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Quantifying Greenhouse Gas Emissions from Australian Piggeries

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2   Executive Summary

This document details two related literature review conducted as one brief project: a review of greenhouse gas emissions measurement techniques to be applied to intensive pig production; and a review of nitrous oxide emissions and processes from pig production. The review has aimed to be comprehensive and rigorous. However, in order to increase the value to APL, comments and recommendations have been added, including some speculation to allow selection of future directions.

Measurement Techniques and Instruments
- In applications where measurements may challenge greenhouse gas assumptions, the most rigorous recognised high accuracy techniques is required
- The Backward Lagrangian Stochastic techniques' flexibility with regard to emission source and scale is extremely attractive. Advantages include robustness, the body of publications applying it, software support, and modest analytical requirements. The choice of this technique for measurements for the intensive livestock industry in Australia and overseas make the Backward Lagrangian Stochastic method a strong candidate for the primary measurement approach for the pig industry.
- Flow through, non-steady state chambers (a chamber placed over an emissions source — such as a deep litter stock pile or suspended over a pond) combined with real-time analysis are probably the best small scale process-based mitigation investigation tool, they allow easy separation of adjacent emissions sources, and also are a critical tool for process evaluations.
- Most mass balance techniques are more measurement intensive than is desirable, though some techniques may be useful to eliminate the effects of adjacent emissions and to verify the BLS techniques.
- Closed path Fourier Transform Infra Red (FTIR) or Tuneable Diode Laser (TDL) instruments will provide the capability to measure emissions adequately in real-time experiments at laboratory, small field scale, and during BLS trials.
- Expensive open path tuneable diode laser techniques have proven capability for methane emissions — but instruments are currently not available for nitrous oxide measurement.
- Gas chromatograph techniques (including GC-MS techniques) are extremely reliable methods suitable for calibration, comparison, and method development roles.

Nitrous Oxide Emissions
- Emissions of nitrous oxide occur via both direct and indirect paths.
- Direct nitrous oxide emissions can occur from both the nitrification and denitrification processes, and may be delivered through the activity of microbes such as bacteria and fungi, or through purely chemical means.
- Denitrification processes are capable of consuming and emitting nitrous oxide.
- The major factors controlling emissions from deep litter, effluents, and from effluent/deep litter amended soils are likely to include:
  - Factors that alter the redox potential of the soil, such as changes in soil moisture and substrate texture/gas permeability. These are factors that are open to a range of manipulations. Interactions with methane emission need to be considered in any mitigation development research.

- Organic carbon availability and quality. This is a mitigation opportunity in that the quantity and "availability" of carbon may be manipulated or altered through managements. Research is required.
- Supply of mineral N. This factor is also open to manipulation, and offers potential for the development of mitigation managements. Any management approach that defers nitrate formation or mineralisation until rapid plant uptake is likely will tend to decrease nitrous oxide emissions. Covered anaerobic digesters have advantages in this area, if subsequent nitrogen management steps extract N or allow rapid uptake as nitrate is formed. Systems where effluent or solids ammonia is captured (on smart sorbers or zeolite) or extracted and managed as a high nutrient use efficiency fertiliser would also facilitate a decrease in nitrous oxide emissions.
- Soil temperature. Temperature can directly increases denitrification rates, but also via indirect means such as increased respiration rate — resulting in an increase in the volume of anaerobic zones. However, temperature behaviour may not be this simple, as temperature optima do exist. Temperature dependence is more likely to follow a trend of several superimposed relationships. While not readily manipulated in many points in the effluent/deep litter/solids management system, there are likely to be some mitigation opportunities. For example handling, covering, and aeration approaches during composting or stockpiling are capable of altering the temperatures developed. Temperatures in digesters and covered ponds may also be feasible.
- Soil pH. The acidity of the soil environment has a controlling influence on nitrification, denitrification, and the ratio of products derived from these processes — directly influencing N_2O emissions — and may also influence other nitrogen transformations, such as immobilisation and mineralisation — that have an indirect influence on emissions. Microbial populations may change or adapt to different pH conditions, and may do so within days. This characteristic is readily manipulated and could form the basis of mitigation development.

- Indirect emissions of N_2O are likely to be substantial (of the same order of magnitude as direct emissions), via ammonia volatilisation, deposition, nitrification/denitrification.
- A range of reasonably simple mitigation measures to prevent ammonia volatilisation are at a stage where trials may prove some of them practical. These include the use of urease inhibitors, pH modification, use of inexpensive cation exchange materials, and separation of solids from urine.
- Piggery effluent nitrous oxide emissions following land application are often larger than those from other waste streams.
- Effluent treatment and separating slurry into solid and liquid fractions tends to decrease N_2O emissions.
- Slurry incorporation and co-application of effluent and inorganic-N sources can greatly increase nitrous oxide emissions.
- Nitrous oxide emissions can be particularly problematic from deep litter systems relative to conventional ponds. However Australian data is required.
- Permeable pond covers, while potentially valuable in the control of odour, may increase nitrous oxide emissions — though data is scarce.
- Opportunities exist to control emissions through diet manipulation. However diet manipulations may affect productivity.

- Nitrous oxide emissions from slatted floored housing are likely to be slightly less (in greenhouse gas equivalence terms) than methane emissions. Nitrous oxide dominates GHG emissions from deep litter systems.
- Current nitrous oxide emission models are designed for use in soil systems, and tend to be reliant on empirical approaches. The few truly mechanistic models may be over-parameterised. Adaptation to effluent/manure systems would be valuable. Sensitivity analyses could be conducted to remove unwarranted, non critical complexity — revealing the critical factors for manipulation through mitigation managements.

Acknowledgements

3   Introduction

Activities across the spectrum of industries are set to encounter considerable pressure for decreased greenhouse gas emissions. While a decision on whether to include agriculture in the Australian carbon trading scheme will not be made until 2013, the lead time to develop the technologies required to make an impact on emissions necessitates that R&D should commence promptly. Even if some portions of the agricultural sector are exempted from the scheme at that time, carbon offset opportunities within the sector may be considerable and a potential source of industry income.

However, even the most basic data is currently not available for the Australian pig industry. For example, emissions data from pig production in Australia has not been collected. Australian Pork Limited has channelled significant funding into specific research areas (capture of methane from covered ponds) related to this deficit, and this will probably be the first relevant data to become available. Availability of the full range of needed data is vital to inform debate around the possible exemption of pig production from the emissions trading scheme. The collection of this vital data may require a substantial investment from the pig industry, and it is therefore important that an appropriate suite of emissions measurement techniques is selected to provide the needed rigorous data at minimum cost.

This literature review will investigate the range of relevant emissions measurement techniques available. A suite of techniques appropriate to the pig industry will be proposed for development of a measurement protocol. The emissions measurement and mitigation issues operating in the realm of pig production have significant commonality with those apparent in other intensive livestock production systems. The review will propose methods with due consideration of the value of a cross industry approach.

Greenhouse gas emissions from intensive livestock enterprises may soon be a major operational consideration. Up to the point of land application, the manure and effluent waste streams from the pig industry are likely to be relatively easy targets for mitigation. Manure and effluent is initially concentrated in sheds, ponds, and spent deep litter or manure solids stockpiles. However, baseline emissions data for the effluent and manure management systems of piggeries is poor or lacking -- both internationally and for Australian conditions.

Relevant data for deep litter systems is almost non-existent. The nitrous oxide emissions that continue after land application of manure/deep litter/or effluent have not been well characterised, and the over-seas data available vary greatly — though it appears that emissions from effluent or manure systems may be much higher than losses from inorganic fertiliser systems with equivalent N applications. Despite the dearth of data, current DOCC guidelines contain techniques for the calculation of piggery manure management emissions — techniques that rely heavily on un-validated emission and conversion factors. In addition to these concerns these calculation techniques do not reward successful mitigation managements. This is a major disincentive to innovation. Ultimately the needs for the pig industry in this area are to accurately quantify the emissions and processes that lead to them, identify the most cost effective points of mitigation, and develop and extend mitigations to producers where required.

The primary objective of this literature review is to provide the first step in this R&D process — a review of measurement techniques and recommendation for a suite of techniques to be used in method and measurement protocol development — and ultimately to be used in the R&D process.

The literature has a secondary goal to review currently available data on nitrous oxide emissions from the pig industry. While APL, DPI&F, and University of Queensland are currently engaged in a significant research program investigating emissions from piggery ponds, the majority of currently published data is likely to only be available from overseas studies.

4   Emission Measurement Techniques

With the mounting international pressures with regard to climate change and greenhouse gas emissions there has been a dramatic acceleration in the development of techniques for the measurement of emissions. It is now possible to choose from a wide range of approaches, with a range of strengths and different niches for appropriate application.

A number of recent reviews have been conducted. One seeking a broad overview for general applications — and stating the appropriate application context for each (concentrations measured may be 100 times higher than for comparable micro-meteorological techniques. Denmead 2008). Other reviews have sought to recommend approaches for very specific emissions contexts — such as monitoring of the performance of geosequestration (Leuning *et al.* 2008).

None of these reviews have investigated the range of techniques for applicability to piggery emissions or even to emissions from confined animal feeding operations. However, there have been a range of comparative experimental studies of two or more measurement techniques' applicability to the intensive livestock context (Griffith *et al.* 2008; McBain and Desjardins 2005; Sommer *et al.* 2004). These studies will be reviewed.

This literature seeks to comprehensively review the available techniques and their applicability in the Australian pig production context, the on farm pig production infrastructure including the land application system — adding the rapidly accumulating science that has been published in the period since the submission of previous more general reviews (e.g. in the 14 months since submission of Denmead 2008).

In selecting techniques appropriate for the piggery context, a range of factors will be considered:
- The scale of measurement. The scales involved for pig production range from point sources (tunnel ventilation exhausts) and process scales (e.g. small laboratory or field trials concerned with modifiable processes that are readily characterised by measurements at the < 1m scale), through pond and shed scales (10's to hundreds of metres in extent), to hundreds or thousands of metres for land application areas.
- Practical application. Where if anywhere would the technique fit in to the need to quantifying emissions or process/mitigation development studies in the pig production context?
- Accuracy and precision.
- Cost.

A wide range of techniques are available and will be reviewed:
- Chamber techniques;
- Mass balance methods;
- Backwards Lagrangian Stochastic Techniques;
- Micrometeorological techniques, including eddy covariance techniques, relaxed eddy accumulation, and flux gradient methods.

4.1 Chamber Techniques

Chamber techniques are the simplest, lowest cost option for portable methods for the capture of greenhouse gas emissions. Implementation varies, but they may be as simple as a dome shaped or cylindrical vessel embedded into a surface from which emissions are to be captured. They are usually of small scale (< 1 m diameter), but have the advantage that they are capable of magnifying changes in concentration of gas in the head space (Denmead 2008) — thus requiring less sensitive analysis techniques or allowing smaller headspace (the air above the surface inside the vessel) concentration changes to be identified.

4.1.1 Flow-Through Steady State Chambers

Flow-Through Steady-State chambers attempt to maintain the concentration of the measured gas in the chamber by a constant known airflow through the chamber.

Emissions are calculated by identifying the difference between the inflow and outflow air concentrations under constant flow conditions. While these techniques are less sensitive when characterising small fluxes than closed chamber techniques, they have the advantage that the constant flow of air can decrease headspace concentration rises that may otherwise inhibit emissions.

While Denmead (2008) comments on the advantages of use of flow through chambers Denmeade's review quotes no papers that use this technique. A major disadvantage of flow through steady state chambers is that related to the pressure gradient that may be induced by the air flow through the chambers (Rochette and Hutchinson 2005). Even small gradients of less than 4 Pa have been demonstrated to result in a several fold increase in CO_2 emission (Kanemasu *et al.* 1974). Indeed, it has been demonstrated that pressure gradients must be maintained below 0.2 Pa for accurate determinations (Fang and Moncrieff 1996). The theoretical advantages of these chambers over non-steady state or non-flow through techniques theoretically include: an ability to maintain headspace gas species at pre-deployment concentrations, control of temperature, and control of humidity. However, it has proven difficult or impossible to capitalise on the theoretical advantages of this form of chamber in many situations. If emissions are large relative to the background atmospheric concentrations, it may be impossible even to maintain headspace gas concentrations at close to pre-deployment concentrations.

However, this method, which is similar to wind tunnel techniques, has recently been applied by Blunden and Aneja (2008) to piggery lagoons overseas in order to determine ammonia and hydrogen sulphide emissions. In addition, the SIS team has used this technique extensively to determine odour, hydrogen sulphide, and other gaseous emissions from piggery ponds and other intensive livestock industry sources. Emissions may be calculated as follows:

$$\text{Flux (kg m}^{-2}\text{ s}^{-1}) = v\,(\rho_{g,0} - \rho_{g,i})/A, \qquad \textbf{Equation 1}$$

where the volume flow rate is designated v ($m^3\,s^{-1}$), outflow and inflow gas concentrations are $\rho_{g,0}$ and $\rho_{g,i}$ (kg m^{-3}), and A (m^2) is the area of the surface contained under the chamber.

Despite the limitations listed here, FT-SS chambers are more adaptable to long-term continuous monitoring of fluxes from small spatial extents than non-flow through designs (Rochette and Hutchinson 2005), due to their lower potential for modifying environmental conditions internally, though emissions can be related to air flow rate (Schwartzkopf 1978), though a relationship can be established between emissions and air flow rate and emissions accurately estimated, or air flow rate controlled to match external conditions.

Figure 1: The DPI&F SIS wind tunnel represents a form of flow through chamber that has been applied to collect pond and surface emissions.

4.1.2   Non-Flow-Through Non-Steady-State Chambers

A recent review (Rochette and Eriksen-Hamel 2008) of data from non-flow through non-steady state chamber studies (one of the two forms of closed chambers) indicated that while the vast majority of nitrous oxide (N_2O) emissions studies have been conducted using these techniques (356 studies reviewed), the data quality of these studies is often poor: poor in terms of absolute measurement accuracy, and poor in terms of methodology. In more recent years, however, the quality of these studies has improved — and the reviewers indicated six factors that can be controlled to improve the quality of N_2O flux measurements:

1.   Use insulated and vented base-and-chamber designs.
2.   Avoid chamber heights lower than 10 cm,
3.   Insert the chamber into the emissions source a minimum of 50 mm,
4.   Use pressurized fixed-volume containers of known efficiency for air sample storage (i.e., avoid plastic syringes),
5.   Include a minimum of three discrete air samples during deployment, including one at time zero, and
6.   Test nonlinearity of changes in headspace concentration with time for estimating dC/dt at time zero.

Indeed Rochette and Eriksen-Hamel (2008) indicate a list of chamber characteristic and technique issues that should be considered in the implementation of any chamber measurement campaign:

- Surface disturbance related to insertion of chambers into surfaces, and diffusion of gas around this barrier (leakage). Insertion into soils should exceed 120 mm per hour of deployment. There are advantages of a semi-permanent base, over which the chamber is fitted at measurement time.
- The height/measurement period ratio of the chamber should exceed 400 mm h^{-1}.
- Chamber area to perimeter ratio determines the importance of leakage relative to emissions — it is therefore recommended that cylindrical chamber diameters exceed 400 mm.
- Duration of deployment determines the degree of perturbation of soil and air temperature, humidity, gas leakage, and inhibition of emissions. Deployment durations should ideally be kept to less than 40 minutes.
- Insulation/heating effects of the chamber on the soil area enclosed — these effects should be minimised.

- Venting — pressure must be able to equalise, without significant leakage occurring.
- Quality control of air samples — since chamber studies are often associated with off-line analysis rather than in-field analysis. This includes restricting storage periods. However if exetainers are used it has been shown that < 1.5 % change in concentrations will be observed. Where other techniques are applied, a container life/contamination study should be conducted.
- Fixed volume sample containers are to be preferred, followed by glass syringes. Plastic syringes are not desirable.
- Positive pressure in sample containers minimises contamination risks.
- Use non-linear modelling of the concentration increase within the chamber where a linear increase with time is not observed. This requires four or more samples to be collected, allowing extrapolation to time zero emission should significant emission inhibition be detected.
- Samples should be taken as soon as possible after deployment time.
- Ensuring that reported emission rates exceed the detection limit or are simply reported as sub-detection, rather than quantified.
- Correct gas analysis for changes in gas temperature during analysis according to the ideal gas law (Rochette and Hutchinson 2005).

Closed chamber techniques have effectively been evolving over several decades, and their value as a means of monitoring relative changes (for example with different treatments in process and mitigation studies) is well established (Rochette and Eriksen-Hamel 2008).

