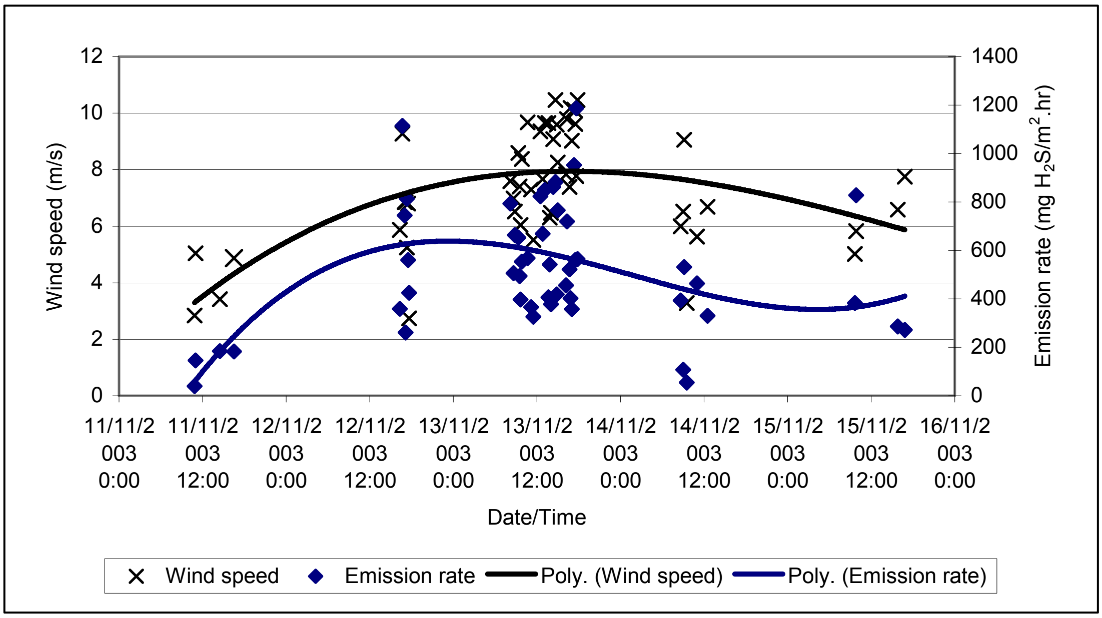

Figure 20: Wind speed and emission rates derived using the STINK model

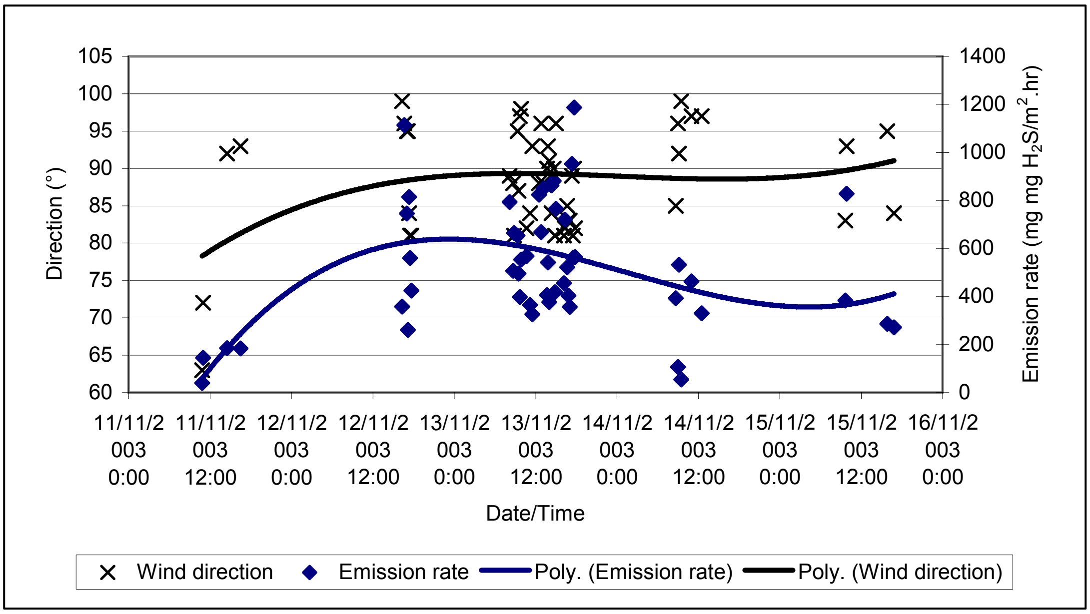

Figure 21: Wind direction and emission rates derived using the STINK model

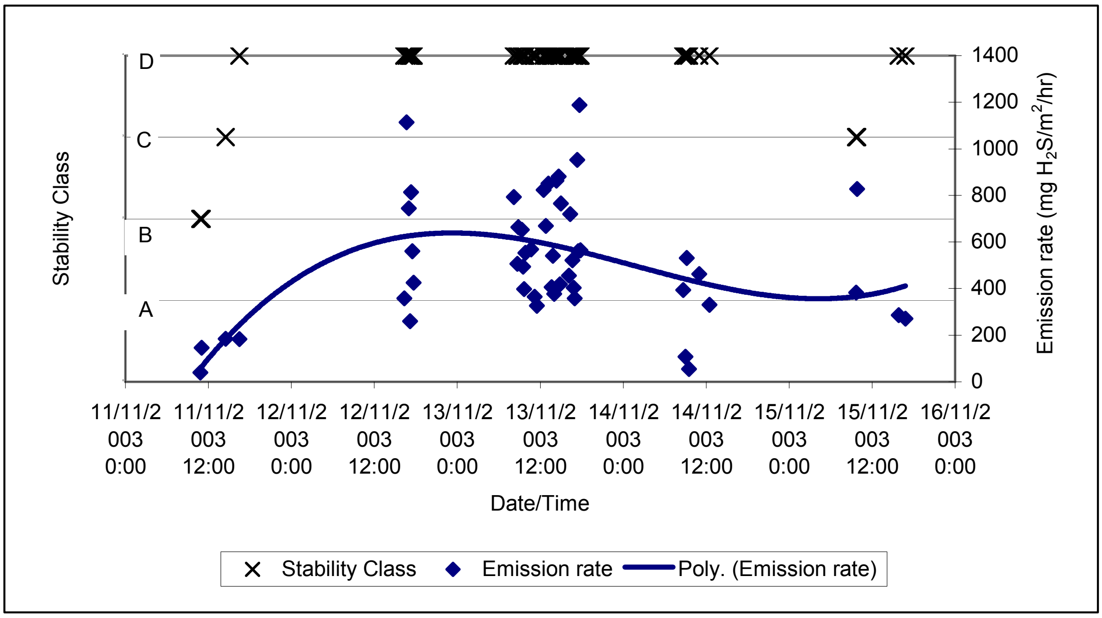

Figure 22: Stability class and emission rates derived using the STINK model

The short and long term emission rates calculated using the STINK model are compared as a box and whisker plot in Figure 23.

