# Quantifying poultry litter conditions and relationships with odour emissions

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#### Abstract

Litter conditions are managed during poultry rearing to provide a comfortable environment for the chickens and reduce the potential of odour impact on surrounding communities. This study aimed to identify and quantify the properties of poultry litter in Australian meat chicken sheds that influence odour formation and emissions. Litter conditions were evaluated in terms of litter moisture content, pH, water activity and oxygen concentration. Litter samples collected from meat chicken sheds during the eight week grow-out period showed that litter conditions varied spatially, within the litter profile, during the grow-out and between grow-outs. Litter conditions were measured at discrete positions across the litter and within the profile to describe the full range, rather than measuring average conditions.

Water affects many of the chemical, physical and microbial properties of litter and yet research revealed a lack of knowledge in terms of the water balance within meat chicken sheds and litter properties, especially moisture content, water holding capacity and water activity. An equation combining theoretical and empirical inputs was developed to estimate the water addition to litter during a grow-out. This was combined with experimental measurements of water holding capacity and evaporation rate to identify periods of the grow-out when litter conditions were at risk of deteriorating. Addition of manure during a grow-out was found to increase the water holding capacity of litter and reduced water activity, which is a measure of the availability of water within litter that affects friability and microbial growth.

Odorant emission rates were measured for different litter conditions in meat chicken sheds and during a laboratory based study where meat chickens were reared in a pen with a litter floor. Emission rates of volatile organic compounds and sulfur compounds (VOC and VSC) from the litter surface were measured using flux hoods and analysed by a combination of TD-GC-MS, TD-GC-SCD and PTR-TofMS methods. Emission rates of some odorants were found to be significantly affected by litter conditions (when litter was characterised as 'wet' or 'dry') and the length of the grow-out. Odour activity values indicated which individual odorants made the biggest contribution to wet and dry litter odours.

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# Abstract

Litter conditions are managed during poultry rearing to provide a comfortable environment for the chickens and reduce the potential of odour impact on surrounding communities. This study aimed to identify and quantify the properties of poultry litter in Australian meat chicken sheds that influence odour formation and emissions. Litter conditions were evaluated in terms of litter moisture content, pH, water activity and oxygen concentration. Litter samples collected from meat chicken sheds during the eight week grow-out period showed that litter conditions varied spatially, within the litter profile, during the grow-out and between grow-outs. Litter conditions were measured at discrete positions across the litter and within the profile to describe the full range, rather than measuring average conditions.

Water affects many of the chemical, physical and microbial properties of litter and yet research revealed a lack of knowledge in terms of the water balance within meat chicken sheds and litter properties, especially moisture content, water holding capacity and water activity. An equation combining theoretical and empirical inputs was developed to estimate the water addition to litter during a grow-out. It was shown that average water addition ranged from 1.0–3.2 L/m²/day during normal conditions. This was combined with experimental measurements of water holding capacity and evaporation rate to identify periods of the grow-out when litter conditions were at risk of deteriorating. Addition of manure during a grow-out was found to increase the water holding capacity of litter, decrease air-filled porosity and reduced water activity, which is a measure of the availability of water within litter that affects friability and microbial growth.

Litter conditions were found to vary spatially, temporally and within the litter profile. Wet litter was characterised by having a compacted or crusted surface, low pH at the surface and high pH at the base, and low oxygen concentration. When fresh excreta was added to the surface of wet litter, the compacted and cohesive surface prevented it from being incorporated, which resulted in a layer of manure forming on the surface. Dry friable litter, in comparison, had neutral to alkaline pH, and was a homogeneous mixture of excreta and bedding materials. When fresh excreta was added to the litter surface of dry friable litter, the excreta rapidly dried and bird action broke the excreta into smaller pieces that were then worked into the litter.

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Odorant emission rates were measured for different litter conditions in meat chicken sheds and during a laboratory based study where meat chickens were reared in a pen with a litter floor. Emission rates of volatile organic compounds and sulfur compounds (VOC and VSC) from the litter surface were measured using flux hoods and analysed by a combination of TD-GC-MS, TD-GC-SCD and PTR-TofMS methods. Emission rates of some odorants were found to be significantly affected by litter conditions (when litter was characterised as 'wet' or 'dry') and the length of the grow-out. Emission rates of sulfides were greater from wet, caked litter than dry friable litter. Differences in emission rates were associated with acidic and anaerobic conditions in the surface of wet, caked litter.

Single compound odour activity values were calculated to determine which odorants made the biggest contribution to odour emitted from different litter conditions. Odorants including 2,3-butanedione, methyl mercaptan, hydrogen sulfide, butanoic acid, trimethylamine and dimethyl sulfide had the highest OAVs for litter and excreta odours. Summing the OAVs for each litter type provided a strong indication that wet, caked litter was more odorous than dry friable litter.

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- Dunlop, M.W., Blackall, P.J., Stuetz, R.M., 2015. Water addition, evaporation and water holding capacity of poultry litter. *Science of the Total Environment 538, 979-985.*
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- Dunlop, M.W., McAuley, J., Blackall, P.J., Stuetz, R.M., 2016. Water activity of poultry litter: Relationship to moisture content during a grow-out. *Journal of Environmental Management 172, 201-206.*
- Dunlop, M.W., Moss, A.F., Groves, P.J., Wilkinson, S.J., Stuetz, R.M., Selle, P.H.,
  2016. The multidimensional causal factors of 'wet litter' in chicken-meat production. *Science of The Total Environment 562, 766-776.*

#### Peer reviewed conference papers

Dunlop, M.W., Stuetz, R.M., 2016. Wet litter — factors associated with the shed microenvironment and litter properties. In 'Proceedings of the 27th Annual Australian Poultry Science Symposium', pp. 21-28. Sydney, NSW, 14-17 February 2016, University of Sydney. from <u>http://sydney.edu.au/vetscience/apss/proceed.shtml</u>.

#### **Conference papers**

- Dunlop, M., 2014. Moisture holding capacities of various litter materials, 'Proceedings of the Poultry Information Exchange (PIX2014) Litter Management Workshop'. 25-28 May 2014, Gold Coast, Australia, pp. 25-34. PIX Committee.
- Dunlop, M., 2014. Studies on odour emissions and their impacts, '*Proceedings of the Poultry Information Exchange (PIX2014)*', 25-28 May 2014, Gold Coast, Australia, PIX Committee.
- Dunlop, M., 2015, 'Managing litter' workshops for growers. *Poultry CRC Ideas Exchange*, September 2015, Nerang, Queensland, Poultry Cooperative Research Centre.
- Dunlop, M., 2016. The challenge of managing litter, *'Proceedings of the Poultry Information Exchange (PIX2016)'*, 29 May–1 June 2016, Gold Coast, Australia. PIX Committee
- Dunlop, M., 2016. Water activity and strategies for litter management, 'Proceedings of the Poultry Information Exchange (PIX2016)', 29 May–1 June 2016, Gold Coast, Australia. PIX Committee.

#### **Industry workshops**

- Dunlop, M., 2013, Odour emissions, odour impacts and litter management. Mareeba, Qld, July 2013.
- Dunlop, M., 2014. Litter management and odour emissions/impacts, Broiler Farm Sector—Technical workshop. Department of Environment and Primary Industries (DEPI), Attwood, Victoria, August 2014.
- Teitzel, S., Dunlop, M., Sansom, G., 2015, Litter management workshops, Australian Chicken Growers Council, Brisbane, Adelaide, Mareeba, June-October 2015.

# Acronyms and abbreviations

Aw	Water activity
DMS	Dimethyl sulfide
DMDS	Dimethyl disulfide
DMTS	Dimethyl trisulfide
MW	Molecular weight
O <sub>2</sub>	Oxygen concentration of air (%, note O <sub>2</sub> concentration of
	ambient air is approximately 21%)
OAV	Odour activity value
OTV	Odour threshold value
Ou/m³	Odour concentration unit (odour unit per cubic metre)
Ou/m²/s	Odour emission rate units (odour units per square metre per
	second)
RH	Relative humidity
PTR-TofMS	Proton transfer reaction time-of-flight mass spectrometer
TD-GC-MS	Thermal desorption-gas chromatography-mass spectrometry
TD-GC-NCD	Gas chromatography-nitrogen chemiluminescence detector
TD-GC-SCD	Gas chromatography-sulfur chemiluminescence detector
VOC	Volatile organic compound (may be odorous or non-odorous)
VSC	Volatile organic sulfur compound

# Glossary

Bedding	Bedding materials are placed on the floor of a meat chicken shed at the start of a grow-out. Materials may include wood shavings or sawdust, rice hulls, peanut shells, straw, shredded paper products and in this document will usually refer to materials that contain no manure (because then it is termed 'litter'). However, litter from previous grow-outs, which may be partially or completely composted or pasteurised, may also be used at the start of a grow-out.
Cake / caking	The formation of a layer of excreta on the surface of the litter. This manure cake is typically dense and compacted, may be up to 10 cm thick and can have high moisture content. While it is often wet, it may also be dry and hard.
Condition (of litter)	Litter condition is a general term used to describe a range of litter properties including pH, O <sub>2</sub> concentration within the pores, compaction, friability, moisture content, water activity, temperature, manure content, microbial activity and nutrient content.
Excreta	Excreta is a mixture of faeces and urine, which for birds is excreted simultaneously. In this thesis, excreta is the term used for freshly discharged waste. After being incorporated into the litter, terminology tends to change and it is referred to as 'manure'.
Grow-out	The 5–8 week long rearing period when meat chickens are raised from 1 day old chicks until they are removed for slaughter. This may be otherwise known as a batch or rearing period.
Litter	In this thesis, the term 'litter' refers to 'meat chicken litter'. Litter is a mixture of bedding materials and poultry manure. It is used on the floor of poultry sheds to provide a cushioned surface and insulation between the birds and the ground; to absorb and release moisture; and allows birds to display behaviour such as dust bathing.
Meat chicken	Otherwise known as a 'broiler', is a type of chicken that has been selectively bred to produce chicken meat. Meat chickens are commonly reared on a litter covered floor in meat chicken sheds.

Moisture content	Moisture content (wet basis) is the mass of water in a sample
	divided by the mass of the moist sample.
	$Moisture \ content = \frac{mass \ of \ water + mass \ of \ over \ dried \ solids}{mass \ of \ water + mass \ of \ over \ dried \ solids}$
	In this thesis, any reference to dry basis moisture content will
	be explicitly noted:
	Dry basis moisture content = $\frac{mass of water (kg)}{mass of oven dried solids (kg)}$
Odorant	An odorant is a chemical compound that is odorous. It may
	be a VOC, reduced sulfur compound or other gas (e.g.
	ammonia). Each odorant has a specific character and odour
	threshold (the minimum concentration at when the odorant
	can be detected). Many odorants combine together to
	produce the smell that is recognised as 'poultry' odour
	Detie of the concentration of a simple company dubit.
value	Ratio of the concentration of a single compound to its odour
Value	detection threshold. Conceptually, the larger the OAV the
	greater potential for that individual odorant compound to
	contribute to the overall odour.
Pickup	The process for removing birds from the shed for slaughter. It
	may otherwise be known as a 'thin-out', 'split', or 'catch-out'.
	Pickups during the grow-out cycle are scheduled to meet
	market demands for quantities and specifications of meat
	products but also regulates the maximum stocking density.
Reused litter	Litter that was used in a previous grow-out and is being used
	again for a subsequent grow-out. Litter may be re-used many
	times. Sometimes the litter is treated before being used again
	(dried, pasteurised, composted, chemically amended,
	de-caked or screened).
Volatile organic	VOCs are molecules that contain at least one carbon and one
compound	hydrogen atom (i.e. organic compounds) that vaporise easily
	at room temperature (i.e. volatile).
Watar activity	Symbolic advite A and is also known as the aquilibrium
water activity	relative humidity (EPH). A is a ratio of the fugacity of water
	in a comple compared to the fugacity of water from pure liquid
	in a sample compared to the rugacity of water north pure liquid
	water at the same temperature. Fugacity is a measure of the
	escaping tendency of the water. A <sub>w</sub> is unit-less and measured
Wet litter	Litter that has high enough moisture content to have
	detrimental effects in terms of disease, food safety risks, bird
	comtort, production efficiency and/or environmental outcomes
	(e.g. odour and ammonia).

# **Chapter 1. Introduction**

# 1.1 Chicken meat industry challenges—litter management and odour impacts

#### 1.1.1 Industry description and consumption of chicken meat

The Australian chicken meat industry is comprised of a small number of large, vertically integrated enterprises and hundreds of meat chicken farms. Approximately 620 million birds are slaughtered annually to produce 1.2 million tonnes of chicken meat (ABARES, 2016). Demand for chicken meat has steadily increased at a rate of 2–4% for several decades, with average per-capita consumption estimated at 47 kg of chicken meat per year (ABARES, 2016). Increasing demand for chicken meat necessitates industry growth and consequently the construction or expansion of meat chicken farms. With this growth comes the increased potential for odour nuisance.

The chicken meat industry is comprised of breeder farms, hatcheries, 'grow-out' farms and abattoirs. The focus of this research is the grow-out farms where meat chickens, received as one-day old chicks from the hatchery, are raised and fattened in specially designed sheds for a period of 5–8 weeks before being transported to the abattoir. Details about chicken meat farms and sheds are readily available (ACMF, 2013). In summary, a typical meat chicken 'grow-out' farm is comprised of 3–10 sheds each housing 30,000–50,000 chickens. Assuming average per-person consumption, each chicken shed produces enough chicken meat for 6,000–13,000 average Australians.

Modern meat chicken sheds are designed specifically to create a comfortable environment for the chickens so that they grow quickly and efficiently. Production efficiency of chicken meat, in terms of feed conversion, is unmatched by any other intensive animal industry. Meat chicken sheds are well insulated and are fitted with a sophisticated climate control (ventilation) system incorporating a programmable controller, heaters, exhaust fans, inlet vents and evaporative cooling pads. The ventilation system is operated to regulate temperature and in-shed air quality by exhausting heat, moisture, dust and foul gases. Figure 1 is an example a typical, modern, meat chicken shed.



Figure 1. Example of a typical, modern, meat chicken shed

Before the day-old chicks are placed in the shed at the start of each grow-out, the floor of the shed is covered with a friable absorbent bedding material. Fresh excreta is added continuously during the grow-out and is worked in by the birds, resulting in a mix of excreta and bedding materials, i.e. litter. Litter is thought to be the primary source of 'offensive' odours emitted from meat chicken farms, and it is these offensive odours that most likely contribute to odour impacts and complaints.

## 1.1.2 Odour from meat chicken production

Smell from meat chicken sheds can upset neighbours and is the leading cause of complaints against meat chicken farms. The smell originates from the litter, fresh excreta (mixture of faeces and urine, which in birds is excreted simultaneously) and from the birds themselves.

A history of complaints about odour has led to environmental regulators and development assessment authorities (i.e. local councils and state government departments) taking a precautionary approach with the approval of new or expanding meat chicken farms. The intention to minimise the potential for future odour impacts is commendable, but restricts growth of the chicken meat industry and places pressures on the supply of chicken meat to Australian consumers.

One odour impact reduction strategy that is applied to meat chicken farms (and other odorous enterprises) in Australia and internationally is to separate the meat chicken sheds from receptors, allowing odours to disperse in the ambient environment to a level that shouldn't cause nuisance. Separation distances are typically determined using atmospheric dispersion modelling combined with odour impact criteria. This strategy has been largely successful; however, there are cases where individual meat
chicken farms receive ongoing odour complaints once they begin operating. In these cases, odour emissions from the farm may be greater than was anticipated during odour impact assessment; the environment surrounding the farm may have anomalies that prevent odours from dispersion in the way predicted by odour dispersion modelling; or the receptor is sensitive to the odour. For these cases, other odour impact reduction strategies are required. Strategies may include capturing and treating odours as they exit the sheds or reducing the formation of odour at the source, primarily the litter. The chicken meat industry has investigated air treatment technologies to capture and treat odour emissions as they exit the sheds (Dunlop, 2009); however, large ventilation rates required for cooling the birds makes conventional air treatment technologies such as biofilters, bio-scrubbers, chemical scrubbers, particulate filters, ozonation, thermal incineration and odour masking agents impractical or uneconomical. The most promising strategy to effectively and economically reduce odour emissions from meat chicken sheds is to reduce the formation of odorants within the litter; however, there is limited understanding of:

- which specific odorants (ammonia, NMVOCs, VSCs) cause odour impacts downwind from the meat chicken shed and if these are the same odorants that dominate and contribute to odour concentration within the shed;
- the conditions/properties of the litter that lead to the formation of the odorants that are most likely to cause downwind impacts; and
- whether or not conditions within the meat chicken shed (i.e. temperature, humidity and static pressure) as well as ventilation airflow dynamics (i.e. air velocity and turbulence) promote accelerated release of odours from the litter that contributes to odour impacts.

### 1.1.3 Challenges for researching meat chicken litter conditions and odour

In summary, litter conditions and odour production in meat chicken sheds are complex and there are many factors to consider when quantifying litter conditions or investigating how litter conditions relate to odour emissions. Some of these include:

- broad range of fresh bedding materials
- spatial variability and non-homogeneity
- temporal trends
- difficulties in measuring representative odour emission rates from meat chicken sheds and/or directly from the litter surface
- difficulties in collecting, storing and analysing the complex mixture of odorants.

# 1.1.4 'Wet litter'

'Wet litter' is a term specifically used when litter has sufficient moisture to result in detrimental outcomes in terms of bird health, diseases, food safety risks, bird comfort, production efficiency and/or environmental outcomes (including odour emissions). It is internationally recognised terminology and yet it is poorly defined in terms of exactly what litter conditions are necessary to be classified as 'wet litter' (Dunlop et al., 2016c). In this thesis, the topic of 'wet litter' is explored in terms of the reported causes of wet litter, how it affects the properties of litter and what effect it may have on odour emissions.

# 1.2 Thesis overview

The central theme of this thesis is that *'the condition' of litter in meat chicken sheds affects odour emissions* and the potential to cause odour nuisance. While this statement is generally accepted, previous measurements of odour emissions from meat chicken sheds has produced inconsistent results that cannot be adequately explained by the measured litter conditions (Dunlop et al., 2011) and the many other factors suspected to affect emissions including ventilation rates, weather conditions, bird health, bird activity and diet (Dunlop et al., 2010). It is suggested that litter conditions and related effects on odour emissions are not well understood, are inadequately measured and are poorly characterised. There is therefore a need to investigate the conditions and properties of litter while it is being used during meat chicken rearing.

The initial intention of this research program was to measure the odorant emissions from different litter conditions to improve the understanding of which odorants are produced. A further intention was to measure the effect of litter compaction, caking and bird activity on the diffusion of odorants through the litter profile. While these were the intended research topics, it became evident that there was a knowledge gap about litter conditions that needed to be addressed first. Following a review of the literature and discussions with researchers that specialise in agricultural wastes and odour emissions, the focus of this research strategically changed to focus on litter properties, especially water dynamics within litter, and to characterise the conditions at different depths within the litter profile. Water has a direct effect on many litter properties including pH, oxygen (O<sub>2</sub>) concentration, microbial activity, friability and temperature and has been a central focus in this investigation. The focus on water included estimating the amount of water being added to litter during a grow-out and measuring:

- the water holding capability of litter and bedding materials;
- the evaporation rate from litter under a range of conditions;
- water availability within litter in terms of water activity (A<sub>w</sub>); and
- the effect of water on the pH of litter at different depths within the litter profile (pH has previously being related to the emission of some odorants).

Following the investigations into the effects of water on litter properties, scoping experiments were carried out to measure odorant emissions from wet and dry litter using a flux chamber techniques and a combination of analytical instruments including thermal desorption-gas chromatograph-mass spectrometer (TD-GC-MS), thermal

desorption-gas chromatograph-sulfur chemiluminescence detector (TD-GC-SCD) or proton transfer reaction-time-of-flight mass spectrometer (PTR-TofMS). These scoping experiments provided a strong indication that wet and dry litter conditions affected odorant emission in a way likely to affect the odour impact potential of meat chicken production. These findings provide a foundation for future research to focus more specifically on odorant formation and emissions within litter and to consider the effects of litter compaction and bird activity on the mass transfer of odorant through the litter and from the litter surface.

Strategically focussing on the water cycle in meat chicken sheds, litter properties, effects of water and measurement of water activity has resulted in new knowledge that can be applied to litter management practices in meat chicken sheds. The benefits of applying this knowledge extend beyond considerations about odour emissions, and can be related to production efficiency, welfare and waste management. The knowledge developed in this study has been communicated to the chicken meat industry in formal publications, conference presentations and workshops.

### 1.2.1 Aim of this research

The aim of this research was to improve understanding about poultry litter conditions and the relationships between litter conditions and odour emissions. This would enable litter management strategies to be tailored to minimise odour. The intent was to examine litter in greater detail than has previously been achieved to improve knowledge about the range of conditions that occur spatially, temporally and throughout the depth of the litter profile.

A further aim was to improve understanding about 'wet litter' including what causes it and what changes within the litter when it becomes wet. The water cycle and water dynamics within litter were a primary focus.

### **1.2.2** Experimental objectives of this research

The following research objectives were attempted to achieve the research aims:

- Develop a method to estimate the amount of water added to litter during a typical grow-out period.
- Experimentally determine the water holding capacity of litter materials.
- Develop a method to experimentally measure the rate of evaporation from litter materials under controlled conditions.

- Assess the variability of litter conditions spatially, temporally and through the litter depth, and the effect of localised conditions on emission rates. The focus will be placed on measuring litter moisture content and pH.
- Apply flux chamber sampling techniques combined with TD-GC-MS, TD-GC-SCD and PTR-TofMS to experimentally determine the odorant composition and measure the emission rate of odorants from a selection of different poultry litter conditions.

# 1.2.3 Thesis layout

This thesis is presented in multiple sections. Chapter 1 introduces Australian chicken meat production and the challenges faced by this industry relating to odour impacts and maintaining litter conditions that are conducive to production of healthy birds and comply with increasingly stringent welfare requirements.

Chapter 2 provides a foundation to this thesis by reviewing existing knowledge about litter conditions, especially 'wet litter', and the emission of odour from litter. This chapter includes a detailed list of known poultry odorants and discussions about the microbial origins of odorants and the diffusion of odorants from porous litter. This chapter draws together information from two published literature reviews (Dunlop et al., 2016a; Dunlop et al., 2016c).

Chapter 3 describes a method developed in this study to estimate the amount of water being applied to poultry litter during a grow-out. Understanding how much water is applied to the litter on each day of a grow-out is important for strategically managing litter conditions, which is required on each day of a grow-out. Information in this chapter was derived from Dunlop et al. (2015).

Chapter 4 describes experiments to measure the water holding capacity and evaporation rate from bedding and litter materials. Evaporation rates were found to depend on moisture content. It has previously been demonstrated that odour emission rates can be related to evaporation and therefore the results from this experiment are valuable for demonstrating how moisture content of the litter may affect odour emission rates. Information in this chapter was derived from Dunlop et al. (2015).

Chapter 5 focuses on measurements of the water activity in poultry litter. Water activity is known to directly affect microbial growth and is responsible for water movement between excreta, litter and ventilation air. It is therefore an important consideration

when investigating the relationships between odour emissions and litter conditions. The information in this chapter was derived from Dunlop et al. (2016b).

Chapter 7 and Chapter 8 present the results of two scoping experiments to gather preliminary data on the effect of litter conditions on odorant emissions, and to hypothesise how the mixture and strength of these odorants may affect the odour impact potential of different litter conditions. The second of these experiments included the use of PTR-TofMS, which was the first time that this technology had been used in conjunction with a flux chamber to measure odorant emissions in real-time from poultry litter. The experiment described in Chapter 7 focussed on measuring odour emissions from a variety of litter conditions using litter sourced from a commercial meat chicken shed. Odorants were sampled using a flux chamber placed on the litter. The litter was either in-situ in the shed (undisturbed) or removed from the shed for sampling in a laboratory setting (disturbed). Odorants were analysed using TD-GC-MS and TD-GC-SCD. In contrast, the experiment discussed in Chapter 8 focussed on measuring odorants from litter in an experimental pen at a research facility in which meat chickens were raised for approximately 5 weeks. Litter conditions were able to be more closely observed in this experimental setting than was possible in a commercial meat chicken shed. Odorant emissions from wet and dry litter conditions were compared and the litter was closely examined in terms of moisture content, water activity and pH. These scoping experiments did not investigate the effects of some factors, such as bird activity and litter compaction, which leaves these complex issues to be the subject of future research.

Conclusions and recommendations for future research are in Chapter 9, and the thesis ends with appendices and a list of references used in this study.