In its simplest form, emissions are calculated according to the following formula (Denmead 2008):

$$Flux = (V/A) \, d\rho_g / dt \hspace{4cm} \textbf{Equation 2}$$

where the volume is designated V (m^3), gas concentrations are ρ_g (kg m^{-3}), and A (m^2) is the area of the surface contained under the chamber. The term t represents time (s). While not explicitly stipulated by the formula, previous applications of the method have tended to use a linear relationship to model the increase in gas concentration over time (e.g. Hendriks *et al.* 2007; Ruser *et al.* 1998). However, there is credible evidence that the slope of increase of gas concentration with time ($d\rho_g / dt$) (Healy *et al.* 1996; Kroon *et al.* 2008) is best assumed to be non-linear as increasing concentrations can inhibit further emissions (Kroon *et al.* 2008). A non-linear equation fitted to the chamber measurements can be used to determine emissions at time 0, allowing quantification of the undisturbed emission flux (Pattey *et al.* 2005).
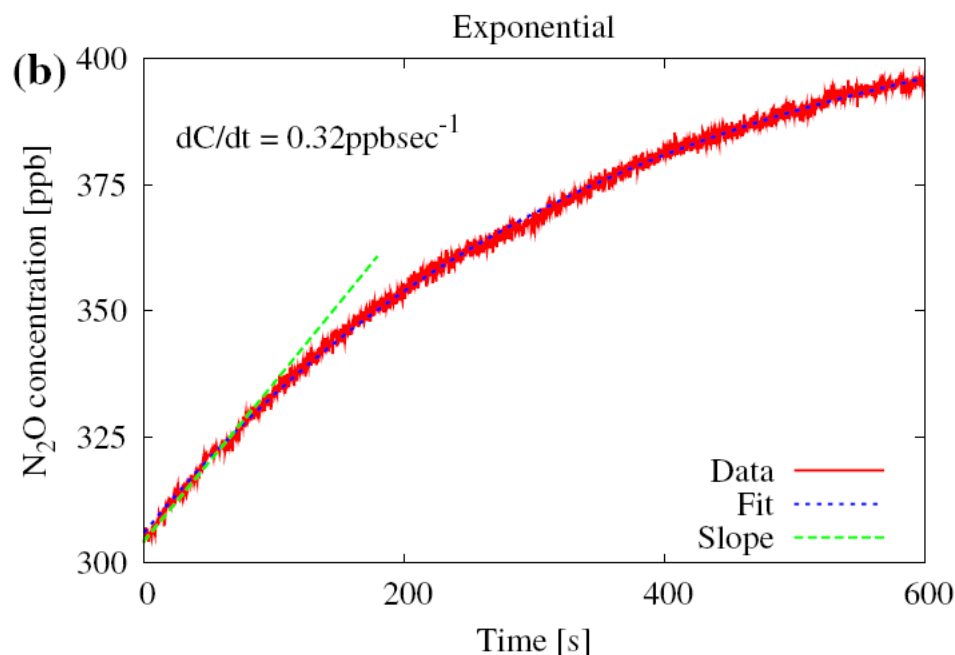
Figure 2: Example of the non-linearity of the gas concentration change under a closed chamber (from Kroon *et al.* 2008).

Rather than being portable many of the chamber designs are set in place and caused to (automatically) open and close. This is very unlikely to be suitable for trafficked areas in the intensive livestock context. Also, it is likely that this approach would violate some of the heat transfer and shading conditions for good measurements that have been recommended (Rochette and Eriksen-Hamel 2008).

Chamber NFT-NSS techniques remain a key method in the arsenal — fitting situations where no other methods are available. They naturally exclude emissions from other sources, they have low power requirements compared to many other techniques, and they provide greater measurement sensitivity than more expensive techniques. These techniques are also particularly adept at detecting relative treatment differences, and are well suited to process-based mitigation studies — and are capable of measuring emissions at small scale. While Denmead (2006) indicated that there was a factor of 2 variations in emission values for N2O from six chambers, the daily means of the emission values from the chambers was very close to those measured by the aerodynamic technique. Where sufficient replicate chambers are applied it appears that they can be used to quantify emissions from larger sources — suitable for situations where confounding emissions from adjacent sources are a significant problem, or where maximum measurement sensitivity is required.

4.1.3   Flow-Through Non-Steady-State Chambers

A subset of the closed chamber group are those where air is circulated in a closed loop between the head space and a gas analyser, permitting the rate of gas concentration to be monitored so as to detect any inhibition of the flux through a build-up in head space concentration and unwanted environmental changes such as increased temperature or pressure (Rochette and Hutchinson 2005). Mixing has also been applied to some chambers by other means (Woodbury *et al.* 2006), however, this does not necessarily qualify the technique as a flow through technique, but may be critically important in these flow through systems (Rochette and Hutchinson 2005).

Since the characteristics of these chambers are otherwise similar to those for non-flow-through non-steady-state chambers, the same range of advantages and disadvantages apply with the added advantage of being able to continuously monitor concentrations in real time.

> **Observation**: FT-NSS chambers combined with real-time analysis are probably the best small scale process-based mitigation investigation tool.

4.1.4   Application Contexts
Given appropriate methodology chambers are known to produce accurate and acceptable results, though many studies have to date been conducted inadequately, or documented inadequately (Rochette and Eriksen-Hamel). The small spatial extent of chamber techniques (e.g. cylindrical chambers with diameters of 400 mm; Rochette & Eriksen-Hamel 2008) suggests a significant disadvantage for larger scales.

However, it is known that replication can overcome this issue where chamber use is necessary, or where chambers have been deployed for another purpose but information is also required at a larger scale. For example, a factor of two variation in emission values for N2O from sugar cane soils with six chambers was observed, though the daily means of the emission values from the chambers was very close to those measured by the aerodynamic micrometeorological technique (Denmead *et al.* 2006). Comparisons were less encouraging in this case for methane emissions, due to spatial variability or detection limit issues, however, similar successes with replicated chamber studies are also reported elsewhere (Laville *et al.* 1999).

Some issues to note in the application of these techniques to pig industry research:
- Conventional shed emissions. Practical applications in this context are not immediately evident.
- Deep litter sheds. Application of this technology within deep litter sheds to measure emissions from the floor space is likely to be practical, inexpensive, and may enable elimination of the influence of other nearby sources. Where nearby sources are not significant or can be eliminated other techniques detailed later in this review may be more suitable.
- Ponds. These types of technologies have already been applied to measuring emissions from ponds, and technologies could be similar to those associated with the DPI&F SIS wind-tunnel. While there is likely to be an application for these techniques in eliminating the influence of adjacent emissions sources, it is also probable that other mid scale approaches detailed in this report will be less adversely affected by spatial variability, and will entail lower labour costs due to the need for high replication.
- Sludge and solids stockpiles. Similar to the comments above, where discrimination of sources is required, chamber techniques may have application in this context for fairly impermeable stockpiled materials (Pattey *et al.* 2005). However, where stockpiled solids have significant gas permeability non-steady-state chambers are likely to be completely inappropriate, due to a strong effect in inhibiting evolution of gasses (Sommer *et al.* 2004).
- Land application areas. Similarly to above, measurements can be conducted where sufficient replication is applied (Denmead *et al.* 2006; Laville *et al.* 1999).
- Process scale mitigation studies conducted in the field, laboratory, or greenhouse. Process studies and studies seeking to develop mitigation techniques frequently need to eliminate the interfering influences, or to decrease the number of varying factors to a limited number that can be controlled. Chamber studies are likely to be particularly valuable in this context.

4.1.5 Strengths and Weaknesses

Chamber methods encompass a range of techniques that are quite inexpensive relative to the other options reviewed in this document. These techniques are extremely portable, and do not require fast response analysers, nor do they require highly sensitive analysers (concentrations measured may be 100 times higher than for comparable micro-meteorological techniques. Denmead 2008).

Weaknesses associated with pressure differences that may result in large errors (Denmead 1979) can be overcome through appropriate venting (Meyer *et al.* 2001; Rochette and Eriksen-Hamel 2008) or the use of electronic pressure and flow control (Denmead 2008). Turbulence in the chamber may affect the flux (DenmeadReicosky2003), or the flux measured may not reflect the wind speed derived flux from outside the chamber. The solution appears to be to relate emissions to a regular wind speed pattern or to a relationship function as described in Denmead (2008).

The short recommended duration of measurement for NSS chambers implies a large labour requirement for measuring piggery enterprise components where there are large diurnal (Jury *et al.* 1982), seasonal, and nutrient input-related variations that must be characterised by in a comprehensive measurement campaign (Kroon *et al.* 2008). Indeed Denmead in his review (2008) points out that due to diurnal cycles – the minimum measurement collection period should be 24 hours of contiguous measurements.

> **Recommendation:** NFT-NSS chambers are a key technique for process investigations and development of mitigations in laboratories. They may also be used to separate emissions sources where these adjacent emissions may otherwise be intermingled and expensive or impossible to differentiate.

4.2 Mass Balance Techniques

These analytical techniques are guided by the principle:

$$\text{GHG emissions = GHG exit from area - GHG entry into area,} \quad \textbf{Equation 3}$$

Or more formally, mean horizontal flux F_h (kg m^2 S^{-1}) at level z for unit width:

$$Fh,z = \text{mean over time}(u_z(\rho_{g,z} - \rho_{g,u})) \quad \textbf{Equation 4}$$

where u_z is horizontal wind speed, and $\rho_{g,z}$ and $p_{g,u}$ are the gas concentration downwind and upwind. An effective rule of thumb according (Denmead 2008) is that in neutral atmospheric conditions (early morning and sunset, conditions where there is no gradient of air temperature in the near ground atmosphere, and hence no density gradient and no buoyancy) the height of the plume Z is likely to be 1/10 of the fetch (the upwind distance of airflow over the source; X). This ratio will be larger in unstable conditions (daytime), but less in stable conditions (night-time when colder dense air is associated with the ground surface). In highly unstable conditions Z/X was observed to be close to 1/3 (Desjardins *et al.* 2004). A numerical integration is necessary to determine surface flux from equation 4 (estimating F_0, the surface flux density; kg m^{-2}s^{-1}). A necessary term in these calculations is the time mean of (uρ_g), commonly represented in equations as $\overline{u\rho_g}$, but estimated for convenience as:

$$\overline{u\rho_g} = \overline{u} \times \overline{\rho_g} \qquad \textbf{Equation 5}$$

However, there is a significant error in this formula, which would more accurately represented as:

$$\overline{u\rho_g} = \overline{u} \times \overline{\rho}_g + \overline{u'\rho'}_g \qquad \textbf{Equation 6}$$

where, u' represents the deviation from the mean of wind speed, and likewise ρ_g' the deviation from the mean for gas concentration, and the term $\overline{u'\rho'}_g$ represents a turbulent diffusive flux in the upwind direction. The magnitude of $\overline{u'\rho'}_g$ is between 5 to 20 % of the value of $\overline{u} \times \overline{\rho}_g$ (as reviewed by Denmead 2008) as confirmed in field trials and wind tunnel experiments (e.g. Desjardins *et al.* 2004). Denmead (2008) recommends a decrease in the horizontal flux estimated by 10 to 15 % or the use of fast response anemometers (Desjardins *et al.* 2004), such as 3d sonic anemometer apparatus.

> **Recommendation:** In applications where measurements may challenge greenhouse gas assumptions, we recommend that the most rigorous approach involving the use of fast response anemometers.

The turbulent diffusion flux, however, is the only complication to what is otherwise a fairly simple theoretical basis for the "closed" and "open" forms of mass balance methods.

Some ambiguity is evident in the classifications of techniques described by several of the most recent and comprehensive reviews. Leuning *et al.* (2008) refers to "Three dimensional transport" measurement systems, and includes in this measurement methods that are certainly mass balance methods — referring to the range of these mass balance techniques as "integrated horizontal flux methods", including together under this title methods that Denmead (2008) refers to as "closed" and "open" mass balance methods. McGinn's (2006) separation of "integrated horizontal flux" techniques seems more logical, discussing "mass difference" methods and "integrated horizontal flux" techniques.

4.2.1   Closed or Mass Difference Systems

Closed mass balance approaches seek to measure concentrations both upwind and downwind of a source by means of a grid of samplers, and are suitable for small well defined source areas. They are suitable even for source areas of heterogenous character (Denmead 2008) or complex topography (Leuning *et al.* 2008). A key advantage of these methods is their ability to represent three dimensional transport (Leuning *et al.* 2008), making them suitable for measurement of emissions from ponds where there is significant wind disturbance over the surface, where one dimensional methods (such as the flux gradient methods described below) are known to fail (Wilson *et al.* 2001). When applying these methods, wind velocity (speed and direction) is measured and emissions samples analysed at enough sampling heights to define the concentration profile from the ground surface to the full height of the emission plume.

Denmead *et al.* (1998) successfully applied a mass difference form of these methods, drawing air at equal rates into sampling tubes located in a 3 dimensional matrix surrounding the emission area. This air was passed to a gas analyser for measurement, determining the mean concentration at each sampling height on each face of the square test area.

These methods have been used by Denmead *et al.* (1998) to measure emissions of CO2, CH4, N2O from landfill. They have also been applied to measure methane emissions from penned and free ranging cattle and sheep (Harper *et al.* 1999; Leuning *et al.* 1999), and nitrous oxide emissions from a grazed pasture (Denmead *et al.* 2001). The enclosed areas investigated by Harper *et al.* (1999) and Leuning et al. (2001) were square with 24 m sides, with measurement conducted at 0.5, 1, 1.5, 3.5 m, or 0.5, 1, 2, and 3.5 m above the ground.

4.2.2   *Open or Integrated Horizontal Flux Systems*

Integrated horizontal flux techniques (Denmead *et al.* 1977) utilise a single tower upwind (or known background concentrations), and a single tower downwind of the source (McGinn 2006), and configuration in relation to wind direction determine the completeness of emission characterisation. These techniques are most appropriate in situations of limited upwind source and uniform surface flux and are suitable for measurement of emissions from animal herds and buildings, and from manure management activities such as spreading, effluent lagoons, manure piles, and waste sites (Denmead 2008).

Integrated horizontal flux techniques have been applied to measure emissions from cattle manure stockpiles (Sommer *et al.* 2004), from grazing cattle (Griffith *et al.* 2008), from dairy cow herds (Laubach and Kelliher 2005; Laubach and Kelliher 2004), and from grazing sheep (Leuning *et al.* 1999). Integrated horizontal flux techniques are sometimes used as a reliable reference technique for comparison to other methods (Sommer *et al.* 2005). Integrated horizontal flux techniques have proven ideal for measurement of manure storages and other point sources (McGinn 2006).

As for mass difference techniques, it is necessary to measure emissions downwind at sufficient height to define the shape of the concentration profile to the top of the emission plume.

As part of the Meat Quality CRC program (early 2000's; figure 3), we applied this technique to ammonia volatilisation from a beef lot-feed pad (unpublished research, Ken Casey and Matt Redding, DPI&F Queensland), using passive ammonia samplers (Leuning *et al.* 1985).

Figure 3: Ammonia emissions measurement using integrated horizontal flux techniques and passive samplers, during a measurement campaign by the DPI&F SIS team.

Desjardins *et al.* (2004) used IHF techniques and could detect a change in methane emission rate of 9% ($P <= 0.05$), with potential to improve this to detection of 5% changes. Their mass balance technique relied on an open path laser technology, with detectors mounted at six heights to 6 m and a laser path length of 50.5 m. They anticipated several practical difficulties in implementing the approach on farm: the need for clear lines of sight for the laser (common to all long, open path measurement methods), an undisturbed fetch without interrupting features and infrastructure (a requirement integrated horizontal flux techniques), and a requirement for measurement heights in

excess of 6 m. In general, these open mass balance techniques encounter difficulties where wind direction shifts outside a pre-set limit. Where uniform circular emission plots are feasible, this problem can be eliminated by locating a sensor tower at its centre, thus ensuring that the length of fetch is always the same (Beauchamp *et al.* 1978). In addition to this pioneering work on ammonia emissions from sewage sludge application, the technique has been applied to other emission situations (examples listed in Denmead 2008). Recently the circular source variation of the IHF technique was successfully was to ammonia emissions from piggery effluent applied in a circular plot (Warren *et al.* 2006). Accuracy deteriorates with decreasing plot radius, and the recommended minimum radius for the technique is 20 m or more, providing accuracy to within 20 % for ammonia volatilisation (Wilson and Shum 1992).

An evolution of the integrated horizontal flux technique provided by Wilson *et al.* (1982) allows gas flux to be determined from measurements of wind speed and gas concentration at just one height above the surface. This development is reliant on the observed relationship that $\overline{u}\,\overline{\rho}\,/\,Flux$ is almost constant at a specific height (ZINST) despite changes in stability conditions. The height of ZINST is dependent on plot radius and surface roughness (z_0). The authors of this development also provided a procedure to estimate errors due to selection of inappropriate ZINST values (e.g. due to poor values of z_0). The method was relatively insensitive to errors related to inaccuracies in z_0, with these error values being less than or comparable to errors for the more measurement intensive circular plot techniques (e.g. Wilson and Shum 1992).