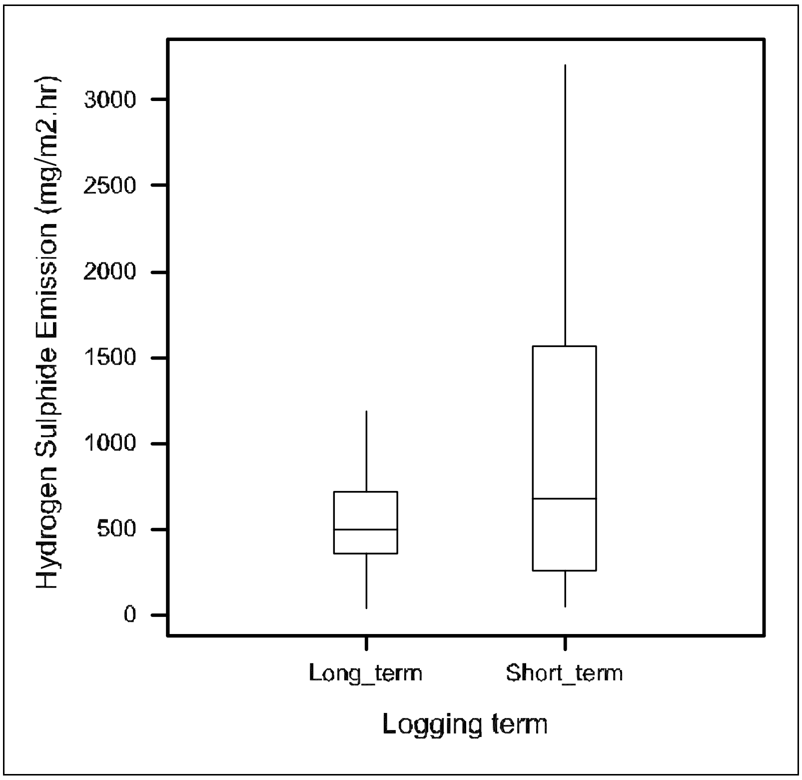

Figure 23: Comparison of short and long term logging

The median value for each sampling event (horizontal line within the box) indicates that both events (different sampling periods) had a similar median emission rate. The median emission rate was 500 mg/m^2.hr for the short term and 676 mg/m^2.hr for the long term. Whilst the box plots in Figure 23 appear to be similar in terms of range and median values, the data sets were significantly different when evaluated using an ANOVA ($P<0.001$, 95%).

As expected, the emission rates were again shown to vary with time. Zahn *et al.* (2002) and more recently Sommer *et al.* (2004) observed similar patterns with respect to time. The data shown in Figure 19 to Figure 22 do not show a direct relationship between ambient temperature, wind speed, direction or stability class. However when all of these components are combined in the Gaussian equation (Equation 1) they interact to enable the prediction of a downwind concentration.

Therefore, fluctuations in any of these can influence the modelled emission rates. Whilst the stability class remained reasonably constant over the sampling period, slight variations in wind speed and direction would have been enough to cause the observed changes in back calculated emission rate (Sattler and McDonald 2002).

The downwind logging units could only detect hydrogen sulphide when the wind was blowing across the lagoon towards the sensors. This effect was confirmed by correlating the weather data and hydrogen sulphide concentrations. Whilst the trend lines for temperature and hydrogen sulphide emission rate (Figure 19) visually indicate that the emission rate may be linked to ambient temperature, a linear regression showed a poor relationship ($R^2 \approx 0.07$) between ambient temperature and hydrogen sulphide emission rate. Similarly a linear regression showed a weak relationship ($R^2 \approx 0.3$) when wind speed and emission rate were compared, thus highlighting that emission rate is a function of many factors not any one factor such as temperature or wind speed. The emission rates in Figure 18 and Figure 19 are greater than those recorded previously at the site (Stage 1 – between 22 and 580 mg/m^2.hr) using similar methodology.

Effluent analysis

The effluent analysis results for the Valley Beef site are shown in Table 10.

Table 10: Effluent analysis results Valley Beef

Characteristic	Inlet	Outlet
Alkalinity (mg/L)	373	1410
COD (mg/L)	5560	1130
Total Iron (mg/L)	2.66	1.86
pH	6.6	7.0
Sulphate (mg/L)	4	<1
Sulphide (mg/L)	0.31	8.33
Total Solids (mg/L)	3980	10
Temperature (° C)	47.8	23.0

Sunland Proteins

Hydrogen sulphide emissions

Sampling was undertaken on two separate occasions. On the initial sampling day (20 November 2003), the gas concentration in the duct was greater than 50 ppm, which meant that the Jerome meter could not be used. As the sampling methods needed to be changed, further analysis could not be undertaken and sampling was undertaken on 7 January 2004. The hydrogen sulphide concentration in the duct was measured using a modified SAEPA (1995) protocol and by collecting grab samples for GC analysis. The average velocity inside the duct was 5.2 m/s (0.022 m^3/s). The average velocity for the initial visit was 7.0 m/s (0.029 m^3/s). Minimal variation in the velocity over time was observed on both sampling days. Sampling is shown in Figure 24 and the results of the GC analysis are shown in Table 11.

Wet chemistry sampling using chemical trapping solutions

Drawing gas from the source into a sample bag using a hand pump

Figure 24: Sampling at Sunland Proteins

Table 11: Results of GC analysis of samples from Sunland Proteins

Analyte	Analyte concentration (ppm)				
	Lower reporting limit (ppm)	Bag 1	Bag 2	Bag 3	Bag 4
Hydrogen sulphide	0.2	130	130	120	110
Carbonyl Sulphide	0.2	0.4	0.4	0.5	0.5
Methyl Mercaptan	0.2	3.8	3.8	3.3	3.4
Ethyl Mercaptan	0.2	<0.2	<0.2	<0.2	<0.2

GC analysis for Valley Beef samples (Table 5) indicted that reduced sulfur species were not being emitted in high levels from the lagoon. This was not the case for the Sunland Proteins lagoon (Table 11) as the GC analysis showed low concentrations of the compound, methyl mercaptan (<4%). The emission rates of hydrogen sulphide from the lagoons calculated from the GC and impinger concentration determinations are shown in Table 12.

Table 12: Hydrogen sulphide emission rates for Sunland Proteins

	Measurement technique	
	GC	Wet chemistry
Number of analyses	4	3
Average	**22.6 mg/m^2.hr**	**2.4 mg/m^2.hr**
Standard deviation	1.8 mg/m^2.hr	1.4 mg/m^2.hr

Table 12 shows:

- The emission rates calculated using the wet chemistry and GC techniques are significantly different ($P<0.0001$, 95%); and
- Variation between methods is more important than variation with time when determining emission rates.

The emission rates measured at Sunland Proteins were much less than those measured at Grantham. The effluent characteristics (Table 13) of the Sunland Proteins site were found to be different to those at Valley Beef. This would be expected, as one site is an abattoir and the other is a rendering plant.

The cover on the lagoon at Sunland Proteins may cause the emission rates to be lower at the Sunland Proteins site when compared to the Grantham site. Gao and Yates (1998b) showed that enclosing emitting surfaces with a flux chamber reduced gaseous emissions due to a decrease in amount of air flushing over the surface. This is in line with the work of Sattler and McDonald (2002) who reported that higher concentrations of hydrogen sulphide in the air above an emitting surface reduced the transfer of hydrogen sulphide from the wastewater to air. As the cover on the lagoon has a much higher air exchange rate than a flux chamber, it is likely that suppression would occur, however, the emissions would not be suppressed as much as by covering a surface with a flux chamber.

