



# Low Cost Options for Reducing Effluent Pond Methane

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## **Executive Summary**

## What is the Report about?

Technology is available for the mitigation of pond methane emissions through biogas capture using impermeable covers and energy recovery. The high capital cost has limited the application of this technology from mid to large sized pig farms. This report reviews the current understanding and advances in low cost options for pond methane reduction that may be economically attractive to the smaller farm systems. Promising mitigation options will be identified for further research and assessment.

#### Who is the Report Targeted at?

This report has been developed for Australian Pork Limited. Dissemination of the results to secondary target audiences (i.e. pork producers or the general public) will be at the discretion of the funding body.

#### Background

The Australian pork industry operates a variety of intensive piggery farming systems which include the conventional shed, deep litter, outdoor rotational and outdoor feedlot piggeries. This report focuses on the conventional flushing system that usually incorporates an anaerobic pond in the effluent pond treatment system.

The anaerobic pond is a significant source of methane in the piggery effluent treatment process. Methods to reduce pond methane emissions including reductions in the volatile solids load, diet modification, covering the pond and establishing a pink pond microbial environment are reviewed.

A wide variety of permeable pond covers have been trialled to determine the performance of the cover at mitigating pond odour, and ammonia emissions and to a lesser extent pond methane and nitrous oxide emissions. This review assembles the published mitigation performance information for the range of cover systems trialled and determines which cover systems show potential for further research.

Methanotrophic microbes consume methane gas and this group of naturally occurring microbes can exist in pond crusts or artificially formed pond covers. The performance of the pond cover that supports a colony of methanotrophic microbes at reducing methane emissions has been reviewed.

Pink and purple ponds occur when the sulphate reducing microbial population become dominant in the anaerobic pond and the pond biochemistry alters. A literature search was undertaken to determine if there are any results which suggest that this type of pond biochemistry can result in decreased methane emissions.

## Aims/Objectives

The project aimed to search and identify potential lower cost pond methane gas emission mitigation strategies. For the more promising strategies, the possible effects of shifting the burden of gas emissions to a different position in the waste handling process were reviewed.

The project considered alternative methods of reducing pond methane gas emissions by modifying current farm management practises, such as feed methods and diet composition.

The project investigated the known reported performance of phototrophic microbes and purple pond environments to determine if GHG mitigation has been investigated or quantified.

## **Methods Used**

The project conducted a comprehensive literature review to investigate the reported tests and trials of permeable pond covers exhibiting methane mitigating performance and phototrophic microbes.

Estimates were made based upon DCC methodology to quantify the expected reductions in pond methane emissions by modifications to pig farm management.

## **Results/Key Findings**

Small but significant reductions in pond methane emissions can be achieved by modifications to feed diet composition and feeding system technology.

A significant reduction in the pond methane emissions can be achieved by implementing solids separation technology. The removal of 25% of solids before entering the pond will reduce pond methane emission by 25%, reducing overall manure emissions by 23%. The separated solids would require good compost management to avoid additional GHG emissions occurring from the wet solids produced by the solids separator. The expected reductions are based upon calculated estimates. The overall position of greenhouse gas emissions for the effluent system using solid separation technology requires confirmation by further research.

Based on the available literature on methane mitigation performance of permeable pond covers, this survey demonstrates that a significant level of investigative work has been undertaken, but in many cases the results vary widely and cast doubt on the reliability of the covers' performance. Part of the reason is the difficulty in performing trials on site and obtaining scientifically repeatable results. The majority of the investigations have been undertaken at the pilot scale and focused on measuring the input cause and output results. A better understanding of the biochemical mechanisms is required.

Formation of a natural pond crust on an anaerobic pond receiving piggery effluent system has been demonstrated to reduce methane gas emissions at the pilot plant scale. A pilot scale study by Petersen (2005) presented evidence that methanotrophic activity occurs in naturally forming crusts. Sommer (2000) reports a methane emissions from an uncovered pond are 38% higher than a pond with a natural crust. No evidence of nitrous oxide emissions were measured when the cover was wet, but nitrous oxide emissions occurred when the cover dried during the warmer summer period. Establishing a pond crust to mitigate GHG emissions is appealing as a low cost option, as the crust material can be formed through pond design and management rather than establishing an artificial cover. It has been observed during site visits to Australian piggeries that the crusts tend to thicken with time and often a steady state thickness is reached where thickening does not continue. Some thick crusts have been observed to crack open exposing the liquid slurry below which provides a direct path for methane emission from the slurry. The performance and buoyancy of a thick crust during very heavy rainfall events is unclear. Further research of pond crust performance for Australia's hot and dry conditions is required to determine the overall GHG performance and indentify how significant the nitrous oxide emissions may become. The research work should focus on the biological mechanisms occurring in the crust.

Laboratory scale experiments showed that expanded clay (LECA) pond covers decreased methane emissions between 9% and 16% and increased nitrous oxide emissions (Guarino et al. 2006). Expanded clay covers are durable but are expensive as the expanded clay balls were imported for the overseas trials. Thicker layers of LECA improved methane mitigation performance but establishing a thick layer on a pond may be difficult.

Scheutz et al. (2004) investigated the methane mitigating performance of combinations of composted material with sand or woodchips. The combination of compost and woodchips demonstrated the highest methane mitigating performance and a steady state methane oxidation rate 161 g.m<sup>2</sup>/day was reported. An investigation of the methane mitigating performance of a pond cover formed from spent composted material supported by a permeable cover may provide a workable low cost option for pond methane mitigation. Composted material provides little available energy for other forms of microbes to become dominant, hence methanotrophic microbes are favoured.

The methane mitigation performance of straw covers is unclear with some studies suggesting a significant methane reduction (Peterson et al. 2004) and other studies showing significant increases (Cizek et al. 2003). Thicker straw covers performed better than thin covers (Guarino et al. 2006) and straw covers tended to increase nitrous oxide emissions (Sommer et al. 2000). Further research is required to scientifically confirm the methane mitigation performance of straw covers and clarify the underlying biochemical mechanism occurring in the cover. The straw cover appears to increase nitrous oxide emissions in a similar manner to the naturally formed crust

(Sommer et al. 2000), however reliable data is scarce. Straw is readily available but to produce a uniform cover thickness over a pond is challenging and preventing the straw from sinking is a problem. The lack of long term durability and disposal of the straw cover must be considered. If a reliable methane mitigating performance of the straw cover can be determined then the viability of a straw cover as a low cost methane mitigating option can be assessed.

Synthetic covers such as BioCap and organic woodchip covers show promise and should be investigated further to provide rigorous and repeatable scientific data to determine GHG mitigation performance.

There is a knowledge gap in the biochemical processes occurring in permeable covers. Further research is required to better understand the biological and mass transfer mechanisms involved to identify optimum specifications for permeable covers.

The microbial environment that exists in a purple pond environment can convert carbon directly to carbon dioxide instead of producing methane. The effects on nitrous oxide emissions and subsequent GHG emissions produced during land application are not reported. There is little reported research work available. Further research to understand the biochemistry involved and how to manage the biochemical system may lead to a workable GHG mitigation process.

#### Recommendations

Reductions in pond methane emissions are achievable from changes in feed diet composition and feeding system technology. It is recommended that these suggestions should form a part of good piggery management practise.

Significant reductions in the pond methane emissions can be achieved by implementing solids separation technology. However, the overall greenhouse gas emission position requires confirmation by research.

Permeable pond covers including naturally formed crusts, spent compost covers with a permeable supporting cover, expanded clay, synthetic covers such as BioCap and wood chip covers show promise at reducing pond methane emissions. The reported results are widely variable. It is recommended that more rigorous investigation is undertaken to provide confidence that a covers methane mitigation performance is reliable.

The reported methane mitigating performance for straw covers vary widely. If a straw cover is to be considered, then further work is required to verify the methane mitigating performance. The challenges of establishing a uniform cover thickness, lack of cover durability and cover disposal must be considered.

Little research has been reported for purple pond phototrophic microbes and GHG mitigation performance. Further research is recommended to improve our understanding of the biochemistry involved in this option as it may hold the potential to achieve significant pond methane reductions by converting carbon directly to carbon dioxide simply by changing the way anaerobic ponds are managed. Further investigation of the addition of gypsum to pig slurry and the effects on methane and nitrous oxide emissions may also provide a low cost GHG mitigation strategy.

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## I. Introduction

The intensive animal farming industry adds a significant contribution towards Australia's greenhouse gas (GHG) emissions. For the majority of pig farms in Australia, the treatment of the animal waste stream involves digestion of the organic component of the waste stream in an anaerobic lagoon. This process is regarded as a low cost and successful method of handling the large volumes of piggery waste produced in these facilities.

A well designed and operated anaerobic pond will reduce the organic load of the waste stream, but can also produce significant quantities of greenhouse gases (GHG) in the form of methane. As a result of climate change science and the known effects of GHG emissions on the world's climate, there is increasing pressure to reduce the level of GHG emissions from all sources. The Australian agricultural industry is exploring options available to improve GHG emission performance and is demonstrating commitment to this objective by conducting research projects, such as this.

There are two pathways for pork producers to follow to address pond methane emissions. The first low cost step is mitigation where pond methane emissions are reduced by some mechanism without energy recovery. The second step is utilisation where pond methane is captured and used for energy recovery. The implementation of methane utilisation can be expected to be more expensive than mitigation. Utilisation technology is now well established to capture methane from a lagoon surface using an impermeable pond cover and transform the gas into a renewable energy source, such as heat and electricity. The high capital cost of this technological solution means that it is generally only economically viable for the medium to large pig farming operations. There is a need to find low cost mitigation options to reduce GHG emissions from lagoons that can be successfully implemented by the smaller farm operations.

The objective of this project is to conduct a comprehensive literature search to identify potential lower cost pond methane gas emission mitigation strategies. For the more promising strategies, the possible effects of shifting the burden of gas emissions to a different position in the waste handling process will be reviewed.

The project will also consider alternative methods of reducing pond methane gas emissions by modifying current farm management practises, such as feed methods and diet composition.

## 2. Background on Pond Emissions

## 2.1. Current Industry Practice

The conventional method of intensive pig farming in Australia is to house pigs in sheds. The sheds are often separated into breeding sheds where boars, gilts and gestating sows are housed and farrowing sheds where sows give birth and suckle the young pigs until they reach weaning age. The weaner pigs are then moved to a grower shed and finishing shed.

A pig farm can be a farrow to finish piggery or specialise in pig breeding, weaners, growers and finishers or a combination of these.

## 2.1.1. Conventional Piggery

What is termed a 'Conventional Piggery' usually has large sheds with underfloor drainage such as slatted floors and channels. The waste stream produced by pigs includes faeces, urine, and water and spilt food which accumulates in the underground drainage channels. A well managed piggery would flush the drains and channels regularly to remove the waste stream from the sheds.

Medium to large conventional piggery operations have rows of sheds. The drainage system from each shed is typically collected in a common sump, which is pumped out to the primary effluent pond, or the shed drains flow by gravity to the primary effluent pond. Some piggeries utilise solids separators to remove a proportion of the volatile solids (VS) from the stream supplied to the anaerobic pond. This reduces the pond loading but also creates an additional solids handling requirement, which may be another source of odour and GHG emissions unless managed properly.

Most primary effluent ponds are designed to operate under anaerobic conditions. A well designed anaerobic pond provides enough volume to support a colony of anaerobic microbes, which digests a significant proportion of the VS and this improves the quality of the liquid effluent stream and produces a stable organic sludge. Large quantities of methane and carbon dioxide gas are emitted from the pond surface.

The primary effluent pond is sometimes followed by a facultative pond, which provides a mixture of anaerobic (oxygen starved) treatment at lower levels and aerobic (oxygen rich) treatment nearer to the surface of the pond. A range of microbial processes in the facultative pond further breakdown the remaining organic material. This further improves the liquid effluent stability and reduces odour emissions. Treated effluent can be used as a source of flushing water to clean the drains in conventional sheds or irrigated onto farm land.

Aerobic ponds can be used to further polish the liquid effluent. Aerobic ponds are either shallow with a large surface area to enhance the natural movement of oxygen into the liquid phase or are

equipped with aerators to mechanically force air containing oxygen into the liquid phase. The aerobic process does not produce methane but converts organic material into carbon dioxide.