# **Chapter 2. Literature review**

# 2.1 Introduction

The emission of odour from litter is affected by many things including the meat chicken rearing process, the management of the in-shed environment and litter management. This chapter contains a discussion of each of these contributing factors and how they relate to odour emissions. Biochemical production of odorants, molecular diffusion and exchange of odorants from the litter also need to be thoroughly understood to fully appreciate how litter conditions contribute to the formation and emission of odours. Managing litter to minimise odour emissions is challenging and there are many fundamental and practical considerations.

# 2.2 Overview of chicken meat production

Meat chickens (*Gallus gallus domesticus*, otherwise known as broilers) are specifically bred and raised for meat production. They are hatched from fertile eggs and then transported to a grow-out farm where they grow for approximately 35–56 days before being transported to an abattoir for slaughter. The major commercial breeds of meat chickens grown in Australia include Ross 308 (<u>http://en.aviagen.com/ross</u>) and Cobb500<sup>™</sup> (<u>http://www.cobb-vantress.com</u>). Detailed information about housing, management, nutrition and growth of the birds during the grow-out cycle is available through the breeding company web sites. Every aspect of the grow-out phase of the production system will influence odour emissions, as explained in the following sections.

# 2.2.1 Meat chicken growth cycle

One-day-old chicks are placed in the grow-out shed on the day they hatch in the hatchery. The shed is pre-heated and the chicks are given immediate access to feed and water. Meat chickens grow rapidly due to selective breeding, high quality feed and being provided with an ideal growing environment, especially in terms of maintaining thermal comfort and lighting cycles. Figure 2 shows the approximate growth rate and body weight for meat chickens. Chickens are placed in the shed at a density of 12–18 birds per square meter (based on the floor area of the entire shed); however, during the first few weeks, the chicks are often restricted to a portion of the shed (for example ½ of the shed until day 7 then ¾ of the shed until day 14) in order to conserve energy and improve uniformity of the in-shed environment. This portion of the shed is known as the brooder or brooding section and is temporarily separated from the remainder of the

shed using a floor-to-ceiling curtain. Dividing the shed during the brooding phase results in different manure and moisture deposition in the two areas, which may have short-term and long-lasting effects on litter conditions and odour emissions and require different management practices.



Figure 2. Daily weight gain and body weight for meat chickens during a grow-out (average of breeds for mixed-sex birds (Aviagen Inc., 2014a; Cobb-Vantress Inc., 2012b))

# 2.2.2 Length of production cycle

The exact length of a grow-out may be different for each batch of chickens depending on market demands and other factors, but typically lasts for 35–56 days. A portion of the flock is commonly removed on day 35 of the grow-out for slaughter. Removing birds for slaughter is called a 'pickup' (otherwise known as a 'thin-out', 'split', or 'catchout'). Pickups during the grow-out cycle are scheduled to meet market demands for quantities and specifications of meat products but also control the maximum stocking density as required by various standards and for different grow-out types:

- 28 kg/m<sup>2</sup> for naturally ventilated farms (FREPA, 2012; SCARM, 2002)
- 30 kg/m<sup>2</sup> for free range farms (with mechanically ventilated sheds) (Barnett et al., 2008)
- 34-40 kg/m<sup>2</sup> for mechanically ventilated farms (FREPA, 2012; SCARM, 2002).

Stocking density influences the deposition rate of manure and moisture into the litter as well as management of the shed and ventilation system. In turn, this may influence odour emissions from the litter.

#### 2.2.3 Feed and water consumption

Water plays an important role in the formation and emission of odorants, which will become evident later in this thesis. It is therefore important to understand the water cycle within litter—water addition from spillages and excreta deposition as well as water losses through evaporation due to ventilation.

Feed consumption during the grow-out cycle is affected by bird age, sex and stocking density. Figure 3 shows typical daily and cumulative feed consumption on a per bird basis.



Figure 3. Daily and cumulative feed consumption per bird (average of breeds for mixed-sex birds (Aviagen Inc., 2014a; Cobb-Vantress Inc., 2012b))

Water consumption for meat chickens is related to the feed intake. On a daily basis, the ratio of water to feed consumption changes throughout the batch. Williams et al. (2013) measured water and feed intake for meat chickens and reported that the ratio of feed to water intake ranged from 1.5–2.6 (L water:kg feed), with the peak occurring on day 7 (Figure 4) (although data prior to day 7 was thought to be inaccurate due to the use of additional feed and water pans). The batch average water:feed ratio at the end of the 41 day batch cycle was 1.74. Grow-out periods for Australian flocks are more

commonly 56 days. If an assumption were made that the water:feed intake stabilised after day 41 at a value of 1.50–1.55, the average water:feed intake ratio at the end of the 56 day grow-out period would be approximately 1.66.



Figure 4. Ratio of water:feed intake throughout a grow-out period (Williams et al., 2013) (average water:feed ratio for days 0–41 was 1.74).

Other researchers have estimated water consumption to be on average 1.5–2.0 times as much water as feed (on a mass per mass basis) over the course of a grow-out cycle (Collett, 2007; Manning et al., 2007; Watkins and Tabler, 2009; Williams et al., 2013). The daily water:feed intake ratios shown in Figure 4 are at the lower end of this range. Estimations of water consumption for Australian meat chickens may need to be higher given our warmer climate. A grow-out average water:feed ratio of 1.8 is likely to be a reasonable assumption for Australian flocks. Figure 5 shows the daily and cumulative water intake per bird during a grow-out when the average water:feed intake ratio is 1.8 (based on water and feed intake during a 56 day grow-out).



Figure 5. Daily water consumption by each bird and cumulative amount over the grow-out period (assuming the bird consumes an average of 1.8 L of water for every kg of feed)

It has been estimated that approximately 50–80% of the water consumed by the birds will be excreted in the manure and therefore applied directly to the litter (Collett, 2007; Czarick and Fairchild, 2012). Together with estimations of feed intake and typical bird density, it is possible to estimate the quantity of water that is added to the litter daily (Figure 6) (Dunlop et al., 2015).



-Daily water deposition (50%) —Cumulative water deposition (50%)

Figure 6. Water applied to the litter daily per square meter and cumulative total over the entire batch—for the brood section of the shed where birds are always present (These are based on the following assumptions: feed consumption of as-hatched birds (averaged for Ross 308 and Cobb 500 birds (Aviagen Inc., 2014a; Cobb-Vantress Inc., 2012b)); water to feed intake ratio as shown in Figure 4; 75% of water consumed is deposited to litter; stocking density 17.0 birds/m<sup>2</sup>; birds restricted to 50% of shed floor area until day 6, 66% until day 10, 75% until day 14; 33% of birds harvested on day 35 with 33% of the remaining birds harvested on day 45 to maintain live weight density under 36 kg/m<sup>2</sup>) (Dunlop et al., 2015)

# 2.2.4 Grow-out shed design

Different styles of meat chicken sheds are used in the Australian chicken meat industry, including:

- mechanically ventilated, including 'tunnel' ventilated and cross-flow;
- 'naturally' ventilated; and
- free-range, which may be mechanically or naturally ventilated.

In Australia, tunnel ventilated sheds are the most common and modern design. As such the description below focusses on this style of shed. Many of the design features are similar between the different styles of sheds.

Mechanically ventilated meat chicken sheds are designed to provide the birds with a comfortable environment and many design features of modern sheds will affect odour and dust emissions. Correct ventilation is essential for bird health, bird comfort, efficient production and control of odour and dust emissions.

Tunnel ventilated sheds are typically 100–150 m long, 12–20 m wide, have 2.4–2.7 m tall walls and low roof profiles. These sheds are stocked with 20,000–50,000 chickens. The shed floor is usually constructed with compacted earth, road-base or concrete. The roof is usually insulated and insulated panelling or impermeable curtains are used for the walls. The selection of wall material depends on the age of the shed and design preference; however, most new farms are constructed with solid, insulated walls.

The ventilation system installed in poultry sheds is very complex and comprises a central control unit, primary ventilation fans, duty ventilation fans, mini-vent inlets, tunnel ventilation inlets, evaporative cooling pads and ceiling baffles (Figure 7).

Large diameter axial fans (1200–1525 mm diameter, called primary or tunnel ventilation fans) are installed on the narrow end of the shed and provide the majority of the ventilation. Maximum ventilation rate is approximately 8–12 m<sup>3</sup>/h per bird. Additional fans (referred to as minimum ventilation or duty fans) are installed in the walls along the length of the shed, on the wall opposite the primary fans, or through the roof to improve air-exchange and air-flow uniformity during low levels of ventilation. All ventilation fans are fitted with back-draft shutters to prevent fresh air entering the shed through inactive fans.

Mini-vent inlets are installed at equal spacing along the walls on each side of the shed. Air is drawn through these vents when low levels of ventilation are required. Tunnel ventilation inlets are positioned on the opposite end of the shed from the tunnel ventilation fans. Air is drawn through these large vents when the shed transitions into tunnel ventilation mode.

Evaporative cooling pads are usually installed in front of the tunnel ventilation inlets. When the weather is hot and maximum cooling is required, water runs over these cooling pads, creating a cooling effect as the air passes through them. Foggers—high pressure nozzles designed to atomise water droplets and create a fine mist—or low pressure sprinklers may also be installed inside the shed and are activated when additional cooling is required.

Some sheds may be fitted with circulation fans or destratification fans in the ceiling. These are designed to mix air within the shed to reduce destratification and improve uniformity of air quality within the shed.



Figure 7. Meat chicken shed showing components of the ventilation system (Dunlop et al., 2016a): (*top*) inside shed with roof removed (*bottom*) outside shed. *Note:* the long axis of the shed has been drawn at ½ to ½ scale for improved presentation

Mechanically ventilated sheds are operated under negative pressure (ranging from 0– 50 Pa) which draws fresh air into the shed through the inlets. Stale air is exhausted from the shed through the fans. There are primarily three modes of ventilation:

- 1. mini-vent ventilation;
- 2. tunnel ventilation without evaporative cooling; and
- 3. tunnel ventilation with evaporative cooling.

# 2.2.5 Ventilation

# 2.2.5.1 Mini-vent ventilation

Mini-vent ventilation is used when low levels of cooling are required and is also used in conjunction with heaters. It allows stale, moisture laden air to be removed from the shed. Mini-vent ventilation is designed to exchange the air in the shed without creating airspeed or drafts. This is achieved by drawing fresh air into the shed through mini-vents.

The mini-vents are an opening (commonly 20–30 cm tall and 40–120 wide) that has an adjustable flap that closes to seal the vent and opens to allow air to enter through the vent (Figure 8). Correct design and operation of mini-vents by having the correct static pressure and vent-flap angle is required for this mode of ventilation to be effective.



Figure 8. Mini-vents as viewed from the inside of the shed. These mini-vents are open to allow air to enter the shed.

The amount of opening through the mini-vents is controlled to maintain a slight vacuum in the shed (approximately 20 Pa depending on shed width and inlet design). The negative pressure ensures that an even amount of fresh air is introduced along the

entire length of the shed. Incoming air is projected along the ceiling so that the air is warmed by utilising heat from the birds and in-shed heaters, to lower relative humidity of the incoming air and to increase the water holding capacity (Figure 9). Fresh air is introduced into the shed in this manner to help remove excessive litter moisture and prevent condensation.



Figure 9. Correct airflow through mini-vents is required to increase the temperature and water holding capacity of incoming air before it contacts the litter (*image modified from Aviagen Inc. (2014c*))

At the lowest levels of mini-vent ventilation, duty fans cycle on and off, removing stale air (containing moisture, dust and odour) while maintaining the internal shed environment. As the level of mini-vent ventilation increases, duty fan activity will increase and the primary fans will start to activate. Depending on the number and size of mini-vents and fan capacity, 50–75% of the primary fans can normally be activated before tunnel inlets need to be opened.

# 2.2.5.2 Tunnel ventilation with and without evaporative cooling

Tunnel ventilation is used when large amounts of cooling are required. During tunnel ventilation, mini-vent inlets are closed and tunnel inlets are opened. This creates airspeed along the length of the shed of up to 4.0 m/s, introducing a wind chill effect for the birds. Wind chill is effective for improving bird comfort during warm weather by reducing the temperature experienced by the birds below the dry-bulb temperature of the air in the shed.

The tunnel inlets (Figure 7) may be opened or closed with a mechanically operated curtain or hinged rigid flap. Ceiling baffles are installed in many sheds to reduce the cross-sectional area of the shed, increasing airspeed at a given ventilation rate.

When extra cooling is required during tunnel ventilation, water runs over the cooling pads, creating an evaporative cooling effect. Evaporative cooling is most effective when ambient relative humidity is low. Evaporate cooling cells are typically installed on both sides of the shed and may be 15–30 m long and 1.8 m tall. The size required depends on the maximum ventilation rate of the shed.



Figure 10. Evaporative cooling cells on a meat chicken shed *(left)* and using water to cool the air entering the shed *(right)* 

While evaporative cooling reduces the air temperature to prevent heat stress, it increases relative humidity in the shed (for example to greater than 80%) and this can influence litter moisture content, drying rate and litter conditions. The effect on litter conditions is expected to affect odour emissions.

# 2.2.5.3 Features of naturally ventilated and free-range sheds

Naturally ventilated shed and sheds used on free-range farms are usually very similar to tunnel ventilated sheds apart from a few design features.

Naturally ventilated sheds do not have ventilation fans that extract air from the shed (or may have only a very limited number that are used during brooding). Fresh air enters the shed and stale, moisture laden air exits the shed due to prevailing winds. The sides of naturally ventilated sheds are usually made from curtains or hinged flaps that are opened and closed to maintain the optimum conditions within the shed, as determined by the bird's needs and weather conditions.



Figure 11. Naturally ventilated sheds have curtains or flaps on the walls that are opened or closed to maintain the correct conditions within the shed.

One challenge with naturally ventilated sheds is the inability to control air exchange rate and wind speed, because it is weather dependent. Naturally ventilated sheds may have stirrer fans installed throughout the shed that can be operated to induce wind currents within the shed, especially during hot weather.

Free-range sheds may be mechanically ventilated (tunnel-ventilated) or naturally ventilated. One design feature of free-range sheds is the installation of 'pop-holes' along the wall of the shed. These pop-holes are opened to give the chickens access to a fenced, grassed range area outside the shed. For mechanically ventilated sheds, opening the pop-holes can impede control of in-shed static pressure and therefore air flow rate, turbulence, mixing and conditioning (relative humidity reduction) within the shed. This may affect litter conditions and odour emissions.



Figure 12. 'Pop-hole' on the wall of a free-range shed that is opened to allow the birds access to the range

The design features of naturally ventilated and free range sheds may affect litter conditions and odour emissions because they reduce the level of control that the grower has over the in-shed conditions and litter drying.

### 2.2.6 Temperature control

Mechanically ventilated poultry sheds are specifically designed to allow precise temperature control for the birds. An example of the temperatures recommended during a grow-out is provided in Figure 13 (Cobb-Vantress Inc., 2012a).

The temperature shown is the effective temperature experienced by the birds following adjustments for humidity and wind-chill. Increased humidity decreases the ability of the bird to dissipate excess heat, which makes the bird feel warmer. Increased shed airspeed creates wind-chill, which reduces the temperature felt by the birds. Consequently, the 18 °C target temperature recommended for 56 day old birds may be achieved with a dry bulb temperature greater than 18 °C, assuming that humidity is low and shed airspeed is high, hence the reason for tunnel ventilation.



Figure 13. Target temperatures during a grow-out (Cobb-Vantress Inc., 2012a)

The change in temperature during a grow-out is an important consideration for odour emissions and litter conditions because temperature affects water evaporation, microbial activity, water activity as well as chemical volatility and equilibrium (relating to Henry's Law (Section 2.5.4).

### 2.2.7 Feed and water supply

Feed and water is supplied to the birds through specialised feeding and drinking systems.

Feed is delivered to the farm and stored in silos. Auger systems controls the flow of feed into the shed, where it is distributed to the birds using lines of feeding pans (Figure 14). The composition of the feed in terms of energy, protein and nutrients is changed several times throughout the grow-out cycle to meet the requirements of the birds. Feed is usually always available to the birds.

Water is supplied to the birds using specially designed nipple drinkers (Figure 15). These drinkers are specifically managed to meet the bird's requirements as they change throughout the grow-out cycle (drinker height and flow rate) and are maintained to prevent leakage. Old drinker designs, known as bell or cup drinkers are rarely used anymore because they were prone to excessive water spillage, resulting in wet litter. Wet litter is recognised as a possible cause of excessive odour generation. For this reason, drinker design, management and maintenance are essential to maintain good litter conditions and control odour.



Figure 14. Picture of a modern feeder pan (Dunlop et al., 2011)



Figure 15. Picture of a nipple drinker (fitted with evaporation cup) (Dunlop et al., 2011)

# 2.3 Litter

Litter is a friable, absorbent material that is used on the floor of meat chicken sheds to provide thermal insulation, absorb moisture, provide cushioning from the earth/concrete floor and allow birds to demonstrate some natural behaviours such as scratching and dust bathing (Collett, 2012; Shepherd and Fairchild, 2010). In addition to absorbing moisture, litter needs to readily release moisture to enable reasonable drying time (Bilgili et al., 2009; Grimes et al., 2002), it must be free of toxins (Tasistro et al., 2007) and must be suitable for use after it is removed from the shed because it has value as a fertiliser (Sistani et al., 2003; Tasistro et al., 2007).

# 2.3.1 Description of litter materials

The term 'litter' is used to describe many different conditions and ages of litter from fresh bedding material through to the time after it is removed from the meat chicken shed. From the perspective of investigating how the properties of litter affect odour emissions there is need for more specific terminology. In this thesis, the following terms will be used (Figure 16):

- bedding materials
- litter
- cake
- reused litter.

All of these may be found existing in a meat chicken shed simultaneously and the proportion of the shed floor covered by each of these states will vary with time. 'Spent litter' is another term that may be used to describe litter once it is removed from the meat chicken shed and will no longer be used to rear meat chickens.



Figure 16. Photographs of bedding material (*left*, pine shavings), litter (*centre*) and cake (*right*). *Note:* litter and cake images show the top surface and exposed side surface following excavation (Dunlop et al., 2016a)

# 2.3.1.1 Bedding materials

*'Bedding materials'* are the base/original materials, free of manure, that are used at the beginning of the litter use cycle. Bedding materials may also be used as a supplement during or after a grow-out to increase litter quantity or improve litter properties. Bedding materials are usually organic (e.g. wood shavings, saw dust, bark, rice hulls, peanut hulls, straw, shredded paper) but some inorganic materials have also been used (e.g. sand or clay such as vermiculite or bentonite) (Bilgili et al., 1999; Bilgili et al., 2009; Cengiz et al., 2011; Davis et al., 2010; Garces et al., 2013; Grimes et al., 2002; Miles et al., 2011b). Not all bedding materials are equal and the choice of bedding materials has an effect on litter physical properties, structure, ammonia production, water absorption capacity, water release rate, biochemical processes and bird health (Benabdeljelil and Ayachi, 1996; Bilgili et al., 2009; Grimes et al., 2002; Miles et al., 2008; Miles et al., 2011a; Shepherd and Fairchild, 2010; Torok et al., 2009).

The properties and suitability of a variety of bedding materials for meat chicken production have previously been investigated (Bilgili et al., 1999; Bilgili et al., 2009; Cengiz et al., 2011; Davis et al., 2010; Garces et al., 2013; Miles et al., 2011b; Reed and McCartney, 1970). There has been interest in how various bedding materials have different moisture holding capacity and physical properties (Grimes et al., 2002; Reed and McCartney, 1970); contribute to bird health and production parameters such as feed conversion ratio, weight gain and carcass properties (Bilgili et al., 1999; Bilgili et al., 2009; Cengiz et al., 2011; Davis et al., 2010; EI-Wahab et al., 2012; Malone et al., 1983); or influence ammonia and other gaseous emissions (Miles et al., 2011b; Tasistro et al., 2007).

#### 2.3.1.2 Litter

*'Litter'* is a friable mixture of bedding materials, fresh excreta, partly decomposed manure, spilt feed, feathers and water (Miles et al., 2011a; Sistani et al., 2003). The amount of excreta in the litter increases during a grow-out period and corresponds with changes in physical and chemical properties of the litter over time (Dunlop et al., 2015; Miles et al., 2008; Miles et al., 2011a).

The properties of bedding materials change with the accumulation of manure and therefore data collected on bedding materials may not be applicable throughout a grow-out period or over multiple grow-out periods (Garces et al., 2013; Meluzzi et al., 2008; Reed and McCartney, 1970; Tucker and Walker, 1992). Even though properties of litter change with manure addition, characteristics of the original bedding materials may be enduring throughout the life of the litter (Andrews and McPherson, 1963; Garces et al., 2013; Meluzzi et al., 2008).

#### 2.3.1.3 Cake

'*Cake*' is a compacted layer/crust that forms on the surface of the bedding materials or litter that contains most of the moisture and faecal matter and may be 5–10 cm thick (Miles et al., 2011a; Shepherd and Fairchild, 2010; Sistani et al., 2003). Miles et al. (2011a) differentiated litter conditions according to 'friable litter' or 'heavy cake'. Cake is not normally considered the same as wet litter but tends to be described as coinciding with wet litter. Cake contributes to undesirable consequences including contact dermatitis because it increases the surface moisture in contact with the birds (Meluzzi et al., 2008; Miles et al., 2011a). Miles et al. (2011a) described cake as providing a slippery, disease sustaining surface.

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Cake formation is reported to be related to litter moisture content, but is also dependent on bedding material (Andrews and McPherson, 1963; Grimes et al., 2002). It tends to form in high-traffic areas (Miles et al., 2008) (presumably due to localised high stocking density) and on litter with higher moisture content (Grimes et al., 2002). Particle size and shape of bedding materials also contributes to cake formation with particles larger than 2.5 cm accelerating cake formation because the litter particles tend to 'bridge' or 'mat over' quickly (Grimes et al., 2002). Materials such as straw, rice hulls, wood fibre products, bagasse and pine needles have been reported to contribute to more severe caking than pine shavings (Grimes et al., 2002; Tasistro et al., 2007). Cake can be broken up by bird scratching (Grimes et al., 2002) or by mechanical turning/cultivating with machinery. Sistani et al. (2003) reported that at the end of a 49 day grow-out period 43% of the mass of floor material was cake with the remaining 57% being friable litter.

Presence of cake has been found to coincide with reduced gas emission rates compared to friable litter and it has been hypothesised that this is related to the formation, thickening and compaction of cake due to bird excretion and traffic (Lin et al., 2012; Miles et al., 2008; Miles et al., 2011a; Tasistro et al., 2007). It has also been shown that gas emission rates and litter properties vary spatially across the floor of a meat chicken shed (Miles et al., 2008; Miles et al., 2011a).

Cake has been described as having high moisture content (relative to the friable litter around it). Sistani et al. (2003) reported cake with moisture content 44.0–47.7% compared to 25.6–29.7% for litter. Miles et al. (2008; 2011a) reported cake with moisture content 55–60%, which was influenced by location, with cake that formed between feeder/watering lines having lower moisture content than surrounding litter while cake that formed near the exhaust fans had higher moisture content than the surrounding litter. Some of the inconsistency regarding reported cake/litter moisture content is possibly due to the cake formation processes and yet these have not been explained in detail in the literature. The litter formation/development process will likely also affect odour and gas formation and emission and is therefore pertinent to this investigation.

Miles et al. (2008) reported that cake formation is currently unavoidable in meat chicken sheds and is typically managed or removed between grow-outs by processes known as de-caking, tilling or conditioning (Miles et al., 2008; Sistani et al., 2003). Decaking removes the cake from the shed and leaves the friable litter for the following

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flock whereas tilling and conditioning mechanically chop and incorporate the cake into the friable litter. These processes aerate the litter, releasing trapped gases and moisture (Miles et al., 2011a; Topper et al., 2008). It is suggested, however, that cake is likely to reform following mechanical treatment if the litter moisture content is still high enough because the litter will not be friable.

# 2.3.1.4 Reused litter

*'Reused litter'* is litter that is used for multiple grow-our periods. In some growing areas litter may be re-used multiple times, for example 8–10 flocks (Sistani et al., 2003). Litter re-use is so common in some countries (i.e. United States of America) that reference to litter in published literature commonly refers to re-used litter that has been used for multiple grow-out periods (even though it is not clearly distinguished). This needs to be recognised because differences in the properties between re-used litter and litter that commenced as bedding material may affect odour emissions (Dunlop et al., 2010; Wathes et al., 1997), especially during the first weeks of a grow-out period (Brewer and Costello, 1999).