Lastly the GC and wet chemistry methods did not provide similar concentrations for samples taken from the same source. As the GC method was calibrated against a hydrogen sulphide standard in the laboratory, there are two possible causes of the variation:

1. A interferent was present with a similar retention time to hydrogen sulphide on the GC column (Environment Agency 2001); or
2. An error was present in the collection process or analysis component of the wet chemistry method.

Communication with SIMTARS (Usher, 2004) has ruled out the presence of interferent in the GC analysis as two methods were used (GC-FPD and micro GC) to determine concentrations.

Not shown in Table 12 is that the three wet chemistry runs, each drawing 1 litre of air per minute, ran for 10, 20 and 30 minutes respectively. In theory if a concentration in the air stream remained constant over time (such as that shown for the GC analysis in Table 11) the three runs would have produced concentrations in the solutions that were 1 time, 2 times and 3 times the concentration of each other respectively. This is due to the fact that the amount of material trapped per cubic metre of air should remain constant, however, this was not the case.

Analysis of the concentrations of the trapping solutions showed that the first impinger trapped the majority of the hydrogen sulphide, with the second impinger trapping much less. This was the case for two of the three samples. The third run had the highest concentration in the first impinger, with the second containing a lower concentration. From this it can be concluded that the trapping of the gaseous hydrogen sulphide is not the issue as there is little breakthrough of hydrogen sulphide from the first to the second impinger that indicates a suitable sampling period. The United Kingdom Environment Agency (2001) reported that for the USEPA Method 11 which is almost identical to the SAEPA method, a number of interferences were possible. These included bias due to high concentrations of thiols or reduction, or oxidation of iodine ions. It is unknown whether high levels of thiols or iodine ion are an issue for abattoir ponds. The author has spoken to a number of specialists in this area without determining a reason for the discrepancy. At this point in time the issue has not been resolved.

Effluent analysis

The effluent analysis results for Sunland Proteins are shown in Table 13.

Table 13: Effluent analysis results for Sunland Proteins

Characteristic	Inlet	Outlet
Alkalinity (mg/L)	1020	2320
COD (mg/L)	2980	994
Total Iron (mg/L)	2.75	0.16
pH	7.5	7.5
Sulphate (mg/L)	200	2
Sulphide (mg/L)	1.52	10.4
Total Solids (mg/L)	339	281
Temperature (°C)	37	30

Conclusions

1) Hydrogen sulphide emission rates for Sunland Proteins were significantly higher than those measured at Valley Beef.
2) Covering of the Sunland Proteins lagoon inhibited the transfer of hydrogen sulphide from the wastewater to air.
3) The wet chemistry method used may not provide for quantitative measurement of hydrogen sulphide from abattoir lagoons.

Stage 3

Valley Beef

Downwind

While it had been concluded in Stage 1 that the USEPA flux chamber was not suitable for determining emissions from abattoir lagoons, rainfall in the weeks leading up to the Stage 3 sampling meant that the lagoon surface was smooth. As the smooth surface eliminated difficulties related to poor surface seals, this provided an excellent opportunity for additional comparison using the chamber in addition to the preferred downwind method.

Long-term downwind sampling was again undertaken using the Odalog units. Due to equipment failure, the sampling had to be undertaken over two periods (9-12 March and 18-26 March 2004). The units were located side by side on the edge of the lagoon as described in the methodology. The meteorological data for the sampling period is summarised in Figure 25.

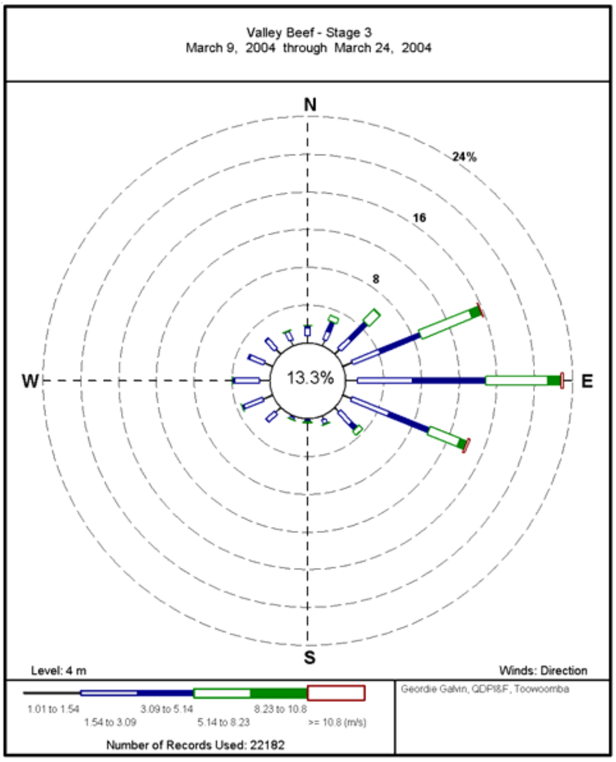

Figure 25: Wind rose of meteorological data Stage 3 - Valley Beef

Figure 25 showed:

- that winds varied from east of north east to east of southeast; and
- a large component of the wind from the east, indicating that the middle of the western side of the lagoon was the optimum downwind sampling location.

The back calculated hydrogen sulphide emission rates for the Valley Beef site are summarised in Figure 26 and Table 14.

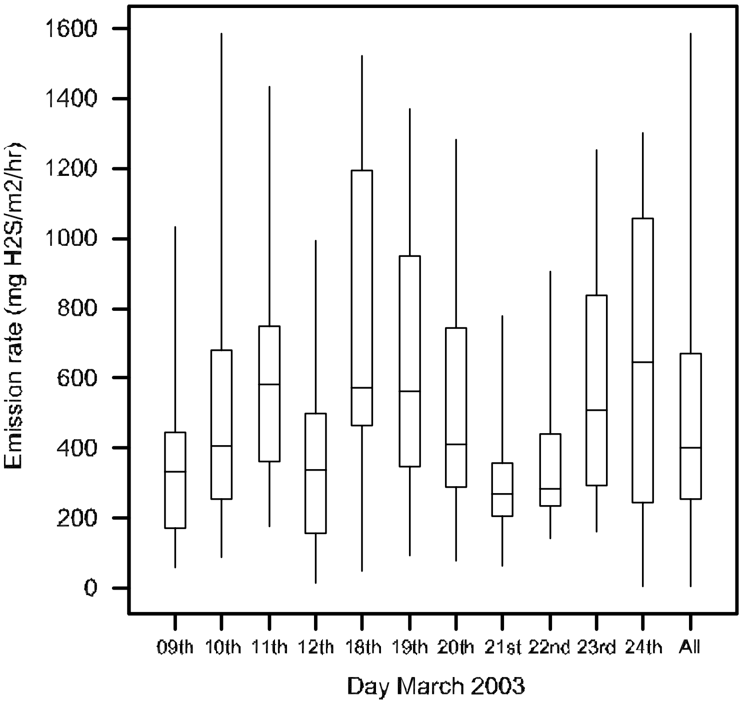

Figure 26: Summary of emission rates calculated using downwind method

Table 14: Summary of back calculated emission rates for Stage 3 Valley Beef

All Values (9 – 24 March 2003)	Emission rate (mg/m^2.hr)
Mean	486
Median	400
Standard Deviation	318
Minimum	7
Maximum	1587

The average emission rate for the period 9 –24 March 2004 was 486 mg/m^2.hr (median 400 mg/m^2.hr). The average emission for Stage 2 for the same source was 522 mg/m^2.hr (median 500 mg/m^2.hr). An analysis of variance was undertaken on the data in Figure 26 and showed a significant difference for both time and date for the dataset, indicating that both time and date were important with respect to emission rates. Obviously the variation by time and date is linked to variation in meteorological conditions. The median value for each sampling day (horizontal line within the box in Figure 26) indicates that some days had higher emission rates than other days, but given the variation shown from the box plots, the median emission rates suggest that the emission rates were not necessarily different (Moore and McCabe 1993).