4.2.3   Application Contexts for Mass Balance Techniques

Observations on the application of these techniques to the pig industry:

- Overall emissions from conventional and deep litter sheds. Mass difference mass balance approaches may be effective in measuring emissions from sheds. Sensitivity to disturbance of air flow over the sheds themselves is unknown, and may increase plume heights, or result in other negative effects. The technique should be capable of eliminating the effects of adjacent sources. Integrated horizontal flux techniques are unlikely to be applicable due to the heterogeneous nature of the source areas.
- Ponds. Mass difference techniques have been successfully applied to pond emission measurement. Integrated horizontal flux techniques may be applicable if disturbance due to banks and structures is not significant. Ponds are unlikely to be circular sources, so these latter techniques would not be able to take advantage of the simplifications that a circular source might enable, and fetch length to the downwind measurement tower will vary with wind direction.
- Sludge and solids stockpiles. Both forms of mass balance techniques are likely to be applicable to these measurements. The integrated horizontal flux method requires more ingenuity in this application, however, the technique has been applied to a circular plan stockpile with good results, using a weather-vane-like upwind and downwind sensor apparatus suspended above the stockpile (Sommer *et al.* 2004).
- Land application areas. Small to moderate plot sizes (0 to 90 m) could be investigated by either one or other of the mass balance techniques, based on comments in the Denmead (2008) review and other reviewed literature.
- Process scale mitigation studies conducted in the field, laboratory, or greenhouse. The mass difference approach may be conducive to this type of study on the small plot scale.

4.2.4 Strengths and Weaknesses of Mass Balance Techniques

Mass balance techniques are appropriate for small to mid scale source areas with well defined boundaries (several metres to 90 m according to Denmead 2008). Both homogenous and heterogeneous emissions source measurements can be accommodated with one or other mass balance approach. As Denmead (2008) notes that both homogenous and heterogeneous sources can be measured using:

- closed path analysis instruments in combination with mass difference measurement techniques
- open path measurement instruments in combination with an integrated horizontal flux approach

Integrated horizontal flux techniques employing closed path single point measurement instruments require a homogenous source distribution.

Rapid response instrumentation is not required. However, slow response instrumentation requires the application of a correction for diffusive flux (decrease estimated flux by 10 to 15 % as discussed in section 2.2). This type of correction is not necessary where fast response instrumentation is applied (Desjardins *et al.* 2004). No assumptions are made about the wind profile or stability characteristics of the system.

Circular plots offer a considerable simplification of the integrated horizontal flux technique, overcoming the need to continuously monitor wind direction — since fetch distances are always equal. Where this is not possible measurements and post possessing is greatly complicated, and wind direction may render tower placement in a given configuration completely inappropriate.

Mass balance methods are most likely to be effective where strong contrast exists between background concentrations and wind concentrations exiting the plots.

At least 5 profile measurements are required over pastures, or fallow soil (Denmead 2008). However more are probably required where surface airflow is disturbed (such as over a banana plantation, Prasertsak *et al.* 2001). This suggests that greater profile heights and more samplers may be required for measurements around sheds and ponds.

> **Recommendation**: Most mass balance techniques are more measurement intensive than is desirable. However the ability of mass difference techniques to eliminate the effect of adjacent emission sources may be valuable, and integrated horizontal flux techniques provide a relatively simple technique to which to compare emissions measurements conducted using other techniques. These advantages may make these techniques unavoidable in some circumstances, however, the measurement efficiency of some of the following techniques make mass balance methods less attractive.

4.3 Backward Lagrangian Stochastic Techniques

Many micrometeorological techniques have two major drawbacks. Firstly they require expensive and extensive instrumentation: equipment not only capable of measuring meteorological variables at higher frequencies than 10 times a second, but also means of measuring or sampling gas concentrations at these high frequencies also, together with a requirement for multiple measurement heights. The configuration of source area required, however, may be a more restrictive consideration in the pig production context. Micrometeorological techniques often require large, flat, homogenous source areas — sources not likely to be encountered in piggery

enterprises apart from large effluent or solids re-use areas. This latter problem was recently explored for a cattle lot-feed (Baum *et al.* 2008).

The backward Lagrangian stochastic technique (BLS) is one means of overcoming these difficulties and introducing significant measurement flexibility.

The "Lagrangian" of a dynamic system is equal to system kinetic energy minus potential energy. Where the conditions of Lagrangian Mechanics apply, the motion of particles in a system can be represented (using the Euler-Lagrange equation) if this Lagrangian value is known.

A Lagrangian model of atmospheric dispersion can be used to calculate the flux of a gas given measurements of atmospheric turbulence and concentrations of the gas of interest in air at any height downwind — under any stability condition (Flesch *et al.* 2004; Flesch *et al.* 1995).

This translates, in practical terms, to considerable measurement flexibility, and has the added advantage that the technique may be applied with line averaged concentration measurements or with point measurements. The method is likewise applicable to both point and area sources.

The BLS technique is applicable to well defined source areas of moderate size, and any shape — and has already proven very applicable in the measurement of emissions from various beef lot-feed sources (Loh *et al.* 2008).

Lagrangian mechanics is used to trace detected "air-packets" through their trajectories back from the sensor to the emissions source, using fast response anemometer data (10 Hz measurements; Figure 4). A large number of these simulations are conducted (commonly 50,000). "Touchdowns" are noted as being inside or outside the source area of interest, as the vertical velocity of the particle calculated. The following relationship is used to describe the system:

$$(\rho_g / F_0)_{simulated} = (1/N)\sum |2/w_0|,$$ **Equation 7**

F_0 is surface flux density, N is the number of particles simulated, w_0 is the vertical velocity of particles at touchdown. The surface flux density is derived from:

$$F_0 = (\rho_g - \rho_{g,b})/(\rho_g / F_0)_{simulated},$$ **Equation 8**

where $\rho_{g,b}$ represents the background gas concentration. The application of the BLS technique is greatly streamlined and simplified by the use of the Windtrax model (Crenna *et al.* 2008).

Inputs to the model (Crenna *et al.* 2008) include the surface roughness height (z_0), source area geometry, and the three dimensional location of the gas sensor, wind speed, direction, and turbulence statistics such as the Obukhov length (L) and friction velocity u^*.

If background concentrations are known, then observations along one line or at one point can be used in a determination. If not, then two points or lines are required, preferably with one point intercepting little of the emissions from the source, and the other's measurements dominated by these emissions. The best approach is to "overdetermine" the emissions by collecting data from more than two measurement points or paths — thus decreasing the effect of errors in measurement, and allowing more touchdowns across the source area to be simulated. By using

overdetermination techniques, a CV of 10% has been achieved for ammonia emissions measurement from grazed cattle (Denmead *et al.* 2004).
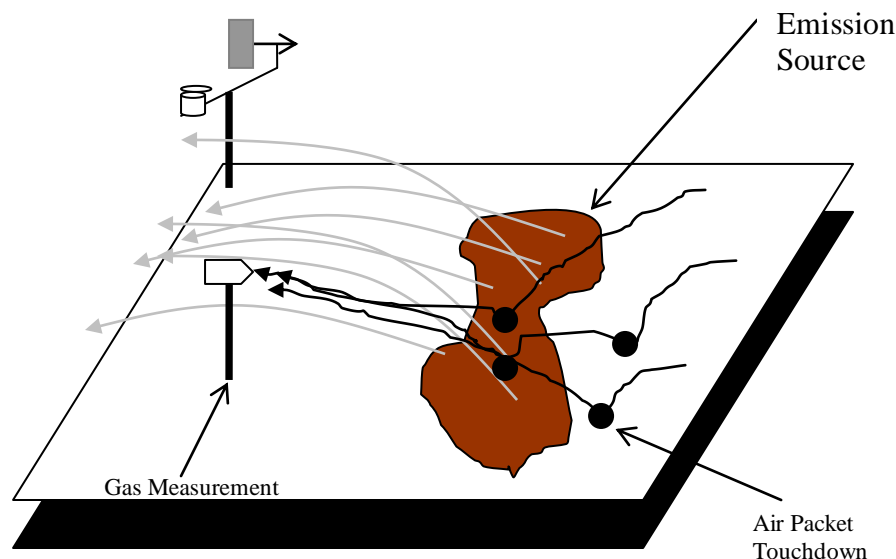
Figure 4: The BLS technique functions by using high resolution meteorological measurements to trace the "packets" of measured gas back to touchdowns within or outside the source area (figure is a modification of diagrams from Flesch and Wilson 2005).

4.3.1   Robust Measurement

Underlying Lagrangian dispersion modelling and the BLS technique are assumption of the Monin-Obukhov hypothesis (Monin and Obukhov 1954). This theoretical base suggests that over flat terrain, atmospheric surface layer turbulence is determined by a few key parameters, including height, buoyancy, kinematic surface stress, and surface temperature flux (Kaimal and Finnigan 1994). These assumptions are least satisfied during severe atmospheric stratification or during transition periods such as sunrise and sunset. Estimates conducted during periods of extreme stability may also be problematic (Flesch *et al.* 2004).

Flesch and Wilson (Flesch and Wilson 2005) suggest that where the terrain is "tolerably" homogenous and amenable to the assumptions of Monin-Obukhov theory, the BLS approach can be applied.

In fact, research has already gone a long way to demonstrate just how tolerant and robust the BLS technique is. For example, it has been demonstrated that the technique is insensitive to obstructions between the measurement point and the source — so long as the obstruction was placed more than 25 times it's height from the measurement point (McBain and Desjardins 2005). Measurements of ammonia emissions from the banks surrounding piggery ponds (Dzikowski *et al.* 1999) have been found to be quite accurate (Flesch and Wilson 2005), within 15 % of measurements conducted using an integrated horizontal flux technique during largely overlapping time periods (McGinn and Janzen 1998). The departures from ideal Monin-Obukhov similarity assumptions caused by the banks of the piggery pond had an insignificant effect on final measurements (Flesch and Wilson 2005).

Divergence from Monin-Obukhov similarity assumptions at the emission source has also been investigated. The effect of obstacles at the source could be overcome by placing the detector an

appropriate distance downwind (Flesch *et al.* 2005) — suggesting that measurements of shed sources may be effective. Other options for these types of measurements are likely to be far more expensive (e.g. the intensive sampling required for mass difference techniques on this relatively large scale). A combination of the BLS technique with tracer gas release may be ideal.

Near continuous data sets can be obtained by placing sampling equipment within an emission source area, producing superior data for some source configurations, including beef lot-feed pads (Flesch *et al.* 2007).

The nature of the BLS model is that measurements conducted at the margin of the emission plume are least likely to produce accurate flux estimates. Adjacent emission sources that disrupt the uniformity of the background concentrations introduce the need for additional sampling and measurement. For example a study has been successfully conducted that separated emissions from adjacent grazed and ungrazed paddocks (Denmead *et al.* 2004).

One criticism of possible numerical errors in some BLS models (Cai *et al.* 2008) may simply indicate that the impressive performance of the BLS approach demonstrated in comparison trials *could* be improved upon. Flesch and Wilson (Flesch and Wilson 2005) suggest that the upper limit of single time-point based flux estimates with this technique is around ± 10 % (assuming perfect wind statistics, which do not exist). Where continuous measurements are conducted with multiple sample points or multiple sample lines, the upper limit of potential for accurate representation is even better. Ultimately the limitation may be the accuracy of the wind statistics available.

4.3.2   Application Contexts for BLS Techniques

As indicated by Denmead (2008), this technique is particularly suited to measurement of intensive animal systems and land application areas. Thus it is one of the primary techniques recommended in this review -- for ponds, sheds, and effluent/solids re-use areas. Pilot trials in conjunction with tracer release (Griffith *et al.* 2008; Sneath *et al.* 2006) will help ensure accurate representation of disturbed emissions sources.

Importantly, the technique is already in use in Australian studies of intensive livestock emissions from other industry sectors (beef lot feeding, Loh *et al.* 2008; McGinn *et al.* 2008).

4.3.3   Strengths and Weaknesses of BLS Techniques

The mounting body of experimental evidence suggests that while assumptions of appropriate conditions for MOST theory are made for the application of the BLS technique, the technique is robust and measurements conducted using it are accurate. Applications to date have been demonstrated for piggery ponds and beef lot feeding.

The technique is sensitive to poor sampling position relative to the plume, and measurements conducted close to the margins of plumes should be discarded. Similar data filtering should be applied to periods of extreme atmospheric stability, transition periods, and periods of extreme atmospheric stratification.

Multiple adjacent sources may pose a problem to the technique, necessitating collection of more measurements. This is therefore a problem of expense — in contrast to the likely impossibility of conducting measurements in these situations with many micrometeorological techniques. Indeed greater flexibility of source configurations and topography are possible with the BLS technique than are practical with the other techniques reviewed here.

The availability of the Windtrax model is also a significant advantage to the implementation of the BLS technique (Crenna *et al.* 2008).

> **Recommendation:** The source and scale flexibility, robustness, body of publication, software support, modest analytical requirements, and choice of this technique for measurements for the intensive livestock industry in Australia and overseas make the BLS method a strong candidate for the primary measurement approach for the pig industry.

4.4 Landscape Scale Micrometeorological Methods

Micrometeorological approaches apply where fluxes are nearly constant with height and concentrations change vertically but not horizontally. These approaches are therefore unlikely to apply to pig production and other intensive livestock systems, except where effluent, manure, or manure solids are land applied very broadly in homogenous flat terrain.

The area contributing to the flux measured by a technique is called its "footprint". Under the limitations of micrometeorological techniques, the footprint must logically be smaller than the homogenous source area, and superimposed on it. The footprint of the source contributing to measured gasses at a height z is strongly influenced by surface roughness and thermal stability (Denmead 2008). Several rules of thumb have been observed to apply (Leclerc and Thurtell 1990; Schuepp *et al.* 1990), producing conditions where flux is nearly constant with height of z, and representative of the flux at the surface (Denmead 2008):

- In neutral conditions 85 % of the flux measured at z originates from within 100 z upwind, with the biggest contributions coming from around 10 z. The practical fetch to height ratio to use is 100:1.
- In unstable conditions the footprint is somewhat smaller, however, in practical terms the appropriate fetch to height ratio to use is once again 100:1.
- In stable conditions this footprint is much larger. Fetch to height ratios expand to 200 to 350:1.

In effect this means that opportunities to use these techniques for the pig industry are probably restricted to homogenous (in terms of topography, soil, and management), large land application areas — where it may be possible to select a fairly regular measurement area with hundreds of metres of upwind extent.

Techniques include eddy covariance, eddy accumulation, and relaxed eddy accumulation.

4.4.1 Eddy Covariance

In many ways, eddy covariance techniques are the most direct way to measure emissions: they determine the vertical flux at the point of measurement, are unaffected by the stability considerations that must be applied to many other methods, and do not require simplifying assumptions (Denmead 2008).

These techniques pose particular problems for greenhouse gas measurement, since they require gas analysis instrumentation with very fast response times (Denmead 2008). Closed path tuneable diode laser can be used for CO2, CH4, N20. Not many other options currently exist.

The problems related to greenhouse gas emissions measurements using this technique are:

- Complications related to simultaneous fluxes of heat and water vapour. Constant sample temperatures can be used to eliminate this issue in closed path analysis using heat exchangers or minimum tube lengths (Leuning and Judd 1996). Air sample dryers can likewise be used to eliminate water vapour issues (Laville *et al.* 1999).
- Since high frequency gas analysis and meteorological data is required there is a need to account for lag between vertical wind measurements and gas concentrations.
- While closed path analyses seem to be the only current option, the sample tubes conducting gas to the instrument have the effect of damping important concentration fluctuations due to wall sorption behaviour (Ibrom *et al.* 2007). Advice on how to deal with this issue has been published (Leuning and Moncrieff 1990) and also means of estimating the impact of this behaviour (Leuning and Judd 1996).
- The general difficulty with these "landscape scale" methods — large fetch lengths relative to sampling heights.
- Selection of vertical and wind direction alignment of the sonic anemometer to prevent negative effects of flow distortion errors around the instrument given that wind direction will vary (Coppin and Taylor 1983; Kaimal *et al.* 1990).
- The influence on flow due to neighbouring equipment and structures (Moore 1986, as cited in Denmead 2008)
- The extremely high frequency of sampling required.