### 2.3.2 Formation processes for friable litter and cake

# 2.3.2.1 Effects of cohesion

Water affects cohesiveness (the attractive forces between particles) and consequently compaction and flowability in granular materials such as litter. Water both lubricates and provides cohesion between soil particles (Burger et al., 1985) and assists with agglomeration in food ingredients (Roudaut, 2007). Compaction will be enhanced or inhibited at particular moisture contents and high moisture contents will allow deformation to occur with less resistance (Burger et al., 1985). Agnew and Leonard (2003) reported that moisture content affects porosity and thermal conductivity and aids compaction/compression in composts. The effect of water on cohesion and compaction can also be applied to litter.

Bernhart and Fasina (2009) measured the cohesiveness and compaction of litter for moisture contents ranging from 10.3% to 30.9%. They observed that drier litter (10.3% moisture content) was less compressible and had higher flowability (as a result of requiring lower ultimate yield stress to shear litter samples) compared to wetter litter (30.9% moisture content). They described litter with 10.3% moisture content as 'easy-flowing' whereas litter with 30.9% moisture content was described as 'non-flowing'. In another application involving litter, Way et al. (2013) found that litter based on wood shavings flowed well when moisture content was less than 35% but adhered and

clogged parts in an implement when moisture content was greater. It is suggested that the increased compressibility and cohesiveness along with decreased flowability that occur with increasing moisture content contribute to cake formation.

The moisture content of litter at the time of compaction also influences the amount of energy required to break up a piece of compacted litter once it has dried. Bernhart et al. (2010) reported that the force required to break compacted samples of litter increased substantially when the moisture content was higher at the time of compaction. They concluded that moisture acted as a natural binder during the agglomeration process because the coating of moisture on particle surfaces improved cohesion between the particles. This suggests that the difficulty in breaking up the cake by the birds (Grimes et al., 2002) is related to the strong adhesion between particles described by Bernhart et al. (2010) that forms when litter/cake is compressed while wet.

# 2.3.2.2 Formation of friable litter

Poultry excreta is a mixture of faeces and urine (Collett, 2012) and has a moisture content ranging from 55% (Miles et al., 2011b; Stephens and Hampson, 2002) to 83% (van der Hoeven-Hangoor et al., 2014) (for birds that were free from illness or disease). Excreta is deposited on the surface of the litter but what happens to it from that point depends on the litter properties, especially moisture content.

Excreta will be worked into the litter and dispersed by bird activity and scratching if the litter is near the 'optimal' moisture content of 25% (Collett, 2012), is friable and the surface of the bedding material is not matted or compacted. When this occurs, the average moisture content of the combined excreta/litter mixture will be less than that of the fresh excreta and the litter will develop a texture that might be described as a moist crumble. The final moisture content will be proportional to the volumes of excreta and bedding that are combined. The litter will likely remain friable and uncompacted because the birds can readily scratch and dig in the litter (because of litter flowability and lower ultimate yield stress required to shear litter particles (Bernhart and Fasina, 2009)). This aids the drying process by maintaining porosity and exchanging litter particles at the litter surface where they are most effectively dried by shed ventilation.

### 2.3.2.3 Formation of caked litter

Litter may have insufficient capacity to absorb the moisture being applied and the birds may not be able to mix the excreta into the litter if:

- the rate of excretion increases (e.g. due to disease or localised high stocking density);
- the litter is moist (e.g. greater than 35-45% moisture content); or
- the litter/bedding material has a matted or compacted surface.

When this occurs, the surface of the litter may 'slick' over (Miles et al., 2008) and cake will begin forming on the litter surface. While friable litter remains uncompacted and dries readily, cake has low porosity (Lin et al., 2012; Miles et al., 2008) and dries slowly (slow drying of cake was inferred by Topper et al. (2008) who reported that cake is removed in the inter-batch period to allow litter to dry).

Reduced friability associated with wet litter (Bernhart and Fasina, 2009; Lister, 2009) reduces the ability of the birds to incorporate fresh excreta into the litter resulting in the formation of an excreta layer on the litter surface. Cake then becomes a physical barrier that prevents fresh excreta being incorporated into friable litter by bird activity and consequently the thickness of cake increases. If the rate of excretion exceeds the rate at which the ventilation system can remove the moisture then the cake will grow thicker and remain wet. On the other hand, if the rate of excretion is less than the evaporation rate due to ventilation, the surface of the cake will dry and eventually the moisture in the wet cake will evaporate from the surface and the entire layer of cake will slowly dry. With wet cake being greater than 55–60% water by mass (Miles et al., 2011a) a substantial volume of the cake is water and therefore drying the cake will reduce cake thickness and overall litter volume.

Another important consideration in litter/cake formation is in-shed ventilation. Average litter moisture conditions are similar, in general, from day to day (Dunlop et al., 2010; Miles et al., 2008; Miles et al., 2011a), which suggests that 24 hour average evaporation rates generally match the amount of water deposited on the litter in the same period. However, ventilation rates fluctuate diurnally in meat chicken sheds to match cooling requirements and ambient conditions. Ventilation rates have been observed to fluctuate from 20 m<sup>3</sup>/s at night to 80 m<sup>3</sup>/s during a single day (Dunlop et al., 2010; Sohn et al., 2010). In this review it will be assumed that meat chickens do not have a preferred time of day for excretion (no information was found in the literature on this subject). Consequently, litter moisture content is likely to increase at night due to higher relative humidity and lower ventilation rates (low potential for evaporation) and decrease during the day due to lower relative humidity and higher ventilation rates (high potential for evaporation). Because excreta are applied at the surface of the litter, any deficit in evaporation will result in the surface moisture content increasing and a

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wetting front will move in a downward direction through the litter profile. This will likely contribute to an increased tendency for cake to form at night. Scheduling the timing for measurement of litter properties and gas emission rates during experimental studies is therefore critical, even within the course of a day, due to anticipated diurnal fluctuations in litter conditions (Powers et al., 2005).

It is evident that existing litter conditions, bedding material properties, excretion rates, bird activity and ventilation all contribute to litter conditions and cake formation. Miles et al. (2008) stated that formation of cake in meat chicken sheds is 'unavoidable'. Additionally, it must be recognised that the majority of water and excreta addition and evaporation occur at the litter surface and therefore it is likely that there will be differences in conditions at the surface of the litter compared to the rest of the litter profile.

# 2.3.3 Variability in the properties of litter

Litter environments in meat chicken sheds are rarely at equilibrium and this creates many challenges for managing litter conditions and measuring, understanding or mitigating the formation and emission of odours from the litter. Litter properties change diurnally, temporally and spatially during each grow-out period and are affected by manure accumulation; moisture addition (bird excretion, condensation and leaking drinkers); moisture loss due to ventilation; and bird activity (scratching, sitting, mixing and preferential use of some parts of the shed).

Physical and chemical properties of litter that are typically measured during in-shed investigations include temperature, moisture content, pH, nitrogen (N) and carbon (C) content. These have been found to change during the grow-out period (Dunlop et al., 2010; Miles et al., 2006; Tasistro et al., 2007). Koerkamp and Groenestein (2008) reported that the history of litter conditions during the growing cycle—including the litter structure (friability), presence of cake and stratification of the litter—had such a strong influence on the emission of ammonia that the most important parameters controlling ammonia emissions (pH, moisture, temperature and ammonia concentration) were not able to be related to the emission rates. Historical records of litter conditions are seldom reported in research papers.

Miles et al. (2008) stated that a lack of homogeneity in litter conditions creates difficulties in accurately estimating gas volatilisation from the litter surface. Spatial nonhomogeneity of litter conditions, in particular, has been reported to significantly affect gaseous emissions in different locations across the floor in a meat chicken shed (Brewer and Costello, 1999; Miles et al., 2008; Miles et al., 2011a). Miles et al. (2011a) concluded that the "highly variable spatial distribution of most parameters cannot be adequately characterised by average values".

The formation of a 'crust' or 'cake' also needs to be considered because it results in a duplex structure in the litter with friable litter and caked layers having substantially different physical and chemical properties that can affect odorant formation and emission (Miles et al., 2011a). Consequently, there will be changes through the depth profiles in addition to the diurnal, temporal and spatial changes previously mentioned.

### 2.3.4 Water activity in litter

Water activity (A<sub>w</sub>) is a thermodynamic property relating to the relative freedom or availability of water in a sample and its tendency to escape. It is considered to be a better measure of water in litter than moisture content since it is more closely related to microbial, chemical and physical properties of litter (van der Hoeven-Hangoor et al., 2014) and has been associated with changes in colour, aroma and texture in other materials (Chirife and Fontana Jr., 2007). A<sub>w</sub> can be directly related to the mixing of fresh excreta with bedding/litter, litter cohesion, cake formation, and relationships between in-shed relative humidity and litter properties (Bernhart and Fasina, 2009; van der Hoeven-Hangoor et al., 2014).

Reid (2007) defined  $A_w$  as "the ratio of [the fugacity of water] in a system, and the fugacity of pure liquid water at the same temperature" and can be approximated by the equilibrium or steady state relative humidity of a substance (Carr et al., 1994; Reid, 2007). Fugacity is a measure of the escaping tendency of a substance (Reid, 2007).

A<sub>w</sub> is approximated by the steady state or equilibrium relative humidity (ERH, expressed as a %) of a substance (Carr et al., 1995; Reid, 2007). In fact the two terms, A<sub>w</sub> and ERH, are interchangeable (A<sub>w</sub> = ERH / 100). A<sub>w</sub> is temperature dependent and generally increases with temperature when moisture content is constant, although the relationship can reverse at high A<sub>w</sub> (Labuza and Altunakar, 2007a). A<sub>w</sub> is measured by placing a sample in a sealed chamber (that is preferably temperature controlled), allowing conditions to equilibrate and then measuring the relative humidity (ERH) of the chamber headspace.

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Relationships between A<sub>w</sub> of litter moisture content have has previously been reported in relation to effects on microbial activity as well as structural and handling properties (Bernhart and Fasina, 2009; Carr et al., 1994; Carr et al., 1995; Chinivasagam et al., 2012; Eriksson De Rezende et al., 2001; Hayes et al., 2000; Macklin et al., 2006; Opara et al., 1992). Additionally, van der Hoeven-Hangoor et al. (2014) measured A<sub>w</sub> in excreta and litter as a response to different diet formulations. More recently, Dunlop et al. (2016b) showed that the relationship between water activity and litter moisture content changed during a grow-out, with fresh bedding having the highest water activity. This has implications for managing litter moisture and surface conditions at different stages of a grow-out, and for re-using litter for multiple grow-outs.

Bernhart and Fasina (2009) reported that litter  $A_w$  increased non-linearly from 0.25 to 0.90 as moisture content increased from 10 to 31%. Data collected by Carr et al. (1995) and van der Hoeven-Hangoor et al. (2014) showed that  $A_w$  increased to 0.98–0.99 when litter moisture content reached 38–55%. By comparison, fresh excreta had high moisture content (up to 83%) with correspondingly high  $A_w$  0.96–0.99 (van der Hoeven-Hangoor et al., 2014).

Labuza and Altunakar (2007b) explained that different materials can have the same A<sub>w</sub> but have different moisture content. Potential effects of using different bedding materials or additives to reduce A<sub>w</sub> in litter have not been explored in the literature. Dunlop et al. (2016); however, recently showed that bedding materials tended to have relatively high A<sub>w</sub> that decreased during the grow-out with the addition of excreta and breakdown of the organic materials.

Additional research is required to explain litter properties, drying and cake formation in terms of water activity and how these relate to odour emissions.

### 2.3.4.1 Relating water movement to water activity

Theoretically, the two main factors controlling moisture transfer between porous materials (i.e. excreta and litter) are A<sub>w</sub> and resistance to diffusion (Labuza and Altunakar, 2007b). Resistance to diffusion increases when there is low porosity or the path that the water vapour needs to travel is long or tortuous (Schwarzenbach et al., 2003). (Section 2.5.4.3 provides further discussion about tortuosity and molecular diffusion.) Water molecules move from a material with higher A<sub>w</sub> to a material with lower A<sub>w</sub> (Figure 17) until the A<sub>w</sub> of the two materials are equal, at which point the system is in thermodynamic equilibrium (Labuza and Altunakar, 2007b). Additionally if

the materials are in a sealed, isothermal chamber, the relative humidity in the chamber will equalise with the  $A_w$  (e.g. if  $A_w = 0.75$ , relative humidity is 75%) and no more water will transfer from the air to the materials or vice-versa.

The relationship between A<sub>w</sub> and steady state relative humidity has important implications for the management of litter moisture content and the in-shed environment. If in-shed relative humidity is higher than the litter A<sub>w</sub>, water will migrate from the air into the surface of the litter. Condensation will also occur if the litter surface is below the dewpoint temperature (Tucker and Walker, 1992). Conversely, water will diffuse through the litter and into the air (raising in-shed relative humidity) if litter A<sub>w</sub> exceeds the in-shed relative humidity. External temperature and humidity, shed ventilation rate and shed heating (including heat released from the birds), will each contribute to inshed relative humidity, litter A<sub>w</sub> and litter moisture content. The effect of increasing air velocity in the poultry shed is likely to reduce water absorption into the litter surface, resulting in lower litter moisture content for a given relative humidity condition (Foong et al., 2009).



Figure 17. Movement of water through the litter and into the ventilation air (Dunlop, 2016)

Fresh excreta has high  $A_w$  of 0.96–0.99 (van der Hoeven-Hangoor et al., 2014). Comparatively, dry litter has lower  $A_w$  ( $A_w$  was 0.25–0.90 when moisture content was 10.3%–30.9% (Bernhart and Fasina, 2009)). When the two come into contact, moisture from the fresh excreta will migrate to the litter and the resulting  $A_w$  of the mixture will be less than the initial  $A_w$  of the fresh excreta but higher than the initial  $A_w$  of the litter. But if litter is wet, the  $A_w$  will be higher and possibly match that of fresh excreta. This will result in little exchange of moisture between the excreta and litter, because they will be at or near thermodynamic equilibrium, and consequently the fresh excreta and litter will remain wet. Relative humidity of the in-shed air also needs to be considered. Water exchange between the litter and in-shed air will occur until the A<sub>w</sub> of the litter matches the relative humidity of the air (assuming isothermal conditions) (Labuza and Altunakar, 2007b). Consequently, if the relative humidity of the air at the litter surface is less than the A<sub>w</sub> of the litter (or fresh excreta) the moisture will diffuse from the litter into the air. If the situation is reversed, moisture will migrate from the air into the litter until thermodynamic equilibrium is reached. When high in-shed relative humidity results in water migrating into the surface of the litter (which may also occur when water vapour condenses on cool litter), the increased A<sub>w</sub> at the surface of the litter increases cohesion between the litter particles resulting in a higher tendency for cake formation.

#### 2.3.4.2 Relating water activity to friability and caking

'Stickiness' and 'caking' of granular or powdery materials has previously been related to A<sub>w</sub> (Roudaut, 2007), especially for materials with high levels of sugars, minerals or proteins (excreta is approximately 20% crude protein (van der Hoeven-Hangoor et al., 2014)). Roudaut (2007) described the process in which increasing A<sub>w</sub> (as a result of increasing moisture content) causes the surfaces of particles to plasticise and this contributes to inter-particle bridging, cohesion and eventual formation of a solid mass with low porosity. Roudaut (2007) explained that there is a '*critical hydration level*' at which caking will commence and suggested that one strategy to prevent caking is through competition for water (i.e. mixing material with low A<sub>w</sub> with materials with high A<sub>w</sub> to force water to migrate from the material with high A<sub>w</sub>).

Bernhart and Fasina (2009) related the cohesiveness and flowability of poultry litter to moisture content and A<sub>w</sub>. They showed that the cohesive strength of litter rapidly increased (the observed change in cohesive strength also depended on the consolidation pressure applied to the litter), and the litter changed from 'free-flowing' to 'cohesive' when the moisture content increased from 18.0% to 22.1% (~0.75 to ~0.85 A<sub>w</sub>, respectively). Based on the theory of Roudaut (2007) and observed properties of poultry litter by Bernhart and Fasina (2009) (and taking into consideration that our values of A<sub>w</sub> were approximately 0.05 greater than theirs), poultry litter reaches the *critical hydration level* between 0.75–0.90 A<sub>w</sub>. Based on our data, this corresponds with moisture content ranging from 12–24% depending on the day during the grow-out. It is therefore likely to be beneficial to keep the A<sub>w</sub> of litter below the *critical hydration level* so the litter remains friable, enabling excreta to be worked into the litter to maximise the rate of moisture transfer away from the excreta.

### 2.3.4.3 Relating water activity to microbial activity

A<sub>w</sub> has previously been related to microbial activity in meat chicken litter by Carr et al. (1994), Carr et al. (1995), Eriksson De Rezende et al. (2001), Hayes et al. (2000), Himathongkham et al. (1999), Macklin et al. (2006) and Opara et al. (1992). The growth of bacteria and fungi can be controlled by keeping the litter A<sub>w</sub> below the minimum limit for microbial growth (Figure 18), nominally: 0.86–0.90 for *Staphylococcus* spp., 0.92–0.95 for *Salmonella* spp., 0.95 for *Escherichia coli*, 0.9–0.97 for *Clostridium* spp., 0.98 for *Campylobacter* spp. and 0.75–0.85 for *Aspergillus* spp. (Fontana, 2007; Taoukis and Richardson, 2007). These growth limiting A<sub>w</sub> values depend on other factors including acidity, temperature, oxygen, nutrient availability and presence of inhibitors (Tapia et al., 2007). All microbial proliferation ceases when A<sub>w</sub> is below 0.61 (Tapia et al., 2007).

Carr et al. (1994) reported that new bedding material (sawdust) had higher A<sub>w</sub> than litter and this was associated with the presence of *Salmonella*. Similarly, Chinivasagam et al. (2012) reported that litter being used for a first grow-out (when fresh bedding was used at the start) had higher A<sub>w</sub> and *Salmonella* levels than litter that had already been used in a previous grow-out (re-used litter). In addition to restricting the growth of microbiota, maintaining low A<sub>w</sub> in poultry litter should, in general, reduce bacterial odour production (Macklin et al., 2006).





Fresh excreta contain a diverse microbial community from the gastrointestinal tract of the birds (Lu et al., 2003a; Singh et al., 2014) and reducing A<sub>w</sub> of excreta may have a positive effect on reducing microbial growth within the litter. It has previously been recommended that the A<sub>w</sub> of poultry litter should be kept below 0.84–0.91 (20–35% moisture content) to restrict the growth of *Salmonella* and other microbiota created a more hygienic environment for poultry production (Carr et al., 1995; Chinivasagam et al., 2012; Eriksson De Rezende et al., 2001; Hayes et al., 2000; Payne et al., 2007).

# 2.4 'Wet litter'

This section discusses the factors that contribute to 'wet litter' in chicken-meat production to improve understanding of how wet litter may contribute to environmental or amenity problems relating to odour or other gaseous emissions. The causative factors are multidimensional including housing, micro- and macro-environmental factors, disease, health and nutrition. The contribution of disease, health and nutrition to wet litter have previously been reviewed by Collett (2012) and Dunlop et al. (2016c). This section will focus on how the environment, shed management, ventilation and litter properties contribute to the occurrence of wet litter.

There is no universally accepted definition for 'wet litter'. One precise definition is that once litter moisture content exceeds 25%, its cushioning, insulating and water holding capacity is compromised (Collett, 2012). Or, additionally, Collett (2007) stated that wet litter results when rates of water addition (excreta, spillage) exceed the rates of removal (evaporation). A European Directive requires that "all chickens shall have permanent access to litter which is dry and friable on the surface" (Lister, 2009). In Australia, the RSPCA has issued requirements in respect of acceptable litter quality (RSPCA, 2013).

Dann (1923) expressed the opinion that "wet litter in the poultry house is a rather troublesome problem to most poultrymen". Wet litter was deemed to be "a favourable medium for the development of colds, catarrh, roup, and like maladies". The author listed six causes of wet litter, all of which were directly related to providing birds with "good housing"; hence the focus of housing and ventilation management in this study.

The occurrence of 'wet litter' in meat chicken sheds is associated with concerns regarding animal welfare, flock health, food safety, environmental impacts and reductions in production efficiency (Table 1).

Animal welfare:	
Increased contact or footpad dermatitis	Bilgili et al. (2009); de Jong et al. (2014); Mayne et al. (2007)
Bird health and comfort:	
increased ammonia concentrations in the grower sheds	Elliott and Collins (1982); Liu et al. (2007); Miles et al. (2011b); Weaver and Meijerhof (1991)
dysbacteriosis	Collett (2012); Hermans et al. (2006)
reduced thermal insulation	Agnew and Leonard (2003)
Litter properties	
reduced friability and more compaction	Agnew and Leonard (2003); Bernhart and Fasina (2009); Tucker and Walker (1992)
Food safety:	Eriksson De Rezende et al. (2001)
Environmental impacts:	Al Homidan et al. (2003); Clarkson and
Increased odour	Misselbrook (1991); Murphy et al. (2014); Wadud et al. (2012)
Litter microbiology:	
Accelerated microbiological growth (increased health risks, food safety risks and odour)	Agnew and Leonard (2003); Wadud et al. (2012)

#### Table 1. Challenges and problems associated with wet litter

The term 'wet litter' is not the only term used in the literature, it has also been described as 'litter deterioration' (Bruce et al., 1990), 'poor litter' (McIlroy et al., 1987), or is inferred during specific discussions implicating wet litter as a key cause of specific conditions including contact dermatitis (de Jong et al., 2014; Shepherd and Fairchild, 2010).

Wet litter is prone to the formation of manure 'cake' (or 'cap' or 'crust') that forms on the surface of the litter and sustains a wet surface. Cake is therefore a consequence of wet litter but also sustains surface conditions that increase the risk of the above issues associated with wet litter. 'Wet litter' and 'caked litter' may be considered by some to be separate, but the consequences of both conditions are likely to be similar and interrelated.

Mitigating wet litter requires thorough understanding of the multidimensional causal factors. This requires a multi-disciplinary approach to understand how the following contribute to wet litter:

- the hydrology in the meat chicken shed micro-environment;
- the biological response of the chickens to nutrition and the production environment; and
- the contributions of:
  - o illness
  - o production equipment
  - o housing design
  - shed/ventilation management
  - o the intensiveness of chicken meat production.

#### 2.4.1 Environmental and housing factors

Key environmental and management factors that contribute to wet litter are multidimensional (Lister, 2009; Tucker and Walker, 1992; van der Hoeven-Hangoor et al., 2013a; 2013b; 2013c; 2014) and have been reasonably well documented in the literature. Table 2 is a summary of research into the various factors that contribute to wet litter. It is unlikely that one dominant cause exists given the numerous interrelated contributing factors.

It is suggested that the contribution of the many factors listed in Table 2 is subject to their management. For example, litter type or quantity and wet or moist bedding material may contribute to wet litter if not appropriately managed but may not contribute to wet litter if they are appropriately managed. Additionally, it may be possible to compensate for a deficiency in one of the factors with additional management or investment in others. As an example, poor litter water holding capacity may be compensated by adding more litter or by increasing ventilation or heating. Increasing ventilation, or its effectiveness, reduces in-shed humidity and increases evaporation of excess water that has accumulated from excretion, condensation or direct application (e.g. drinking system or shed leaks). Also, it may be possible to prevent wet litter with changes to on-farm management or equipment maintenance, for example maintaining drinker lines or managing water pressure. Therefore the knowledge, skills and attitudes of farm staff as well as on-farm procedures and maintenance programs contribute to wet litter but are seldom the subject of formal research or investigation. Overall, identifying the exact cause(s) of wet litter is extremely challenging.