Flux chamber

Prior to sampling from the exhaust air stream, the sensor in the Jerome meter was regenerated. When operating the Jerome meter, a series of bars are evident on the display screen indicating the degree of saturation of the sensor. There was concern because the display indicated that the sensor was becoming overloaded. As a result, the ambient air upwind of the site was also analysed every few minutes to act as a reference. This assumes that upwind concentrations are zero or emission rates would be adjusted accordingly. The measured values are shown in Figure 27.

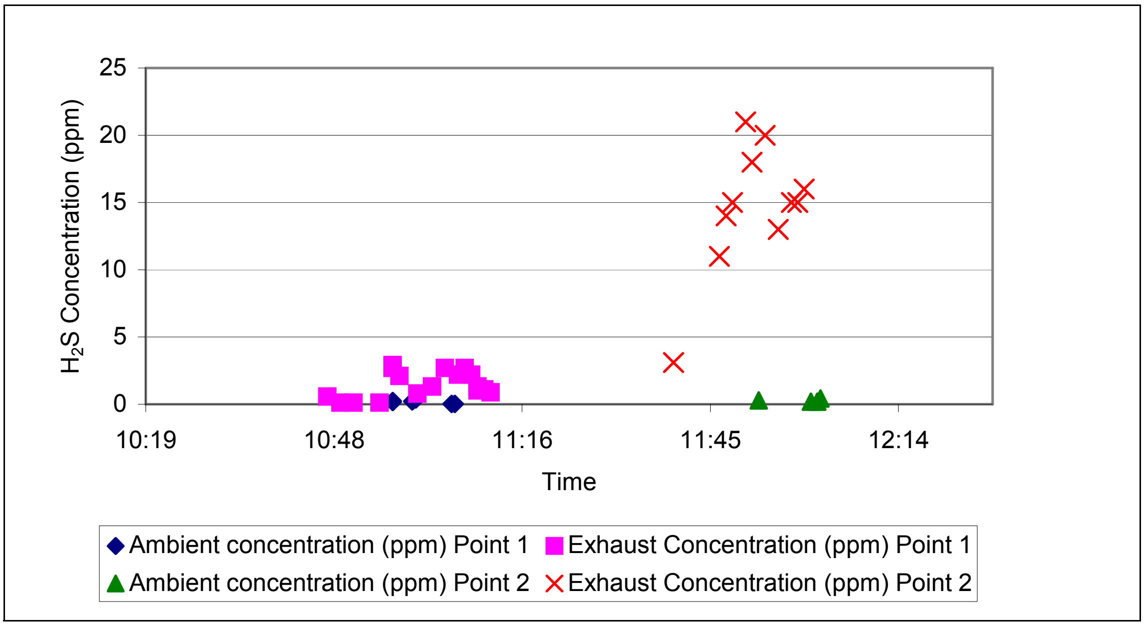

Figure 27: Gas concentration data

Concentrations measured in the exhaust of the flux chamber were significantly greater than those measured in ambient air (P<0.001, 95%). From this it was concluded that the unit was not becoming overloaded by the hydrogen sulphide gas in the exhaust, as the difference between the concentrations measured in the ambient air and the flux chamber remained relatively constant. The calculated emission rates are shown in Figure 28.

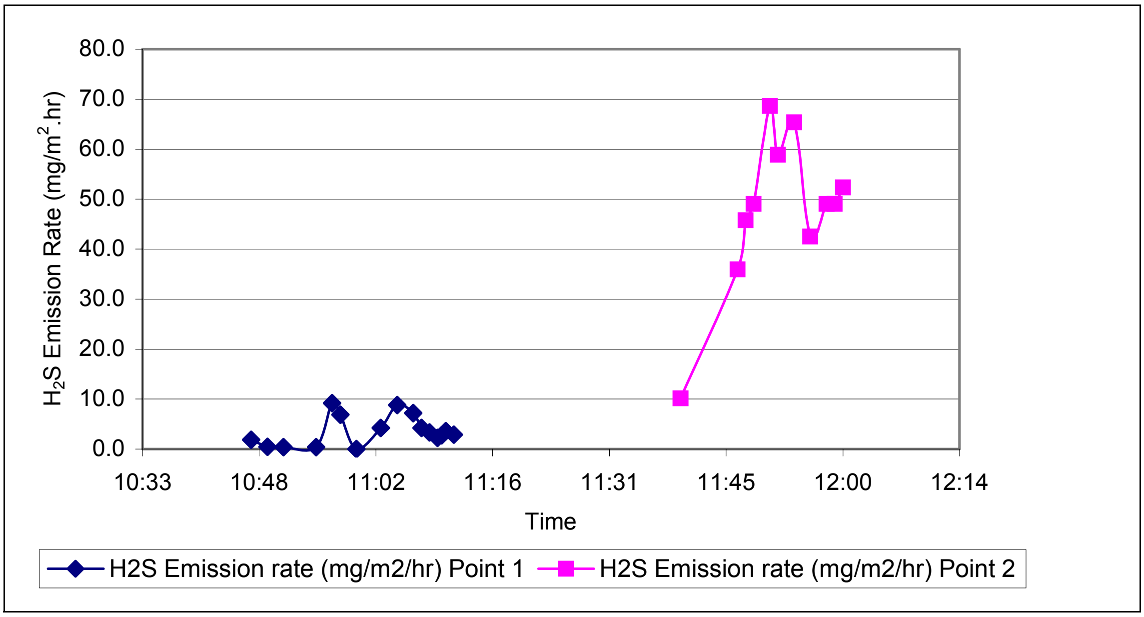

Figure 28: Emission rates calculated using flux chamber

The emission rates for points 1 and 2 are at least an order of magnitude higher than those measured using the flux chamber during Stage 1. The difference is most likely due to the poor seal between the flux chamber base and the cracked surface of the lagoon observed during Stage 1.

The data in Figure 28 shows that the rate of hydrogen sulphide emission varied over the sampling period and by sample point. This mirrors the findings from Stage 1. Again the data indicates that spatial variability is an issue for emission from abattoir lagoons, as the two flux chamber points were significantly different (P<0.001,95%). Spatial variability is taken into account by downwind methods, which assume a spatially averaged emission rate. This issue may, to a certain extent, explain the difference in the predicted emission rates as the limited footprint of “direct” methods could under or over predict emissions depending on the amount of spatial variability.