In stable conditions (e.g. night) eddy covariance techniques were found to be preferable to flux gradient techniques for nitrous oxide emissions from grazed pastures (Phillips *et al.* 2007). However, error due to the micrometeorological technique and analysis combined were about 60 % at night. Similarly errors determined by (Laville *et al.* 1999) were about 25 % for 15 min flux estimates for N_2O using eddy covariance and flux gradient measurements.

4.4.2 Eddy Accumulation

Researchers developed this technique as a solution to the high frequency of sample analysis required to conduct eddy covariance studies (sample analysis required 10 times every second, McInnes and Heilman 2005). Samples are collected with apparatus that collect separate updraft and downdraft samples, proportional to the magnitude of their vertical velocities — that are then analysed (Desjardins 1972). While this solution appeared attractive, there was a practical difficulty in maintaining constantly proportional sampling throughout the range of vertical wind-speed fluctuations that occur in the field (McInnes and Heilman 2005). The relaxed eddy accumulation technique is this methods successor.

4.4.3 Relaxed Eddy Accumulation

The concept behind this approach is similar to that for the eddy accumulation technique, however, sampling proportional to the vertical wind speed is not required. Samples are simply collected at constant flow into one of two bins representing updrafts and downdrafts.

High precision measurements of vertical wind speed are required, and offsets between sample collection times and wind speed measurements cannot be eliminated with latter processing (Leuning *et al.* 2008). High quality plumbing and flow control is critically important. The emission flux for this technique is calculated as follows (Businger and Oncley 1990):

$$F = \beta \sigma_w \overline{d_a} (\overline{\chi \uparrow} - \overline{\chi \downarrow}) = \beta \sigma_w \overline{d_a} \left(\frac{m \uparrow}{ft \uparrow} - \frac{m \downarrow}{ft \downarrow} \right),$$

Equation 9

where over-bars represent time means, β is a proportionality factor, χ is the mixing ratio for the gas analysed, d_a is the density of dry air, σ_w is the standard deviation of the vertical wind velocity, f is the mass flow rate of dry air, t represents the sampling period, and $m \uparrow$ and $m \downarrow$ represent the masses of upward and downward accumulated gas to be analysed.

Published literature suggests that the relaxed eddy accumulation technique is a viable alternative to eddy covariance methods for greenhouse gas measurement (McInnes and Heilman 2005). The fact that measurements are conducted at a single height rather than several heights is a slight advantage over flux gradient techniques (described below).

Recently, the relaxed eddy accumulation technique has been applied in an aircraft mounted application to measure landscape scale methane emissions (Pattey *et al.* 2006).

4.4.4 Flux Gradient Methods

These methods are reliant on an analogue of gas diffusion — gas parcel diffusion. While diffusivities of molecules can be around 0.00001 m^2 s^{-1}, parcel diffusions, however, will be on the order of 0.1 m^2 s^{-1}, with this diffusion constant being represented by K_g (Denmead 2008). The value of K_g is influenced by wind speed, height of the point of interest, atmospheric stability, and "aerodynamic roughness". The result of these interactions is that K_g is site and example specific — it must be determined *in situ*. The underlying relationship for gas emission flux is:

$$F_g = -K_g \partial \overline{\rho_g} / \partial z,$$

Equation 10

and similar equations apply to fluxes of heat and momentum (H, τ), where the eddy diffusivities are represented by K_h and K_m:

$$H = -c_p \overline{d_a} K_h \partial \overline{\theta} / \partial z,$$

Equation 11

$$\tau = \overline{d_a} K_m \partial \overline{u} / \partial z,$$

Equation 12

where θ is the potential temperature of the air (the temperature of an air parcel if it was brought to a standard reference pressure, 1 atmosphere, without heat loss or gain) and c_p is the specific heat of air at constant temperature (energy required to raise the temperature of a mass of air by a unit of temperature).

In the **aerodynamic method** the gas concentration and the flux of momentum between the atmosphere and the surface are used to estimate gas concentrations. The diffusivity in Equation 10 is substituted as follows:

$$K_g = ku_* z / \varphi_g,$$

Equation 13

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where k *is* von Karman's constant, the function φ_g represents the stability conditions of the atmosphere (as summarised in Prueger and Kustas 2005), and u_* is the friction velocity. Gas concentrations are usually measured at two levels, and the difference between the concentrations at the two heights used in calculations.

Significantly, this technique allows measurement from smaller plot sizes (1-2ha) than from eddy covariance techniques. Since sonic anemometer readings are not required, anemometer readings can be conducted with other devices — that may be mounted closer to the ground surface. This leads to a smaller fetch — and small footprint (smaller plot size)(Wagner-Riddle *et al.* 2005). Since 3-d sonic anemometry is not required, emissions measurements using cup or 2-d anemometers can also be conducted during fog, dew, and rain. Since synchronisation of high frequency anemometer and gas analysis is not required, buffering effects and high frequency damping of gas concentrations in sample tubes is no longer important — and long sample tubes can be used with closed path analysis techniques (Denmead 2008). McGinn (2006) suggests that aerodynamic methods may be appropriate for effluent pond measurements — but only large lagoons of appropriate footprint (given the above footprint information, presumable larger than 2 ha, which are probably rare or non-existent in the pig industry), and the method is probably inappropriate for any other pig industry point source. While not recommended by McGinn (2006) his review indicates that aerodynamic methods have been applied by a number of researchers in relevant contexts: piggery effluent ponds (Harper *et al.* 2000; Harper *et al.* 2004) manure holding facilities, dairy cow emissions from a grazed field — though with additional corrections (Laubach and Kelliher 2004).

A major disadvantage of using aerodynamic techniques is inaccuracy when wind speeds are low — leading to inaccurate estimates of wind speed gradients and large errors in calculated emission fluxes (McGinn 2006). However, in terms of measurements for the pig industry, possibly the greatest downfall of the methods is their suspected inaccuracy due to the difference between the real values of K_g and K_m which are normally assumed to be equal or comparable in calculations (estimated emissions only 0.6 of true emissions, Flesch *et al.* 2002).

While the aerodynamic method uses momentum as a tracer, the same sort of approach can be applied to other tracers: water vapour, CO2, and heat (**Tracer methods**). The **Bowen ratio** or energy balance method uses energy as the tracer flux.

Net radiation, or the energy balance, is dependent on the flux density of sensible heat from the surface to the atmosphere, the flux density of latent heat (due to evaporation), the flux density of heat into the soil's surface, and storage of energy. The technique requires measurement of the flux density of heat into the soil, usually with soil heat flux plates. Where accuracy is important, measurements of other sources and sinks of energy are required. The result is a suite of high accuracy measurement requirements.

One advantage of this approach is that it also provides information on evaporation rate. The Bowen ratio method, however, is very error prone around sunrise and sunset (Denmead 2008). The same potential inaccuracies related to differences between K_g and K_m as effect the aerodynamic method also effect the Bowen ratio method (Flesch *et al.* 2002) — and could be severe. Additionally the method assumes that transfer behaviour of the tracer (in this case energy) is similar to the transfer behaviour of the gas of interest (McGinn 2006). McGinn (2006), however, suggests that the technique may be applicable to large ponds (several hectares), and presumably to emissions from homogenous land application areas larger than the techniques emission footprint. Denmead (2008) and Leuning *et al.*'s (Leuning *et al.* 2008) recommendations appear to concur.

Experienced practitioners with any of these flux gradient methods recommend a suite of sampling approaches to minimise errors between measurements at the different heights, including the use of reference gas cells in analysers and using the same analyser for all heights of analysis by switching gas supplies (Wagner-Riddle *et al.* 2005).

In unstable atmospheric conditions (e.g. day), it appears that the aerodynamic technique (using friction velocity measured by eddy co-variance) is the most appropriate flux gradient approach, and in stable conditions (e.g. night) eddy covariance techniques were preferable to flux gradient techniques for nitrous oxide emissions from grazed pastures (Phillips *et al.* 2007). Error due to the micrometeorological technique and analysis combined were about 25 % during the day to 60 % at night. Phillips *et al.* (2007) were forced to correct for footprints that were larger than plot sizes, and filter data based on factors like wind direction — the complex nature of this calculation may be a deterrent to further use of the technique in similar applications in the pig industry. Similarly errors determined by (Laville *et al.* 1999) were about 25 % for 15 min flux estimates for N2O using eddy covariance and flux gradient measurements.

> **Recommendation:** Micrometeorological approaches apply where fluxes are nearly constant with height and concentrations change vertically but not horizontally. These approaches are therefore unlikely to apply to pig production and other intensive livestock systems, except where effluent, manure, or manure solids are land applied very broadly in homogenous flat terrain. Relaxed eddy accumulation may be applicable to large land application areas. The accuracy questions associated with some micrometeorological approaches to greenhouse gas quantification would rule them out of consideration (flux gradient and eddy covariance).

4.5   Online, Offline, Closed Path or Open Path Analysis?

One of the decisions to be made regarding the application of any of the above micrometeorological, BLS, mass difference, or integrated horizontal flux techniques is the type of gas analysis technique to apply.

Offline technologies, where gas samples are collected and transported to an analyser are applicable for some types of studies. Indeed gas chromatography has been applied as a "gold standard" comparison or as the primary line of analysis in range recent studies at different scales (Harvey *et al.* 2008; Mkhabela *et al.* 2006; Skiba *et al.* 2006). Offline analysis via gas chromatography is adaptable to the range of scales, though other techniques are less labour intensive where large numbers of samples are collected a long way from the laboratory. Gas chromatography may be the most appropriate means of measuring some common tracer gasses such as SF_6 (McGinn *et al.* 2006).

A recent review appeared to suggest that off-line analysis (possibly gas chromatography) remained the standard for chambers studies, though this issue was not discussed directly (Rochette and Eriksen-Hamel 2008). While the DPI&F team has several conventional gas chromatographs, the team's Gas Chromatograph-Mass Spectrometer equipped with a PLOT column for greenhouse gas analysis has proven to have added advantages with respect to simultaneous analysis and discrimination of the range of gases in a single sample (Figure 5). This GC-MS technology is not regarded as portable and is therefore suitable for off-line analysis and real time analysis only where laboratory experiments can be co-located.

For long-running analysis in the laboratory, or analysis of experiments in-field, on-line or real-time analytical approaches have real advantages. A wide range of closed path techniques are available and

include in-field or experiment connected gas chromatography, photo-acoustic analysers (Philippe *et al.* 2007a), chemo- luminescence, and quantum cascade lasers (Kroon *et al.* 2007). Fourier transform infrared techniques are particularly attractive in this role, as a single instrument is capable of determining the range of concentrations of the gasses of interest, and scan times are sufficiently short to be practical for BLS determinations (Wagner-Riddle *et al.* 2005). Detection limits for nitrous oxide are likely to be the most exacting, and detection limits using FTIR were found to be equivalent to about 20 ng N m^{-2} s^{-1} in one trial (Griffith and Galle 2000), sufficient to quantify emissions of nitrous oxide from a manure treated soil in a micrometeorological trial. However, recent chamber trials suggest that control emissions of nitrous oxide could be as low as 1 ng m^{-2} s^{-1} (Luo *et al.* 2008, though this measurement was conducted using a chamber technique), though control emissions for other soils were ten times this concentration.

Trials with FTIR have succeeded in accurately monitoring fluxes of 2 ng m^{-2} s^{-1}, though this used the nocturnal boundary layer method, and measurements by more conventional flux gradient methods during the day struggled to quantify 17 ng m^{-2} s^{-1} (Griffith 2002). Company data suggests that detection limits for a state of the art FTIR gas analysis system would be < 10 ppbv for methane and carbon dioxide, and < 5 ppbv for nitrous oxide – on a system with total cost of around $150 000.

Closed path tuneable diode laser analysers exhibit faster response analysis (10 hz) with very low detection limits — at a cost of approximately $230 000. Precision of differences between presented samples of ±0.01 ppb N$_2$O is achievable, and minimum fluxes measured by the flux gradient method are around 3 to 10 ng N m^{-2} s^{-1} (Harvey *et al.* 2008). It is suggested that closed path FTIR cannot reach the same sensitivities in micrometeorological approaches as closed path tuneable diode laser due to the long scan times required for FTIR (Wagner-Riddle *et al.* 2005), though this evaluation from several years ago is at odds with recent manufacturer claims (and is possibly related more to response times than sensitivity). The full potential for analysis accuracy may be more available using closed path FTIR with BLS techniques — where rapid scans are not required, and differences between background and the sample may be larger. Both closed path methods (FTIR and TDL) are capable of quantifying carbon isotope ratios is carbon dioxide (Campbell manual) (Griffith 2002)— providing opportunities for residence time studies where resolutions of greater than 0.2 parts per thousand δ^{13}C is acceptable for FTIR and 0.5 parts per thousand δ^{13}C for TDL.

Importantly, background atmospheric nitrous oxide concentrations are around 300 ppbv, well within the detectable range using FTIR. To conduct a BLS measurement on an intensive livestock source (pond, land application area etc), the same extreme precision requirements as for flux gradient methods will not be required. Downwind measurements of concentration are compared with upwind measurements — rather than gradient measurements at two closely separated heights at the same land surface point. Where measurement frequencies are relatively low (ie for BLS techniques), closed path FTIR is capable of precisions as good or better than those achievable with closed path TDL (Wagner-Riddle *et al.* 2005).

There can be significant advantages to the use of open path measurement techniques to obtain measurements (Flesch and Wilson 2005). Most notably, open path determinations allow path averaged measurements of a length comparable to the dimensions of these intensive livestock sources (100 to 300 m). In the Windtrax BLS software, this is then represented by 30 or more point sources. This line averaging ability, where the laser path crosses the entire emission plume amounts to the measurements being insensitive to errors in modelled lateral dispersion of the plume, contributing to the robustness of estimates of the ratio of emitted concentration: emission flux (the primary parameter in BLS determinations). These advantages of open path analysis approaches can

be achieved by simulating an open path analysis technique with closed path instruments, with a mixed multiple inlet gas sampling arrangement as used very successfully in previous trials by McGinn (*pers. comm*. Dr T. Flesch).

Open path measurements can be conducted for methane using expensive tuneable diode lasers. Critically, the manufacturers investigated do not currently manufacture open path lasers for nitrous oxide measurement though lasers are available for methane and carbon dioxide (Boreal Lasers, Canada). Additionally each gas analysed simultaneously requires another laser — so where monitoring of two gasses is required plus background measurements, four lasers are needed (at a total cost of about $230 000).

Open path FTIR has the advantage of being able to measure the range of GHG's of interest with the one unit (Russwurm and Childers 2002). The analysis process appears far less straight forward than for TDL approaches (Thoma *et al.* 2005); water vapour interferences cannot be removed as they can with closed path units; integrated systems appear to be lacking from the market place. Few publications are available that use this approach.

> **Recommendation:** Closed path FTIR or TDL techniques will provide the capability to measure emissions adequately from real-time experiments at laboratory and small field scale, and can also be used effectively for nitrous oxide, carbon dioxide, and methane emissions for BLS techniques and the range of piggery sources. Sampling techniques can simulate an open path analysis, and capture many of the same advantages. Expensive open path tuneable diode laser techniques have proven capability for methane emissions — but instruments are currently not available for nitrous oxide measurement. Gas chromatograph techniques (including GC-MS techniques) are extremely reliable methods capable in the calibration, comparison, and method development roles.
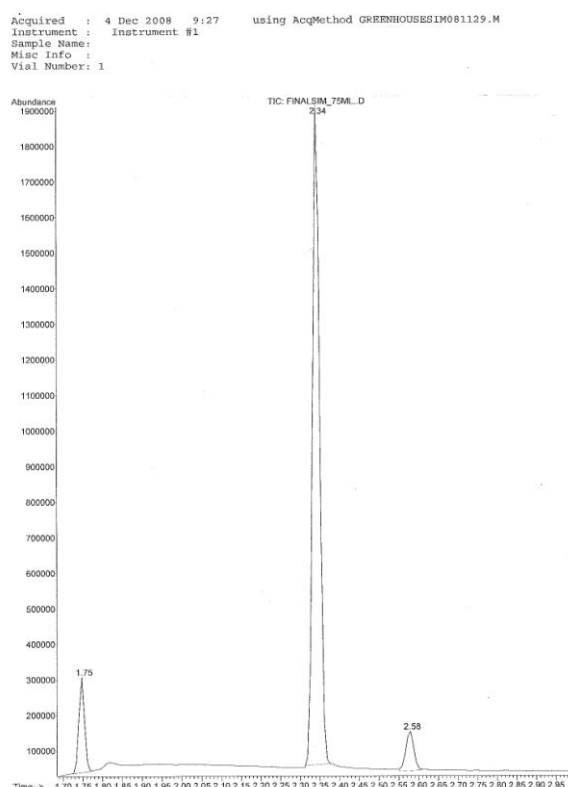
Figure 5: Simultaneous analysis and discrimination of methane (leftmost peak), carbon dioxide (middle peak), and nitrous oxide (right peak) is practical and rapid using GC-MS techniques, as demonstrated using the DPI&F GC-MS.