Key contributing factors	References
Rising damp through floor, leaking walls/roof	Dann (1923); Tucker and Walker (1992)
Drinker spillage (normal)	Bilgili et al. (1999)
Drinker spillage (leaks) mismanagement, pressure, height, design	Bilgili et al. (1999); Dann (1923); Shepherd and Fairchild (2010); Tucker and Walker (1992)
Normal excretion, varying throughout a grow-out period	Collett (2012); Dann (1923); McIlroy et al. (1987); Tucker and Walker (1992); van der Hoeven-Hangoor et al. (2013a); Weaver and Meijerhof (1991)
Stocking density	McIlroy et al. (1987); Meluzzi et al. (2008); Shepherd and Fairchild (2010); Tucker and Walker (1992)
Increased water excretion Nutrition imbalance or ingredients, disease e.g. dysbacteriosis, increased water consumption, water quality; feed supply interruption, gut microbiota	Bruce et al. (1990); Collett (2012); Dann (1923); Eichner et al. (2007); Francesch and Brufau (2004); Guardia et al. (2011); LaVorgna et al. (2014); McIlroy et al. (1987); Shepherd and Fairchild (2010); Tucker and Walker (1992); van der Hoeven-Hangoor et al. (2013a)
Increased in-shed relative humidity Exhaled moisture, wet litter, high ambient humidity, poor in-shed temperature control	Bruce et al. (1990); Dann (1923); Hermans et al. (2006); McIlroy et al. (1987); Payne (1967); Shepherd and Fairchild (2010); Tucker and Walker (1992); Wang et al. (1998); Weaver and Meijerhof (1991)
Season	Bruce et al. (1990); Hermans et al. (2006); McIlroy et al. (1987); Wang et al. (1998)
Condensation on walls, ceilings and in- shed equipment	Dann (1923); Hermans et al. (2006)
Lighting equipment or program	Meluzzi et al. (2008)
Insufficient shed ventilation/air exchange	Dann (1923); Hermans et al. (2006); Tucker and Walker (1992); Weaver and Meijerhof (1991)
Farm biosecurity and cleaning practices	Hermans et al. (2006)
Litter/bedding material type	Andrews and McPherson (1963); Bilgili et al. (2009); Bruce et al. (1990); Davis et al. (2010); Meluzzi et al. (2008); Shepherd and Fairchild (2010); Tucker and Walker (1992)
Insufficient litter depth	Meluzzi et al. (2008); Shepherd and Fairchild (2010); Tucker and Walker (1992)
Excess litter depth	Dann (1923); Ekstrand et al. (1997)
Cool/warm litter and cool/warm in-shed air	Dann (1923); Tucker and Walker (1992)
Litter moisture content / water holding capacity	Andrews and McPherson (1963); Bilgili et al. (2009); Shepherd and Fairchild (2010)

#### Table 2. Key contributing factors and causes of wet litter and cake

The volume of water added to litter, evaporated from litter and able to be stored in litter can each contribute to the occurrence of wet litter. A large quantity of water is added to the litter by excretion and normal drinking spillage due to the high water intake and commercial stocking densities of modern meat chickens. Dunlop et al. (2015) estimated that the amount of water added to litter could be as much as 3.2 L/m<sup>2</sup> per day, with a cumulative total of over 100 L/m<sup>2</sup> during a 56 day grow-out. Collett (2012) estimated that a flock of 20,000 birds can excrete up to 2500 L of water per day onto the litter. On its own, this normal quantity of water excretion tends to be manageable with modern farming practices including shed design and ventilation management; however, avoiding wet litter may not be possible if additional water is added to the litter due to ill-health, imbalanced diet, use of certain feed ingredients or if evaporation is reduced by extended periods of high humidity.

#### 2.4.2 Contribution of litter material properties to wet litter

Essential properties for all bedding materials to avoid wet litter problems include having good water holding capacity and reasonable drying rates (Grimes et al., 2002; Tucker and Walker, 1992). Litter friability, susceptibility to cake formation and water activity are also important properties (Garces et al., 2013) as these contribute to the undesirable side-effects associated with wet litter.

The properties of bedding materials and their suitability in meat chicken sheds have previously been assessed (Andrews and McPherson, 1963; Bilgili et al., 1999; Davis et al., 2010; Garces et al., 2013; Grimes et al., 2002; Meluzzi et al., 2008; Miles et al., 2011b; Reed and McCartney, 1970). The range of parameters investigated varied but included maximum moisture content, water holding capacity, drying rate, compressibility, bulk density, particle size distribution, thermal conductivity, equilibrium moisture content (water activity), friability and caking. It should be noted that testing of these litter properties is often not undertaken according to a reference standard, and irrespective of methods used, the results from laboratory testing may not be representative of conditions that form within the production setting of a meat chicken shed. Bedding materials used included various pine and other wood products (shavings, sawdust bark, bark and chips, stump chips, pine needles, chopped pine needles), rice hulls, peanut hulls, ground corn cobs, sand, straw (wheat, barley, grasses), sugarcane (tops and bagasse), shredded newspaper and clay. Pine shavings were usually found to be the most suitable bedding material due to high absorbency, reasonable drying time and high friability. Other materials ranked in different orders depending on the priority given to different properties measured.

Some bedding materials have properties that require specific management to reduce the risk of wet litter and other problems. For example, sand may require more preheating prior to the placement of chicks at the start of the grow-out period to provide the correct temperature and to reduce moisture condensation issues, whereas straw products need to be cut shorter than 2.5 cm to avoid matting of the surface, which can increase cake formation (Grimes et al., 2002). It is suggested that these examples reinforce the concept that materials are not necessarily suitable or unsuitable for litter, but some may require specific management or treatments.

Moisture content is one property that is commonly measured with litter and bedding materials but care is required when moisture content is used to compare the water holding capacity of different bedding and litter materials. This is because moisture content (mass of water divided by mass of moist litter, expressed as a percentage, %), is calculated on a mass basis when litter in meat chicken sheds is purchased. distributed across the shed floor, and disposed on a volumetric basis. Differences in the bulk density of the dry material (mass of dry material divided by the volume) may vary. Data collected by Reed and McCartney (1970) can be used to illustrate this issue. Pine sawdust and peanut hulls both had a moisture content at saturation of 67% but had dry bulk densities 211 kg/m<sup>3</sup> and 96 kg/m<sup>3</sup> respectively. While the moisture content was the same, the water holding capacity per square metre of litter on the floor (assuming a 5 cm depth) can be calculated to be 21.4 L/m<sup>2</sup> for pine sawdust and 9.7 L/m<sup>2</sup> for peanut hulls. For comparison, pine shavings at saturation point were found to have a moisture content of 63%, dry bulk density of 98 kg/m<sup>3</sup> and water holding capacity of 8 L/m<sup>2</sup>. The calculation is further exaggerated with dense bedding materials such as sand, which have a dry bulk density of 1500 kg/m<sup>3</sup> (Miles et al., 2011b). Despite sand having apparently low moisture content at saturation of 12% (Miles et al., 2011b)., the actual water holding capacity for litter depth of 5 cm is 9.8 L/m<sup>2</sup>, which exceeds that of pine shavings and is approximately equal to peanut hulls.

Friability is another important litter property because it influences the way that the birds interact with the litter (Lister, 2009) and affects litter drying rate (Collett, 2012; Miles et al., 2011a). Lister (2009) related friability to the ability to reduce a substance into smaller pieces. Therefore, friable litter is not caked or sticky and should fall apart. Friable litter can be 'worked' by the birds as they scratch, dig and forage (Lister, 2009). This maintains aerobic conditions and accelerates moisture loss (Lister, 2009). As an alternative to friability, Bernhart and Fasina (2009) used the term 'flowability' to

describe the cohesion between litter particles (i.e. the force between particles causing them to stick together). It is suggested that flowability and friability should be considered similar with respect to the way that individual litter particles hold together and the external forces required to overcome inter-particle bonds. Bernhart and Fasina (2009) concluded that litter moisture content was directly related to the force required to overcome cohesion between particles, with that greater force required to separate particles as litter became wetter. They also reported that litter flowability reduced as moisture content increased and described litter with a moisture content of 10% as freeflowing, 18% as easy flowing and 22–31% as cohesive. An explanation for the relationship between moisture content and particle cohesion was provided by Roudaut (2007) related the 'stickiness' and 'caking' of granular or powdery materials to water activity by explained that increasing water activity (as a result of increasing moisture content) causes the surfaces of particles to plasticise and this contributes to interparticle bridging, cohesion and the eventual formation of a solid mass with low porosity. Roudaut (2007) further explained that there is a 'critical hydration level' at which caking of granular materials will commence.

#### 2.4.3 Contribution of water activity to wet litter

A<sub>w</sub> directly contributes to the negative effects of wet litter because is enables the growth of pathogenic organisms (bacteria, fungi, mould), increases the bird's contact with available/free water in the litter and is responsible for changing the properties of the litter, especially friability, compaction and formation of cake. The latter contribute to slow-drying of the litter surface and resulting slippery, disease sustaining surface as described by Miles et al. (2011a).

#### 2.4.4 Housing and ventilation

Design and management of shed and ventilation system are all-important for litter conditions because they control in-shed temperature, humidity and airflow. Controlled laboratory studies have shown that exposure to in-shed relative humidity of 75% was sufficient to cause wet litter (Weaver and Meijerhof, 1991). Similarly, Payne (1967) found that 72% relative humidity resulted in litter surface caking. Payne (1967) further explained that in-shed relative humidity was able to be controlled by regulating in-shed temperature and ventilation rate using adequate shed insulation and a thermostatically controlled ventilation system. Control of in-shed relative humidity reduces water absorption by the litter and also reduces drips from water that condenses on in-shed surfaces (Hermans et al., 2006; Payne, 1967).

To determine the prevalence of wet litter and identify the predisposing risk factors, Hermans et al. (2006) surveyed meat chicken farms in the UK. Numerous interrelated variables that contributed to wet litter were identified. The only variable associated with the design of meat chicken sheds that contributed to wet litter was side ventilation (where air is drawn into the shed on one side and extracted from the opposite side). Hermans et al. (2006) also reported that inadequate ventilation can lead to high relative humidity in the shed and to poor patterns of air movement such that low incoming airspeed will fall to the ground and create condensation. Conversely, Payne (1967) suggested that too much air flow was not appropriate either because it caused birds to crowd together. What is required is to provide uniform airflow throughout the shed to achieve uniform temperature (Hermans et al., 2006; Payne, 1967) and presumably have uniform litter drying. It is therefore suggested that it is not only the amount of ventilation that is important but the effectiveness of the ventilation system in bringing in air, conditioning it to increase its moisture holding capacity and then getting that air to the litter so it can dry evenly.

With so many housing and ventilation factors that can affect litter moisture (Figure 19), and considering that sheds on different farms are likely to be different, meaningful and specific solutions to wet litter have not been published. Collett (2012) suggested that shed design and ventilation should improve to keep pace with genetics and nutrition that have substantially increased water excretion by birds over recent years.



Figure 19. Graphical summary of factors influencing and affected by wet litter

#### 2.5 Odorant emissions from porous poultry litter

#### 2.5.1 Introduction

Emission of odour from litter in meat chicken sheds (broiler houses) can lead to odour nuisance within the surrounding community and potentially result in complaints (Carey, 2004; Guo et al., 2003; Hayes et al., 2014; Radon et al., 2004). Odour is a normal part of meat chicken production due to anaerobic and aerobic microbial activity in the litter and also due to its release from the animals (Pillai et al., 2012a). Litter is considered to be the primary source of odour from meat chicken sheds because the majority of odorous compounds are released during the decomposition of organic matter (Hobbs et al., 2004; Mackie et al., 1998). Odour from meat chicken sheds is a complex mixture of odorous compounds typically composed of volatile organic compounds (VOCs, including reduced sulfur compounds) and non-VOCs (e.g. ammonia, hydrogen sulfide) (Cai et al., 2007).

Conditions within the litter influence the formation and emission of odorants resulting in changes to the concentration and character of the odour exhausted from meat chicken sheds (Spoelstra, 1980; Wadud et al., 2012). It is suggested that it may be possible to reduce the odour nuisance potential of meat chicken farms by altering this odour mixture in a way that makes the odour less detectable or offensive to the neighbouring community.

Scientific studies and reviews have focussed on general topics about odour from agricultural, industrial and municipal sources (Table 3). This literature provides an understanding of the complexities of odour and odour impacts, but the current specific need is to identify literature that relates to quantifying the properties of meat chicken litter and how these properties influence odour emissions (Dunlop et al., 2016a).

### Table 3.Selected studies on odour from agricultural, municipal and environmental<br/>sources (Dunlop et al., 2016a)

Odour research topics	References
Odour metrics (concentration, intensity, hedonic tone, character)	Fournel et al. (2012); Lebrero et al. (2011); Nimmermark (2011)
Odour measurement (olfactometry)	Hamon et al. (2012); Jacobson et al. (2008); Lebrero et al. (2011); van Harreveld et al. (1999)
Instrumental odorant measurement such as gas chromatography-mass- spectrometry/olfactometry (GC-MS/O), selected ion flow tube-mass spectrometry (SIFT-MS) or proton transfer reaction-mass spectrometry (PTR-MS)	Cai et al. (2006); Hamon et al. (2012); Hansen et al. (2012); Heynderickx et al. (2013); Lebrero et al. (2011); Muñoz et al. (2010); Ni et al. (2012); van Huffel et al. (2012); Zhang et al. (2010b)
Odour sampling methodologies (e.g flux chamber versus wind tunnel methods for area sources, and sample storage prior to analysis)	Bockreis and Steinberg (2005); (2012); Capelli et al. (2013a); Capelli et al. (2013b); Guillot (2012); Hudson and Ayoko (2009); Hudson et al. (2009); Jiang and Kaye (1996); Lebrero et al. (2011); Parker et al. (2013a); Parker et al. (2010a); Parker et al. (2010b)
Odorant chemistry and composition, formation and emission (flux)	Cai et al. (2006); Hamon et al. (2012); Hudson and Ayoko (2008a); Hudson et al. (2009); Mackie et al. (1998); Ni et al. (2012); O'Neill and Phillips (1992); Trabue et al. (2010); Turan et al. (2007)
Odour impacts (frequency, intensity, offensiveness, duration, location/receptor characteristics)	Lebrero et al. (2011); Mackie et al. (1998); O'Neill and Phillips (1992)
Odour management or treatment	Hamon et al. (2012); Lebrero et al. (2011); Massé et al. (2013)

Relatively little information has been reported about the formation of poultry odour compared to other livestock industries, especially pig production (Cai et al., 2007; Trabue et al., 2010). Litter is a very different odour source than other intensive animal bedding/wastes including those from laying hens, pigs and cattle. Unfortunately, even when the focus is 'poultry' wastes, some published research does not specifically identify which production system was involved, instead referring to 'animal wastes' or 'poultry', which does not differentiate between meat chickens or laying hens. There are many differences between meat chickens and laying hens in terms of breed, nutritional requirements, feed formulations, length of production cycle and housing design that are likely to support different odour forming mechanisms. Additionally, some published studies refer to odour emissions from poultry manure or poultry litter/manure composting (Petric et al., 2009; Sweeten et al., 1991; Turan et al., 2007). Accumulation

of manure/litter within meat chicken sheds may be considered a form of stockpiling/composting and there will be some similarity to in-shed litter, but conditions in terms of the environment, microbial activity, surface to volume ratio, fresh manure addition and mechanical mixing due to chicken activity are substantially different.

Litter is a porous material and odorants will be released from the surface (Mackie et al., 1998) but will also diffuse through the pores (Schwarzenbach et al., 2003; Thibodeaux and Scott, 1985; Zhang et al., 2002a). Release of odorants from litter is therefore complex and requires consideration of gas exchange mechanisms and litter physical properties.

The aim of this section is to describe how conditions within litter influence the formation and diffusion of odorants from litter as well as considering how shed and litter management strategies influence litter conditions. Odorants previously identified at meat chicken farms will be summarised. The effect of litter porosity on the exchange of odorants between the litter and ventilation air will also be examined.

#### 2.5.2 Odorant measurement, properties and origins

Litter is considered to be the primary source of odour from meat chicken sheds because it is the source of most odorous compounds (Mackie et al., 1998; Trabue et al., 2010; Wadud et al., 2012) while some odours may be emitted from the birds themselves (Lacey et al., 2004). Meat chicken shed odour is a mixture of dozens of odorous compounds (odorants) (Lacey et al., 2004; Murphy et al., 2014; O'Neill and Phillips, 1992; Trabue et al., 2008b; Trabue et al., 2010) that exist in the gas phase or attached to particulates (Heber et al., 1988; Mackie et al., 1998). These odorants may be VOCs (including reduced sulfur compounds) or non-VOCs (e.g. ammonia, hydrogen sulfide) (Parker et al., 2013b). VOCs are molecules that contain at least one carbon and one hydrogen atom (i.e. organic compounds) that vaporise easily at room temperature (i.e. volatile) (Ni et al., 2012). Trabue et al. (2010) reported that the five most abundant compounds in meat chicken sheds were acetic acid, 2,3-butanedione, methanol, acetone and ethanol. Murphy et al. (2014) reported that the most important compounds for predicting odour from meat chicken sheds were dimethyl disulfide, dimethyl trisulfide, 2,3-butanedione, 3-methyl-1-butanal, 1-butanol, 3-methyl-1-butanol, 2-butanone and 3-hydroxy-2-butanone (acetoin). These are just a few of the many compounds previously reported in meat chicken odour (Appendix A).

#### 2.5.2.1 Odour measurement

Odours are measured and characterised using instrumental and/or sensorial techniques (Capelli et al., 2013b; Lebrero et al., 2011; Zarra et al., 2012). Instrumental techniques include gas chromatography-mass spectrometry (GC-MS), proton transfer reaction-mass spectrometry (PTR-MS) or selected ion flow tube-mass spectrometry (SIFT-MS) whereas sensorial techniques include dilution olfactometry or field-based odour panels (Capelli et al., 2013a; Lebrero et al., 2011). Instrumental techniques are used to characterise an odour in terms of chemical composition by identifying and quantifying the chemical concentration of specific odorants (Capelli et al., 2013a; Lebrero et al., 2011). Instrumental techniques have the benefits of being objective, repeatable and accurate; however, they provide limited information about how the odour may be perceived by human receptors (Akdeniz et al., 2012; Lebrero et al., 2011), especially given that the characterisation of nuisance odour is often subjective (Zavaleta and Wilson, 1976). Another limitation of instrumental techniques is the need to use specialised sample collection equipment, such as sorption tubes or vacuum canisters, which can limit the compounds that are able to be measured and may influence detection limits. Multiple sampling methods may be required to avoid missing a significant fraction of the VOCs associated with poultry production (Trabue et al., 2010).

Sensorial techniques allow odours to be characterised in terms of the way an odour may be perceived by people and how it may contribute to odour annoyance; however the use of human assessors introduces some subjectivity into the odour assessment due to natural variations in sensitivity to smells and preconceptions about odour strength and offensiveness due to previous experience and odour conditioning. Sensorial methods allow an odour to be characterised using four dimensions: concentration, intensity, quality and hedonic tone (Lebrero et al., 2011; Nimmermark, 2011).

#### **Odour concentration**

Odour concentration is measured using dynamic dilution olfactometry and a panel of qualified human odour assessors. Odour assessment is performed using standardized methods such as EN 13725 (European Committee for Standardization, 2003) or AS/NZS 4323.3-2001 (Standards Australia/Standards New Zealand, 2001). According to these Standards, odour assessors qualify if their detection threshold for a reference odorant, *n*-butanol, falls within a specified range. Odour concentration is measured using odour units (ou). One odour unit is determined using a gas mixture containing

132 µg of n-butanol evaporated into one cubic metre of air at standard conditions (0 °C or 20 °C (AS/NZS 4323 or EN 13725 respectively) and 101.325 kPa), which is approximately equivalent to 40 ppbV. One odour unit is defined when this concentration of the reference odorant elicits a physiological response (detection threshold) in 50% of the odour panel. Odour concentration of a sample is then defined by the number of dilutions required to elicit the same physiological response from the qualified panel.

#### **Odour intensity**

Odour intensity "is the intensity of the sensation that is triggered by an odour stimulus" (Schulz et al., 2002) or may otherwise be referred to as "the perceived strength of an odour" (Lebrero et al., 2011). Intensity is measured using a seven point scale: 0=not detectable, 1=very weak, 2=weak, 3=distinct, 4=strong, 5=very strong, 6=extremely strong. A relationship exists between the concentration of an odour (measured by detection threshold) and its perceived intensity according to the Weber-Fechner or Steven's models (Misselbrook et al., 1993; Ouellette et al., 2010; Zhang et al., 2002b). The Weber-Fechner model relates odour intensity to the log<sub>10</sub> odour concentration whereas the Steven's model relates odour intensity to odour concentration using a power function (Zhang et al., 2002b). As an example of what exponent may be required for meat chicken farm odours, (Zhang et al., 2002b) determined that an exponent of 0.57 was required to relate odour concentration to intensity for pig farm odour, although Misselbrook et al. (1993) found that meat chicken farm odours registered a higher intensity score for the same odour concentration compared to pig odours. Ouellette et al. (2010) referred to the exponent used in the Steven's model as 'the persistence' because it relates to how much an odour needs to be diluted to effect a change in the intensity. In practice, the log<sub>10</sub> and power relationships between odour concentration and intensity mean that when the concentration of an odorant is near the odour threshold value, relatively small changes in odour concentration will result in a large change in perceived odour intensity while at much higher concentrations even large changes in the concentration of the odorant will result in small changes to perceived odour intensity.

#### Odour descriptors/character

The third dimension used to describe an odour is odour quality, which provides a description of what an odour or individual odorant smells like. Odour wheels have developed to enable odour qualities/descriptions to be linked to specific odorants or groups of odorants (Decottignies et al., 2013; Suffet and Rosenfeld, 2007). Odour qualities/descriptors for selected meat chicken odorants is provided in Appendix A.

#### **Odour pleasantness**

The fourth dimension used to describe an odour is hedonic tone, which uses a scale to rate the relative pleasantness or unpleasantness of odours (Lebrero et al., 2011; Nimmermark, 2011). The scale ranges from extremely unpleasant to extremely pleasant. One complication regarding hedonic tone is that some odours become less pleasant as the concentration of that odour increases (Nimmermark, 2011).

#### Odour threshold values for individual odorants

Instrumental techniques provide information about the chemical composition of an odour but not the way that it is perceived by human receptors. Single compound odour thresholds (SCOT) (Parker et al., 2012), otherwise reported as an odour threshold (OT); odour threshold value (OTV); or odour detection threshold (ODT), have been determined so the likely contribution of individual odorants to odour impact/annoyance can be estimated. One way to conceptually estimate the relative contribution of an individual odorant to an odour mixture is to calculate its odour activity value (OAV), which is defined as the ratio of the airborne concentration of this compound to its odour threshold (Parker et al., 2012; Parker et al., 2013b; Trabue et al., 2008b). For complex odour mixtures, Capelli et al. (2013b) explained that these individual odorant OAV values can be summed to provide an OAV for the mixture, presumably for comparison to other complex odour mixtures. OAV calculations can be imprecise due to difficulties in finding reliable odour threshold values and the values reported in the literature can vary by several orders of magnitude for individual odorants (Capelli et al., 2013b; Parker et al., 2012) (Figure A. 1 in Appendix A). More sophisticated methods to estimate odour perception from odorant chemical concentrations were explained by Wu et al. (2016); namely sum of individual odour intensities (SOI) and equivalent odour concentration (EOC). These methods require data regarding the slope of the odour intensity-odour concentration relationship. The relationship between odour intensity and odour concentration is not known for many poultry odorants and therefore these more complex methods have not been considered further in this study.

Ruth (1986) explained that some of the differences in reported OT values is related to the way odour threshold is defined. Some authors considered the OT value to be the lowest concentration at which one person can detect an odour while others consider the OT value to be the concentration at which 50-100% of a trained odour assessment panel can detect the odour (Hellman and Small, 1974; Ruth, 1986). Further complicating the use of OT and OAV is that the intensity to concentration relationship (as defined using the Weber-Fechner or Steven's models) is different for different

compounds (Zhang et al., 2010a). This means that even if two compounds/odour mixtures have a similar OAV, one may be perceived as having higher intensity.

The contribution of individual compounds to the perceived odour of an odour mixture in terms of intensity and character is very complex. Ruth (1986) explained that the odour threshold resulting from the mixture of two odorants can be:

- independent (OT<sub>AB</sub> = OT<sub>A</sub> or OT<sub>B</sub>)
- additive  $(OT_{AB} = OT_A + OT_B)$
- synergistic  $(OT_{AB} > OT_A + OT_B)$
- or counteractive (OT<sub>AB</sub> < OT<sub>A</sub> or OT<sub>B</sub>)

(where  $OT_{AB}$  is the odour threshold of the mixture of compounds A and B;  $OT_A$  is the odour threshold of compound A; and  $OT_B$  is the odour threshold of compound B). In contrast, calculations of OAV for individual compounds (Parker et al., 2013b) or complex mixtures (Capelli et al., 2013b) assume the relationship to be simply additive. Considering that odour from litter and meat chicken sheds is known to be a complex mixture of dozens of odorants it would seem unlikely that simple arithmetic would apply to the summation of odorant contributions to the whole odour mixture while assuming no interactions between the compounds.