The issue of the representativeness of different emission rate measurement techniques for area sources has never been resolved. It is well known that certain techniques do not compare favourably with others. The information detailed above points towards underestimation of emissions by the flux chamber technique, thus it is unsuitable for sampling at abattoir ponds.

Effluent analysis

The effluent analysis results for the Valley Beef site are shown in Table 15.

Table 15: Effluent analysis results Valley Beef

Characteristic	Inlet	Outlet
Alkalinity (mg/L)	426	1140
COD (mg/L)	10600	749
Total Iron (mg/L)	1.86	1.52
pH	6.6	7.1
Sulphate (mg/L)	25	2
Sulphide (mg/L)	0.48	5.10
Total Solids (mg/L)	6720	1440
Temperature (° C)	45.0	35.7

Sunland Proteins

Hydrogen sulphide emissions

The site was visited on 30 March 2004. The Jerome meter and GC analysis methods were used, as the reliability of the wet chemistry method had not been confirmed. Velocity in the duct system was 3.9 m/s and varied by approximately 5% over a half hour period. The velocity of 3.9 m/s was approximately 1 m/s less than that measured previously. The results of the GC analysis are shown in Table 16.

Table 16: Results of GC analysis of samples from Sunland Proteins

Analyte	Lower reporting limit (ppm)	Bag 1: 11:48	Bag 2: 11:50	Bag 3: 11:56	Bag 4: 11:59	Bag 5: 12:07
Hydrogen sulphide	0.2	62.0	60.0	61.0	65.0	65.0
Carbonyl Sulphide	0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Methyl Mercaptan	0.2	1.7	1.7	1.7	1.6	1.5
Ethyl Mercaptan	0.2	0.5	0.3	0.3	0.2	0.2

The data in Table 16 shows that low concentrations (<3%) of other sulfur species were present in the gas stream. Again this indicates that interference by other sulfur compounds when using the Jerome meter would be negligible. The hydrogen sulphide concentrations in the ducting are shown in Figure 29. The emission rates are shown in Figure 30.

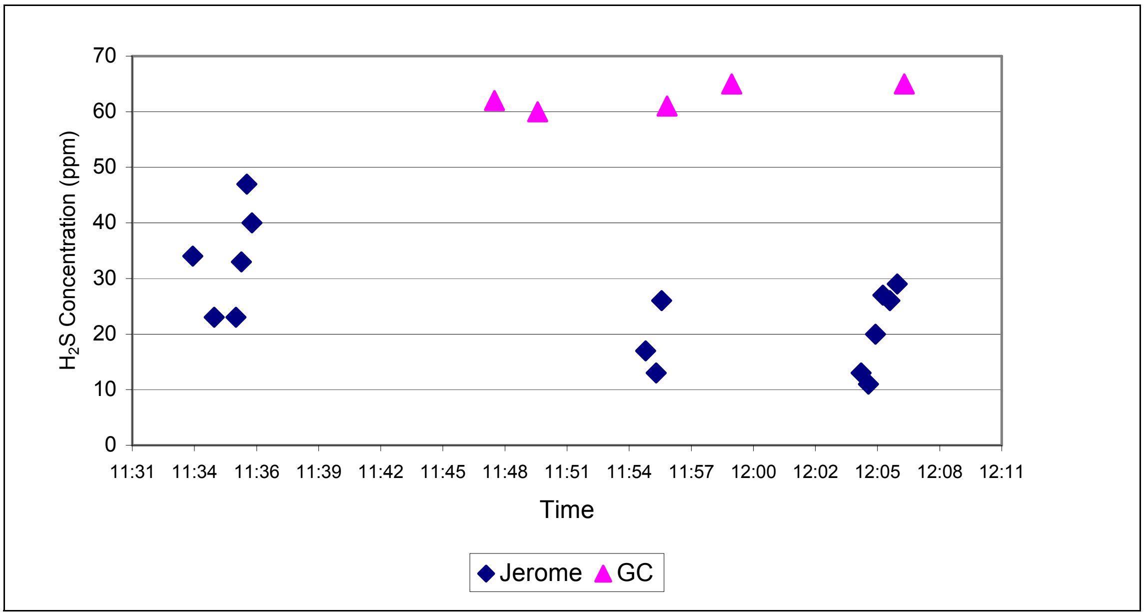

Figure 29: Hydrogen sulphide duct concentrations over time

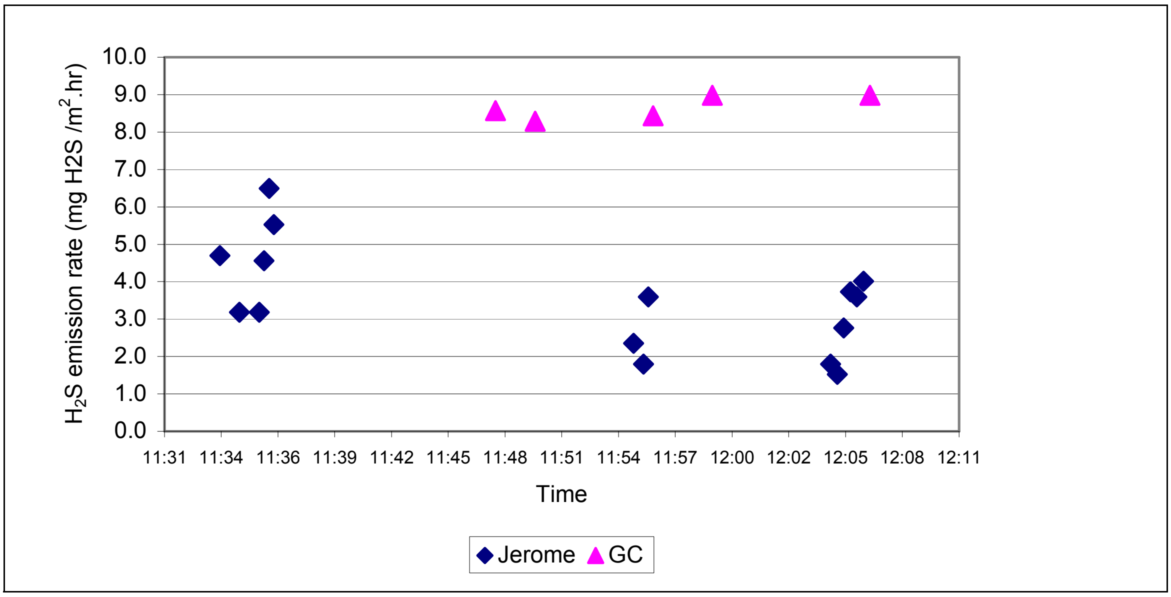

Figure 30: Emission rates for Sunland Proteins

The data in Figure 11 showed that the Odalog and Jerome meters gave similar responses up to 1.6 ppm of hydrogen sulphide. It has also been shown that the Jerome meter gives an accurate and reproducible reading for a standard concentration of 16 ppm. The Jerome meter may not produce reliable results at concentrations >16 ppm in the Sunland Proteins samples because that value exceeds the limits of quantification for the work in this project. The Jerome unit was near new and had been factory calibrated prior to use. Thus, the measurement range of up to 50 ppm quoted by Arizona Instruments (1997) would have been achievable by the unit.