## 2.1.2 Waste Stream Characterisation to Anaerobic Ponds

The composition of effluent from a conventional piggery can vary widely depending upon the design and management strategy employed to run the piggery and the feed composition. For the conventional shed the quality and quantity of flushing water will have an impact on the waste stream characterisation. Table I shows typical manure characterisation data sourced from American piggeries. There is little published Australian data on the characteristics of raw piggery effluent ex-shed.

Component	Expressed as	Flushed	Expressed as
	% or ppm of	From Shed	mg/L
	wet material		
Moisture	%	<b>98</b> ª	
Total Solids	%	<b>2</b> <sup>a</sup>	20,000
Volatile Solids	%	<b>I.6</b> <sup>b</sup>	16,000
Total Kjeldahl Nitrogen	%	<b>0.20</b> <sup>a</sup>	2000
Ammonia-N	%	0.14ª	I 400
Phosphorus	%	<b>0.07</b> <sup>a</sup>	700
Potassium	%	0.17ª	1700
Calcium	%	<b>0.04</b> <sup>a</sup>	400
Sodium	ррт	300ª	300
Magnesium	ррт	<b>290</b> <sup>a</sup>	290
Sulphur	ррт	155ª	155
Zinc	ррт	33.6ª	33.6
Manganese	ррт	<b>14.4</b> ª	14.4
Copper	ррт	31.2ª	31.2

#### Table 1: Typical conventional shed manure characterisation

Source: a) ASAE (2005) b) FSA Consulting estimate

## 2.2. Methanogenesis

## 2.2.1. The Anaerobic Process

Anaerobic digestion is a process where several different populations of microbes convert organic material into methane, carbon dioxide and water. The process will begin to occur when there is little or no available oxygen which would otherwise support an aerobic process of organic material conversion.

For waste streams with high concentrations of degradable organic material, large quantities of oxygen are required to keep the aerobic process functioning at high rates. A lack of oxygen will slow the process down or stop the process and allow the anaerobic microbes to flourish. The

anaerobic digestion process can very efficiently degrade organic material given the right conditions are maintained for the growth and support of the microbial colonies.

Figure I shows an overview of the multistep anaerobic process (Pavlostathis & Giraldo-Gomez 1991).



Figure 1: Anaerobic process

## 2.2.1.1. Hydrolysis, Fermentation and Acidogenesis

Complex organic molecules such as fats and lipids, proteins and carbohydrates, are broken down into smaller and simpler molecules through a process of hydrolysis and acidogenesis.

Several species of microbes produce a range of hydrolytic enzymes that breakdown complex organic molecules. Carbohydrates are converted to simple sugars, proteins are converted to amino acids and lipids are converted to fatty acids. The microbes then successively metabolise the simpler molecules by fermentation to form volatile fatty acids (VFA's) including acetate, propionate, butyrate, lactate and alcohol such as ethanol, carbon dioxide and hydrogen.

The hydrolytic activity of each microbial enzyme is of paramount importance in that polymer hydrolysis may become the rate limiting step and subsequent conversion of that material is inhibited (Miyamoto 1997). If materials that are difficult to digest are present in the feed stream, such as lignin, then undigested material will build up in the sludge and low level methane generation may continue as the difficult to digest material slowly breaks down.

## 2.2.1.2. Acetogenesis and Dehydrogenation

During the acidogenic step long chain fatty acids ( $C_4$  and above) are converted to acetate and hydrogen. In addition, approximately 20% of the acetate is produced by acidogenic fermentation of the sugars and amino acids.

#### 2.2.1.3. Methanogenesis

There are now more than 40 strains of methanogenic Achaea (single celled micro-organisms recently distinguished from bacteria) that have been identified and all produce methane in anaerobic digestion. Although acetate, hydrogen and carbon dioxide are the compounds available, other compounds such as formate, methanol, methylamines and carbon monoxide are also converted to methane (Miyamoto 1997).

Methane can be produced by two paths during this stage. Aceticlastic microbes are one of the slowest growing in the digestion process and produce the majority of the methane by consumption of acetic acid. The performance of these microbes is very sensitive to potential inhibitors including ammonia and a low pH. The digestive activity of these microbes essentially stops below pH 7. Methane is also produced by a different pathway by the action of hydrogenatrohic microbes which combine hydrogen and carbon dioxide.

### 2.2.1.4. Digestion Temperature

Biological methanogenesis has been reported to naturally occur at temperatures of 2°C in marine sediments and above 100°C in geothermal areas. There appears to be an upper temperature limit of 60°C above which there is a rapid reduction in microbial activity (Chynoweth et al. 1998). Anaerobic pond temperatures are typically below 30°C with covered ponds achieving higher temperatures than uncovered ponds due to the insulating effect of the cover. The rate of anaerobic digestion increases with increasing temperature and the ideal range is 30°C to 45°C (Kruger et al. 1995). Biogas plants which use tanks and reactors for digestion typically operate in the mesophilic temperature range 30°C-40°C or thermophilic range from 50°C-60°C. Moving the operation of a digester between mesophilic and thermophilic temperatures is not normally practiced as there is a point at approximately 39°C where microbial activity substantially drops off (Heubeck pers coms 2010).

A piggery effluent lagoon is a large body of liquid and the thermal mass of the pond reduces the influence of the daily and seasonal variations in surrounding ambient temperatures on pond

temperature. The effect of temperature variation on lagoon biogas emissions has been demonstrated during a study conducted in Kansas, United States of America (DeSutter & Ham 2005). The study showed a maximum biogas emission rate (19 mol biogas/m/day) was recorded in the centre of the pond during the period of highest ambient temperatures. During the same period, the emission rate at the edge of the pond was approximately 25% of the peak rate measured at the centre. About half of the total annual biogas produced from the pond during this investigation was recorded over 30 days during the warmest period.

Pond temperatures for covered ponds were measured at Bears Lagoon Piggery, Victoria (Birchall 2009). Pond temperatures were measured at 0.5 m, 1.5 m and 3.5 m depth under the pond cover through an emergency gas vent. Temperature was also measured in the discharge pit on the side of the pond. Temperatures recorded at depths of 0.5 m and 1.5 m was similar to the measurements in the discharge pit. Both pond and pit temperatures were between  $3^{\circ}$ C to  $5^{\circ}$ C warmer than ambient temperatures. The temperatures recorded at a depth of 3.5 m were lower than the surface temperatures during the summer period and generally higher going into the winter period. The ambient temperature ranged from 7°C to 24°C while the pond temperatures ranged from 11°C to 29°C.

During the cooler months, microbial activity in uncovered ponds is considerably reduced and the ponds will tend to function as storage and settling lagoons with little VS degradation occurring. Acid forming microbes are more tolerant to lower temperatures than the methane forming microbes. As the pond temperatures begin to increase with the changing season the microbiological activity resumes. The acidogenic microbes become active first and the formation of VFA's occurs reducing the pH of the pond. The methane producing microbes are slower growing and are also sensitive to reduced pH hence the conversion of VFA's to methane is delayed. During the spring start up period significant odour emissions can occur until the complete set of methanogenic microbes have established populations again (Kruger et al. 1995).

Potential methane mitigation strategies could be related to optimising biochemical pathways that favour phototrophic microbes rather than methanogenic microbes. Control of the rate of change of methane production reactions with temperature is different to that for the sulphate and iron reducing phototrophic microbes with which methanogens compete for degradable organic materials. For example, in soils the relative increase in production rate with a 10°C increase in temperature (the  $Q_{10}$  value) for methanogens is about 4.6 times in anaerobic conditions, while for sulphate reducers it is 1.6 and for iron reducers it is 2.4 (Van Bodegom & Stams 1999).

#### 2.2.1.5. pH and Ammonia Inhibition

The presence of ammonia in the effluent can lead to inhibition of the methanogenesis step of the anaerobic digestion process and this effect increases with increasing temperature. The anaerobic digestion process is very sensitive to the pH level. Ammonia is produced at increasing pH and above a pH of 7.5 the ammonium ion will react with a hydroxyl ion to form ammonia. However,

the increased presence of ammonia will to some extent balance the effect of reduced pH caused by production of acetic acid. At a pH below 6.5 to 7.0 the final step methanogenesis suffers; digestion slows to a stop and fermentation continues (Ponnamperuma 1972). The system enters an acid overload which is very difficult to recover from (Batestone 2009).

Fibrous materials such as straw and wood, which contain lignin and hemicellulose, are more difficult to breakdown than excreted organic waste. Low molecular sugars, VFA's and alcohols exhibit degradation as short as a few hours. Hemicellulose (leafy plant materials), fat and protein are degraded within a few days. The degradation of lignin (plant storks and wood) is hardly noticeable under anaerobic conditions and cellulose breakdown can take several weeks (Steffen et al. 1998).

The addition of spent deep litter bedding into the pond, or a straw cover that sinks into the pond will result in an additional organic load. The addition of this material will result in a reduction in available pond volume and an increase the effective pond loading. If the volume of this material is significant it may have to be physically removed from the pond to allow normal digestion of the piggery waste stream to continue.

Antibiotics and feed additives can impair the digestion process by interfering with the function of some species of microbes.

## 2.2.1.6. Total Solids Concentration

The typical solids concentration of raw piggery waste from a conventional operation is 0.5% to 2%. The method and volume of flushing water used to clean the sheds largely determines the waste stream concentration. Some farms use partially treated effluent as flushing water, which reduces the overall water use but can lead to struvite build up in pipe lines.

## 2.2.1.7. Volatile Solids and Pond Loading

Pond size selection is usually based upon the VS load produced by the piggery. A minimum treatment volume is determined plus an additional volume for sludge build up. The primary anaerobic pond volume can be split into two or more ponds operating in parallel to allow for the effluent treatment operation to continue while one pond is being de-sludged.

The design of the minimum treatment volume for anaerobic ponds has conventionally been based upon the Rational Design Standard (RDS) which determines a minimum volume through a combination of a pond loading rate (100 g VS/m<sup>3</sup>/day) and a climate based K factor. The RDS design results in larger ponds with sufficient volume to allow for longer intervals between desludging. More recently the trend has moved towards a pond volume design based upon higher VS loading rates which results in smaller ponds and encourages the formation of a surface crust to mitigate odour emissions. The underlying premise of the high rate design is good sludge

management to avoid pond odour emission problems and sludge spill over to the second pond. The National Environmental Guidelines for Piggeries (Tucker et al. 2010) suggests a maximum VS loading rate to match the regional variations in the Australian climate ranging from 450 g VS/m<sup>3</sup>/day for the cool climates to 750 g VS/m<sup>3</sup>/day for the hot climate regions.

Properly functioning anaerobic ponds can reduce the VS content of the effluent by up to 70%. The performance of the pond is measurable by determining the reduction in VS from pond inlet to outlet. When VS reduction falls below 50% or the VS content of the treated effluent exceeds 1% then the performance of the pond should be investigated and de-sludging should be considered along with factors that may interfere with the performance of the pond.

Large intermittent slug flows of effluent to the pond should be avoided. Well managed piggeries rotate the shed cleaning cycles on different days so that small loads of VS are flushed to the pond.

## 2.2.2. Sources of Methane

Methane gas is produced from the conventional piggery from four main areas, the animals during digestion, from the shed drains, from the anaerobic pond and during land application.

## 2.2.2.1. Enteric Methane

A significant level of research has focused on reducing methane emissions from ruminant animals, such as cattle and sheep due to the significant quantities of methane released. Pigs are monogastric animals and have a single chambered stomach system. Methane, hydrogen and carbon dioxide is produced by the fermentation of carbohydrates in the gut of the pig. The levels of methane released from pigs was measured during the growth period from 20 kg to 120 kg (Christensen & Thorbeka 1987). The majority of gas produced is excreted at flatus and a smaller quantity is absorbed into the blood stream and is excreted in expired air. The average quantity of methane measured per 20 kg to 25 kg animal was 1 L/day (0.66 g/day) and increased to 12 L/day (7.9 g/day) at 120 kg live weight. The quantity of daily enteric methane emissions from a 120 kg pig is approximately 5% of the enteric methane emission from a 450 kg mature male beef cow (IPCC 2006).

## 2.2.2.2. Shed Drains

Excreted solids, urine and spilt feed collects in the floor drains which if left undisturbed will become anoxic and hydrolyses of complex molecules will begin. VFA's, ammonia and other odour producing compounds are released from the drains and wet surfaces. Small amounts of methane can be released depending upon the intervals between flushing the waste to the ponds although little research has quantified this. An investigation has been undertaken in Europe where the slurry is stored under floor for long periods and cooling of the slurry was recommended as a means of methane emissions reduction (Sommer et al. 2004) (refer to section 2.1.5).