4.6 Recommended Approach

Measurement and mitigation development for the pig industry requires techniques that operate at a range of scales:

- Chamber and headspace trials for mitigation development at laboratory, greenhouse, and small field trial scales.
- Backward Lagrangian Stochastic techniques are well validated and have been successfully applied to point sources, ponds, sheds, and large land application areas. This is the key technique that bridges the likely piggery enterprise scales.
- Most landscape scale micrometeorological measurement techniques are inappropriate for piggery enterprise greenhouse gas studies — due to the source area configurations and

30

scales involved. There may be some application for relaxed eddy accumulation techniques, though the evidence suggests that the BLS techniques can fill the role of emission measurement from land application areas — the largest homogenous source to be encountered in piggery enterprises.

5   The Nitrous Oxide Emission Processes

In order to assess the potential to mitigate Greenhouse Gas Emissions, it is vital to understand the processes by which nitrous oxide is formed in the piggery production system, and how it is emitted. Process understanding will enable intervention points to be identified and intelligent measures to reduce losses to be developed. Most of the research conducted on nitrous oxide processes has been done within the context of soil emissions and, usually, fertiliser applications. While important elements of this context are not transferable to the pig production system, the underlying processes probably are. However, there has been a body of research conducted overseas on nitrous oxide emissions from a range of manure types, including piggery manures, slurries, and effluents. Often this research has been dominantly observational. This review section seeks to outline the processes underlying nitrous oxide emissions, and investigate how those processes may have influenced the emissions observed from piggery relevant systems.

5.1   Nitrogen Transformations and Processes

The nitrogen cycle is composed of a range of nitrogen transformations that may occur in soil or manure substrates. In terms of emission processes, it is important to understand something about these processes (Bolan *et al.* 2004):

- Mineralisation, the conversion of plant unavailable organic N to available inorganic forms via a microbial processes. Nitrogen mineralisation from faeces is slower than from the plant matter from which it was derived or from urine. Manure tends to contain more fibrous carbon forms than the original plant matter, which degrades more slowly, though C:N ratios may be similar.

- Aminization, where macromolecules are hydrolysed to simple N compounds such as amines and amino acids. For example, proteins are converted to amines and CO2.

- Ammonification, the process of microbial conversion of amines and amino acids to ammonium ions. An example is urea hydrolysis, as carried out in the presence of the urease enzyme. In this particular case, the reaction also produces hydroxide ions, raising the pH at the reaction site.

$$CO\,(NH_2)_2 => 2NH_4^+ + 2OH^- + CO_2 \qquad \textbf{Equation 14}$$

  The ammonia thus formed may be lost through volatilisation, fixed to soil, immobilized by soil microbes, nitrified by microbes, or taken directly up by plants.

- Nitrification, the two step microbially driven conversion of ammonium-N to nitrate-N is known as nitrification. The first step in this reaction produces nitrite (NO_2^-), but since the reaction rate of this step is much slower than the step to produce nitrate (NO_3^-), plant toxic nitrite is unlikely to accumulate in soils. More H^+ ions are produced during nitrification than OH^- ions during ammonification (per unit of N), and overall the combination of these reactions on urine and ammonifying manures is expected to acidify the soil. Once formed, nitrate can be taken up directly by plants, lost via leaching, immobilised by microbial processes — or it may be subject to denitrification.

- Immobilisation, the microbial process where nitrate and ammonium are converted to organic N forms, unavailable to plants. Addition of carbon rich materials to cultivated soils can promote immobilisation, and the same process may operate during composting where carbon substrates are added to manures. Where the ratio of C:N is high, microbial access to N may become a limitation, and competition for scarce N will tend to occur between microbes and higher plants. Microbes will, if necessary source N from the soil's mineral N —

immobilising it. Microbial C:N ratios are about 8. Where materials added to soils have C:N ratios of > 30, immobilisation is generally dominant. Where C:N is in the range 20 to 30, immobilisation tends to match mineralisation, and below 20, mineralisation dominates.

- Denitrification. Some microorganisms, under waterlogged soil conditions obtain oxygen by reducing NO_3^-. This reduction process, when allowed to continue to completion proceeds through a range of steps, producing NO_2^-, then nitric oxide (NO), nitrous oxide (N_2O), and finally N_2 gas.

The scale of denitrification in soil systems is such that it is of concern as an economic loss of fertiliser N.

Each of the steps in the denitrification process is conducted by anaerobic bacteria, where free oxygen is limiting. The microbes responsible for denitrification are very widespread in soils, and usually facultative aerobes - microbes that prefer to use oxygen as their electron acceptor, but will use nitrate where oxygen is not available (from genera *Pseudomonas, Bacillus, Alculigenes,* and *Flavobacteriuum*; Tiedje 1988) .

The trophic approaches of the organisms responsible can be divided as follows: **Chemoheterotrophs**, where nitrate is used as the primary electron acceptor to source energy form organic compounds; **Autotrophs**, where energy is obtained by oxidising inorganic compounds such as elemental sulphur using nitrate.

Fungal denitrification may be particularly important to nitrous oxide emissions. The widespread ability of fungi to reduce nitrate to nitrous oxide in order to supply energy for other reactions (dissimilatory reduction) has been demonstrated. Critically, the ability to reduce N_2O to N_2 for most fungi is lacking (Shoun *et al.* 1992). The contribution of fungi to nitrous oxide emissions has been demonstrated (Laughlin and Stevens 2002). In fact denitrification in some arid soil systems is dominantly the result of fungal activity (Crenshaw *et al.* 2008). However, data regarding the role of fungi in denitrification from manure or effluent substrates is lacking. One study found a decrease in fungal hyphae in soil treated with manure (Bittman *et al.* 2005), though this was not linked to denitrificaiton measurements. A more recent study involving pig wastes found that treatment of soils did not result in any significant change in fungal populations (Pratt 2008).When the process is allowed to reach its ultimate extent, it may be represented as follows, using glucose as the substrate, resulting in N_2 emission rather than N_2O:

$$5(CH_2O) + 4NO_3^- + 4H^+ => 2N_2 + 5CO_2 + 7H_2O \qquad \textbf{Equation 15}$$

However, organisms do not have a uniform ability to produce the range of denitrification products (nitrate, NO, N_2O, or N_2). Some organisms may produce mixtures of nitrous oxide and N_2, while others may be restricted to N_2O or N_2 (Stouthamer 1988).

The ratios of N_2O to N_2 produced from soils vary according to the substrate, organisms, environmental conditions, and period of denitrification Sahrawat (Arah and Smith 1990; Sahrawat and Keeney 1986). It appears that the proportion of N_2O to N_2 increases as oxygen availability decreases (Firestone 1982), and small nitrate concentrations have been observed to stimulate nitrous oxide reduction in soils more than large concentrations (Blackmer and Bremner 1979) — possibly as a result of the production of nitrous oxide reductase in response to small nitrate concentrations rather than in response to the nitrous oxide itself (Soohoo and Hollocher 1990). The general understanding is that large concentrations of nitrate and or nitrite decrease reduction of nitrous oxide, raising the $N_2O/(N_2O+N_2)$ ratio of the reduction products (Khalil *et al.* 2005). In order for denitrification to proceed, the following requirements must be met:

- Presence of nitrate, nitrite, NO, or N_2O.
- Anaerobic conditions or locally restricted oxygen availability
- Organic compounds suitable as electron donators
- The presence of appropriate microbes.

Promotion of the process therefore occurs under high soil nitrate, moisture contents sufficient to result in water-logging, and in the presence of a ready carbon source. It increases with pH and temperature. Nitrate may also be reduced to N_2 via non-enzymatic reactions under anaerobic conditions.

- NH_3 volatilization. When soil or manure pH is greater than 7.5, ammonium ions dissociate into gaseous ammonia (NH3), which is subject to volatilisation losses:
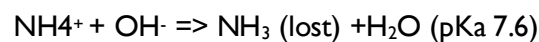
$$NH4^+ + OH^- => NH_3 \text{ (lost)} + H_2O \text{ (pKa 7.6)}$$ **Equation 16**

5.2   Nitrous Oxide Emissions

5.2.1   Direct Emissions

Nitrous oxide emissions can occur as a result of denitrification processes or during nitrification processes.

During denitrifictation, N_2O is formed as an intermediate or final step in the microbial or fungal reduction of nitrate or nitrite under anaerobic conditions (equation 14), providing energy for the metabolic reactions of the driving organisms:

Equation 17   a)   b)   c)   d)

$$NO_3^- \longrightarrow NO_2^- \longrightarrow [NO] \longrightarrow N_2O \longrightarrow N_2$$

energy   energy   energy   energy   energy
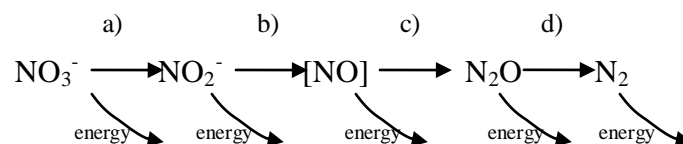
where the letters represent a) nitrate reductase, b) nitrite reductase, c) NO-reductase, d) N_2O-reductase(Saggar *et al.* 2004c). Energy is evolved at each step of this process, and note that gaseous emissions of both N_2O and NO_x (nitric oxides) can occur during this process.

It is important to note that this process can therefore produce or consume nitrous oxide (Blackmer and Bremner 1979) (Chapuis-Lardy *et al.* 2007) (Billings 2008). A comprehensive review of emissions data suggests that the number of reported negative fluxes of N_2O cannot be explained as experimental errors (Chapuis-Lardy *et al.* 2007). Conditions that support nitrous oxide consumption by soils include:
- Low availability of mineral N
- Low oxygen availability — anaerobic conditions

However, the prevalence of these conditions is not always associated with nitrous oxide consumption. Uptake of atmospheric N_2O and full reduction to N_2 (as outlined in equation 14) or solution of N_2O in water is influenced by:

- Low mineral N availability — the raw material for nitrification and denitrification.
- Anaerobic conditions through low availability of oxygen, water content, and redox conditions
- Soil temperature
- pH
- A supply of labile organic carbon and organic N
- Conditions that tend to retard diffusion of nitrous oxide appear to promote consumption.

The lack of resolution on exactly what values of these parameters promotes uptake are a symptom of the probability that a range of processes can be responsible for nitrous oxide uptake, and these processes have not yet been fully defined. Not only can denitrifiers consume nitrous oxide, but evidence suggests that nitrifier can also. While it is not yet known how widespread this ability is, it has been suggested for some time, and recently a range of nitrifiers was identified with this ability (Shaw *et al.* 2006). An illustration of how poorly understood the processes are is the strong nitrous oxide uptake in some dry soils — seemingly contradicting the anaerobic soil requirement.
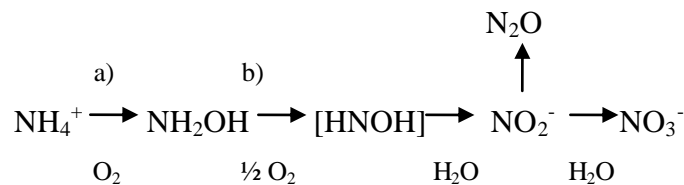
> **Speculatively,** it appears likely that some manure and solids environments may promote consumption of nitrous oxide. However, as will be seen later in this review, any consumption of nitrous oxide from deep litters, etc., appears to be overwhelmed by the processes of nitrous oxide generation.

Production of nitrous oxide may also occur during nitrification, either during NH_4^+ oxidation or through use of NO_2^- as an energy source (by reduction) when oxygen supply is limited:

Equation 18

$$\begin{array}{c}
\qquad\qquad\qquad\qquad\qquad\qquad N_2O \\
\qquad\qquad\qquad\qquad\qquad\qquad \uparrow \\
\overset{a)}{}\qquad \overset{b)}{} \\
NH_4^+ \rightarrow NH_2OH \rightarrow [HNOH] \rightarrow NO_2^- \rightarrow NO_3^- \\
\quad O_2 \qquad\quad \tfrac{1}{2}O_2 \qquad\quad H_2O \qquad\quad H_2O
\end{array}$$

where a) represents that action of ammonium mono-oxygenase and b) hydroxylamine oxidoreductase (Saggar *et al.* 2004c). Note that oxygen is consumed by the initial two steps, while water is consumed in the final two steps.

Major factors in controlling nitrous oxide emissions from soil include:
- Factors that alter the redox potential of the soil, such as changes in soil moisture (Carran *et al.* 1995; Dobbie and Smith 2001). The threshold value for denitrification may be field capacity (DeKlein and VanLogtestijn 1996; Fischer and Whalen 2005). Davidson (1991) demonstrated that at WFPS < 0.60, nitrification was the dominant source of N_2O, while above that level denitrification dominated emissions. Completely saturated soil conditions can promote full denitrification to N_2 — decreasing N_2O emissions (Saggar *et al.* 2004c).
- Soil texture (Saggar *et al.* 2004c), possibly as an influence on the development of anaerobic conditions.
- Organic carbon availability and quality (Fischer and Whalen 2005; Gillam *et al.* 2008; Ineson *et al.* 1998; Kaiser *et al.* 1998). Manipulation of soil organic matter through treatments with or without hay removal or with or without glucose application is capable of altering nitrous oxide emissions from grassland soils, and points to a range of potential mitigations (Tiemann and Billings 2008). In the Tiemann and Billings (2008) case additional available C resulted in

increased emissions, however Sanchez-Martin *et al.* (Sanchez-Martin *et al.* 2008) found that increased available C resulted in more complete denitrification of nitrate to N2 — rather than increased N2O. These authors also speculated that where nitrifiers dominate denitrification and nitrous oxide emissions, additions of highly labile C may depress this activity promoting the activity of denitrifiers.

In general organic carbon inputs to the nitrogen cycle are in the form of dead organisms, plant residues, and manure. These inputs vary in quantity and availability to the activities of heterotrophic organisms (Farquharson and Baldock 2008) — and different chemical paths, transport mechanisms and enzymes are required to break them down. Firestone and Davidson (1989) also propose that soil organic carbon inputs can control the ratio of $N_2O:N_2$ in denitrification emissions (see next dot point).

In addition, increased supply of soil organic matter can increase the rate of respiration of soil heterotrophs — resulting in an increase in soil anaerobic zones where diffusion processes are inadequate in supplying oxygen. This can result in the development of denitrification hotspots (Parkin 1987).

In terms of modelling these processes, decisions on which soil pools of organic carbon are used to control processes continue to be based on conjecture (Farquharson and Baldock 2008), and the importance of role of the different pools may be unrelated to pool size. Three roles of soil organic carbon pools need to be considered: 1) in relationship with biological oxygen demand; 2) as an energy source for denitrifier organisms; 3) as a substrate for N mineralisation under aerobic conditions.

The carbon and nitrogen cycles are inextricably linked. Increased understanding of nitrous oxide emissions processes is likely to shed light on emissions of methane, and soil carbon sequestration behaviour. Fontaine et al.'s (Fontaine et al. 2007) recent influential paper suggests mechanisms that promote the rapid cycling of fresh carbon additions to soils, previously observed as "a priming effect" where fresh carbon additions to soils can promote decay of existing soil carbon. The proposed mechanism suggests that the readily available energy of fresh organic matter additions (e.g. leaf litter) promotes microbial activity.

Management of "available" forms of carbon in manure/effluent/spent deep litter applied to soils or in manure/effluent systems is likely to be able to decrease the emission of nitrous oxide from these systems.

Speculatively, it is possible that composted or otherwise treated piggery manure product streams may have lower available energy and may therefore not participate to the same extent in the carbon priming process (direct discussion with Sebastien Fontaine, INRA, France) — which may be a positive for carbon storage in soils or even emission processes. Newly published research backs up the important potential for carbon sequestration from the treated waste resource such as this (biosolids application was shown to result in carbon sequestration though residence times were not measured; up to 166 t carbon per hectare, Tian et al. 2009).

Research potential: to establish benefits of existing treatments and design improved treatments and managements that decrease nitrous oxide emissions through carbon managements. These investigations should also specifically evaluate treated manure/effluent/and sludge effects on soil carbon sequestration.

Given the dominant content of organic matter in manures, an understanding of which organic matter pools are involved in driving emissions would enable intelligent formulation of effluent and manure solids treatments to mitigate losses, and to enable management responsive estimation of nitrous oxide emissions.

- A supply of mineral N (Ball *et al.* 1997; Fischer and Whalen 2005). If the available oxidised nitrogen (nitrate) greatly exceeds the quantity of the organic carbon to be reduced, the oxidant will be incompletely consumed, emitting N_2O. This is because, as an electron acceptor, nitrate is preferred to N_2O — so N_2O will tend to accumulate when nitrate is in oversupply (Swerts *et al.* 1996).