The data collected during Stage 3 has again shown differences between two flux chamber sample points ($P<0.001$, 95%). This difference indicates spatial variability. The average hydrogen sulphide emission rate at the Sunland Proteins site 3.5 mg/m^2.hr using the Jerome meter or 8.7 mg/m^2.hr using the concentrations determined using the GC. An average emission rate of 486 mg/m^2.hr was determined for the Valley Beef site using the downwind method and an average emission rate of 26 mg/m^2.hr using the flux chamber for the same site.

The variation in predicted emission rates was significant for both on pond measurement (flux chamber $P<0.001$,95%) and the emissions predicted by the different analysis techniques at the same sample point (Sunland Proteins GC vs. Jerome meter $P<0.001$,95%). This research indicates that it is preferable to use a Jerome meter, Odalog unit or Gas Chromatography over wet chemistry methods.

The emission rates for the ponds at Sunland Proteins were on the lower range of those measured at the Valley Beef site. However, the emission rates for the Sunland Proteins site were similar to the emission rates determined using the flux chamber at Valley Beef. It is possible that the emissions were suppressed by covering the surface. Henry's law shows that emissions of hydrogen sulphide from wastewater will increase with temperature (Sattler and Devanathan 2004; Sattler and McDonald 2002). As the effluent inlet and outlet temperatures were essentially the same (Table 13,Table 17), it is unlikely that temperature is the dominant factor affecting the emissions. The difference between the sites is probably caused by a combination of the pond cover suppressing emissions and the lagoon effluent characteristics.

Effluent analysis

The effluent analysis results for Sunland Proteins are shown in Table 17.

Table 17: Effluent analysis results for Sunland Proteins

Characteristic	Inlet	Outlet
Alkalinity (mg/L)	754	1770
COD (mg/L)	3920	896
Total Iron (mg/L)	0.92	1.24
pH	7.3	7.3
Sulphate (mg/L)	39.4	75.8
Sulphide (mg/L)	2.0	3.51
Total Solids (mg/L)	3090	1110
Temperature (°C)	37.7	27.8

The pH of the effluent was different for the two lagoons. The major difference between the sites is that the Sunland Proteins lagoon is covered and has different effluent characteristics to Valley Beef. The measured pH for the sites is summarised in Table 18.

Table 18: Summary of effluent pH

	Valley Beef		Sunland Proteins	
	Inlet	Outlet	Inlet	Outlet
Stage 1	6.5	7.0	N/A	N/A
Stage 2	6.6	7.0	7.5	7.5
Stage 3	6.6	7.1	7.3	7.3

The data in Table 18 shows that:

- wastewater pH at Valley Beef increased (became more alkaline) with treatment;
- wastewater pH at Sunland Proteins remained constant with treatment; and
- the pH levels exiting the treatment lagoon at Valley Beef are lower than those exiting at Sunland Proteins.

Morel and Hering (1993) discussed the concentration of hydrogen sulphide in wastewater. They showed as the acidity of the wastewater increased (pH decreased), the concentration in the liquid phase increased and thus increasing hydrogen sulphide emission rate potential. Sattler and McDonald (2002) also concluded that increasing hydrogen sulphide concentrations in wastewater increased the emission of hydrogen sulphide to air provided the concentration in the air was not high enough to suppress the emissions. The relationship described by Morel and Hering (1993) is shown in Figure 31.

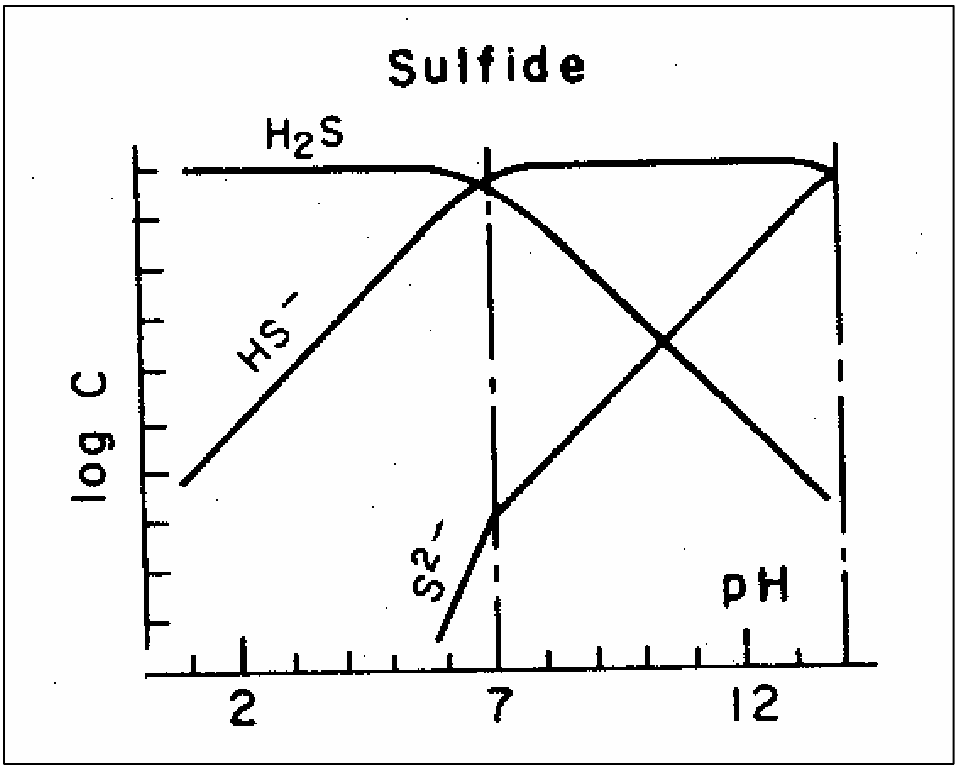

Figure 31: Log C-pH diagram for hydrogen sulphide (HS^- and S^{2-} ions) (Morel and Hering 1993)

Figure 31 shows that at a pH of 7 (Valley Beef) it would be expected that the liquid hydrogen sulphide concentration would be greater than that at a pH of between 7.3 and 7.5 (Sunland Proteins). This concentration difference may be enough to cause the higher emissions at Valley Beef compared to Sunland Proteins. As only two sites were studied in this project, future research may examine this relationship further.

Conclusions

The methods used to determine hydrogen sulphide concentration must be selected with care. The results indicate that:

1) Emission rates determined using a flux chamber emissions were significantly lower than those determined using the back calculation method;
2) The back calculation method is better for determining emissions than the flux chamber as it can encompass the entire source and it does not affect the emissions process;
3) Consideration should be given to limitations of the techniques used to measured hydrogen sulphide concentrations in air prior to future sampling; and
4) The difference in concentrations measured by the GC and Jerome meter techniques is insignificant compared to the difference between the emission rates calculated using the USEPA flux chamber or back calculation techniques.

Measurement of hydrogen sulphide concentrations

A significant issue identified in this research was that each technique used to analyse hydrogen sulphide provided a different concentration.

The Jerome meter reports total reduced sulfur as hydrogen sulphide (Rhoades *et al.* 2003). It has been shown that the low range Odalog unit and the Jerome meter give similar readings up to 1.6 ppm of hydrogen sulphide using a standard. Based on the work of Clanton and Schmidt (2000) it was concluded that the Jerome meter was suitable for measuring hydrogen sulphide where other sulphide species may be present in concentrations up to 2 ppm.