## 2.2.2.3. Pond Methane Emissions

The anaerobic pond can be visualised as having three zones. The heavier particles and the fixed solids such as ash will settle and accumulate in the sludge zone which forms a layer over the base of the pond and is largely inert. A lighter active sludge layer containing a high concentration of VS forms above the inert sludge layer. Above that a supernatant layer forms which is relatively low in suspended solids.

Chemical and biological reactions occur predominantly in the lighter sludge accumulation layer (Kruger et al. 1995). Organic material is broken down by a range of microbes to form VFA's, including acetic acid and under the correct conditions the digestion process continues to form carbon dioxide and methane gas. The carbon dioxide formed either escapes from the pond surface as a gas or is converted to alkaline bicarbonate which helps balance the acid produced to maintain a pond pH between 6.4 and 7.2 (Kruger et al. 1995). Each species of microbes has an optimum environment which includes preferred temperature, pH, salinity, dissolved oxygen levels and light.

The lower layers of the pond are lacking in oxygen and the anaerobic process dominates. Closer to the surface of the pond, oxygen from the air can diffuse into the surface liquid and support colonies of aerobic microbes. The facultative zone between contain microbes that can exist in an aerobic and anaerobic environment.

Figure 2 provides a general overview and diagram of the biological activity occurring in the anaerobic pond.



Key:  $H_{g}S = Hydrogen Sulphide, NO_{g} = Nilrate, SO_{4} = Sulphate, NH_{g} = Ammonia$ 

Figure 2: Anaerobic pond general overview

Source: Kruger et al. (1995).

Methane emissions (M) from pig manure were estimated by the DCC (2007) as follows:

## $M = VS \times Bo \times MCF \times p$

Where:

VS = Volatile solids production Bo = Emissions potential - 0.45 m<sup>3</sup> CH<sub>4</sub>/kg VS (IPCC 2006) MCF = Methane conversion factor (for lagoons = 90%, for 'dry lots' (assumed to cover deep litter systems) the value is 1.5%) P = Density of methane (0.662 kg/m<sup>3</sup>)

Based upon a VS load of 90 kg/yr, the quantity of pond methane emitted from pig manure is estimated to be 24.1 kg/yr per SPU.

The activity of methane producing microbes in anaerobic ponds and sludge characterisation was investigated to determine the uniformity of methane generation and sludge depth (Paing et al. 2000). The influent to the pond was reported as already in an anoxic condition based upon the measured negative redox potential, presence of VFA's, and low concentration of oxygen.

The sludge depth was measured at various points in the lagoon and a three dimensional plot of the sludge depth was produced, which showed the sludge depth was not homogeneous. The sludge depth varied from 0.6 m to 0.7 m at the pond inlet and reduced to 0.1 m to 0.2 m at the outlet. The character of sludge samples was measured and the average concentration of VFA's in the sludge was lower at the outlet to the pond. A mean methane generation rate of 2.9 mL/g of VS/day from pond sludge was measured and the methane production rate was found to be very uneven with an average of 25 L/m<sup>2</sup>/d. Figure 3 shows a plan view of the spatial distribution of VFA's and methane potential of sludge (Paing et al. 2000).



Source: Paing et al. (2000).

Figure 3: Spatial distribution of VFA's and methane emissions from anaerobic pond

The report found that the different stages of anaerobic digestion where spatially separated with acidogenesis occurring near the inlet and methanogenesis occurring nearer the pond outlet. It was suggested that the staged separation of the digestion process appeared to improve the efficiency of the process when compared to other anaerobic systems e.g. septic tanks.

## 2.2.2.4. Methane from Land Application

Where effluent is land applied, methane emissions peak soon after application then decline. Sherlock et al. (2002) investigated the GHG emission rates from land application of pig slurry. 'Methane emissions were highest immediately after application (39.6 g C/ha/h). Methane emissions then continued at a low rate for 7 days, presumably due to metabolism of VFA's in the anaerobic slurry treated soil. The net  $CH_4$  emission was 1052 g C/ha (0.08% of the carbon applied)'. It is likely that entrained methane produced in the pond will be lost soon after application.

## 2.2.3. Sources of Nitrous Oxide

Effluent from a conventional piggery comprises spilt food, faeces, urine and flushing water. The nitrogen content of the effluent is high and mainly in the form of organic nitrogen (urea and proteins). Over half of the nitrogen excreted is in the form of urea in urine and considerable quantities of nitrogen can be lost through volatilisation of urea in the form of ammonia gas (Kruger et al. 1995).

Macromolecules such as proteins are hydrolysed to simple nitrogen compounds such as amines and amino acids then to ammonium ions and ammonia through a process of aminisation and ammonification (Bolan et al. 2004). At a manure slurry pH greater than 7.5, ammonium ions  $(NH_4^+)$  are converted to ammonia gas  $(NH_3)$  and can be lost through volatilisation.

Other groups of microbes change ammonia to nitrite and then to nitrate through the multi-step aerobic process of nitrification. Nitrate is available for use by plants, or can be lost through leaching or immobilised or converted to nitrous oxide or nitrogen gas through a process of denitrification.

Denitrification is an anaerobic process and can only occurring when there is no oxygen or very low quantities of oxygen present. Denitrification requires a source of carbon as an electron donor, the presence of nitrite  $(NO_2^{-})$ , nitrate  $(NO_3^{-})$ , nitric oxide (NO), or nitrous oxide  $(N_2O)$ .

Nitrous oxide is an intermediate by-product of the denitrification process.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Nitrous oxide may also be produced during the nitrification process when oxygen supply is limited. A detailed investigation of nitrous oxide emissions in piggery production systems has been completed by (Redding 2009) and will not be covered here.

There is little published data on nitrous oxide emissions generated inside a piggery shed. Nitrous oxide emissions from an uncovered anaerobic pond are estimated as 0.1% and 0% of nitrogen to the pond (DCC 2007) and (IPCC 2006) respectively. Significant direct nitrous oxide emissions can occur when the treated effluent is applied to land. Indirect nitrous oxide emissions also occur through volatilisation of ammonia and nitrous oxide gases and subsequent re-deposition of these gases to soils and waters or through soil leaching and run off to water ways.

It has been estimated that covering an anaerobic storage pond increases the pond temperature and this results in an increase in pond methane production by 10%, a decrease in nitrous oxide emissions from the covered lagoon by 10% and an increase in nitrous oxide emissions from soils by an average 13% (Brink et al. 2000).

Establishing a permeable pond cover that provides an environment for methanotrophic microbes to consume methane produced by the pond may be an effective method of reducing pond methane emissions however, the effect on nitrous oxide emissions must also be considered to determine the overall position of GHG mitigation for the effluent treatment system.

The burden of GHG mitigation can easily be shifted by achieving moderate GHG reductions at the pond but increases in gas emissions during soil application, or via indirect ammonia volatilisation-related nitrous oxide emissions.

## 2.2.4. GHG Emissions Estimates

GHG emissions for a conventional piggery operating an uncovered anaerobic primary pond and from land application of treated effluent were calculated by Wiedemann et al. (2010) based upon DCC methodology (DCC 2007) and are estimated as follows:

•	Pond Methane	91%
•	Pond Nitrous Oxide	0.8%
•	Nitrous Oxide direct from land	5.1%
•	Nitrous Oxide indirect from land	3.4%

Pond methane emissions clearly form the most significant proportion of GHG emissions from the conventional piggery effluent management system.

## 3. Options for GHG Mitigation

## 3.1. Diet and Feed Wastage

A decrease in the level of protein and carbohydrate in the diet has been shown to decrease ammonia and methane emission from manure during storage. However, this is likely to be counterproductive to desirable animal weight gains. High and low energy feed levels where fed to grower pigs during the growth period from 20 kg to 120 kg (Christensen & Thorbeka 1987). On average low energy feed levels reduced methane excretion by 23% compared with high energy feed levels. When related to dry matter (DM) intake, however the pigs on a low energy feed level excreted 3.1 litres  $CH_4/kg$  dietary DM and pigs on a high energy feed level excreted 2.5 litres  $CH_4/kg$  dietary DM. The addition of polyunsaturated soya bean oil to the diet was found to reduce methane excretion by 26%.

Additives to the diet have different effects on microbial activity in the pond. The addition of copper and zinc to pig feed to determine the effect on pond microbial populations showed that copper resulted in a pond environment which was toxic to methane forming microbes, whereas zinc indicated a healthy microbial pond environment (J. E. Gilley 2000). Since both copper and zinc are potentially toxic trace elements in the environment both of these approaches appear to have considerable disadvantages since they will tend to accumulate in the pond sludge.

During pig feeding it is common that a percentage of food is wasted and finds its way into the effluent system. Using DCC (2007) methodology, it is estimated that a 1% decrease in feed wastage reduces the quantity of methane produced in the pond by 3.8%.

Improvements in feed techniques can lead to decreases in methane generation and savings in the costs of feed supply.

#### 3.2. Separation of Waste Streams

There is a wide range of solids separation equipment available to remove VS from the effluent stream before the anaerobic pond. The equipment includes perforated screens, presses, centrifuges, dissolved air flotation, chemical flocculation and dry scrapping.

Stationary perforated screens have been popular at piggeries as the maintenance requirement is relatively low and they are reasonably inexpensive. The solids removal efficiency is low and the screen produces a wet sludge. The sludge is difficult to effectively handle and cannot be easily composted. The VS rapidly begin to decompose and odour is generated during anaerobic conditions.

The range of separation technologies currently available for piggery waste has been reviewed and solids removal efficiency for screens and separators ranges from 10% to 30% (Tucker et al. 2010). Dissolved air flotation systems and tangential flow separators can achieve 50% to 70% efficiencies but have a high capital cost. A combined gravity settling basin and fan screw press system has been tested and achieved a solids removal efficiencies of 42% and 24% for TS and VS respectively (McGahan et al. 2002). The solids produced are expected to be dry, easily handled and readily compostable.

The removal of 25% of solids before entering the pond will reduce pond methane emissions by 25% reducing overall manure emissions by 23% based on DCC (2007) methodology.

To achieve an overall reduction in GHG emissions for farms using solids separation technology, the separated solids must be treated in an aerobic manner to avoid further methane production. One option for solids composting is to establish a dedicated area and placed the solids in windrows with good drainage. The windrows should be turned periodically to ensure aerobic conditions are maintained.

The research has not been done to confirm a reduction in overall methane emissions using separation technology and the expected reduction may just be an artefact of the DCC method. Therefore from an overall methane emission perspective it could rapidly change.

A Canadian study (Kebreab et al. 2006) of agricultural methane and nitrous oxide emissions reports the following: "The agricultural practice of solid-liquid separation has been to increase the ease of handling and transporting effluent and to reduce odour, but may also be used as a tactic to reduce GHG. Separated solids can be used in conjunction with anaerobic digestion for biogas production. Using only the solid portion of the manure for anaerobic digestion can increase the VS concentration of the substrate and allow for greater  $CH_4$  yield than from the whole manure (Moller et al. 2004). The more complete the transfer of VS from the liquid to the solid portion of the manure, the more  $CH_4$  can be produced. This technique is expensive and little research has been done to determine its practicality and economic efficiency for Canadian conditions."

Betora et al. (2008) investigated pig slurry treatments and the effects on  $N_2O$  and  $CO_2$  emissions after soil incorporation.