#### 2.5.2.2 Measurement of odour emissions from a litter surface

Studies have evaluated wind-tunnels and flux chambers/hoods as area source enclosures to measure the specific emission rate of individual gases or odorous gas mixtures from liquids and porous media (Capelli et al., 2012; Gholson et al., 1989; Gholson et al., 1991; Hudson and Ayoko, 2008a; Jiang and Kaye, 1996; Kienbusch, 1986; Leyris et al., 2005; Smith and Watts, 1994; Witherspoon et al., 2002; Zhang et al., 2002a). The focus of most of these studies has been to evaluate these enclosure devices for their relation to actual emission rates. Smith and Watts (1994) and Zhang et al. (2002a) concluded that wind tunnels and flux chambers/hoods are suitable for comparative studies but will not provide accurate measurement of true emission rates because the conditions created within the enclosure will regulate emissions. A method to address this shortcoming for selected compounds has recently been proposed and tested by Parker et al. (2013a), who simultaneously measured water evaporation inside and outside a sampling enclosure and used the difference in evaporation to scale the measured emission rates.

#### 2.5.3 Microbial production of odorants

The majority of odorants in meat chicken sheds are produced by microbial degradation of organic matter, especially manure (Mackie et al., 1998). The process can occur

aerobically or anaerobically (Powers, 2002) and produces a large number of odorous and intermediate compounds (Mackie et al., 1998; Powers et al., 1999; Zhu, 2000). Odorants are also produced in the gastro-intestinal tract of the chickens by microbiota during anaerobic fermentation of carbohydrates, proteins and amino acids (Rinttilä and Apajalahti, 2013). This is essential in the digestive tract of all animals to recover energy for the host and microbiota (Mackie et al., 1998).

Specific bacterial genera have been identified in the lower gastro-intestinal tract and fresh excreta of meat chickens as well as litter (Appendix B). Lu et al. (2003a) and Wei et al. (2013) reported that the microbiota of the lower gastrointestinal tract (ileum and caeca) were dominated by *Lactobacillus, Streptococcus, Clostridium, Ruminococcus, Bacteroides* and *Eubacterium*, whereas litter microbiota was dominated by *Staphylococcus, Salinicoccus, Virgibacillus, Faklamia, Brevibacterium, Bacillis, Brachybacterium, Aerococcus* and *Corynebacterium* (Lu et al., 2003b; Wadud et al., 2012) (determined using aerobic culturing methods). These organisms produce some of the odorants associated with meat chicken production (Appendix B).

There are similarities between bacterial genera in the lower gastro-intestinal tract and litter. This is not surprising considering meat chickens are known to consume litter as part of their diet (Malone et al., 1983) and this influences the microbial diversity in the gastro-intestinal tract (Torok et al., 2009). Microbiota in the lower gastro-intestinal tract are then deposited in the litter and this influences microbial diversity in the litter (Wadud et al., 2012). Microbial diversity has also been observed to change during the grow-out period in the intestines (Lu et al., 2003a), excreta and litter (Fries et al., 2005).

Microbial interactions between the litter and gastro-intestinal tract can be cyclic with wet litter conditions leading to high bacterial counts in the litter (Fries et al., 2005). This may contribute to dysbacteriosis or other intestinal upset because of an apparent overgrowth of some gastro-intestinal bacteria (Hermans et al., 2006). The result is wet excreta perpetuating wet litter conditions (Guardia et al., 2011). Additionally, susceptibility of the birds to bacterially induced gastric upset is greater in the first 3–4 weeks of a grow-out period (Guardia et al., 2011; Torok et al., 2009), which can exacerbate wet excreta and litter conditions.

Microbial growth and diversity in the litter are influenced by pH, temperature and moisture content (Lovanh et al., 2007; Wadud et al., 2012), bedding material type (Fries et al., 2005) and stocking density (Guardia et al., 2011). Changes in these

conditions and resulting microbial activity can occur within very short distances (a few centimetres) (Lovanh et al., 2007). With respect to odour formation, changes in conditions that affect microbial diversity and activity (pH, moisture content, temperature, manure content) will influence the formation of specific odorants (Spoelstra, 1980; Wadud et al., 2012). In beef feedlot manure, Woodbury et al. (2015) reported that warm, wet, anaerobic conditions resulted in greater emission rates of sulfide compounds, which have offensive character and are more likely to contribute to odour impacts due to low odour threshold values. Zhu (2000) concluded that aeration can be effective in reducing offensive odours because it supports aerobic bacteria that actively decompose odorous compounds.

Odorant emissions change spatially within a chicken shed and temporally during each grow-out period (Miles et al., 2011a); however, it is not possible in a practical sense to link the formation of specific odorants to specific microbial activity because of the complexity of microbial processes and the properties of the waste substrate (Spoelstra, 1980). It is suggested that there are at least three microenvironments with different microbial diversity that contribute to odour from litter. These should to be considered specifically when investigating the origins of odour from litter:

- 1. fresh excreta
- 2. dry friable litter
- 3. wet/caked litter.

Odour from fresh excreta is not well represented in the literature due to 'litter decomposition' historically being seen as the primary odour source. Le et al. (2005a) reported the direct release of indole and phenol compounds from fresh excreta. Because of the differences in microbial diversity between fresh excreta and litter it is likely that fresh excreta and litter will produce different mixtures of odorants (Appendix B). Dominant bacteria in fresh excreta are known to produce many of the odorants in meat chicken shed odour (Murphy et al., 2014). It is therefore suggested that fresh excreta should receive more focus as an odour source in meat chicken sheds.

The potential contribution of odour from fresh excreta can be viewed in context with the manure accumulation processes previously discussed. When fresh excreta mix with dry, friable bedding/litter, the mixing process reduces moisture content (and water activity) of the excreta, exposes the manure to oxygen and supports aerobic microbial activity. Conversely, excreta will remain intact and wet for longer if it mixes with sticky, wet litter or cake. The result is a moist micro-environment that supports anaerobic

microbial activity and production of odorants with offensive characters and low odour thresholds.

#### 2.5.4 Gas exchange from porous media

Formation of odorants within meat chicken litter is one issue that needs to be considered. A second is the mechanisms controlling the emission or flux of odorants from the litter into the air above it and then exhausted from the shed through the ventilation fans. To investigate these mechanisms it is necessary to understand the factors controlling transfer of odorants from the litter to air. The following sections review the fundamental diffusion and emission processes from porous materials.

#### 2.5.4.1 Molecular diffusion and boundary theories

Diffusion and transport of gases from liquid and porous media are complex and dynamic processes that have previously been described or reviewed by Capelli et al. (2012), Hudson and Ayoko (2008b), Jähne and Haußecker (1998), Parker et al. (2010a), Schwarzenbach et al. (2003), Thibodeaux and Scott (1985) and Zhang et al. (2002a). Molecules of a compound move randomly within a medium (e.g. air) and collide with other molecules. The behaviour and movement of molecules within the medium is governed by the ability of the molecule to move within the medium. This is described in terms of molecular diffusivity and quantified using a diffusion coefficient (Schwarzenbach et al., 2003). If there is a concentration gradient of the compound in the medium, the compound will diffuse from the place of high concentration to low concentration at a rate proportional to the gradient. *Fick's law* is used to describe the steady state diffusive flux of the compound by incorporating its diffusion coefficient and the concentration gradient (Schwarzenbach et al., 2003; Thibodeaux and Scott, 1985).

Molecules of a compound will eventually reach the boundary of the medium through which they are diffusing. When they reach the boundary, additional forces will act on the molecules, affecting the rate at which the molecules can travel through the boundary (i.e. provide resistance). Boundaries are considered to be any change in the properties of the medium or boundary/interface of a new medium. The following are some examples:

- changes in temperature (e.g. thermoclines)
- changes in phase (i.e. solid to liquid, solid to gas, liquid to gas and vice-versa)
- changes in density (e.g. compaction of a solid or porous material)
- changes in material (e.g. water to air, film/cover on a liquid surface)
- change in chemical concentration/compound
- change in turbulence.

In the case of poultry litter, the boundary may be the surface of the litter/cake, the surface of individual litter particles, or the surface of a film of moisture surrounding individual litter particles.

Theories on diffusion and boundary transfer are applied to the emission of volatile compounds from liquids, solid and/or porous materials (Schwarzenbach et al., 2003; Thibodeaux and Scott, 1985). One common feature of these models is the assumption that there is resistance preventing the flux of volatile compounds from the source into the airstream and vice-versa. This resistance is commonly viewed as layers. A layer exists in the air phase and is referred to as a boundary layer while the layer in the source is referred to as a surface or sub-surface layer (Schwarzenbach et al., 2003). Schwarzenbach et al. (2003) described three types of boundary, each identifiable by changes in diffusion rate on each side of the boundary or through the boundary:

#### Bottleneck boundary

Bottleneck boundaries are characterised by an abrupt drop in diffusivity at the boundary when the zones on either side of the boundary have relatively unrestricted diffusivity. A classic example of a bottleneck boundaries is the water-air interface, where molecules are relatively free to diffuse within each of the water and air zones, but the movement of molecules between the zones is restrictive.

In the case of water-air interface there are multiple layers to the bottleneck boundary (there will likely be multiple layers at the boundary between any two different media). There is a layer at the boundary of the water (liquid phase boundary layer) and also at the boundary of the air (gas phase boundary layer). Each of these layers can independently influence the diffusivity of molecules through the water-air interface.

Due to the requirement for unrestricted availability of molecules at the boundary, bottleneck boundaries commonly have mixing/turbulence in the zones on each side of the boundary.

#### Wall boundary

Wall boundaries are characterised by a sudden change in diffusivity from one side of the boundary to the other (diffusivity changes by orders of magnitude). Zones on each side of the boundary may be the same media (e.g. a compacted layer) or different media (e.g. water column on top of a sediment layer in a river).

#### Diffusive boundary

Diffusive boundaries are characterised by similar diffusion rates in both zones on each side of the boundary, but reduced rate of diffusion within the boundary. This can occur due to a change in physical property of a single medium (i.e. change in chemical concentration or temperature) or between two media that have similar diffusivity for the compound of interest.

It is suggested that emissions from litter may be described using different boundary types depending on physical litter conditions. Surface and boundary layers exist on the overall litter surface and also on each particle within the litter. Dry, friable litter or cake may be described as a 'diffusive boundary' or 'wall boundary' depending on the amount of resistance to diffusion within the litter compared to the air above it. However, if a layer of cake is present on the litter surface, and the focus is emission of odorants from the base of the litter through the cake, then a 'bottleneck boundary' may be more appropriate (Figure 20).



Figure 20. Diffusivity and concentration profiles through litter (*top*) and caked litter (*bottom*)

Resistance to flux of a volatile compound can occur in either the air boundary layer or surface layer or both, depending on the specific compound, properties of the source (e.g. turbulence of a liquid or porosity and compaction of a solid) and conditions of the airflow above the surface. Convective mass transfer through the air boundary layer above the litter is affected by the thickness and conditions within the boundary layer (Capelli et al., 2012; Thibodeaux and Scott, 1985; Zhang et al., 2002a). Increasing velocity and turbulence of air (as indicated by greater Reynolds number) reduce the thickness of the boundary layer and increase the mass convection of compounds from litter. Litter surface roughness also affects the boundary layer. Zhang et al. (2002a) found that the surface roughness of soil (which is likely to be similar to litter) was sufficient to make the air boundary layer turbulent, thus avoiding laminar flow conditions.

It is a common assumption that gases move from a solid/porous/liquid source into the gas phase above it due to the much higher concentration of compounds in the source; however, the movement of compounds can theoretically be in both directions. The direction of diffusion is affected by:

- changes of concentration with the air or source
- changes to physical conditions (e.g. changes in temperature)
- changes to the boundary layers
- properties of the specific compound
- environmental conditions.

Schwarzenbach et al. (2003) provided examples of how a change in temperature reverses the direction of flux for individual compounds due to changes in solubility and diffusivity of a particular compound in two different media, which occur due to changes in temperature. It may be unlikely that this reversal would occur during normal conditions in a meat chicken shed due to much higher concentration of odorant compounds within litter compared to the relatively low concentration in the air above the litter; however, it may be a consideration with particular area-source sampling enclosures (e.g. flux hoods) that increase the concentration of compounds in the air above the litter to a condition that is closer to equilibrium. In this situation, changes in litter or ambient conditions may be sufficient to reverse the direction of odorant transport.

The 'two-film theory' — also be known as the 'stagnant-film model' (Parker et al., 2010a) — is one boundary layer theory that has previously been used to explain the transfer of gases between the liquid and gas phase (Hudson and Ayoko, 2008b; Parker

et al., 2010a). The two-film theory is applicable to quiescent (still) water bodies and still air conditions at the boundary between the liquid and gas phases. Litter is not a quiescent water body and therefore the two-film theory may have limited applicability for modelling odorant emissions due to litter conditions and ventilation practices. It is suggested that this theory may be applicable when litter has moderate to high litter moisture content because moisture will surround litter particles and fill pores within the litter.

#### 2.5.4.2 Henry's law

Integral with the two-film theory is Henry's law. Parker et al. (2010a) referred to Henry's law when stating "that at equilibrium, the VOC concentration in the air is directly proportional to the VOC concentration in the water". Henry's law constants enable the definition of a steady state ratio in the concentration of a compound in the liquid phase to the concentration of the specific compound in the gas phase above it. Each compound has a different Henry's law constant and will therefore reach equilibrium with different conditions in both the liquid and gas phase. Henry's law constants also provide a guide for which conditions, turbulence and/or phenomena control the emission (Hudson and Ayoko, 2008b; Parker et al., 2010a; Schwarzenbach et al., 2003).

To add a complication, Henry's law constants may be presented using one of four different units, some with dimensions and some dimensionless (Staudinger and Roberts, 1996). Additionally, the value of a Henry's law constant assigned to a compound changes with temperature (published values are usually quoted at either 20 °C or 25 °C), pH, compound hydration, compound concentration as well as the presence of other compounds, dissolved salts, dissolved organic matter and suspended solids (due to adsorption of compounds onto the solids surfaces) (Staudinger and Roberts, 1996). Consequently published values should be considered as approximate only (Hudson and Ayoko, 2008b).

When using Henry's law constants to explain emissions, the dimensionless values (or log<sub>10</sub> of the dimensionless value) is common (Hudson and Ayoko, 2008b; Parker et al., 2010a; Schwarzenbach et al., 2003; Staudinger and Roberts, 1996, 2001) although some of the largest compilations of Henry's law constants tend to use dimensional values (NIST, 2013; Sander, 1999). Henry's law constants for selected meat chicken shed odorants are provided in Appendix A and Figure A. 2. The Henry's law constant assigned to each compound can be used as an indication of the relative importance of

ventilation air speed/turbulence or litter moisture content on odorant emissions from litter.

Emissions of compounds with a dimensionless Henry's law constant value less than  $1.0 \times 10^{-3}$  are driven by physical phenomena in the gas phase (i.e. in-shed ventilation air speed and turbulence), while compounds with a Henry's law constant value greater than  $1.0 \times 10^{-3}$  are driven by physical phenomena within the liquid (Hudson and Ayoko, 2008b; Parker et al., 2010a). Hudson and Ayoko (2008b) further categorised the compounds into three categories: emission rates for compounds with dimensionless Henry's law constant less than  $1.0 \times 10^{-3.3}$  are gas phase controlled; emission rate for compound with dimensionless Henry's law constant between  $1.0 \times 10^{-3.3}$  and  $1.0 \times 10^{-1.3}$  are both gas and liquid phase controlled; while the emission rates for compounds with Henry's law constant greater than  $1.0 \times 10^{-1.3}$  are liquid phase controlled; while the emission rates for compounds with Henry's law constant greater than  $1.0 \times 10^{-1.3}$  are liquid phase controlled; while the emission rates for compounds with Henry's law constant greater than  $1.0 \times 10^{-1.3}$  are liquid phase controlled; while the emission rates for compounds with Henry's law constant greater than  $1.0 \times 10^{-1.3}$  are liquid phase controlled (Figure 21 and Figure A. 2).



Figure 21. Henry's constant (dimensionless units) for selected meat chicken odorants (refer to Figure A. 2 in Appendix A for extended list of poultry odorants)

The two-film theory is traditionally applied to quiescent water bodies rather than moist porous materials such as meat chicken litter or meat chicken litter cake. With porous materials, fluxes of VOCs and water are reduced by internal resistance and by some molecules of the compound being adsorbed on particle surfaces (Ghaly and MacDonald, 2012; Schwarzenbach et al., 2003; Staudinger and Roberts, 1996; Yusheng and Poulsen, 1988; Zhang et al., 2002a). Internal resistance and diffusion from litter are affected by:

- cake (thickness, moisture content and density)
- porosity (affected by particle size, compaction, moisture content, faeces content)
- moisture content (affecting the availability of water for evaporation)
- air conditions above the litter (temperature, humidity and concentration of compounds being emitted that are already in the air).

Evaporation of water has been found to be representative of the emission of gas-phase controlled odorants, which includes many of the odorants identified as contributing to odour impacts (Parker et al., 2013a; Parker et al., 2010a; Parker et al., 2013b). The advantage of using water evaporation (water flux) instead of odorants is the relative ease, low cost and accuracy of measuring water evaporation using a readily available laboratory balance. Further experimental work is required to quantify the effects of temperature, humidity, litter porosity (cake compared to friable litter), litter pH, air speed and other factors on evaporation of water from meat chicken litter so this flux can be related to emission of gas-phase controlled odorants.

Litter is a porous medium comprising solid, liquid and vapour phases. There are complexities of litter that need to be considered, from a gas exchange perspective, with respect to odour emissions including porosity, moisture content, effects of turbulence from ventilation and interactions of the birds with the litter.

#### 2.5.4.3 Effects of litter porosity on odorant emissions from porous litter

Emission of odorants from porous surfaces is a more complex process than from liquids due to phenomena of diffusion within pores and the effects of turbulence above the rough surface (Capelli et al., 2012). When considering porous sources, such as litter, it is commonly assumed that movement of volatile compounds within the pores occurs by the process of random molecular diffusion and then flux from the porous material into the airstream above occurs by convective mass transfer (Zhang et al., 2002a).

Schwarzenbach et al. (2003) explained that diffusion through pores occurs by molecular diffusion because the small diameter of pores suppresses turbulence. Flux of odorants will be less from a porous medium compared to a homogenous fluid or gas (assuming the pores of the porous medium are filled with the same fluid/gas) because the relatively longer and non-linear nature of pores compared to fluids (i.e. air or water) increases the distance that molecules need to travel before they are emitted. This resistance is described in terms of the diffusivity of molecules in the porous medium compared to diffusivity in free air, and is termed 'tortuosity'. In all situations, molecular diffusion within the pores will be less than flux into free air due to resistance that occurs because of the tenuous path through the pores (Zhang et al., 2002a).

Litter has a variety of pore sizes ranging from large cracks and pores that exist between particles down to micro-pores that exist between fine particles or within particles (e.g. pores within the grain structure of wood shavings). Porosity varies spatially, through the litter profile and during the grow-out cycle. This variability occurs as a result of litter compaction due to bird activity (Miles et al., 2008), grinding down of litter particles and the presence of cake or greater manure content (Miles et al., 2008), which can happen for a variety of litter, shed, ventilation and flock management related reasons. Layers in the litter with different porosity, for example cake vs friable litter, will affect the rate of diffusion of compounds through the litter profile (Figure 20).

Litter porosity reduces during the grow-out cycle due to the increasing proportion of very fine manure particles and 'grinding' of the coarser bedding materials that support macro-pores within the litter. Different bedding materials will have a different ability to support pores within the litter and will also have different durability and longevity. Reducing macro porosity increases tortuosity and will slow rates of diffusion of odorants through the litter medium (Schwarzenbach et al., 2003).

In any medium (solid, liquid or gas), molecules of a compound will diffuse in a random manner due to molecular forces until a state of equilibrium is reached. This is known as molecular diffusion. Any movement or mixing of the medium, for example due to ventilation airflow, will introduce another mechanism of diffusion known as turbulent diffusion. Rates of diffusion vary by orders of magnitude depending on the medium and the type of diffusion. Molecular diffusion rates in gas-phase media are in the order of  $10^4$  times greater than in liquids and turbulent diffusion leads to rates of diffusion  $10^8$ –  $10^{13}$  times greater than molecular diffusion (Schwarzenbach et al., 2003).

Litter pores may be filled with air, water or both depending on the litter moisture content (Schwarzenbach et al., 2003). Litter porosity reduces with increasing moisture content due to an increasing amount of water in the pores but also because litter particles swell as they absorb water. It has been observed that the volume of litter particles increases at a greater rate than the mass increases as the litter particles absorb water (Bernhart and Fasina, 2009). As litter becomes wetter, more of the inter- and intra-particle pore space fills with water. Molecular diffusion of gases through the litter will be greatly reduced because diffusivity is orders of magnitude slower in liquids than air, and because the reduction in pore size will increase tortuosity. Consequently, increasing water content in litter reduces porosity and the flux of odorous gases diffusing through the litter pores, which will in turn reduce the flux of odorants being released from the surface (Schwarzenbach et al., 2003; Thibodeaux and Scott, 1985; Zhang et al., 2002a). Zhang et al. (2002a) concluded that reduced porosity reduces the maximum flux rates and this leaves a greater quantity of odorants in the litter matrix that can sustain a longer enduring flux.

## 2.5.4.4 Effects of ventilation and in-shed aerodynamics on odorant emissions from porous litter

Different ventilation conditions are used in meat chicken sheds to optimise the comfort of the birds (especially in removing heat) and manage litter conditions. Air temperatures are reduced during the grow-out period to provide a thermo-neutral environment for the birds. The recommended 'effective' temperature starts at approximately 31 °C (at the start of the grow-out period) and reduces linearly to 20 °C on day 27 where it is kept constant until the end of the grow-out (Figure 13). The 'effective' temperature is not dry-bulb air temperature, but is a comfort temperature considering relative humidity and wind-chill due to air speed (Aviagen Inc., 2014c; Cobb-Vantress Inc., 2012a).

Many meat chicken sheds, for example in the south-eastern region of Australia, are mechanically ventilated (Figure 7). Farm managers vary ventilation programs according to prevailing conditions using their experience and interpretation of biological responses displayed by the birds, such as panting and congregating behaviours.

Air is drawn into tunnel-ventilated sheds using negative pressure (typically 10–40 Pa) through evenly spaced wall-mounted vents (mini-vent inlets), large vents at the front of the shed (tunnel inlets), or both types of vent simultaneously. Air entering the shed through mini-vent inlets is projected across the ceiling where it mixes with warm air

lingering near the roof apex. Warming the incoming air reduces its relative humidity thus increasing its moisture-holding capacity and allowing more moisture to be removed from the litter. Air entering the shed through mini-vents creates turbulence and mixing of the in-shed air but produces minimal air velocity at the litter surface. This minimises wind-chill on the birds, which is essential during the early stages of a grow-out period. When a higher degree of cooling is required, mini-vents are closed and air enters the shed through tunnel inlets at the front of the shed. This air may or may not be cooled using evaporative cooling cells. The air then moves linearly through the shed towards the tunnel fans, reaching air speeds of up to 4.0 m/s depending on the shed design. At these velocities, the air is turbulent. Ventilation strategies are designed to maximise the evaporation potential of the air, either by increasing its moisture-holding capacity or reaching moderate air velocities. Due to the relationships between water evaporation and odorant emissions (Parker et al., 2013a), it is likely that the conditions created by ventilating the shed are likely to influence odour emissions from the litter (Barth et al., 1984).

#### Considerations of the shed as an area source enclosure

Tunnel ventilated meat chicken sheds are effectively a large area-source enclosure that can be operated like a wind tunnel or dynamic flux hood depending on the inlet vents that are used (tunnel or mini-vent inlets respectively). Use of specific inlets and ventilation programs depends on the cooling requirements of the birds. Conditions in the shed are similar to a wind tunnel when operated in tunnel ventilation mode due to turbulent linear air movement or are similar to a dynamic flux hood when operated in mini-vent ventilation mode due to random air movement/turbulence and negligible air speed.

With meat chicken sheds being similar to area source enclosures, it is likely that the airflow conditions within the shed will influence odour emission rates, especially for odorants that are gas phase controlled (relating to Henry's law constant, Appendix A and Figure A. 2). It is suggested that changing the mode of ventilation from tunnel ventilation to mini-vent ventilation may reduce odour emission rate, but it is unlikely that this strategy could be used in a practical way due to considerations of heat stress. Nonetheless, it is surprising that no literature was found specifically relating the air speed or mode of ventilation in meat chicken sheds to odour emissions, although some researchers have reported that higher ventilation rates correspond with higher ammonia and odour emission rates (Dunlop et al., 2010; Le et al., 2005b; Ndegwa et al., 2008; Zhu et al., 2000). Jiang and Kaye (1996) and Hafner et al. (2012) reported

that emissions of gas phase controlled VOCs and water from porous media (manure and silage) increased with increasing turbulence and airspeed of the air over the surface. This again highlights the relevance of Henry's law constants for individual compounds (Appendix A and Figure A. 2) when investigating the effects of ventilation air speed and turbulence on odorant emissions from litter. There is a need for further investigation into the effects of ventilation rate and air speed on the emission of individual odorants from meat chicken litter.