During Stage 3, the GC and Jerome meters gave different results at approximately 50 ppm and during Stage 2, the wet chemistry, Jerome meter and GC methods gave significantly different results. Gay *et al*. (2003) and Koelsch *et al*. (2004) examined hydrogen sulphide emissions from intensive animal operations in the United States using a Jerome meter. They reported hydrogen sulphide concentration as Total Reduced Sulfur (TRS). TRS was defined as the summation of all gaseous unoxidised sulfur compounds, among which hydrogen sulphide was the major constituent (Gay *et al.* 2003). Koelsch *et al*. (2004) found that a comparison of a Jerome meter against a bottled TRS regulatory standard produced high estimates if most of the TRS was in the form of hydrogen sulphide. The work of Clanton and Schmidt (2000) found a good correlation between GC and Jerome meter measured hydrogen sulphide concentrations. This was not observed during this project.

It is not known why the Jerome meter and GC methods gave different results in Stage 3. The GC method measured a much higher concentration than the Jerome meter. If interference by other sulfur compounds was the source, it would be expected, as detailed by Koelsch *et al*. (2004) that the Jerome meter would measure a higher concentration, however, This was not the case. Slight variations in emission with time may have caused the differences, however, the data in Figure 29 shows that when the Jerome meter measured 30 ppm the GC method reported values nearly double this. As both methods provided consistent results (a minimal amount of variation over time) at the end of this project, a firm conclusion has not been drawn.

Spatial variability

Spatial variability of emissions has been previously identified as a significant issue for piggery lagoons (Galvin *et al.* 2003; Galvin *et al.* 2004; Hudson *et al.* 2004). Spatial variability for abattoir lagoons was first identified during Stage 1. It was not identified in the downwind modelling as it is recognised that downwind methods account for spatial variability (Galvin *et al.* 2004; Harris *et al.* 1996; Sarkar and Hobbs, 2003).

Early in the project it was thought that the flux chamber was unable to obtain a good seal on the crust/chamber interface and leakage caused the emissions to vary due to varying flow rates. During Stage 3, the surface of the Valley Beef lagoon was smooth, due to recent rainfall, and two points were sampled using the flux chamber.

The results from Stage 3 again showed that spatial variability could be a significant issue when determining hydrogen sulphide emissions from abattoir treatment lagoons. At present, the extent of the variability is unknown, as a limited number of sample points were used. In addition to the number of sample points, the surface crust makes it difficult to sample from the points toward the middle of the lagoon using a direct method without a large truck mounted crane or cableway system.

Influence of COD and BOD loading on emissions

The influence of BOD or COD loadings on the amount of hydrogen sulphide generated by a treatment system is important. It is proposed that the percentage of COD removed by the system is a good indicator of the potential to emit hydrogen sulphide. The BOD and COD loadings per hectare per day for the two sites are shown in Table 19. The data for BOD loading and the conversion factor were supplied by Dr Mike Johns.

Table 19: BOD and COD loadings

Site	Kg BOD/ha.day	Factor	Kg COD/ha.day
Valley Beef	10,000	2	20,000
Sunland Proteins	2,500	2.5	6,250

The effluent treatment efficiency and emission rates are summarised in Table 20

Table 20: Summary of emission rates and effluent data

	H2S emission rate (mg/m2.hr)	% COD Removed	BOD loading (kg /ha.day)
Sunland Proteins stage 2	23	67	2500
Sunland Proteins stage 3	9	77	2500
Valley Beef stage 2	486	80	10000
Valley Beef stage 3	522	93	10000

The data in Table 20 was used to plot emission rate versus COD removed and emission rate vs. BOD loading. These are shown below as Figure 32 and Figure 33 respectively.