The treatment of manures may improve their agricultural value and environmental quality, for instance with regards to greenhouse gases mitigation and enhancement of carbon (C)sequestration. The present study verified whether different pig slurry treatments (i.e. solid/liquid separation and anaerobic digestion) changed slurry composition. The effect of the slurry composition on N<sub>2</sub>O and CO<sub>2</sub> emissions, denitrification and soil mineral nitrogen (N), after soil incorporation, was also examined during a 58-day mesocosm study. The treatments included nontreated pig slurry (NT), the solid fraction (SF), and the liquid fraction (LF) of pig slurry and the anaerobically digested liquid fraction (DG). Finally, a non-fertilized (N0) and a treatment with urea (UR) were also present. The N<sub>2</sub>O emissions measured represented 4.8%, 2.6%, 1.8%, 1.0% and 0.9% of N supplied with slurry/ fertilizer for NT, LF, DG, SF and UR, respectively. Cumulative CO<sub>2</sub> emissions ranged from 0.40 g CO<sub>2</sub>-C kg(-1) soil (0.38 Mg CO<sub>2</sub>-C ha(-1)) to 0.80 g CO<sub>2</sub>-C kg(-1) soil (0.75 Mg CO<sub>2</sub>N<sub>2</sub>O and CO<sub>2</sub> emission patterns as well as denitrification processes and nitrate availability. In particular, the solid fraction obtained after mechanical separation produced the most pronounced difference, while the liquid fraction and the anaerobically digested liquid fraction did not show significant difference with respect to the original slurry for any of the measured parameters. Combining data from the different fractions, the study showed that separation of slurry leads to reduced  $N_2O$  emissions, irrespective of whether the liquid fraction is digested or not. Furthermore, the results suggested that the default emission factor for N2O emissions inventory is too low for both the non-treated pig slurry and its liquid fraction (digested or not), and too high for the separated solid fraction and urea."

#### 3.3. Pre-Treatment of Waste Streams

Pig manure is largely a conglomeration of reasonably small particles and should allow for reasonably rapid hydrolysis, however there are cases where pre-treatment of the solids is required to enable the anaerobic process to become established. During a site visit to AJ Bush rendering plant it was observed that ultrasonic pre-treatment of the waste was required to allow the anaerobic process in the pond to commence. It has recently been reported that the inclusion of ultrasonic pre-treatment enabled the digestion process to handle the fat and oil from the rendering process which also resulted in an increase in biogas production (Lamb 2006).

Ultrasonic pre-treatment of the pig slurry can increase the solubilisation of organic material and improve the degradation efficiency of the aerobic or anaerobic digestion process. The effect of ultrasonic pre-treatment on soluble chemical oxygen demand and methane generation was evaluated for beef feedlot manure, dairy manure and pig manure (Wu-Haan et al. 2009). Two ultrasonic power levels and amplitude settings were trialled on the manures. The results for the pig slurry showed an increase in soluble chemical oxygen demand of 23% and an increase in

methane yield of 56%. The greatest methane yield achieved was 394 mL of  $CH_4/g$  of VS by using the highest power and longest treatment time, although this was also at the highest power requirement.

This type of waste stream pre-treatment improves the efficiency of the anaerobic process and increases the level of pond methane generated.

#### 3.4. Natural Organic Pond Crusts

The formation of a pond crust can occur naturally under the correct conditions and normally at high VS loading rates. The process behind crust formation is not well understood but a mechanism is suggested where a portion of the solids in suspension are collected on the surface through the action of gas bubbles rising through the liquid (Misselbrook et al. 2005). An alternative explanation for the accumulation of organic matter at the pond surface is related to the density difference between organic matter and water. If organic matter accumulates at the pond surface then a crust forms through the action of evaporation of liquid from the surface, and partial drying, and binding of the remaining solid particles. During pilot plant studies there were no crusts formed with total solids (TS) concentrations less than 1% (Misselbrook et al. 2005). Additional factors including temperature, wind speed, solar radiation and rainfall that influence surface drying appear to also be important. The study (on dairy effluent) reported that a robust crust only occurred after 250 mm of evaporation had occurred.

Misselbrook et al. (2005) suggests that the affect of a crust on slurry storage tanks is to provide a physical barrier between the liquid surface and air. This provides a barrier to reduce the gas transfer of oxygen from the air into the liquid surface, which supports anaerobic digestion, reduces pond odour and reduces ammonia emissions by 50%. The methane mitigating performance of methanotrophic microbes in the crust was not considered in this report.

The occurrence of methane oxidation in a naturally forming crust formed over cattle slurry was investigated and confirmed in a laboratory study (Petersen et al. 2005). Untreated cattle slurry naturally forms a surface crust. Samples of crust were collected at the end of a 140 day storage experiment and tested for methanotrophic activity. In this experiment, samples of artificially formed crusts over digested slurry were also collected. As a crust does not appear to form over digested slurry, a loosely packed layer of straw was established as an artificial crust. After a four day lag for the untreated slurry and seven to 10 day lag for digested slurry, all of the treatments demonstrated a reduction in methane gas content in the headspace above the crust. The reported methane oxidation rates ranged from 0.1 to 0.5 mg/kg organic matter/h. Partial drying of the crust increased the level of methane oxidation in some treatments. The moisture content, pH, electrical conductivity (EC), total ammoniacal nitrogen, nitrite, and nitrate of the crust were tested at different depths (for the naturally forming crusts). The pH ranged from 8.1 to 8.8 for all crusts.

There was a significant increase in the level of EC and mineral nitrogen for the digested slurry. This study presents direct evidence for methanotrophic activity in slurry storages. It was suggested that the presence of nitrite and nitrate provide evidence of nitrification in the surface crust although no firm conclusions are drawn.

The addition of a crust forming slurry to non crusting slurry was investigated in an attempt to stimulate crust formation (Mannebeck 1985). The addition of cattle slurry to non crusting slurry was investigated (Sommer et al. 2000) but the crust was found to crack and breakup within weeks. Gas was observed to be held under the crust and was released when the crust breaks up (Bicudo et al. 2001). This results in a delay in emissions rather than a reduction in emissions.

Sommer (2000) measured methane and nitrous oxide emissions from stored cattle slurry and fermented slurry. A 7 to 10 cm thick layer of crust naturally formed on the slurry. During this trial methane emissions from uncovered cattle slurry were compared to emissions from slurry covered with leca, straw or a natural crust. It is reported that methane emissions were 38% higher from the uncovered slurry compared to any of the covers tested. Individual results for each cover are presented in a graph which shows significant variation. No nitrous oxide emissions were reported during the autumn period where rain fall exceeded evaporation and the covers appeared saturated. In the summer period where the evaporation rate exceeded rainfall, significant levels of nitrous oxide emissions were measured of up to 25 mg  $N/m^2/h$  for the surface crust. Sommer (2000) suggests that the mechanism for nitrous oxide emissions is related to the crust drying and forming areas in the crust where oxygen can diffuse down into the crust and dissolved  $NH_4^+$  is drawn up into the crust and is then oxidised by nitrifying microbes in this oxic zone. In the lower anoxic zones denitrifying microbes can produce nitrous oxide. Sommer (2000) cites studies that suggest that the majority of nitrous oxide emitted is produced through nitrification. During periods of increased rainfall and crust moisture content, the concentration of  $NH_4^+$  in the cover is reduced and this is offered as the reason why no nitrous oxide emissions are detected.

## 3.5. Modified Manure Management

During a European study of cattle and pig manure handling system algorithms are developed which link carbon and nitrogen turnover and predict  $CH_4$  and  $N_2O$  emissions (Sommer et al. 2004). Pig slurry was stored in house for 15 days before being transported to an outside storage area. Two manure management processes were considered. The first was methane collection from the animal shed and manure store and nitrous oxide emissions from the manure store and field application. The second management system incorporated anaerobic digestion with methane collection for farm heating. The results from the simulations indicated that daily flushing of the cattle houses would reduce the total annual methane and nitrous oxide emissions by 35% ( $CO_2$ equivalent) and cooling of the pig slurry channels inside the sheds would reduce total annual methane and nitrous oxide emissions by 21% ( $CO_2$  equivalent). If manure is anaerobically digested prior to external manure storage, and the biogas that is produced is consumed, then the simulation predicts a 90% reduction in methane emissions from outside storage and greater than 50% reduction of nitrous oxide after spring field application.

If methane emissions from the shed are reduced by cooling the pig slurry then the level of pond emissions are likely to increase. Cooling of pig slurry could be part of an overall methane mitigation strategy if a pond methane sink can be established.

## 3.6. Impermeable Covers

Impermeable covers are fitted over an anaerobic lagoon to trap and prevent gas from escaping the enclosed space. A range of synthetic cover materials are available and can be fabricated from low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP) or polyester scrim reinforced polypropylene, XR-5 or similar (Craggs et al. 2008). The cover material must be robust to enable assembly and layout on site which may involve towing on and off the pond. The material should also be repairable on site, resistant to ultraviolet light, durable and be leak free over a long service life.

The collection of methane gas from an effluent pond fitted with an impermeable cover is an established practice in Europe, with several benefits, including:

- reduction in the methane emissions
- reduction of odour generation
- recovery of energy from gas burning
- production of a stable, valuable soil additive (Kruger et al. 1995).

A review of a anaerobic pond which is specifically designed to be covered for GHG gas capture is provided by the National Institute of Water and Atmospheric Research - NIWA (Craggs et al. 2008). The review labels this pond design as a covered anaerobic pond (CAP) design. A traditional uncovered anaerobic lagoon is designed with a lower organic loading rate and has a larger surface area. The CAP design has a smaller volume and surface area than the traditional anaerobic pond; therefore the cost of covering the smaller pond is lower. The NIWA article provides a range of gas production rates and gas compositions which is shown in Table 2.

Table 2. Blogas composition from a covered anaerobic point				
Parameter	Units	CAP		
<b>Biogas Production rate</b>	$m^3/kg VS_{added}$	0.26 - 0.38		
<b>Biogas Composition</b>				
CH₄	%	55 – 70		

## Table 2: Biogas composition from a covered anaerobic pond

CO2	%	30 - 40
O <sub>2</sub>	%	0 - 0.3
N <sub>2</sub>	%	
Other	%	I - 4
Methane Production Rate	$m^3/kg VS_{added}$	0.20 - 0.28
Source: Craggs et al. (2008).		

Typical costs for the establishment of a CAP pond including cover, pond liner and gas generator are presented in the NIWA article and are shown in Table 3

Component		Lifespan	Unit Cost
		(yrs)	(\$ NZ)
Anaerobic Pond (earth lined)	(\$/m <sup>3</sup> excavated)	> 20	8 – 10
Pond Liner	(\$/m <sup>2</sup> installed)	20	15 – 20
Biogas Collection Cover	(\$/m <sup>2</sup> installed)	20	20 - 25
Generator (CHP unit)	(\$/kW)	5 - 10	1000 – 1500

Table 3. Typical costs to establish a covered anaerobic pond

Source: Craggs et al. (2008).

The National Environmental Guidelines for Piggeries (Tucker et al. 2010) provides recommendations for pond lining based upon achieving a minimum design permeability target. Ponds constructed from soils that contain less than 20% clay will require sealing with liners made from imported clay or synthetic liner. The inclusion of a pond liner makes the de-sludging operation more difficult as the liner can be easily damaged by heavy machinery.

Cost estimates have been selected from the NIWA study and are based in New Zealand currency to determine the installation cost for a gas collection and energy production system for a small and medium sized piggery. Table 4 shows the estimates.

Table 4: Cost estimate for gas co	llection cover and energy recov	very system
Pond Dimensions	CAP	CAP
	Small operation	Medium

			Operation
No of sows		400	2000
TS Produced	(kg DM/day)	1,512	7,562
Total VS to Pond (screened)	(kg DM/day)	1,093	5,463
CAP Pond Volume	m <sup>3</sup>	3642	18211
CAP Pond cover area	m²	1109	4108
CAP Earth Lined Pond	\$	31,138	147,687
CAP Cover Cost	\$	24,708	59,400
Generator Cost (CHP unit)	\$	56,286	221,430
Total Investment Cost	\$	112,132	428,518
Estimated annual operation and	¢	0.007	0.007
maintenance costs	φ	8,887	8,887

Source: Craggs et al. (2008).

Estimates of the costs recovered through energy generation and greenhouse gas credits that will offset the investment cost for the cover, pond and energy production system, have not been provided in this report. Depending upon the estimated value of GHG credits, the payback period is estimated to be between two to three years (Craggs et al. 2008).

This short payback period is attractive if the NIWA system and similar costs can be applied to the smaller Australian pig growers. It should also be noted that a part of the short payback period is based upon the operation of a solids separator and no costs associated with handling the separate wastes, and 20% of the heat generated by the CHP equipment is used on site. For electrical control reasons at this site, the electricity generated from biogas is used in parallel with the mains supply to maintain a minimum 9 kW mains load. Electricity generated from biogas can be used during peak load periods to minimise electrical costs.

If an impermeable cover is established over an existing traditional anaerobic pond there would be reduced costs (compared to figures in table 4), as the pond is already formed but increased costs attributed to the increase in cover size.