#### 2.5.4.5 Effects of moisture on odorant emissions from porous litter

A substantial quantity of water is added to litter and evaporated from litter on a daily basis during a grow-out cycle (Collett, 2012; Dunlop et al., 2015). This is balanced by evaporation rates that vary throughout the day. As such, litter moisture content is constantly changing. The presence of water in litter has multiple effects on the emission of odorants by reducing porosity of litter (physical resistance) and by altering the emission potential of odorants from the liquid phase within litter.

The rate of water evaporation is influenced by litter porosity and the internal mass transfer resistance of water to the evaporation surface (Ghaly and MacDonald, 2012; Yusheng and Poulsen, 1988). The rate of evaporation reduces as the litter dries due to its resistance to diffusion of water vapour through litter pores as the drying front moves from the litter surface down through the litter profile (i.e. increasing thickness of the sub-surface boundary layer) and eventually due to unavailability of free water for evaporation (Aminzadeh and Or, 2013).

Many odorants are water soluble (Appendix A and Figure A. 3) and therefore the water held within the litter will absorb and retain odorants (Cai et al., 2006; Woodbury et al., 2015) that are then subject to air-water exchange processes. Relatively large amounts of water are added and evaporated from litter daily (kg of water per m<sup>2</sup> per day) and it is suggested that this contributes to the substantial movement of odorous molecules within the litter (molecular diffusion within litter water and air-filled pores) and from the litter into the ventilation air. Woodbury et al. (2015) concluded that additional research is required to evaluate the effects of wetting and drying cycles on emissions.

Litter is unlikely to be completely saturated, i.e. all pores filled with water, with the exception of wet cake. If saturated, compounds diffuse slowly through the liquid-filled pores to the litter surface where they would be available for emission into the ventilation air above the litter. The tortuous path through the pore spaces provides

resistance to diffusion from the litter depths. More commonly litter may be damp, in which case it could be expected that a film of water would be present within and around each litter particle, creating an extensive emission surface, with greater surface-to-volume ratio than may exist in a body of water (Valsaraj, 1994). Valsaraj (1994) explained that the increased surface-to-volume ratio of water film in a non-saturated zone changes the rate of gas exchange at the liquid-air interface, which can result in considerable adsorption or release of gases. Additionally, Valsaraj (1994) suggested that water molecules compete with VOCs for sorption sites on mineral surfaces. It is suggested that in the case of litter this may result in the release of VOCs that are bound to dry litter surfaces. Gases emitted from dry surfaces or from the liquid film into air-filled pores or at the litter surface are subject to random molecular diffusion through the litter pores (Schwarzenbach et al., 2003; Thibodeaux and Scott, 1985; Zhang et al., 2002a).

Volatile compounds are emitted from the water held within litter in a similar way to larger bodies of water (such as liquid waste ponds), with the main difference being that the amount of liquid surface available for emission depends on the moisture content of the litter (Thibodeaux and Scott, 1985; Valsaraj, 1994). The emission of these compounds is governed by the properties of the liquid and air above the liquid, and the rate of emission will depend on the specific compound. Liang and Liao (2004) measured the effective diffusion rate of odorants from pig manure and found that Henry's law constants for specific compounds affected their emission rate as manure moisture content changed. Henry's law constants enable the definition of a steadystate ratio in the concentration of a compound in the liquid phase to the concentration of the specific compound in the gas phase above it (Parker et al., 2010a). Specifically, the diffusion rate of a compound with a small Henry's law constant (p-Cresol, dimensionless Henry's law constant value 1.0 x 10<sup>-4.5</sup>, which makes it an air phasecontrolled compound) increased as moisture content of the manure increased while the diffusion rate of other compounds with larger Henry's law constant (toluene and pxylene, dimensionless Henry's law constant value  $\sim 1.0 \times 10^{-0.53}$ , which makes them liquid phase controlled compounds) decreased as moisture content increased. It is suggested that this finding reinforces the application of the emission theories and Henry's law to moist porous materials and also indicates that litter moisture content is likely to influence the diffusion rate (and therefore the emission rate) of individual odorants, which in turn will lead to differences in odorant concentration.

#### 2.5.4.6 Effects of the birds on odour emissions from the litter

The birds deposit manure and moisture onto the litter surface and then mix it in. Nutrients in the excreta are the catalyst to odorant emissions and some odorants will be emitted directly from the excreta. The addition of nutrients to the litter also fuels the degrading/composting processes that release odorants (Mackie et al., 1998).

The birds produce substantial heat and warm the litter when they sit down. It is suggested that warming the litter will accelerate evaporation from the litter and will also increase the rate of microbial activity. Changes to temperature of an emission source can influence the emission or re-absorption rate of specific odorants (Woodbury et al., 2015).

Resistance to emission of gas phase compounds through pores in the litter is reduced when emitting surfaces (i.e. manure particles and liquids) are raised to the surface of the litter. This is because the odorants are not subjected to the tortuous path through the pores (Zhang et al., 2002a). Normal bird activities such as scratching and dust-bathing increase the exposure of emission sources at the litter surface, which in turn will likely result in higher emission rates from those sources. Trabue et al. (2010) reported that the presence of birds in a meat chicken shed corresponded with sevenfold higher VOC concentrations than an area of a shed without birds. Trabue et al. (2010) concluded that this demonstrated the importance of characterising odour emissions from animal facilities while the animals are present because there were distinct differences in both odorant diversity and concentrations in the presence or absence of birds.

The presence of birds affects the airspeed and turbulence at the litter surface, which in turn may affect emission rates of certain odorants (Trabue et al., 2010). No information could be found regarding or quantifying the specific effect that the birds have on micro-turbulence at the litter surface. It is suggested that they may reduce air velocity at the litter surface but would increase turbulence. The overall effect of this on the air boundary layer and mass convection of odorants from the litter is unknown and requires investigation.

# 2.5.4.7 Management strategies that interfere with or inhibit odorant formation and emission from litter

There have been limited studies of management strategies that reduce the formation and emission of odorants from meat chicken litter. Few investigations, if any, have considered the "litter physical and chemical properties, gas evolution, bird effects, as well as meat chicken house management and structure" as recommended by Miles et al. (2011a) for the development of "comprehensive mitigation strategies".

A review by Ullman et al. (2004) focussed on the use of litter amendments but mostly from the perspective of reducing ammonia emissions. In their review, the discussion of odour reduction strategies primarily focussed on air scrubbing, misting, filtering, ionizing, oxidising and dispersing technologies. (Bouzalakos et al., 2004) also focussed on misting technologies combined with the use of masking agents, counteractants, neutralisers and surface-enhanced absorption agents to reduce airborne odours. These end-of-pipe strategies target airborne odours and have not necessarily been shown to be effective at reducing odour formation or emissions from litter, i.e. the source of the odour, and are beyond the scope of this study; however, they warrant further investigation and development for when strategies to reduce odour from the litter are ineffective. Table 4 list selected odour reduction management strategies and expected efficacies.

Strategy	Reported or expected efficacy
Maintaining dry litter and	Expected efficacy:
friable litter	<ul> <li>Less offensive odour due to aerobic conditions (Barth et al., 1984)</li> </ul>
	• Lower emission of water soluble odorants due to lower water evaporation rates (Barth et al., 1984; Woodbury et al., 2015)
	<ul> <li>Reduced odour formation due to less microbial activity (Wadud et al., 2012)</li> </ul>
Litter in-situ aeration	<ul> <li>Odour concentration reduced by 6–36% (not significant or consistent)</li> </ul>
In-shed windrowing/	Compared to non-windrowed litter (Harmel et al., 2014):
pasteurising (only applicable	<ul> <li>58–65% reduction in odour concentration</li> </ul>
for litter-reuse in subsequent	Changed odour character from 'manure' to 'earthy'
batches or land application of	Reduced odour offensiveness when land applied
spent litter)	<ul> <li>Some odorant compounds decreased but others increased</li> </ul>
Acidifying litter additives	<ul> <li>Inconsistent reduction of volatile fatty acids by 14–83% (Kim et al., 2011)</li> </ul>
	<ul> <li>Reduced ammonia (considered an odorant) by up to 99% (Ullman et al., 2004)</li> </ul>
Litter adsorbent addition	In laboratory trial conditions (Pillai et al., 2012a):
(activated carbon, silica gel or zeolite)	<ul> <li>Reduced emission of some odorant compounds but not all. Concluded that no one product was universally effective.</li> </ul>
Enzyme addition combined with heated incubation	Greatly reduced odour (but economic viability unknown) (Enticknap et al., 2006)
Clinoptilolite addition to feed and directly to litter	• No odour reduction (Amon et al., 1997)
Yucca extract based feed additive	No odour reduction (Amon et al., 1997)

#### Table 4. Selected management strategies to reduce odour emissions from litter

In a broader context, absorption and adsorption of odorants onto organic material for microbial degradation have been investigated with respect to biofiltration of odours (Chen and Hoff, 2009; Kennes et al., 2009; Ralebitso-Senior et al., 2012). Biofiltration is an odour reduction technology in which odorous air is passed through a moist, biologically active and commonly organic medium. Microbes within the biofilter consume and convert the odorant compounds into less odorous compounds thereby reducing the concentration and intensity of the released odour. Interestingly, the review by Chen and Hoff (2009) highlighted the importance of moisture content, porosity, temperature, microbial activity, pH and VOC diffusion on the odour removal efficiency of biofilters. If conditions within the biofilter bed are sub-optimal, for example anaerobic, odorant removal efficiency is reduced and the biofilter may emit its own odours (Chen and Hoff, 2009). It is suggested that biofilters, like litter, are a porous organic medium that is interacting with volatile odorants and therefore further review of the literature

concerning biofiltration may reveal knowledge that can be used to develop new strategies to reduce the emission of odorants from litter.

Nahm (2005) suggested that reducing moisture content, changing pH or adding fresh shavings or zeolite (or other clay materials with high adsorption properties) can be effective at reducing emissions of gases such as ammonia. Unfortunately, these treatments may not be effective for reducing the emission of all of the odorants that contribute to odour impacts downwind from the shed (Barth et al., 1984). Pillai et al. (2012a) tested several litter additives to reduce odorant emissions and found adsorbent materials including activated carbon and silica gel to be effective on some odorants, but not all. Loyon et al. (2016) reported strategies to reduce emissions (especially ammonia) from meat chicken sheds, which were based on good housekeeping and litter management practices including the reduction of water loss from drinking systems and using forced manure drying (with ventilation air). This further supports the strategy of maintaining dry and friable litter to minimise odour emissions. Further research and development is required to translate this strategy into practical techniques that will assist meat chicken growers to achieve dry and friable litter conditions in sheds. Improved techniques are also required to reverse wet and caked litter so that dry and friable conditions can be maintained.

#### 2.6 Summary

Litter is considered the primary source of odour in meat chicken sheds. Odour emissions from litter are complex due to the existence of multiple odorant sources within litter (i.e. fresh excreta, friable litter and cake), formation and emission of numerous odorants, and significant spatial and temporal variability of moisture content, porosity, pH, ventilation air-flow, temperature, humidity and bird activity (Figure 22). There is limited published information relating specific litter conditions to odour emissions.

A list of more than 130 meat chicken related odorants was compiled along with selected properties including odour threshold value, odour character, Henry's law constant, water solubility and vapour pressure (Appendix A). This list serves as a reference for odorants considered in this thesis.



Figure 22. Graphical summary of the factors affecting odour emissions from litter

Litter formation mechanisms are not well described in the literature despite the fact that the resulting conditions, especially friable litter or cake, are known to significantly affect odours. Mechanisms for the formation of cake and friable litter have been proposed in this chapter after considering the contributions of litter friability, flowability, moisture content, water activity and compaction.

'Wet litter' is an issue that not only affects odour emissions but also bird health, comfort and welfare. Strategies to reduce the occurrence of wet litter are likely to have many benefits.

#### 2.6.1 Specific findings from the literature

- Bedding materials are not necessarily suitable or unsuitable, but each may require specific management.
- The properties of bedding materials may be enduring through a grow-out, but in general the addition of manure substantially changes the litter properties.
- Some of the challenges in researching litter conditions and odour emissions include:
  - broad range of fresh bedding materials
  - spatial variability and non-homogeneity
  - temporal trends
  - difficulties in measuring representative odour emission rates from meat chicken sheds and/or directly from the litter surface
  - difficulties in collecting, storing and analysing complex odour mixtures.
- Maintaining litter friability is a key objective for avoiding wet litter, promoting rapid drying and preventing the formation of low odour threshold odorants. This is most

productively achieved by birds 'working' the litter bit may also be achieved by conditioning the litter with machinery.

- An effective ventilation system is crucial for litter management and reducing odour emissions.
- A substantial quantity of water is added to the litter daily due to bird excretion and from 'normal' drinker spillage. The estimates available in the literature are from overseas production systems where stocking densities and grow-out durations differ from Australian production.
- Microbiological activity is responsible for the production of many odorants.
- Litter conditions regulate microbial growth in the litter, which affects odour formation.
- Water activity (A<sub>w</sub>) is closely related to microbial, chemical and physical properties of litter. Lower A<sub>w</sub> occurs with reused litter and has been found to play a role in microbial dynamics in the litter.

#### 2.6.2 Research opportunities

- Opportunities exist to improve understanding of odour formation processes and emissions from litter. Research is required to specifically identify and quantify the emission rate of odorants from litter with known physical conditions and history.
- Research is required to relate the evaporation of water with odour emissions, and considering the effects of air speed, temperature, relative humidity (i.e. the factors normally considered to control evaporation rate).
- There is need for a method to estimate the amount of water added to litter from bird excretion and drinking spillage in Australian meat chicken sheds—to improve understanding about how much water needs to be evaporated daily during a grow-out. This may be important for relating to odour emissions.
- More thorough investigation of water activity in litter is required to improve understanding of how litter properties affect water activity and vice-versa.
- Odour from fresh excreta are not well understood and yet may be an important odour source.
- Research is required to develop practical litter management techniques that maintain dry and friable litter, which is likely to minimise odour emissions and reduce the potential for odour impacts.

### Chapter 3. Water additions to litter from excreta and normal drinking spillage

#### 3.1 Introduction

Water is routinely added to the litter on every day of a grow-out from excretion and spillage from drinkers. Collett (2012) estimated that a flock of 20,000 birds can excrete up to 2500 L of water per day onto the litter. This quantity of water is relevant for the later stages of a grow-out, but is not applicable to the early stages of a grow-out when ventilation rates and therefore evaporation rates are substantially lower. Managing litter moisture content is necessary on every day of a grow-out and therefore a method is required to estimate how much water is added to the litter on every day.

This chapter outlines a method that was developed to calculate the amount of water being added to the litter on every day of a grow-out.

# 3.2 Calculating litter wetting due to excretion and normal drinking spillage

Daily water additions to litter from bird excretion and normal drinking spillage were calculated using an equation that drew on empirically derived relationships between feed intake, water usage and water losses (exhaled moisture and excretion) for commercial meat chickens (Eq. 1). The calculation includes water inputs ( $w_{drinking}$ ,  $w_{feed}$  and  $w_{metabolic}$ ), retention ( $w_{growth}$ ) and evaporation losses ( $w_{latent}$ ) from each bird plus adjustments to account for stocking density, percentage of shed in use (relevant for part-shed brooding) and percentage of the flock remaining in the shed (relevant for when a percentage of the flock is harvested for slaughter during the grow-out). Water applied to litter was calculated on a square metre ( $m^2$ ) basis (assuming a litter depth of 5 cm) to enable direct comparison of water addition to litter, storage within litter and evaporation from litter (Chapter 4). Using this equation requires assumptions that the birds are healthy, have an optimal diet, are evenly distributed across the floor of the shed and are in a thermo-neutral environment.

$$w_{litter} = \frac{\left(w_{drinking} + w_{feed} + w_{metabolic} - w_{growth} - w_{latent}\right) \times \rho_{stocking} \times f_{remaining}}{P_{shed}}$$
Eq. 1

Where:

*w<sub>litter</sub>* is the water applied to litter through bird excretion and normal drinking spillage (L/day/m<sup>2</sup>)

*w*<sub>drinking</sub> is the water used in the shed for drinking (including spillage) by each bird (L/bird/day) (Eq. 4)

- *w<sub>feed</sub>* is the water ingested by birds in the feed (L/bird/day) (assumed that feed has 10% moisture content, 100g/kg 'as-fed' feed)
- *w<sub>metabolic</sub>* is the water released during metabolism and available for excretion (L/bird/day) (Eq. 5)

 $w_{growth}$  is the amount of water retained by the birds (L/bird/day) (assumed water accounts for 70% of daily growth)

*w*<sub>latent</sub> is the water evaporated from the bird during thermo-regulation (i.e panting and losses through the skin) (L/bird/day) — under thermo neutral conditions this is assumed to be half of total available water:

 $W_{latent} = 0.5 \times (W_{drinking} + W_{feed} + W_{metabolic} - W_{growth})$ 

 $\rho_{\text{stocking}}$  is the stocking density for the entire shed floor area (birds/m<sup>2</sup>)

P<sub>shed</sub> is the percentage of the shed in use in the case of part-shed brooding (%)

fremaining is the percentage of flock remaining after each thinning (%)

The following production values were used in this study. These values are commonly used on in Australian meat chicken farms, but any reasonable production values can be used in the calculations. Stocking density used in this example was 17 birds/m<sup>2</sup>, with allowable maximum live mass density limited to 36 kg/m<sup>2</sup>. The stocking density was varied during the grow-out to accommodate partial shed brooding and thinning. Partial-shed brooding in this example included using only 50% of the shed for days 1–6 of the grow-out, 66% of the shed for days 7–10 and 75% of the shed was used for days 11–14. This study also included flock thinning (a production process where a portion of the flock is removed from the shed for slaughter) by removing 33% of the flock on day 35, and 33% of the remaining flock on day 46 to maintain live mass density under 36 kg/m<sup>2</sup>, with all birds removed for slaughter at the end of the grow-out on day 56. Feed consumption and growth rate data were averaged from as-hatched data for Ross 308 and Cobb500<sup>™</sup> breeds.

#### 3.2.1 Estimating daily water consumption

Water consumption was related to feed intake using the water:feed ratio over the course of a grow-out (*wfr*, total water used in drinker lines divided by total feed consumed). The water used in drinker lines inherently includes water consumed by the birds plus normal drinking spillage. This ratio is typically 1.8 L/kg but can vary from 1.5–2.0 L/kg (Collett, 2007; Feddes et al., 2002; Manning et al., 2007; Watkins and Tabler,
2009; Williams et al., 2013). The water:feed ratio increases with temperature (Manning et al., 2007), stocking density (Feddes et al., 2002) as well as certain dietary imbalances, feed ingredients and health issues (Collett, 2012). It is also affected by type of drinker, with nipple drinkers (without evaporation cups) producing the lowest ratio (Manning et al., 2007).

The water:feed intake ratio varies during a grow-out. Williams et al. (2013) measured water usage in commercial broiler shed using nipple drinker systems (combination of Lubing Systems, Cleveland, TN; and Cumberland Poultry Systems, Assumption, IL). Water intake measured in this way inherently includes normal drinking spillage. Williams et al. (2013) demonstrated that for days 7–42 of a grow-out, daily water:feed ratio (*wfr<sub>daily</sub>*, which is the amount of water used in drinking lines on a particular day divided by the mass of feed consumed on that day) reduced from 2.53 on day 10 to 1.73–1.83 after day 25 for 2010–2011 Cobb<sup>TM</sup> strain commercial flocks (Figure 23). The water:feed ratio did not show a clear trend prior to day 10, so in the current analysis it was assumed to have a constant value of 2.53. After 42 days, it was assumed that the water:feed ratio remained constant. This assumption was supported by water consumption data published by Watkins and Tabler (2009) when used in conjunction with published feed consumption data for the appropriate breed (Cobb500<sup>TM</sup>).



Figure 23. Subset of daily water:feed ratio ( $wfr_{daily}$ ) from Williams et al. (2013) for '2010–2011 flocks', multiplier (*m*) of grow-out used to calculate  $wfr_{daily}$ from the grow-out water:feed ratio (wfr), and predicted  $wfr_{daily}$ assuming wfr of 1.83 ( $r^2$ =0.94 for days 10–42).

To calculate the daily water:feed ratio, a relationship was established between the daily water:feed ratio and the grow-out water:feed ratio (Eq. 2), using a multiplier m (Eq. 3) based on data by Williams et al. (2013). This allows an appropriate grow-out water:feed ratio to be selected in anticipation of changes to growing conditions. The water:feed ratio for a grow-out is also affected by the batch length due to higher water:feed ratio at the beginning and a greater quantity of feed and water consumed during the later stages.

 $wfr_{daily} = wfr \times m$ Eq. 2Where:<br/>wfr\_{daily} is the daily water:feed ratio (L/kg)<br/>wfr is the grow-out water feed ratio (L/kg) for days 1–56<br/>m is the multiplier applied to the grow-out water:feed ratio to calculate the daily water:feed<br/>ratio (Eq. 3).Eq. 3For d < 9,<br/>m = 1.385Eq. 3For  $9 \le d < 32$ ,<br/> $m = -2.7226 \times 10^{-5} \times d^3 + 2.7500 \times 10^{-3} \times d^2 - 9.2711 \times 10^{-2} \times d + 2.0205$ 

For  $d \ge 32$ , m = 0.975

Where:

d is the day of the grow-out (days)

*m* is the multiplier applied the grow-out water:feed ratio to calculate the daily water:feed ratio that was derived from data in Williams et al. (2013).

Eq. 4

The amount of water consumed daily by each bird was calculated using readily available daily feed consumption per bird data for commercial breeds (Eq. 4).

 $W_{drinking} = Wfr_{daily} \times fc_{daily} W_{drinking} = wfr_{daily} \times fc_{daily}$ 

Where:

 $w_{drinking}$  is the water consumed by each bird (L/bird/day)  $wfr_{daily}$  is the daily water:feed ratio (L/kg) (from Eq. 2)  $fc_{daily}$  is the daily feed consumption (kg/bird/day)

### 3.2.2 Estimating water ingested with feed and released during metabolism

Feed contains approximately 10% moisture content (100 g/kg 'as-fed' feed) (Collett, 2012) therefore water ingested with feed was estimated using published daily feed consumption data.

In addition to water directly ingested in feed, metabolic water is released from the feed as it is metabolised by the bird. Metabolic water production (Eq. 5) is limited by diet formulation (33.44 g/MJ of dietary energy) (Collett, 2012). Dietary energy in feed for commercial broiler feeds is nominally 12.65–13.40 MJ/kg (Aviagen Inc., 2014b).

$$w_{metabolic} = \frac{33.44 \times E_{dietary} \times fc_{daily}}{1000}$$
 Eq. 5

Where:

 $w_{metabolic}$  is the water released during metabolism and available for excretion (L/bird/day)  $E_{dietary}$  is dietary energy of the feed (MJ)  $fc_{daily}$  is the daily feed consumption (kg/bird/day)

# 3.2.3 Estimating water retained during bird growth or evaporated for temperature regulation

Some of the water ingested by birds will not be available for excretion on the litter. It was assumed that water accounts for 70% of daily growth rate (Goldstein and Skadhauge, 2000) and was therefore not available for excretion.

Meat chickens also use water to regulate body temperature. They remove latent energy from their body by evaporating water through panting and passive losses through the skin (Collett, 2012; Yahav et al., 2004). Collett (2012) estimated that evaporative losses were approximately half of total water losses during thermo neutral conditions, leaving the other half to be excreted as liquid onto the litter. However, during times of heat stress, evaporation losses can account for as much as 80% of total water losses, leaving only 20% available for excretion as liquid. Commercial meat chickens housed in tunnel ventilated sheds are likely to be close to thermo-neutrality so it was assumed that 50% of total water losses would be excreted onto the litter.

# 3.2.4 The amount of water that meat chickens excrete or spill when drinking during a grow-out

The equations presented in this chapter (Eq. 1–Eq. 5) were included in a Microsoft Excel<sup>®</sup> spreadsheet (Appendix C) to simplify the calculation process and allow the effect of alternative input values to be explored. Figure 24 shows the daily rate of litter wetting due to bird excretion and normal drinking spillage calculated using Eq. 1 and the described model inputs. Daily water deposition ranged from 0.5 L/m<sup>2</sup> on day 1 to a maximum of 3.2 L/m<sup>2</sup> on day 35. Over the course of a 56 day grow-out the total quantity of water excreted onto the litter was 104 L/m<sup>2</sup>.