Effluent and manure managements that tend to defer nitrate formation until rapid use or uptake occurs (e.g. through plant uptake) favour lower nitrous oxide emissions. Covered anaerobic digesters have advantages in this area, if subsequent nitrogen management steps extract N or allow rapid uptake as nitrate is formed.

***Speculatively**, systems where effluent or solids ammonia is captured (on smart sorbers or zeolite) or extracted and managed as a high nutrient use efficiency fertiliser could be used in conjunction with conventional ponds or with digesters. Alternatively stripped ammonia could be rapidly nitrified and used to manufacture slow release fertilisers based around smart sorbers manufactured from recycled materials. This is an area of **research potential,** where DPI&F has current skills and experience.*

- Soil temperature (Dobbie and Smith 2001; Fischer and Whalen 2005; Grant and Pattey 2008). Temperature increase directly increases denitrification rates according to the

Arrhenius equation (a simple equation for temperature dependence of the rate constant), but also via indirect means such as increased respiration rate — resulting in an increase in the volume of anaerobic zones (DeKlein and VanLogtestijn 1996). This temperature dependence is extreme, with Q10 values (emission rate at $(T + 10)°C$/emission rate at $T°C$) for temperature changes from 5 to 12 degrees being around 50, and 8.9 for 12 to 18 $T°C$ (Dobbie and Smith 2001). It is also known that the form of N applied and irrigation management alter temperature dependence. For example the positive relationship with temperature is accentuated in unirrigated systems relative to irrigated systems (DeKlein and VanLogtestijn 1996). DeKlein and VanLogtestijn suggested that this was related to the two mechanisms via which temperature tends to increase denitrification, where increased respiration causing anaerobic microsites has a bigger potential where a high proportion of the soil is not already anaerobic. Grant and Pattey (2008) were able to model short term nitrous oxide emission rate changes with temperature increase (5 fold increase over a 10 degree temperature change) by combining the known effects of temperature (via the Arrhenius equation) on microbial C and N transformations (responsible for a 2 fold rate increase over a 10 degree temperature change) with the effects of temperature on gaseous solubilities and diffusivities, and with water effects on gaseous diffusivities, interphase gas transfer coefficients, and diffusion path lengths. Farquharson and Baldock (2008) also note that the temperature relationship is likely to be an aggregate relationship of this kind.

Farquharson and Baldock (2008) particularly emphasise that relationships such as the Arrhenius equation fall well short of representing temperature relationships over a range of temperature values. Temperature optima exist, and emission rates are not likely to continue to rise indefinitely as temperature increases. Also microbes are known to be adapted to the climatic conditions at a particular site.

> The potential to change the temperatures applied to most points in the piggery production system is small. However, temperature change of impermeably covered ponds, digesters, and composting operations is conceivable.
>
> **Research potential:** Temperature optima for minimised greenhouse gas emissions in manure/effluent storage and treatment, and for decreased emission+ increased residence time of carbon in soils are targets for investigation with potential practical outcomes.

- Soil pH. The acidity of the soil environment has a controlling influence on nitrification, denitrification, and the ratio of products derived from these processes — directly influencing N_2O emissions — and may also influence other nitrogen transformations, such as immobilisation and mineralisation — that have an indirect influence on emissions (Farquharson and Baldock 2008). Many of the processes involved in the nitrogen cycle involve the consumption or release of acidity, which results in positive or negative feedbacks that influence nitrous oxide emission processes. Farquharson and Baldock note that the concept of optimal pH for nitrification and denitrification is worthy of further attention.

Simek and Cooper (2002) conducted a review of the effect of pH on denitrification rates. They drew three process conclusions. 1). Total denitrification rates (N_2+N_2O) are higher in neutral conditions than in neutral or even slightly alkaline soil conditions — though this may have been an indirect influence of pH due to decreases in available carbon and mineral N in the acidic conditions. 2) The concepts of optimum denitrification pH and the possibility that microbial populations may adapt to shifts in pH require further investigation. 3) The

consensus view is that decreases in pH increase the ratio of $N_2O:N_2$ in emissions. This may explain the inhibited reduction of N_2O to N_2 under acidic conditions.

There is good evidence for adaptation or development of better adapted microbial populations. Optimum pH for dentrification activity in short denitrification enzyme activity incubations was found to be around the initial soil pH in one trial. However, denitrification potential incubations over a number of days revealed an optimal potential under near neutral conditions, with the change in optimum soil pH occurring after 1 – 2 days(Simek *et al.* 2002).

> **Research potential:** *Modification of the pH in portions of the effluent/manure/deep litter system may be a relatively simple matter. Understanding how these systems may be optimised for minimum greenhouse gas emissions may produce economical, simple mitigations.*

- Soil management practices that effect the above by compacting the soil or changing moisture contents (Saggar *et al.* 2004c).

The first six influences above appear to be the primary controlling factors, which may be indirectly influenced by other factors (such as the last dot point above). For example, the effects of compaction (such as animal treading) can be dramatic. A seven fold increase in nitrous oxide emission has been observed compared to an uncompacted comparable treatment, with 10 % of the applied nitrate being emitted as N2O (Bhandral *et al.* 2003). These emissions may represent the upper limit of N loss as N2O emissions as the soils were wet throughout the study. In this case it is likely that the effect of compaction on gaseous diffusion rates in soils may have promoted the development of anaerobic soil conditions.

The wide seasonal variability of nitrous oxide emissions (Luo *et al.* 1999; Ryden 1981; as reviewed by Saggar *et al.* 2004c) can often be explicable in terms of variations of the controlling factors already discussed (Saggar *et al.* 2004c). Water filled pore space appears to have the strongest influence.

5.2.2 Indirect Emissions through Ammonia Volatilisation

While ammonia is not regarded as a greenhouse gas, there is good reason to consider volatilisation as an indirect greenhouse gas emission. Gaseous ammonia emissions may undergo transformation in the atmosphere, but will rapidly be re-deposited (Krupa 2003) as a gas dissolved in rain, rain deposited aerosols, or depositions as nitrate or ammonia compounds, which are then subject to the range of soil transformation processes. Indirect emissions of greenhouse gasses were estimated to be about 14 % of direct emissions (Mosier *et al.* 1998). Recent investigations of indirect emissions from beef lot feeding suggests that these emissions may be much higher — with 59 % of all excreted N being volatilised largely as NH_3, and estimated emission of nitrous oxide following deposition estimated to be of the same order as direct emissions (Denmead *et al.* 2008). Comparable investigations have not been conducted for entire piggery systems. Pain *et al.* (1989) studied emissions following pig slurry application to soil, finding volatilisation of 5 to 27 % of the N applied, with the majority occurring within 12 hours of application, and volatilisation rates of up to 12.1 kg N ha⁻¹ h⁻¹. In another land application trial, 574 kg of N ha⁻¹ was applied as liquid swine manure, with 65% of this being volatilised when it was applied to a plastic liner (Hoff *et al.* 1981). Smith *et al.* (2001) found that in an Australian silage cropping system irrigated with piggery effluent (2300 kg /ha/year) only about 12 % of the N loading was volatilised.

Overall system ammonia volatilisation will be larger than these land application observations, and it seems that similar losses through secondary emissions to those discussed by Denmead *et al.* (2008) are likely.

5.2.2.1 Decreasing Ammonia Volatilisation

A likely major source of ammonia in piggery systems is urea hydrolysis as catalysed by the urease enzyme. This process follows the following reaction path:

$$(NH_2)_2CO + 2H_2O \rightarrow (NH_4)_2CO_3 \qquad \textbf{Equation 19}$$

$$(NH_4)_2CO_3 \rightarrow NH_4^+ + CO_3^{2-} \qquad \textbf{Equation 20}$$

$$CO_3^{2-} + 2H_2O \rightarrow HCO_3^- + OH^- \qquad \textbf{Equation 21}$$
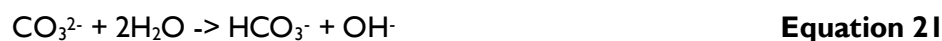
Thanks to this process, the half life of urine-urea in soil is very brief, with a value of 3.0 h being observed (Sherlock and Goh 1984). Urine-urea half lives tend to be briefer than other urea sources due to the hippuric acid, high urine pH (8.6), and probable urease content of some livestock urines (as reviewed by Bolan *et al.* 2004). However, it appears that pig urine may not contain the urease enzyme (Beline *et al.* 1998), and since the majority of waste N from cattle and pigs is excreted in urine (as much as 97 %), separation of pig urine from pig faeces (which does contain urease) is a logical mitigation, though it presents practical difficulties

In addition, decreasing urine pH via introduction of dietary organic (benzoic) acids or Ca and P salts can decrease urinary pH and NH3 emissions. Urine/faeces separation has demonstrated about a 50 % decrease in ammonia emissions for pig wastes for a range of pilot and full scale trials (Ndegwa *et al.* 2008).

Use of urease inhibitors is another logical approach — preventing the hydrolysis process by inhibiting the effectiveness of the urease enzyme. A range of chemicals exist, and have been recently reviewed (Ndegwa *et al.* 2008), and have been found to be effective when correctly applied — for example directly to effluent storages. In New Zealand experimentation has been conducted on the use of urease inhibitors to increase fertiliser-N efficiency and I believe commercial products are now available (authors personal experience). A review of use of urease inhibitors to enhance fertiliser effectiveness has recently been published (Chen *et al.* 2008a), suggesting a range of options.

Dietary manipulations may also prove fruitful, though the economics of such manipulations may not be favourable. Decreased dietary crude protein (with or without supplemental amino acids), or increased fibre tends to shift the dominance of urine N to higher proportions of faeces N, inducing 28 to 79 % decreases. Apparently an 8 % decrease in N excretion is achieved for each 1 % decrease in CP.

Other potential approaches include the modification of pH to favour retention of ammonia in solution, sorbing ammonia on zeolites and other cation exchange media, pond covers, covers with sphagnum moss, and the use of saponins (these latter have had variable success).

While a range of options exist for decreasing ammonia volatilisation, and there is good reason to believe this can decrease secondary nitrous oxide emissions, it should be noted that decreasing ammonia emission from one point in a chain of effluent/manure management may simply shift the emission to another point in that chain. Prevention of volatilisation to the point of land application (where urease inhibitors could be used to increase nutrient use efficiency) is required. Another option to be considered is stripping ammonia from the waste stream in order to produce a secondary product or fertiliser from it.

> **Research potential**: Indirect emissions of N_2O are likely to be substantial (of the same order of magnitude as direct emissions), via ammonia volatilisation, deposition, nitrification/denitrification. However, a range of reasonably simple mitigation measures have already been conceived, and trials may prove some of them practical. However to be successful, mitigations must not simply shift emission to another point in production.

5.3 Data Regarding Manure and Effluent Application to Land

Process investigations of nitrous oxide emissions from effluent and manure sources are less common. Some observations at the process level are available for various manures, and are briefly reviewed in (Kebreab *et al.* 2006):

- Ratios of nitrous oxide-N to N_2-N emitted from manures have been observed to range from 0.09 to 0.21 (Mahimairaja *et al.* 1995), and emissions from fresh manure are unlikely to be significant due to the lack of nitrate

- One study found that, as for soil emissions, increasing temperature resulted in higher nitrous oxide emissions (Brown *et al.* 2002), though other studies have shown that this dependence disappeared after several weeks (Petersen *et al.* 1998). Optimum temperature conditions are yet to be established, and the factors on which this temperature depends.

- As manure solids content rises, so do nitrous oxide emissions, and incorporation of straw into the manure can increase aeration and improve diffusion of nitrous oxide from the manure (Brown *et al.* 2000) — with optimum conditions for maximum nitrous oxide emissions occurring at 55 to 70 % water content (redox potential 150 to 250 mV Eh).

- Under high water content conditions, nitrous oxide emissions were limited by low nitrate contents, (Brown *et al.* 2000).

- High ammonia contents were not observed to inhibit nitrous oxide formation from piggery slurry, in a system where nitrifier denitrification dominated (Beline *et al.* 1999). In other systems very high ammonia can inhibit nitrification.

Since applications of manures and effluents have the ability to influence critical factors for nitrous oxide emissions simultaneously (for example, soil moisture and waterlogging behaviour, mineral nitrogen availability, and organic carbon availability) it is predictable that these materials may behave differently than inorganic fertiliser applications to soil — as found in studies such as Whalen *et al.* (2000). Saggar *et al.* (2004c) review emissions from excretal deposition from grazed pastures. Some of this material is relevant to understanding the processes prevalent in the land application areas of Australian piggeries.

Nitrous oxide emissions are highly time-variable, particularly with time after manure application, and they are strongly influenced by the application technique, and also by the quantity of water applied (effluent, irrigation, or rain) as evident from NZ research on piggery manure slurry application to soils (Sommer *et al.* 1996).

Nitrous oxide emissions from effluents and slurries tend to peak very rapidly — within 24 hours — then gradually fall to control levels over several days or weeks. This has been the observation with dairy effluents (Barton and Schipper 2001; Saggar *et al.* 2004b). Fischer and Whalen (2005) observed peak N_2+N_2O emissions due to denitrification within 1 day of application rising from 200 to as high as 2850 mug N m^{-2} hr^{-1} — though this only lasted a short period (<=3 days; pig effluent). In another study, losses due to denitrification in 8 to 12 days (when rates returned to pre-fertilisation levels) were < 2 % of the total N applied. Thompson and Pain (Thompson and Pain 1991, as cited in Saggar

et al. 2004) found that nitrous oxide emissions didn't peak until 30 hours after the initial piggery effluent application, but responses were more rapid for subsequent effluent applications (8 hours). Sharpe and Harper (Sharpe and Harper 1997) and Whalen *et al.* (Whalen *et al.* 2000) observed much more rapid responses to piggery effluent application (within several hours). In another trial of liquid dairy effluent injection, nitrous oxide emissions were highest immediately after injection, with a subsequent switch to N_2 emission (Comfort *et al.* 1990). For U.S. coastal plain and Appalachian Plateau soils, swine effluent irrigation similar observations held true (Bender and Wood 2007) — the greatest emissions were immediately following application.

While the ratio of N_2 to N_2O in manure and effluent related emissions are variable, it appears that emissions related to manure applications fit into the range of 3:1 (dairy cattle (Jarvis and Pain 1994)) to nearly 1:1 (cattle (Jarvis *et al.* 1994)). This ratio can change during the course of processes at a site. For example, application of a cattle manure slurry increased the mole fraction of N_2O from 0.5 to 0.85 in the first 12 hr after application. More than 94% of the N_2O emitted arose from reduction of NO_3^- (Stevens and Laughlin 2001). These emissions were attributed to aerobic nitrate respiration as well as respiratory denitrification.

Importantly, it appears that irrigation to very dry soil can result in extremely low nitrous oxide emissions — as attributed to water filled pore space relationships (J. Luo, AgResearch NZ, quoted in Saggar *et al.*2004). However, an understanding of nitrogen use efficiency suggests that applying effluent under conditions where there is poor uptake results in increased concentrations of nitrate in the soil (Read *et al.* 2008), and ultimately may increase nitrous oxide emissions.
When considering emissions from effluent and manure management and application systems it is necessary to also understand that ammonia emitted from ponds will undergo rapid deposition and a proportion will undergo transformation to nitrous oxide (refer section 4.2.2). Where ammonia emissions are large compared to direct nitrous oxide emissions, this effect can be very significant, and it is reasonable to assume that a few percent of the ammonia-N deposited will be re-emitted as nitrous oxide (Denmead *et al.* 2008).

Pig related overseas data is summarised in Table 1.

Speculatively, the rapid peaking of some slurry, and effluent emissions suggests depletion of some process feedstock that is initially in relatively good supply (such as mineral N), or build up of inhibitory reaction products. This may be related to rapid nitrification of the initial high concentrations of ammonia.

Research potential: Treatments that decrease the rate of initial nitrification may prevent an over-supply of nitrate from piggery effluent. Since an oversupply of nitrate favours nitrous oxide emissions rather than denitrification to harmless N_2, slowing the rate of nitrification could well decrease nitrous oxide emissions from effluent application. Techniques to achieve this could include: introduction of urease inhibitors at the point of manure and effluent collection, use of nitrification inhibitors, stripping ammonia prior to land application, and binding ammonia to sorber materials that promote a slower release to microbial activity.