A case study of Parkville Piggery provided estimates for covering existing anaerobic lagoons (GHD Pty Ltd 2008). The piggery has since closed. Cost estimates to cover the first anaerobic lagoon where based upon a piggery capacity of 1200 sows. The piggery included a solids screening system and supplied a TS load of 3880 kg/day to two anaerobic lagoons operating in parallel. At the time of the study (1998) it was estimated that the cost to cover the two lagoons was AUS\$ 410,000, with a payback period of 11 years. Subsequent work by NIWA has superseded the Parkville Piggery study and payback periods have been significantly reduced. Payback periods of 3 to 4 years or less are typical.

#### 3.7. Solid Covers

It has been recommended that slurry tanks are fitted with solid covers to reduce methane and ammonia emissions, although no figures provided (Amon et al. 2004). Methane, ammonia and nitrous oxide gas emissions were measured from five tanks containing untreated cattle slurry and anaerobically digested cattle slurry. Different cover combinations were tested, a natural crust over the untreated slurry, the same slurry covered with a lid, digested slurry with no lid, digested slurry with a straw cover and finally digested slurry with straw and a lid cover. The results of the gas emissions were individually tabled and also represented as a combined GHG equivalent based upon the relative potency of each gas to carbon dioxide. The factors used were 21 for methane and 310 for nitrous oxide. Two experimental runs were completed, one during the European winter and one during the summer. There were no emission reduction figures specified in the report's conclusion but the discussion of results showed that during winter, covering the untreated slurry decreased the methane and nitrous oxide gas emissions. When compared to the winter batch, the level of methane emissions during the summer period increased significantly (estimated to be 21 times) while there was a small increase in nitrous oxide emissions (estimated to be 10% to 50%). By applying the cover over the untreated slurry, the methane emissions were reduced although the nitrous oxide emissions increased. From an overall GHG perspective, the author concluded that covering untreated slurry with a wooden lid decreased GHG emissions. The report also compared GHG gas emissions from different covers on digested slurry. The results showed that by covering the digested slurry with straw, GHG emissions were unchanged in winter and increased during the summer period. Adding a solid cover over the straw layer decreased the overall GHG emissions.

## 4. Permeable Covers and Methanotrophs

Permeable pond covers allow liquid and gas to move in either direction through the cover. Some cover materials can provide a habitat that enable colonies of microbes to exist which feed on gases released from the pond surface. The combination of a permeable cover that supports microbial activity may be a low cost method to establish a methane mitigation system.

#### 4.1. Methanotrophic Chemistry

Methanotrophic microbes are unique in their ability to utilise methane as their sole carbon and energy source (Hanson & Hanson 1996). The stages in the oxidation process are complex with many electron donors, unique enzymes and intermediates involved. The basic reaction steps are as follows:

$$CH_4 + O_2 \rightarrow CH_3OH + H_2O \rightarrow HCHO \rightarrow HCOOH \rightarrow CO_2$$

Methanotrophs oxidise methane to methanol, then formaldehyde. The microbes then either continue with the oxidisation to form carbon dioxide or assimilate the intermediate to form new

cell material instead (Hettiaratchi et al. 1998). Methanotrophs have been categorised into two main types, low oxidation capacity methanotrophs and high capacity methanotrophs. A third group, type X, shares metabolic features with both of these groups (Petersen et al. 2005).

Each methanotrophic strain of microbes includes a range of individual microbial species. The cell morphology of type I methanotrophs is short rods, some cocci or ellipsoids cell shapes. A comprehensive study on methanotrophic microbes (Hanson & Hanson 1996) reports 13 microbes included in the type I strain.

The differences in characteristics between the strains have been reported by many studies which are summarised (cited in Huber-Humer et al. 2008) as follows:

- Some strains can also metabolise organic substances other than methane.
- The methane concentration that triggers the onset of methane oxidation varies.
- Methane consumption rate varies.
- In some cases the oxygen requirements varies.
- The tolerance to changes in temperature and moisture varies.
- Microbial strains have different propensities for producing exopolymeric substances.

Methanotrophic microbes can produce an exopolymeric substance in certain circumstances. It is suggested that the production of the exopolymeric substance may be a response to excess carbon availability which would otherwise result in increasing levels of formaldehyde formation, which is poisonous to the cell (cited in Huber-Humer et al. 2008).

It is concluded 'that the type I methanotrophs appear to be best adapted to grow at low methane concentrations while the growth of some of the type II methanotrophic microbes is favoured when methane levels are high, with low nitrogen and oxygen levels and when copper is substantially depleted in the media' (Hanson & Hanson 1996).

Methanotrophic microbes utilises formaldehyde as the major source of carbon for cell material production. Chemoautotrophs are microbes that oxidise ammonia to nitrite to obtain energy for carbon dioxide fixation via the Calvin-Benson cycle (Hanson & Hanson 1996). The two groups of microbes operate in a similar way and oxidise a range of compounds including ammonia and methane but at considerably different rates. The presence of methane inhibits the oxidation of ammonia to nitrite by nitrifying microbes. The presence of ammonia inhibits the oxidation of methane to carbon dioxide by reducing the growth rate of all methanotrophs. All methane oxidisers examined oxidised ammonia to nitrite although the rate of ammonia oxidation by methanotrophs was found to be 2 orders of magnitude lower than those of the ammonia oxidising microbes (Hanson & Hanson 1996).

Recently, aerobic oxidation of methane coupled to denitrification (AME-D) has been observed in the laboratory. The AME-D involves aerobic (not anaerobic) methanotrophs oxidising methane and releasing organic material that is used by coexisting denitrifying microbes for denitrification. Recently, anoxic (little or no oxygen) methane oxidation coupled to denitrification has been observed (Modin et al. 2008).

Research into the influencing competition between type I and II methanotrophs was undertaken by Amaerl et al. (cited in Hanson & Hanson 1996) where diffusion columns with opposing gradients of methane and air were established. The experiment attempted to isolate the methanotrophic microbes from a variety of natural sources to study the associations between denitrifying and methanotrophic microbes. At the top of the columns where the concentration of methane was low and the concentration of air was high, the DNA of the microbes was sampled to determine that type I methanotrophs were more prevalent. At the bottom of some of the columns where methane concentration was high, some oxygen leakage accidently occurred and it was found that type II methanotrophs prevailed. Further observations of methanotrophic microbial populations sampled in nitrogen poor and copper poor environments lead to the conclusion that the concentrations of methane, oxygen and combined nitrogen are the primary determinants of the type of methanotrophs present (Hanson & Hanson 1996).

## 4.2. Methanotrophs in Soil Cover Systems

Organic material that is located in a land fill system will normally exist in an oxygen starved environment. Under these conditions, methane gas, carbon dioxide and odour will be produced through naturally occurring anaerobic digestion. Methods have been established to capture the gas and reduce the level of methane and odorous gases escaping the land fill area using biofilters. In 2004, the University of New South Wales established a biofilter trial on an existing landfill at Kelso (UNSW 2007). An impermeable cover was laid over an existing landfill area. Gas drainage lines containing a combination of PVC pipes and crushed concrete, bricks and tiles, were laid under the cover and conveyed the gas from the field to the biofilters.

The biofilters were  $3 \text{ m} \times 3 \text{ m}$  and 1.2 m thick and contained different combinations of composted garden waste, shredded wood and municipal waste. The trial was monitored from 2004 to 2006 and reported methane oxidation rates in excess of 90% and odour reductions of more than 97.5%. The results from the trial indicated that the high levels of methane oxidation (greater than 80%) where achieved at methane loading rates less than 10 g/m<sup>2</sup>/hr. At increased methane loading rates, approximately 30 to 40 g/m<sup>2</sup>/hr, the methane oxidation rate was estimated to be less than 20%.

The development of a "bioactive" cover to mitigate methane emissions from a landfill material was reported (Hileger et al. 2007). This report was the first stage of a project to assess a range of covers at the laboratory scale, including natural sponge, non woven polypropylene geotextile, and

plastic trickling media with polycarbonate membrane and glass beads. The results confirmed that the sponge of geotextile mediums appeared to support methanotrophic colonies.

An investigation into the ability of soil to remove volatile organic compounds reports that soil has a high capacity for methane oxidation and reports oxidation rates of 24 to 112  $\mu$ g CH<sub>4</sub>/g/h (Scheutz et al. 2004). It is also reported that the 'capacity for methane oxidation was related to the depth of oxygen penetration. The methane oxidisers were active down to 500 mm depth and maximum oxidation was observed at a depth of 150 to 200 mm'.

It was estimated that all of the methane gas produced from one landfill site could be oxidised under optimum conditions by a biocover where the temperature is 22°C and moisture content is 25% w/w. It was recognised that high oxidation rates under optimal conditions may not be achieved due to the influences of atmospheric pressure, temperature and rainfall (Scheutz et al. 2004).

To give some perspective, it is estimated that for a 400 sow piggery the gas volume produced would be 240 m<sup>3</sup>/day (Craggs et al. 2008). This equates to 5973 mole/day of CH<sub>4</sub> produced based upon a gas composition of 60% methane and applying the ideal gas law at 20°C and 101.3 kPa. The maximum methane oxidation rates reported for soil landfill systems are 10.4 mol CH<sub>4</sub> /m<sup>2</sup>/day (Kightley et al. 1994). It could be feasible to collect the biogas using an impermeable cover and supplying it to an inexpensive biofilter. Based upon these figures it is estimated that a 25 m x 25 m biofilter operating at optimum conditions would be required. If the biofilter operates well then the gas produced is mainly carbon dioxide. Alternatively a gas flaring system also produces carbon dioxide.

A detailed investigation into gas transport mechanisms leading to attenuation of methane was investigated and a reactive transport model using the Dusty Gas Model were used to establish a multicomponent simulation model (Molins et al. 2008). Experimental data was plotted against calculated values from simulation models and are presented in Figure 4 (Experimental data in represented by symbols and simulated results by lines)

The two plots show the effects of high and low gas flux rates on the position of the zone where methane production is sustained. Similar research is required for permeable covers and would include gas transport and diffusion modelling, and determining optimum conditions to achieve maximum microbiological activity.



Figure 4: Concentrations of  $N_2$ ,  $O_2$ ,  $CO_2$ , and  $CH_4$  at low and high gas flux rates. Source: (Molins et al. 2008)

## 4.3. Permeable Covers

A permeable cover sits in the interface zone between the pond liquid surface and air. The cover allows the passage of gas and liquid to move through the cover in either direction. Permeable covers can be fabricated from a basic thin mat material such as shade cloth, or a more sophisticated geotextile material. Permeable covers can also be established using floating materials such as polystyrene, plastic or clay balls that reduce the open area of the liquid surface interface.

The key to effectiveness of a permeable cover with methanotrophic activity will be maintaining slightly moist, but aerobic conditions. The factors controlling methanotrophic processes in soils are described below. To a large part it is expected that these factors will also be applicable to other systems, such as pond covers.

## 4.3.1.1. Temperature

Temperature affects community structure (Borjesson et al. 2004, Mohanty et al. 2007) and reaction rates of enzymes, microbial activity, and possibly growth (Borjesson et al. 2004, Nedwell & Watson 1995, Nozhevnikova et al. 2001). The  $Q_{10}$  values observed ranged from 3–4 (Borjesson et al. 2004). Subsequent research has found that temperature influence in some systems is of minor importance (Urmann et al. 2009). At atmospheric methane concentrations, temperature dependence appears to be inconsistent but usually small (Borken et al. 2006). At temperatures between -5–10°C this factors influence was increased, and  $Q_{10}$  values varied between 1.1 and 4.8 for the temperature range 4 to 40 degrees in a range of studies (De Visscher et al. 2001, King & Adamsen 1992, Park et al. 2005). At elevated methane concentrations, greater temperature dependence was observed (De Visscher et al. 2001, Jäckel et al. 2005). This is probably more representative of the conditions encountered in digesters or some manure management systems.

## 4.3.1.2. Organic Carbon Content.

In 22 rice soils, methanotroph population was found to be very strongly related to organic carbon content, though activity was not (Joulian et al. 1997).

## 4.3.1.3. Available P, K, and N

Increased available P correlated well with increased methanotrophic activity in rice soils (Joulian et al. 1997).