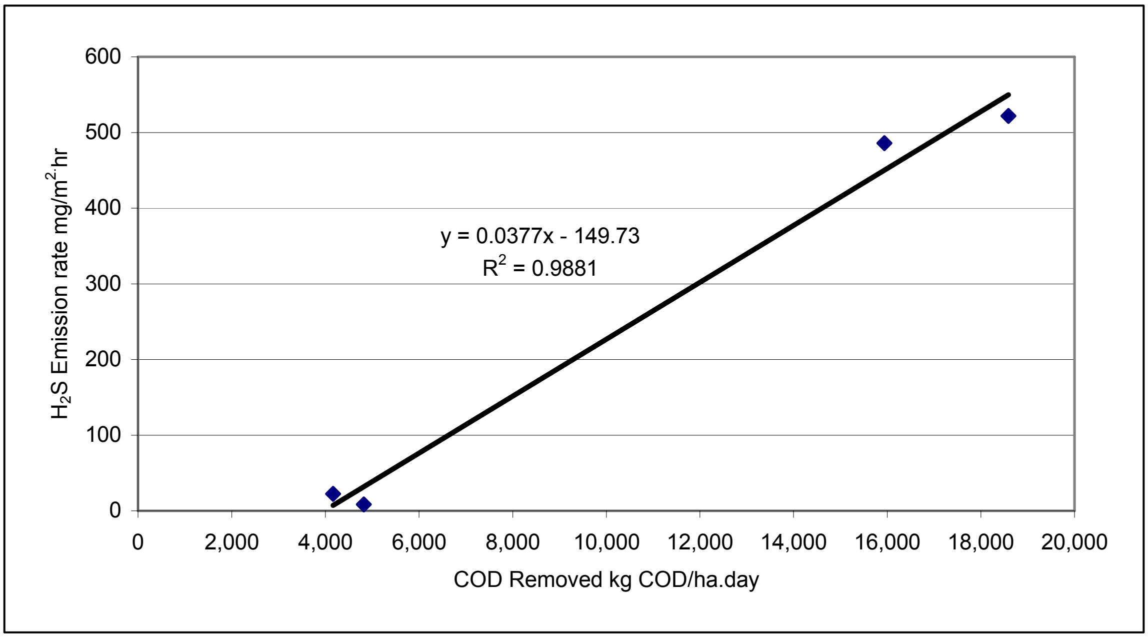

Figure 32: Emission rate as a function of COD removed

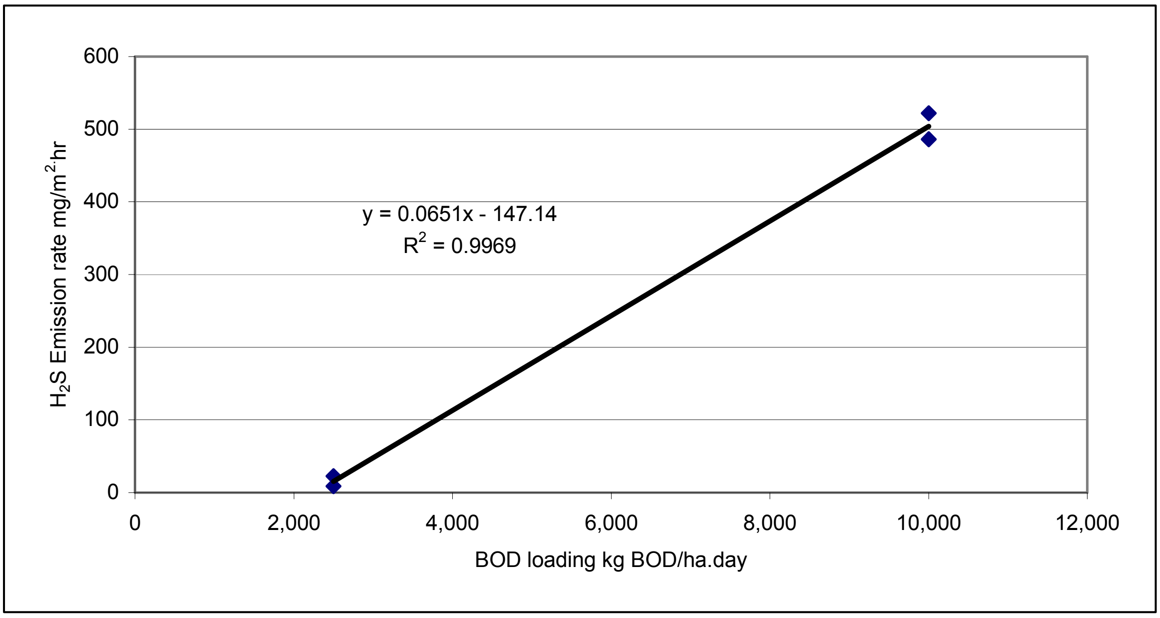

Figure 33: Emission rate as a function of BOD loading

Whilst the data in the figures shows a high correlation (R^2), this was expected due to a limited number of data points. The data, however, does indicate that the emission rates vary with loading rate. As there are only two pairs of data, additional data sets would be required to enable identification/confirmation of any trends. The uncertainties with respect to the determination of a "true" hydrogen sulphide concentration add another level of complexity to this issue.

Emission rate per square metre per year

The emission rate of hydrogen sulphide per square meter is shown in Table 21.

Table 21: Hydrogen sulphide emission rate per square meter

Site and Visit	Median emission rate (kg/m^2.year)	Average emission rate (kg/m^2.year)	Standard deviation
Sunland Proteins Stage 2	0.2	0.2	±0.02
Valley Beef Stage 2	4.4	4.6	±2.30
Sunland Proteins Stage 3	0.1	0.1	±0.003
Valley Beef Stage 3	3.5	4.3	±2.80

Emission rate per HSCW

The average emission rate from the Valley Beef lagoon was approximately 504 mg/m^2.hr. The average emission rate from the Sunland Proteins site was 16 mg/m^2.hr. No HSCW data was available for Sunland Proteins however the Valley Beef HSCW data from January 2003 till April 2004 was 36719 Tons. Based on this the emission of 18428 kg/year of hydrogen sulphide was calculated using the data from the downwind method. Using the alternate flux chamber data, 1842 kg/year of hydrogen sulphide was calculated for Stage 3.

The emission rate per ton of HSCW per year using the downwind method is 0.5 kg hydrogen sulphide per ton of HSCW or 0.05 kg per ton of HSCW using the flux chamber data.

Success in meeting objectives

The project objectives of this research previously listed covered four themes: determining the most suitable methods for quantifying hydrogen sulphide emission rates from anaerobic lagoons, identification of sampling sites, conducting a thorough plan of research to determine hydrogen sulphide emission rates and to develop industry specific median emission rates. Prior to undertaking sampling a number of sites were identified as suitable for the project. Unfortunately only two sites were used, as a third site could not be found prior to commencement of the project.

A thorough review of methods used to determine hydrogen sulphide emission rates from area sources was undertaken prior to the project proposal being submitted. From this a number of “best bet” methods were selected for further assessment during stage 1 of the project. Stage 1 highlighted that emission rates derived from back calculation were significantly higher than those calculated during the USEPA flux chamber irrespective of hydrogen sulphide analysis method. Differences between methods used to measure hydrogen sulphide concentrations were observed but were insignificant compared to the difference between emission rates derived from the downwind and flux chamber methods.

Over the entire sampling period, a number of techniques were trialled with respect to measuring hydrogen sulphide concentrations for incorporation with area source emission rate estimation methods. The results showed that the USEPA flux chamber and a Gaussian back calculation method generated significantly different emission rates using an identical hydrogen sulphide measurement technique. The results also showed that different hydrogen sulphide measurement techniques provided different hydrogen sulphide concentrations when taken at a single source. Overall, it was found that for uncovered ponds, the use of back calculation or a UNSW wind tunnel were preferred for area source emission rate measurement.

The primary objective of the project w2as to determine industry specific median emission factors and ranges. These were detailed in Table 1 above for lagoons with different loading rates and treatment efficiencies.

Impact on meat and livestock industry

The emission of hydrogen sulphide (H_2S) from anaerobic lagoons is a significant issue for the meat industry due to increased community expectations and reporting requirements. Whilst numerous studies have examined hydrogen sulphide emissions from lagoons treating animal wastes (e.g. Clanton and Schmidt (2000), Chen and Parkhurst (1997), Jacobson *et al*. (1997), Bicudo *et al*. (2001) and Zahn *et al*. (2002)) no work has been undertaken on Australian meat industry operations. A search of over 1700 international and Australian journals did not find any articles relating to hydrogen sulphide emissions from abattoir lagoons.

Increased community expectations and regulatory reporting requirements in combination with a lack of data hampers effective management of hydrogen sulphide emissions from the meat industry in Australia. The emission rates presented in this report will assist processors and the community by having:

- hydrogen sulphide emission rates for anaerobic systems;
- hydrogen sulphide emission factors for NPI reporting;
- knowledge which can be translated into the design of processes capturing anaerobic gases from anaerobic ponds; and
- information that can be used to determine ways to reduce hydrogen sulphide emissions from the meat industry.

Conclusions

Rates of emission of hydrogen sulphide from the Valley Beef lagoon and Sunland proteins were 504 $mg/m^2.hr$ and 16 $mg/m^2.hr$ respectively.

This project has undertaken work in a previously unpublished area and inroads have been made into the measurement of hydrogen sulphide emission rates from abattoir lagoons. However, a number of issues have been identified. These include:

1) Flux chambers are not suitable for measuring emissions from anaerobic lagoons, neither practically nor scientifically;
2) Emission of hydrogen sulphide varies across the surface of a lagoon;
3) Emission rates and air flow rates for the covered lagoon varied with time; and
4) Hydrogen sulphide measurement techniques reported different concentrations from similar samples.

At the end of the project, significant progress has been made, however, the issue of relating management or other practices to emission rates has not been quantified. The data, however, gives a good indication of the amount of hydrogen sulphide emitted from abattoir treatment lagoons.

Recommendations

It is recommended that future abattoir lagoon design be undertaken as to:

- maximise depth and thus treatment volume to decrease loading rate; and
- minimise surface area to reduce the emitting area of the ponds.

In addition a number of research themes have arisen from this project. These include:

- Undertaking a definitive comparison of hydrogen sulphide analysis techniques for a range of sources;
- Improving the understanding of the effect of lagoon design and management on hydrogen sulphide emissions;
- Undertaking medium to long term, continuous monitoring at a covered or uncovered lagoon to determine the extent of factors including diurnal changes and variation in effluent characteristics on hydrogen sulphide emission rates; and
- Investigation of techniques for reducing hydrogen sulphide emissions, eg. Use permeable or impermeable covers.

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