Figure 24. Daily and cumulative deposition of water to litter during a grow-out based on the following assumptions: feed consumption of as-hatched birds (averaged for Ross 308 and Cobb500<sup>™</sup> breeds); water:feed intake ratio for the grow-out was 1.80; 70% of growth rate was water retained in the bird; 50% of total water lost from the bird was excreted as liquid onto the litter; stocking density 17.0 birds/m<sup>2</sup>; birds restricted to 50% of shed floor area until day 6, 66% until day 10, 75% until day 14; 33% of birds harvested on day 35 with 33% of the remaining birds harvested on day 47 to maintain live weight density under 36 kg/m<sup>2</sup>.

Water deposition rates decreased after day 35 due to assumptions about thinning regimes. For the first 14 days of the grow-out, restriction of the flock into the brooding section of the shed, in addition to higher water:feed intake, increased the rate of water deposition. Interestingly, the daily water deposition rate on day 47 following the second thinning is similar to the water deposition rate on day 14 (1.7 L/m<sup>2</sup>/day compared to 1.6 L/m<sup>2</sup>/day) despite the live mass density being about twice as much (24 kg/m<sup>2</sup> on day 47 compared to 11 kg/m<sup>2</sup> on day 14). These results suggest that water deposition rates and litter water content should be considered with regard to daily ventilation requirements to ensure the water added daily to the litter is evaporated.

There are limited published examples of water excretion/spillage estimates for comparison. Collett (2012) estimated that a flock of 20,000 meat chickens excretes 2,500 L of water daily onto the litter at maximum density (assumed to be day 35 of the grow-out). In comparison, the method described in this study estimated 3,800 L of

water would be added to the litter. Bolan et al. (2010) estimated total manure production for 35 and 49 day old meat chickens to be 4 kg and 6 kg, respectively, with an assumption that moisture content of excreted manure is 90%. Using these values, the total water excreted up to 35 and 49 days is approximately 3.7 kg and 7.0 kg, respectively per bird, which is similar to our estimates (3.6 kg at day 35 and 5.5 kg at day 49). Discrepancies between our findings and previously published estimates of water deposition may be due to different assumptions in water and feed intake as well as water retention.

Assumptions about the ratio of total water lost from the bird as evaporation and excretion can have a strong influence on the amount of water excreted to litter. By assuming that 80% of water loss is through evaporation compared to 50%, water excreted to litter reduces by 60%. While a 50:50 ratio (evaporation:liquid) was assumed due to thermo neutral conditions within modern meat chicken sheds, it's more likely that this value will fluctuate daily and throughout the grow-out. Overall, the assumptions used in this study are likely to result in the maximum amount of water being excreted to the litter under normal growing conditions, but it is useful to highlight the quantity of water that can be applied to litter on a daily basis.

#### 3.3 Summary

The calculations described in this chapter allowed the amount of water added daily to the litter due to bird excretion and normal drinker spillage to be estimated. Assumptions were based on published values and statements, and the outputs compared reasonably well with published estimates of water excretion. Input values used in the calculations can readily be adjusted to accommodate local production parameters (breed, geographical location, climatic, seasonal, brood and flock thinning specifics) to more accurately estimate water application rates for their operational conditions.

It was identified in the literature review that water evaporation rates can be related to odour emission rates. The next chapter describes an experiment to measure litter water holding capacity and evaporation rates of water from litter. The combination of water addition, storage and evaporation are important for understanding litter conditions and the relationship to odour emissions.

# Chapter 4. Water holding capacity, porosity and evaporation rate

# 4.1 Introduction

Understanding the relationships between water addition (Chapter 3), storage and evaporation throughout a grow-out will improve litter moisture management. Water is removed from litter by evaporation, which can be enhanced with ventilation and litter turning (Collett, 2012). Specific knowledge of evaporation rates from litter is important for managing litter moisture but can also be related to diffusion rates of gases such as ammonia and other odorants from litter. Evaporation of water has been found to be representative of the emission of gas-phase controlled volatile organic compounds (VOCs), which includes many of the odorants identified as contributing to odour impacts (Hudson and Ayoko, 2008b; Parker et al., 2013a; Parker et al., 2010a). The advantage of using water evaporation (water flux) instead of VOCs is the relative ease, low cost and accuracy of measuring water evaporation (Parker et al., 2013a).

The experiments described in this chapter were conducted to measure:

- how much water is able to be stored in litter;
- litter porosity; and
- the rate of water evaporation from litter.

Measurements were repeated on a regular basis during a grow-out to assess the impact of manure accumulation and litter structural changes. In this chapter, water quantities are expressed in units of litres of water per square metre of poultry shed floor area (L/m<sup>2</sup>) (assuming a litter depth of 5 cm), to enable comparison with water application rates (Chapter 3). (*Preliminary investigations that led to the experiments described in this chapter are summarised in Appendix D.*) The objective of this experiment was to see if the physical properties of litter were changing during a growout in ways that assist or hinder litter moisture management.

# 4.2 Methods and materials

#### 4.2.1 Farm description and litter collection

Litter samples were collected at weekly intervals from a tunnel ventilated shed (Table 5) stocked with 39,870 Ross 308 meat chickens. The shed had a floor area of 2,055 m<sup>2</sup> resulting in an initial stocking density of 19.4 birds/m<sup>2</sup>. Fresh pine shavings were used at the start of the batch to a depth of 5 cm. Part shed brooding was used, with day-old chicks being restricted to 50% of the floor area (the brooding section) before being allowed access to more of the shed.

Litter used for analysis was sub-sampled from the brooding section (so all litter collected on a sampling day had a similar opportunity for manure accumulation). Litter was collected from three trenches dug in the litter widthwise across the shed. Trenches were 75–100 mm wide and were equally spaced along the length of the brooding section. The length of each trench was half the shed width, extending from the centre of the shed to one side wall, which was randomly chosen. Litter from all three trenches was placed in a container where it was mixed with a shovel before the sub-sample was collected. Litter was transported in a sealed 20 L bucket for analysis.

Length	137 m
Width	15 m
Floor area	2055 m <sup>2</sup> (incl. brooding section 972 m <sup>2</sup> )
Wall and ceiling apex heights	2.75 m ( <i>walls)</i> , 4.38 m (ceiling apex)
Length of brood section	64.8 m (located in the rear of the shed)
Minivents	68, dimension 1.4 m long and 0.2 m high
Tunnel ventilation inlets	Rigid inward opening flap, 1.2 m high, 25 m long on each side of the shed
Fans	<u>Tunnel ventilation fans</u> 12, Hired Hand 1320 mm diameter, 750 W, fitted with discharge cone <u>Duty fans (one of each type installed near the tunnel</u> fans with the others installed on the front wall of the
	<u>snea)</u> 2, Munters EM50, 1270 mm, 750 W 2, Munters EM36, 915 mm, 370 W
Ventilation computer	Hired Hand Evolution 3000
Roof and wall materials	Metal-clad insulated panels
Floor	Compacted earth/clay
Drinkers	Lubing nipple drinkers with evap. cup
Feed	Big Dutchman feed pans

#### Table 5. Meat chicken shed dimensions and characteristics

#### 4.2.2 Measuring water holding capacity and porosity

AS 3743—2003 (Appendix B method) (Standards Australia, 2003) was used to determine the water holding capacity and porosity of litter samples. In brief, custom apparatus (Figure 25), as described in the Standard, was used comprising two pieces of PVC tube (internal diameter 8.7 cm, length 12.0 cm), one capped on the bottom and the second adapted so it could fit snugly over the top of the first piece (bottom tube and top tube, respectively). Drain holes were drilled in the bottom cap. The volume of the bottom tube was calibrated by filling the tube with water and gravimetrically determining the volume of water added. Litter was pre-conditioned to 45-55% moisture content and then poured into the top of the tube (both pieces joined together at this stage) until the top section was at least half full. The tubes and moistened litter were dropped 5 times from a height of 5 cm to settle the litter. The apparatus was soaked three times in a container of water so that the entire litter sample was completely submerged. The top section of tube and excess litter was carefully removed and the surface of litter levelled in the bottom tube. This was then lowered into water until water was level with the top surface of the litter and tube. The drain holes were blocked as the apparatus was removed from the water. Water was drained for up to 60 minutes into a pre-weighed container. The entire saturated litter sample was then poured into a pre-weighed sample dish and dried at 65 °C until it reached stable weight. Water holding capacity was calculated (Eq. 6) in units L/m<sup>2</sup>. Litter moisture content when saturated was also calculated. Porosity was calculated using Eq. 7.



Figure 25. Custom apparatus used to determine litter porosity: (*left*) top and bottom section; (*centre*) removing top section; (*right*) draining and collecting 'pore' water

Water holding capacity = 
$$\frac{(M_w - M_d) \times 50}{V}$$

Where:

Water *holding capacity* is the volume of water per square metre L/m<sup>2</sup> (assuming 1 L = 1 kg of water and 5 cm of litter depth)  $M_w$  is the mass of the saturated litter in the bottom tube (kg)  $M_d$  is the oven dry mass of the litter in the bottom tube (kg) V is the volume of the bottom tube (L) 50 is the volume of litter per square metre at 5 cm depth (L/m<sup>2</sup>)

Air filled porosity = 
$$\frac{V_{drained} \times 100}{V}$$

Where:

 $V_{drained}$  is the volume of water drained from the mix (L) V is the volume of the sample (the volume of the bottom tube) (L)

#### 4.2.3 Measuring evaporation rates

A custom method was developed to measure the evaporation rate of water from litter samples. The goal was to quantify the change in evaporation potential of litter during a grow-out (due to changes in manure content and litter structural change), with increasing litter moisture content, and increasing air speed. As such, the method involved placing litter samples with defined volume and surface area (3 repetitions each of 10%, 22.5%, 35%, 47.5% and 60% moisture content) in custom wind tunnels (described below; 1 tunnel each with wind speed 0.5, 1.0, 1.5 and 2.0 m/s) within a temperature and humidity controlled cabinet (model TRH-460-SD, Thermoline Scientific, Smithfield, Australia, temperature range 10-60±1.2 °C and relative humidity range 10–90% with 4% variability). The experimental procedure was repeated approximately weekly on progressively older litter samples (collected day 10, 17, 24, 31, 38, 45 and 52 of the grow-out). Testing was replicated (n=2) for each of these litter samples. Testing was also conducted using water to enable comparison between evaporation from a free water surface and litter (water was used as an experimental reference material). Jars of water were handled in the same manner as the litter samples and the testing was replicated (n=5). The temperature and humidity controlled cabinet provided reproducible testing conditions.

#### Custom wind tunnels for evaporation experiments

Custom wind tunnels (485 mm wide x 475 mm long x were 100 mm high) were constructed from galvanised sheet metal (Figure 26). Airflow was provided by five fans (92 mm diameter, maximum airflow 0.035 m<sup>3</sup>/s, Multicomp MC36332). Variable voltage power supplies (TENMA<sup>®</sup> model 72-10481, 0–30V) were used to control the rotational speed of the fans to change the airflow rate as required in the wind tunnels. Flow

Eq. 6

Eq. 7

straightening sections were installed on each end of the test-chamber section of the wind tunnels to reduce air turbulence and rotation (Figure 27). Sample jars were positioned using an evenly spaced grid. Each wind tunnel had a base section that enabled the top of sample jars to be aligned with the bottom of the wind tunnel. Sample jars were evenly spaced within the wind tunnel using a grid pattern.



Figure 26. Custom wind tunnel used to measure evaporation from litter (acrylic panels provide a view of inside)



Figure 27. Left - Flow straightening sections were used to improve airflow uniformity. *Right* - Smoke travelling through the custom wind tunnel. Lines visible at the front of the smoke demonstrate air flow uniformity

Different moisture contents (10%, 22.5%, 35%, 47.5% and 60%) were achieved by drying litter at 65 °C and then adding the required amount of water. After water was added, the samples were mixed, rested for 24 hours in a sealed container and then mixed again prior to testing.

Litter was placed into pre-weighed plastic sample jars (50 mm deep and 41 mm diameter). Jars were over-filled and then the side of the jar was tapped 5 times allowing

the litter to settle into the jar. Any excess was carefully scraped off the top, leaving the litter sample level with the top of the jar. Each jar was weighed and placed in a randomly determined position in the wind tunnels. Each wind tunnel contained three repetitions of all five moisture content samples.

Wind tunnels were placed into the temperature and humidity controlled cabinet Figure 28, which was pre-conditioned to the required test conditions (25 °C, 50% relative humidity). Power was then supplied to each wind tunnel simultaneously. After three hours of drying, each sample jar was re-weighed to determine the moisture loss. Moisture loss from each jar was adjusted to a daily average value for further calculations. Evaporation rates were calculated in terms of evaporation per square metre per day (L/m²/day).



Figure 28. Custom wind tunnels in the temperature and humidity controlled cabinet



Figure 29. Using water to evaluate the drying uniformity between wind tunnels (foam was used to prevent sloshing but was kept below the water surface during tests)

The rate of drying in each of the wind tunnels was investigated using water as the test material. Water was placed into the sample cups (Figure 29, *note:* foam was used to prevent sloshing and care was taken to ensure the foam was below the water surface during testing). Evaporation rates between the wind-tunnels was found to be similar and the assumption was made that this would transfer to the litter drying experiments.

#### 4.2.4 Data analysis

Data from the experiments to measure porosity and evaporation rates were analysed using double split-plot ANOVA tests with *Genstat* (VSN, 2016).

# 4.3 Results and discussion

#### 4.3.1 Litter water holding capacity and porosity during a grow-out

Figure 30 shows the moisture content at saturation, water holding capacity and porosity of litter during the grow-out as the proportion of manure to bedding material increased (data has been standardised for a constant volume and naturally the addition of manure during a grow-out will increase the total amount of litter). Moisture content at saturation (%) remained relatively constant (71–74%) during the grow-out, which is similar to previously reported values for wood shavings based litter (63–72%) (Bilgili et al., 2009; Miles et al., 2011b; Reed and McCartney, 1970). Despite the relatively constant moisture content at saturation, the litter on day 31 of the grow-out was able to hold approximately twice the amount of water as the same volume of fresh bedding. The discrepancy exists because the formula for calculating moisture content is sensitive to the increase in dry bulk density of the litter during a grow-out due to manure addition (Reed and McCartney, 1970).

Litter porosity reduced significantly (*P*<0.05) between sampling days 0, 10, 17, 25, 31 and 38 but there was no significant difference between days 38, 45 and 52 (Figure 30). It is suggested that the reduction in porosity during the grow-out was due to the accumulation of fine manure particles in the pore space between the coarser pine shavings. Diffusion of water vapour and other gases in and out of the litter through the pores may therefore be restricted later in the grow-out.



Figure 30. Moisture content at saturation, water holding capacity and porosity of litter throughout a grow-out (LSD bars show the least significant difference of means at 5% level

### 4.3.2 The amount of water contained within 1.0 m<sup>2</sup> of litter

A significant two way interaction between the length of a grow-out and litter moisture content was found to affect the amount of water contained within 1.0 m<sup>2</sup> of litter (*P*<0.001). Figure 31 shows that the amount of water contained within litter increased throughout the grow-out for the same litter moisture content. This suggests that the increased water holding capacity of the litter during the grow-out was due to the increasing manure:bedding ratio. There also appeared to be a trend in the water contained within 1.0 m<sup>2</sup> of litter to stabilise between days 31–38 of the grow-out (similar to the trend for water holding capacity in Figure 30), presumably because the manure content outweighed the water holding properties/ability of the original bedding material. To confirm this trend it would be necessary to measure the water content of litter re-used for multiple grow-out cycles. The observed trend of increasing water contained within 1.0 m<sup>2</sup> of litter during the grow-out was due to increased water holding ability of the litter material and not due to the increase in litter depth during a grow-out.



Figure 31. The volume of water contained within 1.0 m<sup>2</sup> of litter at different moisture content values throughout the grow-out assuming a litter depth of 5 cm. (LSD bar shows the least significant difference of means at 5% level)

The observed increase in water contained within 1.0 m<sup>2</sup> of litter is important because it can be related to how quickly the moisture content will change at different stages of a grow-out. Water application to the litter is largely independent of the litter material. If starting from the same moisture content, fresh bedding will reach a higher moisture content than litter later in the grow-out when the same quantity of water is applied. Conversely, when drying, more water will need to be evaporated from older litter than fresh bedding to achieve a similar reduction in moisture content (e.g. from 40% to 20%). In general, this might result in greater fluctuations in moisture content earlier in a grow-out.

There was a notable difference in the volume of water contained within 1.0 m<sup>2</sup> of litter depending on sample preparation methods. Water holding capacity (Figure 30) was determined by compacting the sample (as described in AS 3743—2003) whereas the volume of water contained within 1.0 m<sup>2</sup> of litter (L/m<sup>2</sup>) at various moisture content (%) (Figure 31) was determined with samples that were allowed to settle under their own weight ('compacted' versus 'settled', respectively). Maximum water holding capacity of compacted litter was found to be approximately 32 L/m<sup>2</sup> at 71% moisture content. Extrapolating the moisture content of settled litter to 71% produced a maximum water

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holding capacity of approximately 20 L/m<sup>2</sup>. It is hypothesised that the actual water holding capacity of poultry litter within a shed will be between these two values due to continuous and alternating actions of compaction and loosening by chickens walking, sitting and scratching the litter.

#### 4.3.3 Evaporation rate from litter

Significant two way interactions were found to affect evaporation rates of water from litter including: length of the grow-out × moisture content (P<0.001); air speed × moisture content (P<0.001); and length of grow-out × airspeed (P<0.05). Litter evaporation rate increased approximately linearly with moisture content (for all litter ages), linearly with air speed (for all litter ages) and also increased with the length of the grow-out. Figure 32 shows mean evaporation rate increase in evaporation rate with air speed (mean of all litter ages). The observed increase in evaporation rate with air speed (indicated by the slope of the lines) was greatest at high moisture content.





When litter was relatively dry (10% and 23% moisture content), evaporation rate remained similar as air speed was increased (from 0.5–2.0 m/s); however, at high moisture content (47% and 60%) air speed had a much greater effect on the evaporation rate. This result supports the use of higher ventilation air speeds in tunnel-

ventilated poultry sheds to accelerate the drying of litter if it becomes wet. Conversely, if litter is maintained in a drier state, there is reduced need for high ventilation air-speed to dry the litter, which may result in energy savings for chicken meat production. There may also be challenges in maintaining dry litter at the peak of the grow-out because evaporation rates from dry litter were found to be less than peak water application rates (water applied to litter at 3.2 L/m²/day and evaporated at less than 3.0 L/m²/day when litter moisture content was 23% and experimental air conditions were 25 °C and 50% relative humidity). Increasing evaporation rate from litter that contained more manure (measured by length of the grow-out) was presumed to be related to greater volume of water per square meter (L/m²) for the same numerical value of moisture content (Figure 31).

Only initial evaporation rates (first three hours of drying) were measured during this experiment because it was assumed that regular scratching and turning of the litter surface by bird activity would likely expose fresh litter surfaces that would exhibit the initial evaporation rate. In real production situations, litter is rarely homogeneous and wet excretion from the birds is applied to the litter surface. This wet excretion may or may not be incorporated into the litter but with a high moisture content is likely to have a high evaporation rate. Evaporation rates from litter with alternative values of litter moisture content, air speed, relative humidity and temperature can be calculated with a combination of theoretical and empirical equations (Section 4.3.3.1).

Evaporation of water has previously been related to the emission of certain gases and odorants (Parker et al., 2013a; Parker et al., 2010a). In this experiment, evaporation rates from litter were lower than from a free water surface (Figure 32), indicating that the litter material and pore structure provides some resistance to evaporation. Further research is required to determine whether the factors contributing to higher evaporation rates also contribute to higher gaseous emission rates, and how this may contribute to higher concentration of in-shed gases and/or increased potential for odour impacts to the surrounding community.

#### 4.3.3.1 Method to estimate the evaporation rate from litter and free water

Drying rates measured during the experiments need to be used in the context of how they were measured. Unique aerodynamic conditions within the drying apparatus are likely to be different to conditions in a commercial poultry shed. Because of this, water was used as a reference material for comparison and because it may allow future practitioners to measure free-water evaporation in poultry sheds and be able to apply a scaling factor to predict evaporation losses from litter.

Users of these equations should ensure they understand the conditions at which these measurements were made, and take these into consideration when using the following equations:

- Conditions were 25 °C and 50% relative humidity
- Samples had small surface area (13 cm<sup>2</sup>)
- Air flow was turbulent, velocity ranged from 0.5–2.0 m/s
- Evaporation losses were based on a 3 hour measurement period and scaled up to calculated daily losses
- Litter samples were undisturbed during the measurement period.
- Evaporation results were averaged from tests on litter of various age and manure content (litter collected on days 10, 17, 24, 31, 38, 45 and 52) of a grow-out. Evaporation rates tended to be higher for older litter (especially for higher moisture content), but the equations described below represent only the mean value for all litter ages.

Expanding the terms in Eq. 13 and making use of Eq. 8 or Eq. 10 to estimate evaporation rate from litter at 25°C and 50% relative humidity, produces a formula that enables prediction of evaporation from litter with any combination of temperature, relative humidity, litter moisture content and airspeed.

# Regression equation to estimate evaporation rates from litter using moisture content and air velocity

(Applies only when air conditions are 25 °C and 50% relative humidity)

Based on the data in Figure 32, Eq. 8 was derived to enable prediction of evaporation rates from litter and Eq. 9 was derived to enable prediction of evaporation rates from free-water samples (reference material of a free-water surface).

$E_{litter} = 0.1855 \ e^{(4.7683 \times M)} \times V + 7.0684 \times M - 0.1855$	Eq. 8
---	-------

	Ea 0
$E_{water} = 3.9084 \times V + 4.2520$	Eq. 9

#### Where:

*E* is evaporation rate (L/m<sup>2</sup>/day) at 25°C and 50% relative humidity *M* is litter moisture content (%, g/g, wet basis gravimetric moisture content) *V* is air velocity (m/s) *e* is exponential of the natural logarithm

Fitting values calculated from Eq. 8 and Eq. 9 to experimental data (mean of all litter ages, as presented in Figure 32) produced the following statistics.

- For Eq. 8: *n*=20, *r*<sup>2</sup> = 0.98, slope of 1:1 line = 1.09.
- For Eq. 9: *n*=4, *r*<sup>2</sup> = 1.00, slope of 1:1 line = 1.00.

#### Using free-water evaporation rate to predicting evaporation rate from litter

A relationship (Eq. 10) was found between the evaporation rate of free-water and litter, using a multiplier (W, Eq. 11), that enables the prediction of evaporation rate from litter of known moisture content if the free-water evaporation rate is known or can be measured. Figure 33 shows values of 'W' as calculated from experimental data (using the mean of all litter ages for each moisture content and air speed condition).



Figure 33. Multiplier (*W*) to calculate litter evaporation rates from free-water evaporation rate calculated from experimental data (mean of all litter ages).

#### $E_{litter} = W \times E_{water}$

Eq. 10

 $W = [-0.0608 \times (M - 0.022) \times V + 1.5975 \times M - 0.0671]$  Eq. 11

Where:

*E* is evaporation rate (L/m<sup>2</sup>/day) at 25°C and 50% relative humidity *M* is litter moisture content (%, g/g, wet basis gravimetric moisture content) *V* is air velocity (m/s) *W* is a multiplier to calculate litter evaporation from free-water evaporation rate

Fitting values calculated Eq. 10 to experimental data (mean of all litter ages, as presented in Figure 32) using experimentally measured free-water evaporation rates, produced the following statistics: n=20,  $r^2 = 0.98$ , slope of 1:1 line = 1.06.

#### Theoretical effects of temperature and relative humidity on evaporation

Evaporation rates theoretically increase when the drying airflow has greater capacity to hold water. Water holding capacity of the air increases when air temperature increases or when relative humidity decreases (assuming the other conditions are unchanged). This occurs due to a difference between the partial pressure of water vapour in air and the partial pressure of water vapour in air at saturation. Shah (2012) explained that evaporation rate from free-water can be predicted if air speed and the partial pressures of water vapour in air are known (specific for a set of temperature and humidity conditions) according to Eq. 12. Conditions investigated by Shah (2012) typically involved low air speed (*V*<0.15 m/s); however, the linear increase of evaporation rates observed in this investigation (Figure 32) suggest that Eq. 12 is likely to be applicable; however, empirically determined terms in the equation will be specific to the experimental apparatus/conditions.

$$E_{water} = C \times f(V \times (p_w - p_w))$$
 (Shah, 2012) Eq. 12  
Where:  
*E* is evaporation rate (L/m<sup>2</sup>/day) at room/test conditions  
*C* is a constant  
*V* is air velocity (m/s)  
 $p_w$  is the partial pressure of water vapour in air at saturation (Pa)

 $p_r$  is the partial pressure water vapour in air at room/test conditions (Pa)

In this investigation, the constant term  $\bigcirc$  and function of air speed (*V*) can be assumed not to change (because experimental apparatus and air speed are assumed to be constant and we've chosen to ignore air volume increases with temperature change). This leaves only the term ( $p_w - p_r$ ). Since all evaporation data, *E*, were measured at 25°C and 50% relative humidity, changes of evaporation rate with temperature and humidity can be estimated using Eq. 13 and a multiplier (*P*, Eq. 14). Partial pressure water vapour in air at room/test conditions ( $p_r$ ) can be calculated using  $p_w$  and relative humidity Eq. 15). Thus the term ( $p_w - p_r$ ) can be rearranged to include relative humidity (Eq. 16).