## 4.3.1.4. Phosphorus

Phosphorus addition to rice soils has been observed to decrease methane emissions (Lu et al. 1999). Additions of urea-N has also been observed to stimulate methanotrophic activity (Kruger & Frenzel 2003), though plant production also increased, increasing methane emission (*via* increased organic matter availability, though the balance was a decrease in methane emission). Similar effects are related to K additions, combined with methanogenic inhibition in flooded rice soils (Babu et al. 2006). Under conditions of elevated atmospheric carbon dioxide, increasing N additions resulted in a reversal of the balance between methane creation and consumption (Xu et al. 2004).

## 4.3.1.5. Acidity

Soils with pH greater than neutral tended to have increased methanotrophic activity (Joulian et al. 1997). However, methanotrophs have been observed to function at pH values as low as 3.5 (Benstead & King 2001, Price et al. 2004).

## 4.3.1.6. Clay Content

Low clay content was correlated with increased methanotrophy, but not with methanotroph population (Joulian et al. 1997). The relationship with methanotrophy may reflect the relationship between oxygen diffusion rate and clay content.

## 4.3.1.7. Active Manganese

Active manganese was found to be positively correlated with methanotroph population, but not activity (Joulian et al. 1997).

## 4.3.1.8. Water Content, Gas Diffusion Rates, and Aeration

Anything that decreases the size of aerobic zones is likely to influence methanotrophic activity, since methane oxidation is dominantly an aerobic process (Amaral & Knowles 1995). Methanotrophy tends to be favoured by the presence of oxidised zones (Le Mer & Roger 2001), though methane oxidation maximises at field capacity (Czepiel et al. 1995, Le Mer et al. 1996). As water content rises beyond field capacity, methane oxidation decreases (Werner et al. 2006). It is proposed (Dalal et al. 2008) that this is due to the limited methane diffusion observed in wet soils (Ball et al. 1997, Del Grosso et al. 2000). However, methanotrophs remain viable through periods of anaerobic conditions, and with the return of favourable conditions will once again become active (Le Mer & Roger 2001). Indeed, concurrent methane oxidation and methanogenesis can

occur in wet soils (Khalil & Baggs 2005) and net methane oxidation has been observed at water filled pore space values greater than 60% - due to localised aerobic microsites or anaerobic methane oxidation (Dale et al. 2006, Khalil & Baggs 2005).

## 4.3.1.9. Anaerobic Methane Oxidation

Anaerobic methane oxidation is also possible, and occurs in sediments undergoing hydrogenotrophic sulphate reduction and hydrogen oxidation (Dalal et al. 2008). This is especially likely when acetate is depleted by methanogens (Dale et al. 2006, Valentine & Reeburgh 2000) as acetate is a key methanogenic substrate.

One of the major limitations to methane oxidation in soil is the rate of diffusion from the air into the soil (Grant 1999, King & Adamsen 1992, Smith et al. 2000, Templeton et al. 2006, Tyler et al. 1994). Soil texture, compaction, and bulk density are related to air filled pore space and to rates of gas diffusion (a range of supporting references are cited in Dalal et al. 2008). Methane diffusion rates in soil water are also likely to be much lower than diffusion rates in soil air (Dalal et al. 2008 evidence cited as Whalen et al. 1992 however no support was found for this reference).

## 4.3.1.10. Redox Potential

The redox potential of rice-field soils is also influenced strongly by the presence of active Fe and organic matter (as cited in Le Mer & Roger 2001, Neue & Roger 1994). The organic matter relationship probably reflects increased respiration of decomposing microbes — and the ease of decomposition of the organic matter is important (Moore & Dalva 1993).

## 4.3.1.11. Salinity

Salinity more effectively inhibits methane oxidation than it inhibits more general microbial respiration (Saari et al. 2004) or methane production (Denier Van der Gon & Neue 1995). Dalal et al. (2008) suggests that this is related to moisture stress (Saari et al. 2004, Schnell & King 1996) or specific chloride and ammonia inhibition (Price et al. 2004).

## 4.3.1.12. Substrate Limitation

Methane oxidation is an enzyme controlled reaction (as is methane production), and so the availability of the raw materials controls the rate of reaction. For the maximum reaction rate to be achieved, required methane concentrations are in the range ( $\mu$ L L<sup>-1</sup>) of 5–30 for soil (Gulledge & Schimel 1998, Price et al. 2004, Saari et al. 2004), 70–800 in wetland soils (Knief et al. 2006, Saari et al. 2004), and 29–84 for landfills (Park et al. 2005). Methane oxidation rates are known to be methane limited (Chan & Parkin 2001), and increased methane concentrations can overcome some of the rate limitations imposed by gas diffusion rates through increasing soil water contents (Khalil & Baggs 2005). Concentrating methane may be a means to increase methane oxidation efficiency.

#### 4.3.1.13. Mineral Nitrogen and Nitrogen Fertiliser

The understanding of methane consumption and nitrogen effects continues to develop, and some authors suggest that there has been an over-emphasis of the inhibitory roles rather than the importance of stimulatory effects (Bodelier & Laanbroek 2004). The oxidation of methane and the oxidation of ammonia compete for oxygen (Hanson & Hanson 1996) or alternative electron donors (Dale et al. 2006). A range of published observations suggest that soil or fertiliser ammonia inhibit methane oxidation through competitive processes (Bedard & Knowles 1989, Bykova et al. 2007, Chu et al. 2007, Gulledge & Schimel 1998, Powlson et al. 1997, Veldkamp et al. 2001). Conflicting observations have also been published, where ammonia did not have this effect, or where ammonia applications increased methane oxidation (Dalal et al. 2008), possibly reflecting methanotrophic diversity. Nitrogen fertiliser application tends to inhibit methane consumption by Type II methanotrophs, but enhances consumption by type I organisms (Mohanty et al. 2006). The inhibitory effects of ammonia additions are likely to be short lived due to the rapid transformation of ammonia to nitrate (Chu et al. 2007, Dalal et al. 2008). In rice soils at higher initial methane concentrations, the duration of the initial inhibitory effect can be decreased by increasing initial methane concentrations — and be replaced by stimulated oxidation (Cai & Mosier 2000).

## 4.3.1.14. Nitrite

Nitrite also inhibits methane oxidation (Wang & Ineson 2003), but this effect is likely to be shortlived in soils due to the normal lack of persistence of nitrite (Dalal et al. 2008). Nitrate has been found inhibitory only in very high concentrations, which likely give rise to osmotic effects (Bodelier & Laanbroek 2004), or through reduction to nitrite (Wang & Ineson 2003).

## 4.3.1.15. Copper and Potassium Additions

Copper is an essential methanotroph enzyme co-factor, with Type II methanotrophs active at lower Cu concentrations than Type I methanotrophs (as cited in Bedard & Knowles 1989, Dalal et al. 2008, Myronova et al. 2006). Evidence is conflicting as to whether K additions can stimulate methanotrophic activity (Babu et al. 2006, Sanhueza et al. 1994).

## 4.3.2. Spent Compost Cover Material

(Brown et al. 2008) and (Scheutz et al. 2009) reviewed greenhouse gas mitigation using spent compost (which contains an existing methanotrophic population) as a cover material. (Scheutz et al. 2009) reviewed the effect of four cover types including compost and wood, compost and sand (1:1), compost and sand (1:5) and supermuld (a commercial compost product) on the mitigation of volatile organic compounds and methane. The compost was sourced from screening residues of 2 year compost comprised from garden waste. The combination of woodchips and compost showed the highest peak rate 247 g.m<sup>2</sup>/day and highest steady state methane oxidation rate at 161 g.m<sup>2</sup>/day. The study also demonstrated the importance of structure of the cover to provide effective porosity allowing air into the cover to support methane oxidation. The study showed that insufficient structure may lead to the production of exopolymeric substances by the microbes

leading to structure clogging and the development of anaerobic conditions and methane generation.

Further research to review and quantify the methane mitigating performance of a spent compost cover which is supported by a permeable cover that prevents water logging of the compost may provide a workable low cost pond methane mitigating system.

Using a non-wicking (coarse, low water potential) underlying substrate may also help prevent excessive water being drawn up.

#### 4.3.3. Straw and Crop Residue Covers

The performance of a wide range of organic permeable covers such as barley straw and wheat straw, have been investigated. The focus has been to identify low cost cover options which provide a significant reduction in pond odour. Investigations have been completed in Queensland and assessed polypropylene geofabric, polythene shade cloth and supported straw (Hudson N 2005, Hudson et al. 2008). The report confirms that organic covers can reduce the average odour emissions from 41 to 76% depending upon the cover material.

A laboratory study investigating gas emission reduction performance and the effects of straw cover age, moisture content, and microbiological development in straw covers over swine slurry reported that aged straw covers can reduced ammonia emissions by 99%, and some of the gases responsible for odours such as dimethyl sulphide by 81%, phenol by 82%, p-cresol by 95% and benzyl alcohol by 97%. The findings from the study were suggested to support the concept that the main mechanism for reductions in odorant emissions from straw coved slurry is associated with the cover acting as a physical barrier. The emission reduction of specific gases such as ammonia and p-cresol, appeared to be related to the straw acting as a biofilter (Victoria Blanes-Vidal 2009).

An investigation measuring methane and nitrous oxide gas emissions above a straw covered piggery lagoon compared emissions from a similar uncovered piggery lagoon (Cizek et al. 2003). A flux hood was suspended over one corner of the lagoon and gas emission samples were collected on three different days at the same times during the day. Gas samples were analysed for odour, carbon dioxide, methane and nitrous oxide using a gas chromatograph. It was reported that the straw covering decreased odour by 37.8%, had no impact on carbon dioxide emissions, slightly increased nitrous oxide emissions by 7.6% but there was uncertainty in the level of statistical significances with this result. It was reported that methane emissions were increased above the straw covering by 247%. It was suggested in the report that the reasons for the high methane emissions over straw, was an additional anaerobic source due to sunken straw or reduced surface mixing of air and liquid. The report does not consider the effect of methanotrophic activity, straw cover age or cover condition. A photograph of the hood sampling position shows the sampling

site is very close to the edge of a large pond and possibly located in a zone of poor mixing possibly leading to widely variable results.

The economic evaluation of straw covers and straw supported on a geotextile to reduce odour and gas emissions on manure storage basins was reported (Larry D. Jacobson 2001). This work focused on odour and hydrogen sulphide emission reduction.

GHG emissions were measured from two pond cells located at a 600 sow piggery at Saskatchewan, Canada (Peterson et al. 2004). Gas emissions were measured for four years when the pond had no cover, a straw cover and a negative air pressure cover (NAP). Methane emissions from the uncovered pond were approximately 1230 g  $CO_2$ -eq/m<sup>2</sup>/day and this was reduced to approximately 130 g  $CO_2$ -eq/m<sup>2</sup>/day with a straw cover and 100 g  $CO_2$ -eq/m<sup>2</sup>/day with an NAP cover. It was reported that GHG emissions from the exhaust fans of the NAP cover were not significantly different from the straw covered pond.

Straw covers were found to be the least expensive with the shortest durable life. The odour mitigating performance was improved as the cover thickness increased towards 300 mm (Burns & Moody 2008).

## 4.3.4. Expanded Clay (LECA), Perlite and Rubber Chip Covers

Light weight expanded clay (LECA) is made by burning clay particles to form clay balls that are buoyant, water resistant, and have a long service life. The clay balls float and form a partial physical barrier between the air and pond surface. The resulting layer will assume the shape of a liquid surface. Perlite is a light weight low density volcanic glass.

The performance of LECA, ground rubber, geotextile and mineral granules (Perlite) was investigated to determine the potential for mitigating odour, hydrogen sulphide and ammonia emissions on manure storage (Burns & Moody 2008). LECA covers were reported to be the most expensive option tested, however a large proportion of the cost for the LECA cover was in the transportation cost of LECA balls from the manufacturer in Europe to the trial location in the USA. The LECA cover was reported to provide a 90% reduction in odour and reduce ammonia emissions from 65% to 95%. Field tests of ground rubber over a four month period were reported to work well, although no results were given. The mineral granules "Vermiculite" and "Perlite" were found to be unsatisfactory.