5.3.1   *Piggery Manures and Effluents Compared to Other Sources*
The characteristics of the effluent applied can dramatically effect nitrous oxide emissions. For example, the range of constituents of effluents or manure slurries has an influence on nitrous oxide emission behaviour. Nitrous oxide emissions from liquid dairy manure fertilised row crops can

exceed the emissions from row crops fertilised with similar rates of inorganic fertiliser (Lowrance 1992; Lowrance and Smittle 1988). It has been suggested (Barton and Schipper 2001) that this sort of response is due to increased carbon availability or increased anaerobic conditions (caused by increased respiration). Indeed, this effect has also been demonstrated by decreasing the carbon concentrations in a biogas manure slurry — decreasing the nitrous oxide emissions (Petersen 1999). Untreated dairy manure slurries have been related to higher emissions than treated slurries (Saggar *et al.* 2004b; as cited in Saggar *et al.* 2004c).

Piggery effluent appears to be a higher intensity source of nitrous oxide than many other agricultural effluents (Saggar *et al.* 2004). Bhandral *et al.* (2007) observed differences between treated effluents attributable to their C:N ratios in a New Zealand study — pig effluent was greatest emitter of all the effluents (nitrous oxide emissions were 2.17 % of applied) in Autumn (compared to treated and untreated dairy effluent, and treated abattoir effluent), while in winter abattoir effluent emissions were higher. The higher emission rates were attributed to higher concentration of easily nitrifiable ammonia N at effluent application, and to the low C:N ratios in the more intensely emitting effluents. Emission was largely complete within a couple of weeks of application. Similarly, Khan (1999), as quoted in Saggar *et al.* (2004c), observed nitrous oxide emissions of 1.9 % of total applied N from piggery effluent, but only 0.1 to 0.3 % of applied N for diary farm effluent. It was suggested that some of this difference may be attributable to differences in application technique — dairy effluent was applied via flooding, which may promote full denitrification to N2 (Saggar et al. 2004c cites Kester *et al.* 1997, though these authors do not appear to address this issue).

Table 1: Summary of largely overseas piggery production system data.

Reference	Emission Point	CH4	N2O		Ammonia		Location	Observation Period	Comments
Beline *et al.* 1999	Pond	-	30	% of total Nitrogen			France	60 days	Aerobic pond trial
Whalen *et al.* 2000	Land application	-	1.4	% of total N applied			North Carolina	24 days	Emission rate similar to that for inorganic fertiliser; application of 297 kg of N ha^{-1} rapid initial peak
Sommer *et al.* 1996	Land application	30 g ha^{-1} day	40 to 100				NZ	16 days	bare wet soil; control emissions 2g N ha^{-1} day^{-1}; 50 t ha^{-1} of pig slurry, 1.4 g NH4$^+$-N kg^{-1}
Sommer *et al.* 1996	Land application	30 g ha^{-1} day	10 to 60	g N2O ha^{-1} day^{-1}			NZ	16 days	bare dry soil; control emissions 2g N ha^{-1} day^{-1}; 50 t ha^{-1} of pig slurry, 1.4 g NH4$^+$-N kg^{-1}
Sharpe Harper 1997	Land application		13	% of total applied N	82	% volatilised within 24 hours	US		36 kg N ha^{-1} applied to oats from heading stage
Bender and Wood 2007	Land application	14.41-34.76 kg CH4-C ha^{-1} year	1.26 - 3.97	kg N ha^{-1} year^{-1}			Alabama	2 years	112 kg N ha^{-1} year^{-1}; intact soil core study; effluent and ammonium nitrate losses of N2O similar; three different soils; control N2O emissions were .24-.79 kg N ha^{-1} year^{-1}; control NH4 emissions -0.06 to 1.28 kg C ha^{-1} year^{-1}
Pain et al 1989	Land application				5-27	% total N			574 kg of N ha^{-1}
Smith et al 2001	Land application				12	% total N	Australia		2300 kg ha^{-1} year; volatilisation losses.
Bhandral *et al.* 2007	Land application		2.17	% total N			New Zealand	102 days	27 kg N ha^{-1} applied; treated piggery effluent a greater source
Khan 1999	Land application		1.9	% total N			New Zealand		
Velthof et al. 2003	Land application		7.3 - 13.9	% total N			Netherlands	98	incubation trials of incorporation at depth with denitrification optimum moisture; 25 to 200 mg of N kg$^-$

soil

Reference	Emission Point	CH4		N2O		Ammonia		Location	Observation Period	Comments
Bertora et al. 2008	Land application			4.8	% total N				58	mesocosm study 170 kg N ha^{-1}, untreated pig slurry; 60 % water filled pore space; separation and treatment greatly decreased emissions.
Chantigny et al. 2007	Land application			414	g N2O ha^{-1} day^{-1}	22	kg N ha^{-1}	Canada	3 years	field trial, 146 kg N ha^{-1} year^{-1}; These values are those for untreated effluent.
Rochette et al. 2000	Land application			1.23 - 1.65	% total N			Canada		field trial, 125 to 250 kg of effluent N ha^{-1} year;
Thorman et al. 2007	Deep litter stockpile			2.6	% total N			UK	1 year	Stockpile
Thorman et al. 2007	Land application			< 0.01	% total N			UK	3 months	land application of deep litter, 250 kg N ha^{-1}
Harper et al. 2000	Pond	1.3 - 125.8	mg CH4 ha^{-1} day^{-1}	0-3.1	kg N2O ha^{-1} day^{-1}	29 - 239	mg NH4$^+$-N kg^{-1}	US	2 years	four pond system
Harper et al. 2004	Housing					7	% total N inputs to farm	US	3 seasons	percentages of total farm inputs
Harper et al. 2004	Pond			0.1	% total N inputs to farm	8	% total N inputs to farm	US	3 seasons	percentages of total farm inputs, measurement assumptions make a big difference
Harper et al. 2004	Land application			0.05	% total N inputs to farm	2	% total N inputs to farm	US	3 seasons	percentages of total farm inputs
Park et al. 2006	Pond			3.6	g head^{-1} year^{-1}			Canada	2 years	Cold conditions
Szanto et al. 2007	Composting manure+straw			2.5	% total N	3.9	% total N	Netherlands	4 months	with turning
Szanto et al. 2007	Composting manure+straw			9.9	% total N	2.4	% total N	Netherlands	4 months	without turning
Wolter et al. 2004	Deep litter stockpile	2	% of total carbon	1.9	% total N			Germany	113 days	thermophillic, high temperature decomposition occurred; ammonia emission plus denitrification accounted for 26

Reference	Emission Point	CH4		N2O		Ammonia		Location	Observation Period	Comments
Dong et al. 2007	Housing	9.6-58.4	g CH4 (500 kg liveweight)$^{-1}$ day^{-1}	.54-1.29	g N2O (500 kg liveweight)$^{-1}$ day^{-1}			China		non-comparable housing
Blanes-Vidal et al. 2008	Litter based housing	252-297	mg h^{-1} m^{-2}	0-68.8	mg h^{-1} m^{-2}	3.5-60.3	mg h^{-1} m^{-2}	Denmark	37 days	a range of C substrates were added to the manure slurry as rooting materials — increasing methane emissions.
Groenestein and Van Faassen 1996	Litter based housing			0.3 and 0.2	g N h^{-1} pig^{-1}	0.24 and .12	g N h^{-1} pig^{-1}	Netherlands		

Reference	Emission Point	CH4		N2O		Ammonia		Location	Observation Period	Comments
Groenestein and Van Faassen 1996	Slatted floored housing					0.3	g N h^{-1} pig^{-1}	Netherlands		
Amon et al. 2007	Litter based housing	1.24	kg CH4 pig^{-1} year^{-1}	39.9	g N2O pig^{-1} year^{-1}	2.1	kg NH$_3$ pig^{-1} year^{-1}	Austria	1 year	
Phillipe et al. 2007	Slatted floored housing	16	g CH4 pig^{-1} day^{-1}	0.54	g N2O pig^{-1} day^{-1}	6.2	g N2O pig^{-1} day^{-1}	Belgian	4 months	lab scale housing trial
Phillipe et al. 2007	Litter based housing	16	g CH4 pig^{-1} day^{-1}	1.11	g N2O day^{-1}	13.1	G N2O pig^{-1} day^{-1}	Belgian	4 months	lab scale housing trial

In another study where pig manure was applied to a sandy soil with low organic matter, higher emissions resulted than from other manures. This may have been due to the high content of inorganic N, and the easily mineralised N and C that the manure contained (Velthof *et al.* 2003). In this case pig manure emissions (7.3 to 13.9 % of the N applied) were worse than those from cattle (1.8 to 3.0 %) and poultry (0.5 to 1.9%) manures.

It has also been observed that urine-urea may hydrolyse more rapidly than fertiliser-urea, generating greater CO_2 in the soil airspace, triggering greater denitrification and nitrous oxide emission (Sherlock and Goh 1983).

> **Observation:** Piggery effluent nitrous oxide emissions following land application are often larger than those from other waste streams. This may be due to their high ammonia content, mineralisable N, mineralisable C, and low C:N ratios of many of these effluents compared to other sources.

5.3.2 *Effect of Effluent Treatment Process*

Data strongly suggests that the treatment applied to piggery effluent is a major emission influence. Bertora (2008) experimented with separating solids from pig slurry and with the effects of treatment. Nitrous oxide emissions from untreated pig slurry were about 4.8 % of total N, about 1 % for the solid fraction, and 2.6 % for the liquid fraction. For the anaerobically digested liquid fraction, nitrous oxide emissions were 1.8% of total N, while emissions from a treatment of urea alone was about 0.9 % of the total N applied. Solid fraction produced the highest potential denitrification fluxes, however (N_2O+N_2 emissions). Separating slurry into solid and liquid fractions tends to decrease N_2O emissions, whether the liquid is digested or not.

Similarly, Chantigny (2007) found that N_2O emissions tended to be higher with raw liquid swine manure than with mineral fertilizer. This was not the case for digested liquid swine manure, or filtered or separated liquid swine manure.

The large concentrations of inorganic N in fresh pig manure slurry have led to large losses of N2O through denitrification and nitrification in other studies. Yang (2004) found that these emissions were 35 times the emission from yard waste compost, 50 times the emission from fresh pig manure slurry/wheat straw compost, and 76 times that from the untreated soil control.

> **Observation:** Separating slurry into solid and liquid fractions tends to decrease N_2O emissions, whether the liquid is digested or not. Treatment also tends to decrease nitrous oxide emissions following land application. Treatment decreases the concentration of inorganic N contained in the effluent — which may be the reason for the latter effect. Separating the liquid fraction from the solid fraction decreased access to readily degradable carbon for the solids fraction, and decreased organic N in the liquid fraction — these factors may have been related to the overall decrease in N_2O emissions.

5.3.3 The Influence of Application Technique and Combined Inorganic-N Fertiliser Applications on Nitrous Oxide Emissions

Slurry incorporation can dramatically increase nitrous oxide emissions (as reviewed for the dairy industry; Saggar *et al.* 2004c) by creating an oxygen poor environment that is enriched in available C and mineral N. Co-application of inorganic N and piggery effluent can produce a similar effect (Meijide *et al.* 2007; Perala *et al.* 2006). Velthof *et al.* (2003) found that placing pig manure slurry in a strip at 5 cm depth resulted in greater N_2O emissions than other forms of incorporation and surface application.

Counterexamples exist. In one study, injection of pig slurry did not result in different CO_2 production, nor did it alter the emission of N_2O or total denitrification (N2 + N2O, Dendooven *et al.* 1998). A positive benefit of injection in this study was that ammonia volatilisation was decreased by 90 %.

Arcara (1999) combined mineral N and pig slurry and investigated N_2O emission in the field. No large differences were observed between urea and slurry fertiliser plots, and it appears that the effluent application did not remove any additional limitation on nitrous oxide emission. However, combinations of urea and slurry usually produced an increase in both N_2O emissions from denitrification and ammonia emission (leading to potential N_2O losses of about 50 % of the losses due to denitrification, assuming 2% emission from re-deposited ammonia).

However, Chadwick (1997; as cited in Saggar *et al.* 2004c) noted that while nitrous oxide emissions from injection exceeded those from surface application in the period immediately following application, after 89 to 119 days the situation was reversed.

Nitrous oxide emissions tend to increase with application rate of effluents (Rochette *et al.* 2000; Velthof *et al.* 2003). Logically this may be the result of the higher rates of application of mineral N, larger application of water, and greater available carbon application. Velthof (2003) observed this effect with piggery effluent (though percentage losses did not increase), with N rates up to 200 mg N kg^{-1}, observing losses up to 13.9 % of the applied N.

> **Observation:** Slurry incorporation and co-application of effluent and inorganic-N sources can greatly increase nitrous oxide emissions.

5.3.4 Effluent and Spent Deep Litter Storage Emissions

Nitrous oxide emissions also occur from effluent ponds and from pig housing. In fact Thorman *et al.* (2007), having investigated a U.K. straw bedding system suggested that nitrous oxide emissions from manure stockpile storage may be more important sources in some overseas systems than emissions from land application. Losses of nitrous oxide from the stockpile (over a period of 12 months) amounted to 2.6 % of the total N, while losses after land application represented < 0.01 %.

While impermeable pond covers may allow collection of emissions, permeable covers present their own problems. Various permeable cover materials were found to increase nitrous oxide emissions in Germany (Berg *et al.* 2006), though the mechanism was not investigated or discussed. Emissions of nitrous oxide in these systems were up to about 35 % of total carbon dioxide equivalent emissions, while for the uncovered control, nitrous oxide

emissions were only about 10 % of the total carbon dioxide equivalent emissions. Simultaneously acidifying and covering the pond was found to decrease nitrous oxide and methane emissions. Petersen and Miller (2006) reviewed the lack of knowledge surrounding the behaviour of permeable pond covers with regard to nitrous oxide emissions, and indicate their potential for emissions — based on the evidence of the presence of nitrate from a single supporting reference (Sommer *et al.* 2000, which provides evidence of increasing nitrous oxide emission from crusts as they dry out due to nitrate formation).

Nitrous oxide emissions have been observed from a U.S. four pond system at a piggery (Harper *et al.* 2000). Emission from the sludges of the second to fourth ponds at a four pond piggery system in Georgia, U.S., totalled 3.6 kg N_2O ha^{-1} day^{-1}. These emissions were relatively small compared to the corresponding N_2 emissions (emissions totalled 58.1 kg N_2O ha^{-1} day^{-1}). The authors suggest that microbial denitrification may be occurring due to the observed nitrate in ponds 3 to 4 (up to 40 mg kg^{-1} in pond 4). Nitrous oxide emission was negligible in pond 1, even though denitrification is suspected via an undetermined process or via nitrification-denitrification caused by methanotrophs using O_2 as an electron acceptor (where the nitrous oxide is not an intermediate reaction product). The measurements of nitrous oxide, N_2, and methane emissions were trapped below the lagoon surface (nominally representing sludge emissions). Cumulative nitrous oxide emissions from the 4 ponds represented an emission equivalent (CO_2-equivalents) of about a third of the methane emissions (assuming 310 x CO_2 potency for nitrous oxide and 25 x CO_2 potency for methane).

In a later study (Harper *et al.* 2004) measured lower direct nitrous oxide emissions (0.1 % of total N inputs) from effluent ponds, and much lower ammonia emissions than recorded by other studies (much more N_2-N was emitted than methane). The flux gradient measurement approach was employed, and the assumptions made had a significant effect on the emissions calculated.

While most effluent treatment systems at flushed piggeries employ anaerobic processes, it is claimed that solid separation plus aerobic treatment can decrease greenhouse gas emissions by about 97 %, and conserve much of the waste nitrogen for by-product streams (Vanotti *et al.* 2008).

It is important to use data from comparable climates when evaluating the Australian industry. For example, very cold climates (8.4 degrees C average annual), nitrous oxide emissions from anaerobic stored liquid pig manure were found to be quite small (Canadian study, Park *et al.* 2006), amounting to 3.6 g head^{-1} year^{-1}. This is far less than the IPCC-based emission factor of 17 g head^{-1} year^{-1}. Given the temperature dependence of the emissions processes, it is likely that the same pond system located elsewhere would generate greater emissions.

Composting pig manure also generates nitrous oxide emissions. Szanto *et al.* (2007) found that nitrous oxide emissions from turned manure-straw composts piles emitted 2.5 % of total N as nitrous oxide, while unturned piles were much worse, emitting 9.9 % of total N as nitrous oxide. This may have been the result of the enhanced anaerobic conditions prevailing in the static piles. Very low C/N ratios and monthly turning appear to be required to decrease nitrous oxide emissions below significant levels, partly through favouring the emission of N_2. In another trial nitrous oxide was found to be the most significant greenhouse gas emission from a deep litter pig manure stockpile (78.4 % of emissions CO2

equivalent, Wolter *et al.* 2004). Emissions peaked early in the trial when thermophillic microbial conditions dominated (stockpile temperatures at day 10, at the peak of emission were 50 to 70 degrees C). While methane and CO_2 emissions in this trial were strongly correlated with temperature (which varied independently of ambient temperature), nitrous oxide emissions were found to be less predictable. Initial bulk density was found to be a major factor in controlling emissions, due to its influence on gas exchange. Total nitrous oxide emissions from the composting trial amounted to 1.9 % of total N.