A laboratory study to investigate the effects on gas emissions by covering liquid pig waste with granules of perlite (Pegµlit<sup>™</sup>) and lightweight expended clay aggregate (Leca<sup>™</sup>) was reported (Berg 2003). The results of this study were initially reported in 2003 (Berg 2003)and then more fully in 2006 (Berg et al. 2006). Samples of pig manure with a dry matter content ranging from 5% to 8% were stored in 65 litre containers for 162 days. Different combinations of granule layers, all

60 mm thick, were trialled along with the addition of lactic acid, or saccharose or no additive addition. The investigation reviewed the effects of pH and the various combinations of covering and additives on ammonia, nitrous oxide and methane gas emissions. For some of the sample combinations tested, the results varied widely. It was concluded that methane is the most prevalent greenhouse gas emitted from liquid manure storage and nitrous oxide emissions are one tenth the rate of methane but can increase by using straw or granules covers (which lowers ammonia emissions). It was concluded that lowering the pH of the slurry can reduce both methane and nitrous oxide emissions and the combination of a covering layer and acidifying should cause a pH below 6.0 to reduce methane and nitrous oxide emissions effectively.

In a section of the report (Berg et al. 2006), the greatest reductions in methane emission rates were achieved with a combination of a straw or LECA cover and reducing the pH value to around 6. (FSA Consulting note that digestion activity generally slows to a stop at low pH). The reported results (table 2 in the report) show significant reductions in methane emissions with some combinations of treatments (LECA or straw with lactic acid) compared to the control result, but the authors refer to wide statistical variance associated with the results and hence there is no significant emission reduction numbers provided.

The Perlite cover was reported to have little effect on methane emissions. Significant emission rates of nitrous oxide were measured when the samples had developed a surface crust which occurred with straw, Perlite and LECA cover materials. The highest nitrous oxide emission rates were found with the straw samples. The straw crust was destroyed on day 112 and nitrous oxide emissions were reported as "nearly none". As the straw crust became established again, nitrous oxide emissions rapidly increased. Applying water to the surface of the straw to simulate rainfall produced a reduction in nitrous oxide emissions (Berg et al. 2006).

The effect on gas mitigation performance was tested for a LECA cover at two different layer thicknesses, 7 cm and 14 cm. The thicker layer increased methane mitigation from 9% to 16% and carbon dioxide mitigation from 19.5% to 34.9% (Guarino et al. 2006).

A fact sheet describing permeable and impermeable covers for manure storage (Nicolai et al. 2004) describes each covers effectiveness in the reduction of odour, hydrogen sulphide and ammonia emissions. The range of covers includes straw, geotextile, geotextile with straw, "LECA" and "Macrolite" (an expanded clay ball). No information was presented on methane mitigation. The clay ball options were estimated to have an economic life of 10 years but are significantly more expensive that straw covers.

In summary LECA covers decreased methane emissions but increased nitrous oxide emissions with thicker layers further reducing methane emissions (Berg et al. 2006, Guarino et al. 2006).

#### 4.3.5. Woodchip and Wood Based Covers

A floating sawdust cover was trialled but it quickly became water logged and sank. Coating the sawdust with oil was tried in an attempt to improve buoyancy but with no success (Meyer & Converse 1982). A thin layer of woodchips (7 cm) and thick layer (14 cm) was trialled over 190 litre manure samples stored indoors. It was reported that the only significant reduction in methane emission (31.7%) was achieved with a 140 mm layer of wood chips and good chip flotation was observed during the trial.

#### 4.3.6. Peat Covers

Peat is a porous partially decayed organic layer and is found in areas that were once wetland bogs. Studies report reductions in ammonia emissions from 70% to 100% and thick layers perform better than thin layers (Sommer et al. 1993).

#### 4.3.7. Oils and Fats

Fat from an abattoir DAF plant is used to form a permeable layer in the abattoir's primary anaerobic pond. The fat is thick, solid and floats. Vegetable oil is buoyant and self spreads across a smooth liquid surface to form a fairly uniform layer on top of the liquid. Vegetable oil layers showed short term reductions of GHG emissions (Guarino et al. 2006). A long term study found that methane emissions increased by up to 189% (Williams & Sneath 2002) due to increased biological degradation.

Two vegetable oils were trialled, rape seed oil and used cooking oil. Both were found to biodegrade and produce methane (Burns & Moody 2008).

Permeable covers using petroleum based oils have been investigated for ammonia, and hydrogen sulphide mitigation. There has been no test data located for GHG emission reduction.

#### 4.3.8. Hydrophobic Compounds

A mixture of hydrophobic powder was made by mixing ammonium phosphate, ammonium sulphate and hydrophobic silica (Sakamotoa et al. 2006). The powder was used to form a floating cover over digested or raw cattle slurry. The trial lasted for 13 days and reduced ammonia, hydrogen sulphide and methane emissions in general. A longer trial period is required to determine the durability and long term performance of this type of cover.

It may be possible to produce an inexpensive hydrophobic material using any starchy material with appropriate inexpensive treatment. But durability and practicality issues of the compound when used as a pond cover would have to be addressed in particular related to water logging.

#### 4.3.9. Geotextiles and Biocovers

Permeable synthetic covers can provide a uniform cover medium which is buoyant and durable. The covers are fabricated from polyester, polystyrene foam, geotextile, polyethylene fibre and marketed under different brand names.

Sections of a mature permeable 'Bio-cap' cover and the associated biofilm attached to the cover were sampled from three swine waste handling lagoon sites located in the Midwest USA (Miller & Baumgartner 2007). Waste water samples were also taken from below the cover sample locations. The potential nitrifying and denitrifying activities of the mature covers was compared to new cover material in laboratory based aerobic and anaerobic incubators. Details of the semi permeable cover material are not provided in the report although new samples of the material obtained from the supplier (Baumgartner Environics, Olivia MN USA were www.beiagsolutions.com). An experiment to measure the nitrification potential of the mature cover with biofilm, and new cover, nitrification potential of the waste water, denitrification potential of the covers and consumption of NOx in the waste water was undertaken. The study concluded that the semi permeable cover served as a useful medium to support a biofilm that had the capacity to transform ammonia to nitrogen. The methane mitigation performance of the 'Biocap' cover was not reported.

An evaluation was made of a floating permeable composite cover of polyethylene chips topped with a geotextile layer containing zeolite particles (Miner et al. 2003). Laboratory and field evaluation found a reduction in ammonia emissions by 80%. References to methane gas emissions were made in general.

A geotextile cover was trialled over manure slurry and was tested for ammonia and odour control effectiveness. The cover provided a reduction of between 40% to 65% in odour and 30% to 90% reduction in hydrogen sulphide. Results for greenhouse gases were not reported. It was concluded that a geotextile cover with buoyancy aid or straw performed better than the geotextile alone (Burns & Moody 2008).

A Monsanto patent (Tung & Roberts 2004), describing a concept for a foldable, self floating cover system for a body of water. The purpose of the patent design is to reduce odours, emissions of ammonia, hydrogen sulphide, and or volatile organic compounds from lagoons like anaerobic sewage lagoons. The cover has a structure to suitable for growth of biomass into which offensive gases from a sewage lagoon may permeate and be oxidised. The cover provides sufficient buoyancy to support the biomass and maintain a significant proportion above the surface of the lagoon. The cover and cover with biomass are permeable to the rain. The cover material is 3 mm thick. The cover is designed to support aerobic oxidation of the gases. Various options are mentioned for this conceptual design. No specific details are provided for methane or GHG mitigation.

## 4.3.10. Floating Plastic Balls

Siemens are marketing the E Ball floating cover system (Siemens Water Technologies 2009). The manufacturer offers 100 mm diameter polyethylene balls which are poured onto the surface to eventually provide a uniform cover. No specific data is provided on gas emission reduction, however this type of air filled ball could provide a buoyancy aid to a biological layer above.

#### 4.3.11. Biofiltration

Meridian Aquatic Technology offers the AqauMats (Meridian Aquatic Technology 2002). This is a biofiltration mat system that is supported from the pond surface. It is claimed that the mat provides a biofilter for reduction of  $BOD_5$  and total suspended solids. No performance data is provided.

## 5. Purple Pond Microbes

Lagoons with established populations of purple sulphur microbes have the potential to reduce pond odour by oxidising hydrogen sulphide into elemental sulphur during photosynthesis.

Purple sulphur microbes occur in anaerobic environments that have sulphur in the reduced form available and they give the pond a brownish purple to pink colour, depending upon the microbial population present. There are approximately 60 species of phototrophic microbes and they are categorised into one of four groups, purple sulphur, purple non sulphur, green sulphur and green gliding. The microbial species *Bacteriochlorophyll q* (Bchl a) is typically used as a measure of abundance of phototrophic microbes.

Algae and plants use water as an electron source for photosynthesis and produce oxygen. Phototrophic microbes use carbon dioxide or VFA's as a carbon source, light as energy and reduced sulphur compounds such as hydrogen sulphide as an electron source (Hamilton et al. 2006). A wide range of microbial species can coexist in the lagoon environment. Symbiosis exists between acid forming microbes, methanogenic microbes, phototrophic microbes, algae and aerobic microbes. Sulphate reduction by phototrophic microbes is more favourable energetically than methane production by methanogenic microbes. Where low concentrations of sulphate exist then the methane producing microbes dominate. If organic matter is limited then high concentrations of sulphate may inhibit methane production.

The influence of sulphur on gaseous emissions from pig manure, and the competition between sulphate reducing and methanogenic microorganisms was investigated (Berg & Model 2008). The addition of gypsum (CaSO<sub>4</sub>) to pig slurry was investigated at the laboratory scale. The experiment observed the generation of methane gas during a 14 week period from 12 vessels containing fresh manure from fattening pigs. The results indicated that increasing addition rates of gypsum reduced

the level of methane produced and also shortened the time of methane production from the slurry. It is reported that an addition of 4% gypsum to the slurry resulted in almost halving the methane produced. It is also reported that nearly all nitrous oxide emissions were eliminated by this treatment.

In a North American study, 29 swine manure management systems were monitored for gas emissions, VS loading, nutrient and volatile organic compound emissions (J. A. Zahn 2001). The data from the piggery's were divided into groups based upon four manure handling systems which included building confinement, lined earth storage basins, lagoons and phototrophic lagoons. The phototrophic lagoons exhibited populations of bacteriochlorophyll a above 40 nmol m/L. The average VS loading for the lagoons were 300 g VS/d/m and 70 g VS/d/m for the phototrophic lagoons. Reported pond methane emissions for the lagoons were 13,900 g  $CH_4$ /h and 11,990 g  $CH_4$ /h for the phototrophic lagoons. The phototrophic lagoons and lower emission rates of volatile organic carbon compounds.

There is little research available which investigates GHG emissions from lagoons exhibiting a purple pond environment. A better understanding is required of the pond bio chemistry and conditions which can lead to GHG mitigation from the phototrophic pond, and subsequent effluent and sludge quality.

## Conclusions

A range of options have been reviewed to determine which methods of piggery management and new developments in pond cover technology show potential to reduce pond methane gas emissions.

Small but significant reductions in pond methane emissions can be achieved by modifications to feed diet composition and feeding system technology.

A significant reduction in the pond methane emissions can be achieved by implementing solids separation technology. The removal of 25% of solids before entering the pond will reduce pond methane emission by 25% reducing overall manure emissions by 23%. The separated solids would require good compost management to avoid additional GHG emissions occurring from the wet solids produced by the solids separator.

Based on the available literature on methane mitigation performance of permeable pond covers, this survey demonstrates that a significant level of investigative work has been undertaken, but in many cases the results vary widely and cast doubt on the reliability of the covers' performance. Part of the reason is the difficulty in performing trials on site and obtaining scientifically repeatable results. The majority of the investigations have been undertaken at the pilot scale and focused on measuring the input cause and output results. A better understanding of the biochemical mechanisms is required.

Formation of a natural pond crust on an anaerobic pond receiving piggery effluent system has been demonstrated to reduce methane gas emissions at the pilot plant scale. A pilot scale study by Petersen (2005) presented evidence that methanotrophic activity occurs in naturally forming crusts. Sommer (2000) reports a methane emissions from an uncovered pond are 38% higher than a pond with a natural crust. No evidence of nitrous oxide emissions were measured when the cover was wet, but nitrous oxide emissions occurred when the cover dried during the warmer summer period. Establishing a pond crust to mitigate GHG emissions is appealing as a low cost option, as the crust material can be formed through pond design and management rather than establishing an artificial cover. It has been observed during site visits to Australian piggeries that the crusts tend to thicken with time and often a steady state thickness is reached where thickening does not continue. Some thick crusts have been observed to crack open exposing the liquid slurry below which provides a direct path for methane emission from the slurry. The performance and buoyancy of a thick crust during very heavy rainfall events is unclear. Further research of pond crust performance for Australia's hot and dry conditions is required to determine the overall GHG performance and indentify how significant the nitrous oxide emissions may become. The research work should focus on the biological mechanisms occurring in the crust.

Cooling of slurry in pig sheds shows a reduction in methane emissions. This may form a part of a strategy to delay methane emissions until the waste stream arrives at the pond if an effective methane recovery or elimination system at the pond can be implemented. It is not clear how such a system could be established in the warmer parts of Australia.

Laboratory scale experiments showed that expanded clay (LECA) pond covers decreased methane emissions between 9% and 16% and increased nitrous oxide emissions (Guarino et al. 2006). Expanded clay covers are durable but are expensive as the expanded clay balls were imported for the overseas trials. Thicker layers of LECA improved methane mitigation performance but establishing a thick layer on a pond may be difficult.

Impermeable covers are an effective way of capturing and converting methane to an energy source and mitigating pond methane. New pond designs are emerging that incorporate a smaller more highly loaded pond and cover system to minimise the capital costs.

The methane mitigating performance of composted material has been reported (Scheutz et al. 2009). The investigation of the methane mitigating performance of a cover formed from spent composted material supported by a permeable cover may provide a workable low cost option for

methane mitigation. Composted material provides little available energy for other forms of microbes to become dominant. Hence methanotrophic microbes are favoured

The methane mitigation performance of straw covers is unclear with some studies suggesting a significant methane reduction (Peterson et al. 2004) and other studies showing significant increase (Cizek et al. 2003). Thicker straw covers performed better than thin covers (Guarino et al. 2006) and straw covers tended to increase nitrous oxide emissions (Sommer et al. 2000). Further research is required to scientifically confirm the methane mitigation performance of straw covers and clarify the underlying biochemical mechanism occurring in the cover. The straw cover appears to increase nitrous oxide emissions in a similar manner to the naturally formed crust (Sommer et al. 2000) however reliable data is scarce. Straw is readily available but to produce a uniform cover thickness over a pond is challenging and preventing the straw from sinking is a problem. The lack of long term durability and disposal of the straw cover must be considered. If a reliable methane mitigating performance of the straw cover can be determined then the viability of a straw cover as a low cost methane mitigating option can be assessed.

Synthetic covers such as BioCap and organic woodchip covers show promise and should be investigated further to provide rigorous and repeatable scientific data to determine GHG mitigation performance.

There is a knowledge gap in the biochemical processes occurring in permeable covers. Further research is required to better understand the biological and mass transfer mechanisms involved to identify optimum specifications for permeable covers.

The microbe's environment that exists in a purple pond environment can convert carbon directly to carbon dioxide instead of producing methane. The effects on nitrous oxide emissions and subsequent GHG emissions produced during land application are not reported. There is little reported research work available. Further research to understand the biochemistry involved and how to manage the biochemical system may lead to a workable GHG mitigation process.

The addition of 4% gypsum to pig slurry has been reported to almost halve methane emissions and nearly eliminate all nitrous oxide emissions. Further investigation to review the effects of different addition rates is warranted.

## 6. Implications and Recommendations

Low cost pond methane mitigations options are available.

Improvement in feed management techniques and management of diet can result in reductions in pond methane emissions.

Solids separation technology will achieve reductions in pond methane but good management of the separated solids is required to achieve and overall gain in GHG emissions.

Permeable pond covers such as natural pond crusts, spent bedding covers and synthetic covers such as BioCap and wood chips should be researched further. The focus of the research should be to gain a better understanding of the underlying biological mechanisms occurring in the cover as well as determining scientifically rigorous and repeatable results.

Research to understand the GHG reducing potential of purple pond systems is recommended. The ability of phototrophic microbes to produce carbon dioxide instead of methane gas suggests that significant GHG gas reductions may be achievable by a different overall method of pond management. Further investigation of the addition of gypsum to pig slurry and the effects on methane and nitrous oxide emissions may also provide a low cost GHG mitigation strategy.

## 7. Technical Summary

The Australian pork industry operates a variety of intensive piggery farming systems which include the conventional shed, deep litter, outdoor rotational and outdoor feedlot piggeries. This report focuses on the conventional flushing system that usually incorporates an anaerobic pond in the effluent pond treatment system.

The anaerobic pond is a significant source of methane in the piggery effluent treatment process. Methods to reduce pond methane emissions including reductions in the VS load, diet modification, covering the pond and establishing a pink pond microbial environment are reviewed in this report.

Small but significant reductions in pond methane emissions can be achieved by modifications to feed diet composition and feeding system technology. A decrease in the level of carbohydrate and protein in the diet has shown to decrease ammonia and methane emission from manure during storage. However, this is likely to be counterproductive to desirable animal weight gains.

A significant reduction in the pond methane emissions can be achieved by implementing solids separation technology. The removal of 25% of solids before entering the pond will reduce pond methane emission by 25% reducing overall manure emissions by 23%. The separated solids would require good compost management to avoid additional GHG emissions occurring from the wet solids produced by the solids separator. The research has not been done to confirm a reduction in overall methane emissions using separation technology and the expected reductions in methane emissions may just be an artefact of the DCC calculation method. One Canadian research study looked at solid separation and retaining the maximum fraction of VS in the separated solids and then digesting the solids fraction only. This technique is expected to be expensive and little

research has been done to determine its practicality and economic efficiency for Canadian conditions.

Technology is available for the mitigation of pond methane emissions through biogas capture using impermeable covers and energy recovery. The high capital cost has limited the application of this technology to mid to large sized pig farms. The technology is developing and work by NIWA in New Zealand has focused on establishing small highly loaded ponds with steep pond walls to reduce the pond surface area and minimise the cost of covering the pond (Craggs et al. 2008). This will enable some of the small to mid size farms to consider implementing this technology.

Low cost options for pond methane reduction are required that may be economically attractive to the smaller farm systems and promising mitigation options are required for further research and assessment.

A wide variety of permeable pond covers have been trialled to determine the performance of the cover at mitigating pond odour, and ammonia emissions and to a lesser extent pond methane and nitrous oxide emissions. Certain types of permeable pond covers can provide a porous aerobic environment which allows colonies of methanotrophic microbes to become established in the zone between air and the liquid surface.

Methanotrophs consume methane gas and this group of naturally occurring microbes can exist in naturally forming pond crusts or artificially formed pond covers.

Based on the available literature on methane mitigation performance of permeable pond covers, this survey demonstrates that a significant level of investigative work has been undertaken, but in many cases the results vary widely and cast doubt on the reliability of the covers' performance. Part of the reason is the difficulty in performing trials on site and obtaining scientifically repeatable results. The majority of the investigations have been undertaken at the pilot scale and focused on measuring the input cause and output results. A better understanding of the biochemical mechanisms is required.

Formation of a natural pond crust on an anaerobic pond receiving piggery effluent has been demonstrated to reduce methane gas emissions at the pilot plant scale. A pilot scale study by Petersen (2005) presented evidence that methanotrophic activity occurs in naturally forming crusts. Sommer (2000) reports a methane emissions from an uncovered pond are 38% higher than a pond with a natural crust. No evidence of nitrous oxide emissions were measured when the cover was wet, but nitrous oxide emissions occurred when the cover dried during the warmer summer period. Establishing a pond crust to mitigate GHG emissions is appealing as a low cost option, as the crust material can be formed through pond design and management rather than establishing an artificial cover. It has been observed during site visits to Australian piggeries that

the crusts tend to thicken with time and often a steady state thickness is reached where thickening does not continue. Some thick crusts have been observed to crack open exposing the liquid slurry below which provides a direct path for methane emission from the slurry. The performance and buoyancy of a thick crust during very heavy rainfall events is unclear. Further research of pond crust performance for Australia's hot and dry conditions is required to determine the overall GHG performance and indentify how significant the nitrous oxide emissions may become. The research work should focus on the biological mechanisms occurring in the crust.

Laboratory scale experiments showed that pond covers formed from expanded clay balls (LECA) decreased methane emissions between 9% and 16% and increased nitrous oxide emissions (Guarino et al. 2006). Expanded clay covers are durable but are expensive as the expanded clay balls were imported for the overseas trials. Thicker layers of LECA improved methane mitigation performance but establishing a thick layer on a pond may be difficult.

Scheutz et al. (2009) investigated the methane mitigating performance of combinations of composted material with sand or woodchips. The combination of spent compost and woodchips demonstrated the highest methane mitigating performance and a steady state methane oxidation rate 161 g.m<sup>2</sup>/day was reported. An investigation of the methane mitigating performance of a pond cover formed from spent composted material supported by a permeable cover may provide a workable low cost option for pond methane mitigation. Composted material provides little available energy for other forms of microbes to become dominant. Hence methanotrophic microbes are favoured

The methane mitigation performance of straw covers is unclear with some studies suggesting a significant methane reduction (Peterson et al. 2004) and other studies showing significant increase (Cizek et al. 2003). Thicker straw covers performed better than thin covers (Guarino et al. 2006) and straw covers tended to increase nitrous oxide emissions (Sommer et al. 2000). Further research is required to scientifically confirm the methane mitigation performance of straw covers and clarify the underlying biochemical mechanism occurring in the cover. The straw cover appears to increase nitrous oxide emissions in a similar manner to the naturally formed crust (Sommer et al. 2000) however reliable data is scarce. Straw is readily available but to produce a uniform cover thickness over a pond is challenging and preventing the straw from sinking is a problem. The lack of long term durability and disposal of the straw cover must be considered. If a reliable methane mitigating performance of the straw cover can be determined then the viability of a straw cover as a low cost methane mitigating option can be assessed.

Floating sawdust covers were trialled but quickly became waterlogged and sank. The saw dust was costed with oil in an attempt to improve buoyancy but with no success. A layer of woodchips was

trialled over manure samples and a reduction in methane emissions of 31.7% was reported for a 140 mm thick cover with good chip flotation (Meyer & Converse 1982).

Peat material has been reviewed for ammonia reductions but no data on methane reductions have been reported.

Oils and fats are commonly used at abattoirs to form a primary pond cover. Short term studies showed reductions in methane emissions however a longer term study showed an increase in methane emissions due to increased biological degradation (Williams & Sneath 2002).

A hydrophobic powder was made by mixing ammonium phosphate, ammonium sulphate and hydrophobic silica (Sakamotoa et al. 2006) and was used to form a floating cover over digested and raw cattle slurry. The trial lasted for 13 days and reduced ammonia, hydrogen sulphide and methane emissions in general. A longer trial period is required to determine the durability and long term performance of this type of cover. It may be possible to produce an inexpensive hydrophobic material using any starchy material with appropriate inexpensive treatment. But durability and practicality issues of the compound when used as a pond cover would have to be addressed in particular related to water logging.

Permeable synthetic covers such as BioCap are emerging but little scientific data is available to determine methane mitigating performance of these cover materials. Sections of an aged BioCap cover were taken from three swine waste handling lagoons located in Midwest USA. A sample of a biofilm which was attached to the aged covers was also taken. The study focused on the nitrifying and potential denitrifying activities of the cover with biofilm compared to new cover material. The study concluded that the biofilm attached to the cover had the capacity to transform ammonia to nitrogen however methane was not considered. Further research for this type of pond cover to investigate methane mitigation performance and the effect on nitrous oxide emissions for Australian climatic conditions would identify the feasibility and expected cost for a pond cover installation.

There is a knowledge gap in the biochemical processes occurring in permeable covers. Further research is required to better understand the biological and mass transfer mechanisms involved to identify optimum specifications for permeable covers.

Permeable pond covers including naturally formed crusts, spent compost with a supporting cover and expanded clay, synthetic covers such as BioCap and wood chip covers show promise at reducing pond methane emissions. The reported results are widely variable. It is recommended that more rigorous investigation is undertaken to provide confidence that a covers methane mitigation performance is reliable. Pink and purple ponds occur when the sulphate reducing microbial population become dominant in the anaerobic pond and the pond biochemistry alters. A literature search was undertaken to determine if there are any results which suggest that this type of pond biochemistry can result in decreased methane emissions.

The microbial environment that exists in a purple pond environment can convert carbon directly to carbon dioxide instead of producing methane. The effects on nitrous oxide emissions and subsequent GHG emissions produced during land application are not reported. There is little reported research work available. Further research to understand the biochemistry involved and how to manage the biochemical system may lead to a workable GHG mitigation process by converting carbon directly to carbon dioxide simply by changing the way anaerobic ponds are managed.

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