> **Observation:** Nitrous oxide emissions can be particularly problematic from deep litter systems relative to conventional ponds. However Australian data is required. Permeable pond covers, while potentially valuable in the control of odour, may increase nitrous oxide emissions — though data is scarce. Compost and stockpile aeration and bulk density conditions are critically important influences on emissions.

5.3.5   Diet
Diet is also known to be a factor in emissions process — as the availability of mineral and mineralisable N and C would suggest. Literature on the subject is not common, though one study observed that decreasing the protein in the diet was the most effective means of decreasing ammonia and CH_4 emission during storage and N_2O from the soil (Velthof *et al.* 2005).

> **Observation:** Unplumbed opportunities exist for controlling emissions through diet manipulation. However these diet manipulations are likely to effect productivity. For example an effective manipulation has been to decrease feed protein content.

5.3.6   Emissions from Housing
Dong *et al.* (2007) developed emission rates for nitrous oxide from Chinese gestation, farrowing, nursery, and grower-finisher units observing 0.75, 0.54, 1.29, and 0.86 g day^{-1}(500 kg liveweight)$^{-1}$, rates that were comparable in scale to methane emission rates (CO_2-equivalents). Ammonia emissions did not appear to be measured in this study, so it is not possible to account for indirect nitrous oxide emissions.

In a Danish trial of straw additions to pig pens on GHG emissions, the nitrous oxide emissions from the slatted housing were negligible — though ammonia emissions amounted to 1.54 g hour^{-1} [500 kg live-weight]$^{-1}$ (Blanes-Vidal *et al.* 2008). Even allowing for indirect emissions of several percent of ammonia-N as N_2O, it is likely that methane emissions from this system are of greatest concern.

Deep litter production may generate nitrous oxide emissions at higher rates than other production systems. Emissions from a Dutch deep litter piggery were about 7.2 g of N_2O-N day^{-1} pig^{-1}, observed over 112 to 121 days (Groenestein and Van Faassen 1996). This system involved weekly turning of bedding material and manure burial, and two commercial microbial preparations (these commercial products had no significant effect relative to each other). In an Austrian deep litter study, nitrous oxide emissions amounted to about 40 g of nitrous oxide per pig place per year (Amon *et al.* 2007), which represented over half the direct methane emissions in CO_2-equivalents. Ammonia emissions were substantial (2.1 kg per pig place per year), and it is likely that indirect emissions may bring total nitrous oxide

CO_2-equivalent emissions up to the same magnitude as methane emissions from this system (Denmead *et al.* 2008).

Phillipe *et al.* (2007b) conducted a comparative investigation of emissions from slatted floor production versus deep litter production in a Belgian lab-scale animal housing study. Two different production rooms were used for the trial treatments, for a four month observation period. While methane and CO2 emissions from the two systems were very comparable (about 16 g pig^{-1} day^{-1} of methane, 1.7 to 1.9 kg of CO2), nitrous oxide and ammonia emissions from the deep litter system (13.1 g pig^{-1} day^{-1} ammonia, 1.11 g pig^{-1} day^{-1} N_2O) was approximately double the emissions from the slatted floor system (6.2 g pig^{-1} day^{-1} Ammonia; 0.54 g pig^{-1} day^{-1} nitrous oxide). Methane and nitrous oxide emissions in this case were reasonably equivalent in terms of CO_2 comparability in deep litter systems (methane emissions from both systems was around 16 g pig^{-1} day^{-1}), while methane emissions dominated the two gasses in the slatted system.

Nitrous oxide emission can occur during nitrification (which is promoted by aerobic conditions) and during denitrification of nitrate (during anaerobic conditions). Both of these conditions occur in deep litter bedding, something that cannot be said of the conditions in effluent collected beneath slatted floors. The Deep litter system described by Phillipe *et al.* (2007) produced more direct emissions than the slatted production. These nitrous oxide emission values are highly comparable to the other available range of data values (0.03 to 8 g pig^{-1} day^{-1} for deep litter systems; 0.17 to 2.26 g pig^{-1} day^{-1} for slatted floor systems; based on a range of unavailable references reviewed by Phillipe et al 2007, and Osada *et al.* 1998).

> **Observation:** Nitrous oxide emissions from slatted floored/flushed housing are likely to be of the same order of magnitude as methane emissions, but are unlikely to be greater. Nitrous oxide dominates GHG emissions from deep litter systems.

5.4   Process Algorithms

While it is not always necessary to develop a software based model around processes to answer important questions, it is usually beneficial to attempt to place process knowledge in a quantitative framework. These mathematical models can then allow understanding to be effectively validated on a much more satisfactory, quantitative basis than is possible without them — without these mathematical models, research is likely to amount to yes/no answers to merely qualitative research questions. For example, we can go beyond the question "does temperature effect nitrous oxide emissions?" to "does temperature dependence follow the Arrhenius process model?". The usefulness of this approach is not limited to the development of simulation models, but allows more intelligent and effective development of process-based mitigations and relative benefits of various approaches to be estimated. In addition, this sort of approach is essential to improve on the IPCC and Department of Climate Change greenhouse gas inventory calculation protocols.

Comparisons of the mathematical algorithms describing nitrous oxide emissions modelling are lacking in the literature, qualitative in nature, or describe computer simulation approaches without rigorous recourse to mathematics. Chen *et al.* (2008b) recently reviewed the simulation approaches that have been attempted since the mid 1970's. Chen *et al.* classified these approaches according to scale (laboratory, field, and global scales), and particularly notes the value of process-based (rather than empirical) field scale models in

development of mitigation approaches, reviewing the strengths and weaknesses of approaches. However, in terms of my review, any validated process-based simulation model is of note. This otherwise useful review is largely qualitative in nature and non-mathematical. Field scale simulation models, while of direct applicability to the field systems they model, contain much material that is not relevant to the intention of this nitrous oxide emission process review (such as crop growth components). Additionally, piggery effluent and deep litter emissions processes in the shed, at the pond or stockpile, and during and after land application are not considered by such models.

However, the most recent development activity appears to have been concentrated in these field scale models rather than in the laboratory scale process modelling efforts (Chen *et al.* 2008b). Some of the more venerable simulation models have undergone a multi-decadal development process, and have been applied to a wide range of environments, for example the NGAS-DAYCENT model (Del Grosso *et al.* 2008; Mosier *et al.* 1983; Parton *et al.* 1996). This model, however, is reliant on semi-empirical approaches for the modules concerned with the actual N_2O emissions, and therefore will not be considered further here.

Another long lived, continuously developed, and well validated model is DNDC (Li *et al.* 1992a; b; Saggar *et al.* 2004a), which is more mechanistically based than the NGAS-DAYCENT model. An extremely broad ranging mechanistic model dealing with many ecosystem interactions and not focussing solely on nitrous oxide emissions is the *ecosys* model (Grant *et al.* 2001; Grant and Pattey 2003; 2008).

Ideally this review section would focus on one, relatively recently developed model that encapsulates recent advances in process understanding coherently in a small number of recent papers. Unfortunately strictly process driven recent models are less common than models with an admixture of empirical simplifications, such as the CERES-NOE model (Gabrielle *et al.* 2006; Henault *et al.* 2005; Henault and Germon 2000).

The most comprehensive approach to the mechanics of the N_2O emissions process appears to be that used by *ecosys* and described in (Grant and Pattey 2003). The complex approach conducted in this model evaluates emissions and process for each cell in a grid (similar to a finite element approach), integrating time scale from seconds to centuries. Data requirements are extreme, with about 40 parameters required for the N_2O component, alone.

The recent model, WNMM (Water and Nitrogen Management Model) applies an approach that has been relatively successful, has some mechanistic basis, but attempts to minimise mechanistic complications (Li *et al.* 2007). Nitrous oxide emissions in this model is dependent on a semi-mechanistic, semi-empirical, but relatively simple approach (Xu *et al.* 1998). During initial validation this model produced output consistent with field results (overall correlation coefficient 0.78), and represented pig effluent applications to soil quite well (correlation coefficients 0.92, 0.90, and 0.88, for 144, 95, and 48 kg of N ha^{-1}).

Xu *et al.*'s (1998) model is based on the following calculations, which provide a conceptual framework within which to consider the foregoing discussion of emission processes. The nitrification rate is estimated based on the following equation:

$$q_N = k_N f_T f_w t,$$ **Equation 22**

where q_N is a proportion of the ammonia-N contained in the upper soil layers (up to the ammonia-N concentration); f_T is a stress function related to temperature having a value from 0 to 1; f_W is another stress function with a value in the same range, but representing the effects of water stress via a relationship with the water filled pore space; t is the length of the time step.

Calculation of N_2O emissions during nitrification are empirically calculated as a calibrated proportion of nitrification multiplied by the water and temperature stress functions outlined above.

Total denitrification ($N_2O+NO+N_2$) emissions were calculated on the basis of one of two prevailing conditions. Wet period denitrification was represented as:

$$q_W = k_D [NO_3] f_T t_w,$$ **Equation 23**

where k_D is the first-order rate coefficient for denitrification, and is determined by soil organic matter content, soil drainage, tillage applied, presence of manure, climate, and the presence of pans; $[NO_3]$ is the nitrate content of the surface soil, and t_w is the number of wet days within the time step t. The corresponding equation for dry period denitrification is:

$$q_W = k_D [NO_3] f_T f_w' (t - t_w),$$ **Equation 24**

where f_w' is a water stress function for anaerobic processes (value 0 to 1). Partitioning of the total denitrification into N_2, NO, and N_2O is achieved empirically, once again through calibration and coefficients.

While the *ecosys* model (Grant and Pattey 2003) is very highly parameterised, WNMM has the disadvantage of containing a large component of empiricism. A good aspiration goal that will demonstrate effective process understanding is to eliminate the empirical components of algorithms employing a magnitude less complexity than is required to parameterise *ecosys*. While *ecosys* is extremely complex, its comprehensive coverage may make it valuable for sensitivity analysis— where processes found to be poorly related to observed outcomes can be eliminated from a slimmer, more focussed representation of the modelled environment.

Research potential: The model ecosys is perhaps over-parameterised for the representation of nitrous oxide emissions from housing, deep litter/effluent storage, and spent deep litter/effluent application. However, process representations in many other models are heavily reliant on empirical calculations. Where process understanding can eliminate this empiricism by reaching a point where only processes influential in piggery production systems are considered, intelligent mitigation development will be assisted and accurate management responsive emissions calculation will be enabled. A sensitivity analysis of the algorithms on which ecosys is based would be one approach likely to succeed.

6   Conclusions and Recommendations

Measurement Techniques and Instruments

- In applications where measurements may challenge greenhouse gas assumptions, we recommend that the most rigorous approach involving the use of fast response anemometers.
- The Backward Lagrangian Stochastic techniques' flexibility with regard to emission source and scale is extremely attractive. Advantages include robustness, the body of publications applying it, software support, and modest analytical requirements. The choice of this technique for measurements for the intensive livestock industry in Australia and overseas make the Backward Lagrangian Stochastic method a strong candidate for the primary measurement approach for the pig industry.
- Flow through, non-steady state chambers combined with real-time analysis are probably the best small scale process-based mitigation investigation tool.
- Flow through, non-steady state chambers are a key technique for process investigations and development of mitigations in laboratories. They may also be used to separate emissions sources — where adjacent emissions are intermingled and may be otherwise expensive or impossible to differentiate.
- Most mass balance techniques are more measurement intensive than is desirable. However the ability of mass difference techniques to eliminate the effect of adjacent emission sources may be valuable. Integrated horizontal flux techniques provide a relatively simple technique with which to compare emissions measurements conducted using other techniques.
- Closed path Fourier Transform Infra Red (FTIR) or Tuneable Diode Laser (TDL) instruments will provide the capability to measure emissions adequately in real-time experiments at laboratory and small field scale. They can also be used effectively for nitrous oxide, carbon dioxide, and methane emissions for BLS techniques. Sampling techniques can simulate an open path analysis, and capture many of the same advantages as true open path methods.
- Expensive open path tuneable diode laser techniques have proven capability for methane emissions — but instruments are currently not available for nitrous oxide measurement.
- Gas chromatograph techniques (including GC-MS techniques) are extremely reliable methods suitable for calibration, comparison, and method development roles.
- The labour and technical overhead for calibration in Fourier Transform Infra Red analysis techniques seems to be higher than for Tuneable Diode Laser methods, though FTIR techniques are capable of analysis of multiple analytes simultaneously.
- Measurement and mitigation development for the pig industry requires techniques that operate at a range of scales:
    - Chamber and headspace trials for mitigation development at laboratory, greenhouse, and small field trial scales.
    - Backward Lagrangian Stochastic techniques are well validated and have been successfully applied to point sources, ponds, sheds, and large land application areas. This is the key technique that bridges the likely piggery enterprise spatial scales.
- Most landscape scale micrometeorological measurement techniques are inappropriate for piggery enterprise greenhouse gas studies — due to the source

area configurations and scales involved. There may be some application for relaxed eddy accumulation techniques, though the evidence suggests that the BLS techniques can fill the role of emission measurement from land application areas — the largest homogenous source to be encountered in piggery enterprises.

Nitrous Oxide Emissions

- Emissions of nitrous oxide occur via both direct and indirect paths.
- Direct nitrous oxide emissions can occur from both the nitrification and denitrification processes, and may be delivered through the activity of microbes such as bacteria and fungi, or through purely chemical means.
- Denitrification processes are capable of consuming and emitting nitrous oxide.
- The major factors controlling emissions from soils are likely to be related to the factors that control emissions from deep litter, effluents, and from effluent/deep litter amended soils. These soil factors include:
    - Factors that alter the redox potential of the soil, such as changes in soil moisture.
    - Soil texture possibly as an influence on the development of anaerobic conditions, and effecting transport of gasses and solutes within soils.
    - Organic carbon availability and quality.
    - Supply of mineral N.
    - Soil temperature. Temperature can directly increases denitrification rates, but also via indirect means such as increased respiration rate — resulting in an increase in the volume of anaerobic zones. However, temperature behaviour may not be this simple, as temperature optima do exist. Temperature dependence is more likely to follow a trend of several superimposed relationships.
    - Soil pH. The acidity of the soil environment has a controlling influence on nitrification, denitrification, and the ratio of products derived from these processes — directly influencing N_2O emissions — and may also influence other nitrogen transformations, such as immobilisation and mineralisation — that have an indirect influence on emissions. Microbial populations may change or adapt to different pH conditions, and may do so within days.
    - Management practices can influence emission rates by manipulating one or more of the above factors.
- Indirect emissions of N_2O are likely to be substantial (of the same order of magnitude as direct emissions), via ammonia volatilisation, deposition, nitrification/denitrification.
- A range of reasonably simple mitigation measures for ammonia volatilisation have already been conceived, and trials may prove some of them practical.
- Piggery effluent nitrous oxide emissions following land application are often larger than those from other waste streams. This may be due to their high ammonia content, mineralisable N, mineralisable C, and low C:N ratios of many of these effluents compared to other sources.
- Separating slurry into solid and liquid fractions tends to decrease N_2O emissions, whether the liquid is digested or not. Treatment also tends to decrease nitrous oxide emissions. Treatment decreases the concentration of inorganic N contained in the effluent — which may be the reason for the latter effect. Separating the liquid fraction from the solid fraction decreases access to readily degradable carbon for

the solids fraction, and decreased organic N in the liquid fraction. These factors may be related to the overall decrease in N_2O emissions.

- Slurry incorporation and co-application of effluent and inorganic-N sources can greatly increase nitrous oxide emissions.
- Nitrous oxide emissions can be particularly problematic from deep litter systems relative to conventional ponds. However Australian data is required.
- Permeable pond covers, while potentially valuable in the control of odour, may increase nitrous oxide emissions — though data is scarce.
- Opportunities exist to control emissions through diet manipulation. However diet manipulations may affect productivity.
- Nitrous oxide emissions from slatted floored housing are likely to be slightly less than methane emissions. Nitrous oxide dominates GHG emissions from deep litter systems.
- Current nitrous oxide emission models are designed for use in soil systems, and tend to be reliant on empirical approaches. The few truly mechanistic models may be over-parameterised. Adaptation to effluent/manure systems would be valuable. Sensitivity analyses could be conducted to remove unwarranted, non critical complexity — revealing the critical factors for manipulation through mitigation managements.

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