$E_{T,Rh} = E_{25°C,50\%} \times P$	Eq. 13
$P = \frac{(p_w - p_r)_{T,Rh}}{(p_w - p_r)_{25^{\circ}\text{C},50\%}}$	Eq. 14
$p_r = R \times p_w$	Eq. 15
$(p_w - p_r) = p_w (1 - R)$	Eq. 16

Where:

*E* is evaporation rate (L/m²/day)

P is a multiplier to estimate evaporation rate at different temperature and humidity  $p_w$  is the partial pressure of water vapour in air at saturation (Pa)

 $p_r$  is the partial pressure water vapour in air at room/test conditions (Pa)

*R* is the relative humidity at room/test conditions (%)

Subscripts:

T,Rh is at room/test conditions

 $_{\rm 25^{\circ}C,50\%}$  is at 25°C and 50% relative humidity.

At conditions of 25°C and 50% humidity, the term (pw - pr) produces a value of 1582.7 Pa

Partial pressure of water vapour in air at saturation ( $p_w$ ) can be estimated using Eq. 17 (Tang and Etzion, 2004).

 $p_w = 3385.5 \ e[-8.0929 + 0.97608(T + 42.607)^{0.5}]$  (Tang and Etzion, 2004) Eq. 17 Where:

 $p_w$  is the partial pressure of water vapour in air at saturation (Pa)

e is exponential of the natural logarithm

T is the room/test temperature (0 < T < 65°C, (Tang and Etzion, 2004))

Figure 34 shows values of multiplier (P) for selected air temperatures, to enable calculation of evaporation at air conditions other than 25°C and 50% relative humidity using Eq. 13.



Figure 34. Multiplier 'P', which can be used to scale evaporation rates measured at 25°C and 50% relative humidity to any environmental test condition.

#### 4.4 Summary

Litter properties and conditions change constantly within poultry sheds due to manure addition, water application and evaporation (Figure 35). Water holding capacity was found to increase from 15 L/m<sup>2</sup> for fresh pine shavings to just over 30 L/m<sup>2</sup> by day 31 of a grow-out. Conversely, air-filled porosity decreased during the grow-out as fine manure particles accumulated in the pore spaces between the bedding particles. It is suggested that this will increase resistance to gas and water vapour diffusion from deep in the litter profile.

Measuring litter properties to get realistic values can be challenging due to compressibility and varying density. Litter moisture content (%, gravimetric wet basis) is not a good measure of the amount of water stored in litter (L/m<sup>2</sup>) if comparing litter materials with different bulk density, such as when bedding materials or manure content differ. It has been demonstrated that the amount of water stored in litter increased during the grow-out even though the moisture content may be the same (Figure 31).



Figure 35. Graphical summary of the relationships between the amount of water in litter and the trends in water holding capacity, water application rates and evaporation during a grow-out

In Chapter 3, an equation was developed to estimate the amount of water applied to litter on a daily basis throughout a grow-out. This equation was used to show that water applied to the litter due to bird excretion and normal drinking spillage could be as much as 3.2 L/m<sup>2</sup>/day, with the total amount of water applied to the litter during a grow-out exceeding 100 L/m<sup>2</sup>. This is more than three times the water holding capacity of litter, highlighting the importance and necessity of daily evaporation of water from the litter. Litter moisture control early in the grow-out may be challenging due to high daily water:feed ratio, higher stocking density during brooding and use of fresh bedding materials, which have limited capacity to hold water. Recommended ventilation rates throughout the grow-out may require review to ensure that evaporation rates match water application rates at all stages of meat chicken production.

Experiments were conducted to measure evaporation rates from litter during a growout. Evaporation rates increased with litter moisture content and air speed. Poultry farm operators with tunnel ventilated sheds may be able to use this to their advantage if there is a need to rapidly dry-out wet litter. When daily moisture application rates are at their greatest, it may be challenging to maintain litter in a very dry state because evaporation rates from dry litter may be insufficient to remove the required amount of water.

Conditions that result in high evaporation rates may also result in high emission rates of certain gases and odours. Further research is required to investigate the relationship between water evaporation and gas emission rates from porous materials such as poultry litter.

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# Chapter 5. Water activity in poultry litter

## 5.1 Introduction

Water activity (A<sub>w</sub>) is considered to be a better measure of water in litter than moisture content since it is more closely related to microbial, chemical and physical properties of litter (van der Hoeven-Hangoor et al., 2014).

The purpose of the experiment described in this chapter was to explore the relationship between A<sub>w</sub> and moisture content of litter throughout a grow-out period. The relationship between A<sub>w</sub> and moisture content during a grow-out has implications for litter management, the microbial properties of poultry litter and the potential for environmental impacts with the formation of nuisance odours. These are relevant for making decisions regarding litter re-use for multiple grow-outs, setting targets for litter moisture content to minimise microbial risks and to ensure necessary litter physical conditions are maintained during a grow-out.

# 5.2 Materials and methods

#### 5.2.1 Farm description and collection of litter and bedding materials

Litter samples were collected in a previous experiments (Section 4.2.1). In brief, litter samples were collected from a commercial broiler shed that was stocked with Ross 308 meat chickens at a stocking density of 19.4 birds/m<sup>2</sup>. Pine shavings were used at the start of the grow-out at a depth of 5 cm. Litter samples were collected on days 0 (pine shavings), 10, 17, 24, 31, 38, 45 and 52 of a grow-out. Samples were stored at 4 °C until the end of the grow-out period.

Samples of bedding materials (not containing excreta) including hardwood sawdust, rice hulls and peanut shells were also tested and compared with pine shavings. These materials were stored in as-received condition until testing.

### 5.2.2 Sample preparation

A 0.5–1.0 L sample from each litter collection day and each bedding material was dried in an oven at 40 °C until a constant mass was reached. Each sample was then divided into seven sub-samples that were designated with a target moisture content value: 10.0, 16.3, 22.5, 28.8, 35.0, 47.5 and 60%. Target values were arbitrarily chosen to represent the normal range of litter moisture content found in meat chicken sheds. The required amount of water to achieve each target moisture content value was then added to each sub-sample, which were then mixed and sealed in individual containers for 24–48 hours prior to  $A_w$  analysis.

#### 5.2.3 Water activity analysis

A<sub>w</sub> was measured using an AquaLab<sup>®</sup> dewpoint water activity meter (model 4TE, Decagon Devices Inc., Pullman, WA, USA—measurement range 0.030–1.000 A<sub>w</sub>, accuracy ±0.003 A<sub>w</sub>, repeatability ±0.001 A<sub>w</sub>). The temperature controlled sample chamber was set to 25 °C. Between each A<sub>w</sub> measurement, dry activated charcoal was placed in the sample chamber to remove any residual moisture or volatiles.

Litter samples for each of the seven moisture contents from each of the eight sampling days were analysed in random order in triplicate. The experimental design (7×8×3) produced a total of n=168 measurements. Bedding material samples for each of the seven moisture contents for each of the four materials were analysed in random order in duplicate. The experimental design (7×4×2) produced a total of n=56 measurements. When each A<sub>w</sub> measurement was complete, the litter sample was placed in a preweighed tray and dried in an oven (model 8150, Contherm, Hutt City, New Zealand) at 65 °C to determine matching moisture content value for each A<sub>w</sub> value.

#### 5.2.4 Data analysis

#### 5.2.4.1 Non-linear regression analysis

The relationship between  $A_w$  and moisture content of bedding and litter materials was investigated using grouped non-linear (exponential) regression analysis with a grouping factor for bedding material or litter sampling day, respectively. *GenStat* 16<sup>th</sup> Edition (VSN, 2016) was used to fit the exponential function (Eq. 18). Significance of the grouping factor on curve parameterisation was assessed when *p*-values were less than 0.05.

$$A_w = A + B \times (R^m)$$

Eq. 18

Where:  $A_w$  is water activity m is litter moisture content A, B and R are parameters to be estimated.

#### 5.2.4.2 Application of the empirical 'Henderson' model

Theoretical and empirical models have previously been used to describe the relationship between A<sub>w</sub> and dry basis moisture content (Maia et al., 2011). (Note the use of *dry basis* moisture content in this section, where moisture content is calculated from the mass of water divided by the mass of the dry solids. Eq. 21 and Eq. 22 enable convertion between wet and dry basis.) One such empirical model, the 'Henderson model' (Henderson, 1952), has been used extensively to describe the water sorption behaviour of biological materials because of frequent high correlation with experimental data and small number of model parameters (Maia et al., 2011). The model is expressed in Eq. 19 or Eq. 20 depending on whether A<sub>w</sub> or moisture content is the subject, respectively.

$$A_w = 1 - e^{\left(-Tk(M^n)\right)}$$
 Eq. 19

$$M = \left[ \left( ln(1 - A_w) \right) / (-kT) \right]^{1/n}$$
 Eq. 20

Where:

 $A_w$  is water activity (expressed as a decimal) M is the equilibrium litter moisture content (dry basis) k and n are experimentally derived parameters T is the temperature (K) e is exponential of the natural logarithm (*In*).

1 /--

$M_d = M_w \div (1 - M_w)$	(ASABE, 2007)	
$M_w = M_d \div (1 + M_d)$	(ASABE, 2007)	Eq. 22

Where:

 $M_w$  is wet basis moisture content (mass of water divided by mass of moist litter)  $M_d$  is dry basis moisture content (mass of water divided by mass of oven dried litter)

To describe the relationship between moisture content and  $A_w$ , the Henderson model (Eq. 19) was fitted for each day separately using non-linear regression with no linear terms. An exponential curve was then fitted to the parameter estimates of *k* and *n* from the fitted Henderson models for each day, allowing these parameters to be estimated on any day of the grow-out.

### 5.3 Results and discussion

# 5.3.1 Exponential relationship between A<sub>w</sub> and moisture content for bedding materials

Exponential relationships between water activity (A<sub>w</sub>) and moisture content (%, wet basis) were observed for bedding materials with curves differing (P<0.01) among materials (Figure 36; R<sup>2</sup>=0.983; regression parameters provided in Table 6). A<sub>w</sub> increased from 0.70 to 1.00 as moisture content increased from 11 to 60%. The increase of A<sub>w</sub> as a function of moisture content was most rapid for rice hulls. Compared to equilibrium relative humidity (ERH) values published by Reed and McCartney (1970), our A<sub>w</sub> values for pine shavings and rice hulls were similar although our A<sub>w</sub> values for peanut shells appeared to be lower. This comparison was limited due to Reed and McCartney (1970) measuring ERH to a maximum of 93% (0.93 A<sub>w</sub>), which had corresponding litter moisture content of 16–19%.



Figure 36. Mean experimental values and exponential regression curves for bedding materials showing water activity (A<sub>w</sub>) as a function of moisture content (wet basis)

Materials	Regression parameters		
	Α	В	R
Bedding materials			
Pine Shavings	1.010E+00 ± 4.83E-03	-1.562E+00 ± 1.90E-01	3.040E-07 ± 3.23E-07
Hardwood sawdust	1.007E+00 ± 4.95E-03	-2.993E+00 ± 6.23E-01	2.270E-09 ± 4.04E-09
Peanut shells	1.000E+00 ± 5.00E-03	-2.206E+00 ± 3.42E-01	1.540E-08 ± 2.06E-08
Rice Hulls	1.002E+00 ± 4.81E-03	-3.180E+00 ± 1.21E+00	2.930E-11 ± 1.01E-10

Table 6.Regression analysis parameters (Eq. 18) for bedding materials (parameter<br/>value ± standard error (s.e.)).

All the bedding materials displayed high  $A_w$  (> 0.99) when moisture content was greater than 30%, but rice hulls exhibited higher  $A_w$  than the other bedding materials when moisture content was less than 25%. This may make rice hulls more prone to caking and supporting more microbial growth at the early stages of a grow-out. Further testing would be required to confirm whether the relatively higher  $A_w$  of rice hull continues during the grow-out when manure is added.

5.3.2 Exponential relationship between Aw and moisture content for litter

Exponential relationships were also evident between  $A_w$  and moisture content for litter samples (regression curves for selected days shown in Figure 37;  $R^2 = 0.989$ ; regression parameters provided in Table 7 and a method to estimate the regression parameters for litter on any day is provided in Section 5.3.2.1). Curves differed (P<0.001) among sampling days with  $A_w$  reaching an asymptote most rapidly (i.e. at the lowest moisture content) for the pine shavings (moisture content approx. 28%) and less rapidly (i.e. at higher moisture contents) as the grow-out progressed. In other words, there was general trend for  $A_w$  to decrease for the same value of moisture content as the grow-out progressed and the manure content in the litter increased (evident by the curves in Figure 37 shifting downwards and to the right as the number of days during the grow-out increased). This trend has relevance for microbial activity in the litter as well as the management of litter physical properties and moisture content.





Materials	Regression parameters		
	Α	В	R
	Litter collected	during grow-out	
Day 0 (Pine shavings)	1.010E+00 ± 3.47E-03	-1.562E+00 ± 1.36E-01	3.040E-07 ± 2.32E-07
Day 10	9.956E-01 ± 3.38E-03	-1.284E+00 ± 1.28E-01	5.890E-07 ± 5.09E-07
Day 17	9.899E-01 ± 3.36E-03	-1.241E+00 ± 1.23E-01	9.310E-07 ± 7.67E-07
Day 24	9.908E-01 ± 3.56E-03	-1.268E+00 ± 1.23E-01	1.740E-06 ± 1.34E-06
Day 31	9.901E-01 ± 3.91E-03	-9.872E-01 ± 7.15E-02	1.315E-05 ± 7.97E-06
Day 38	9.959E-01 ± 4.94E-03	-5.993E-01 ± 3.60E-02	2.840E-04 ± 1.56E-04
Day 45	9.888E-01 ± 4.00E-03	-1.010E+00 ± 7.35E-02	2.310E-05 ± 1.34E-05
Day 52	9.909E-01 ± 4.32E-03	-8.687E-01 ± 6.47E-02	5.860E-05 ± 3.41E-05

Table 7.Regression analysis parameters (Eq. 18) for litter<br/>(parameter value ± standard error (s.e.)).

One consequence of the trend for A<sub>w</sub> to decrease during a grow-out (Figure 37), is that litter later in the grow-out will absorb more water and equilibrate at higher moisture content for the same relative humidity (evident in Figure 37 by exchanging the name of the vertical axis from 'Water activity' to '[Equilibrium] relative humidity'). This phenomenon was most obvious at very high relative humidity, and litter moisture

content could be maintained below, for example 25%, if relative humidity at the litter surface remains below 92% (and assuming there are no other water inputs).

The curvilinear relationships observed in this study between A<sub>w</sub> and moisture content were similar to those reported by Bernhart and Fasina (2009) and Eriksson De Rezende et al. (2001); however, this study has demonstrated that the relationship changes during the grow-out. Bernhart and Fasina (2009) explained that the observed curvilinear relationship is typical for materials that absorb moisture by capillary forces and for materials that contain significant amounts of soluble components such as sugars and salts. A<sub>w</sub> measured in this study compared well with some published values (van der Hoeven-Hangoor et al., 2014), but was higher than others by about 0.05 Aw (Bernhart and Fasina, 2009; Carr et al., 1995; Eriksson De Rezende et al., 2001; Hayes et al., 2000). Differences observed between studies may be due to differences in the bedding materials, A<sub>w</sub> testing conditions (e.g. temperature), or due to some of the previously tested litter being used for multiple grow-outs. The possibility of measuring lower A<sub>w</sub> in previously used litter is supported by (Chinivasagam et al., 2012), who found that litter used for multiple grow-outs tended to have lower Aw compared to litter being used in its first grow-out (fresh bedding material used at the start of the first grow-out). This further supports our observation that  $A_w$  decreases over the course of a grow-out and also demonstrates that  $A_w$  is likely to be even lower when litter is used for multiple grow-outs.

# 5.3.2.1 Application of the exponential regression parameters for litter throughout a grow-out

This section describes the development of equations to predict the regression parameters, *A*, *B* and *R* (Table 6 and Table 7) for Eq. 18. The purpose of estimating the regression parameters is to enable prediction of  $A_w$  from litter moisture content for any moisture content on any day of a grow-out cycle (limited within the experimental conditions: 10–60% moisture content and Day 0 to Day 52 of a grow-out).

Following non-linear regression analysis to determine values for the parameters *A*, *B* and *R*, these parameters were plotted as a function of the days of the grow-out when litter was collected (Day 0, 10, 17, 24, 31, 45 and 52; *note:* Litter on Day 0 was fresh pine shavings that did not contain any manure; and Day 38 did not fit the relationship and was excluded from the regression analyses). Parameters *A* and *R* were found to

have curvilinear relationships with 'Day of the grow-out' (*d*) and *B* was found to have a linear relationship, Thus:

$A = 0.98968 + 0.0201 \times (0.87^{d})$	$(R^2 = 0.972)$	Eq. 23
$B = -1.4775 + 0.01185 \times d$	$(R^2 = 0.858)$	Eq. 24
$R = 0.00000111 + 0.000000141 \times (1.1222^{d})$	$(R^2 = 0.964)$	Eq. 25

Substituting these parameter estimates into Eq. 18 produced a model that provided strong fit to the mean experimental data (Figure 38): n = 56,  $R^2 = 0.983$ , standard error = 0.0122 A<sub>w</sub>.



Figure 38. Scatter graph of regression modelled water activity and mean experimental water activity of poultry litter

#### 5.3.3 Empirical 'Henderson' model Aw isotherms

The Henderson model (Eq. 19) described the relationships between  $A_w$  and moisture content for each day with  $R^2$  values ranging from 0.975 to 0.994 (Table 8, with selected model curves in Figure 39). The strong fit of the model to the experimental data in this study further supports the application of the model to a variety of biological/agricultural materials as previously demonstrated by Henderson (1952) and Maia et al. (2011).

Materials	Henderson model parameters		
	k	п	R²
Day 0 (Pine shavings)	$0.0438 \pm 0.0064$	1.1271 ± 0.0799	0.975
Day 10	0.0293 ± 0.0013	$0.9005 \pm 0.024$	0.994
Day 17	$0.0255 \pm 0.0018$	0.8397 ± 0.0411	0.980
Day 24	$0.0250 \pm 0.0015$	$0.8606 \pm 0.0348$	0.985
Day 31	$0.0202 \pm 0.0010$	$0.7539 \pm 0.0305$	0.983
Day 38	$0.0156 \pm 0.0006$	0.5764 ± 0.0223	0.984
Day 45	$0.0187 \pm 0.0008$	$0.7469 \pm 0.0283$	0.986
Day 52	0.0173 ± 0.0005	0.6918 ± 0.0200	0.991
Parameter estimation			
equations	k = 0.01727 +	$n = 0.6991 + 0.4173 \times$	<i>k</i> : 0.973
(where <i>d</i> is the day of	0.02613 × (0.9359 <sup>d</sup> )	(0.9434 <sup>a</sup> )	<i>n</i> : 0.928
the arow-out $(0 \le d \le 52)$			

Table 8.Henderson model (Eq. 19) parameters n and k for litter materials (parameter<br/>value  $\pm$  s.e.) and regression equations to estimate these parameters.



Figure 39. Mean experimental values and selected Henderson model curves (Days 0, 24 and 52) for poultry litter showing water activity (A<sub>w</sub>) as a function of moisture content (wet basis)

Parameter estimates for *k* and *n* decreased exponentially during the grow-out (Figure 40) with  $R^2 = 0.973$  and 0.928, respectively (Table 8), which implied that the litter properties did indeed change. (Day 38 data were excluded from the exponential regression analysis between the parameter estimates and day because it had a poor fit with these relationships. It was suspected that the litter sample collected on day 38 may not have been characteristic of the litter in the shed.)



Figure 40. Henderson parameters, *n* and *k*, measured and calculated values using equations in Table 8

The thermodynamic basis of the Henderson model enables the  $A_w$  isotherms to be estimated for other temperatures (Henderson, 1952). It is suggested that the parameter estimates developed in this study will allow the relationships between  $A_w$  and moisture content to be estimated for pine shavings based poultry litter at any stage of a grow-out and for different temperature conditions, although further testing is required to verify this.

#### Application of the Henderson model using parameter estimation equations

This section provides further description of the application of the Henderson model (Eq. 19) using the parameter (k and n) estimation equations (Table 8). Note that in the development of these equations, experimental data from Day 38 were excluded because this day did not fit the relationships observed with the remaining days.

Applying the Henderson model provided a strong fit to the mean experimental data (Figure 41): n = 56,  $R^2 = 0.988$ , standard error = 0.0101 A<sub>w</sub>.



### 5.4 Summary

Meat chickens raised on litter floors interact with their own waste products and therefore litter conditions need to be carefully managed to control the risks associated with this contact. A<sub>w</sub> is an important measure of litter properties, and is closely related to microbial activity, physical properties and in-shed relative humidity/litter moisture management. Greater focus should therefore be placed on measuring A<sub>w</sub> in addition to moisture content.



Figure 42. Graphical summary of water activity in litter

In this study, it has been shown that the relationships between relative humidity, litter moisture content and A<sub>w</sub> changes during a meat chicken grow-out (Figure 42). The relationship between moisture content and water activity was able to be described

using standard exponential regression analysis and through application of the Henderson model. In general, A<sub>w</sub> was greatest with fresh bedding materials and decreased during the grow-out with the addition of excreta and natural break-down of the organic materials. In the absence of measuring A<sub>w</sub>, the methods proposed in this chapter to estimate A<sub>w</sub> from moisture content should be considered.

Poultry excreta and litter naturally contain microbiota. Whilst most of these organisms are ubiquitous and essential in some aspects of poultry production, for example in the chickens' gastro-intestinal tract, once in the litter they contribute to odour production (Section 2.5.3) and increase risks to flock health, worker health and food safety. Aw growth limits for selected microbiota were compared against the Aw isotherms for fresh pine shavings and day 52 litter (Figure 43 and Figure 44). Lower Aw observed later in the grow-out may be beneficial for reducing growth of some microbial organisms (especially those with higher Aw limits), and that it may be less necessary to maintain very low litter moisture content at the start of a grow-out, compared to the end of the grow-out, in order to have the same Aw and respective microbial growth restriction. Further testing under field conditions is required to confirm this.






Figure 44. Water activity vs litter water content (L/m<sup>2</sup>)—Minimum water activity limits for growth of selected microbiota for fresh pine shavings and poultry litter collected on Day 52 of a grow-out— Microbiota include Campylobacter, E. coli, Salmonella, Clostridium, Staphylococcus and Aspergillus (Fontana, 2007; Taoukis and Richardson, 2007)

Maintaining low  $A_w$  (e.g. less than 0.85–0.91  $A_w$ ) in the poultry litter through active litter moisture management should:

- reduce microbial risks to flock health, worker health and food safety;
- reduce microbial odour production and the potential for nuisance odour impacts;
- assist in the transfer of water from excreta, which initially has high A<sub>w</sub> (0.96– 0.99 A<sub>w</sub>), into the litter, thus reducing the A<sub>w</sub> of excreta and the survival of gut-sourced bacteria in the litter; and
- reduce litter particle cohesion and prevent caking thus maintaining friable and free-flowing litter.

High  $A_w$  in fresh bedding materials provides a major challenge early in the grow-out with respect to microbial control. Using litter from the previous grow-out as bedding material at the start of a grow-out (i.e. reused litter) may provide some benefit from a  $A_w$  perspective, although other factors, such as ammonia, need to be considered.

# Chapter 6. Litter conditions—moisture content, pH, oxygen concentration and water activity

# 6.1 Introduction

Quantifying litter conditions was necessary before investigating the relationships between litter conditions and odour emissions. In this study, a variety of litter sampling techniques were used to quantify:

- the average or range of conditions within the meat chicken shed, both spatially and temporally
- the conditions at specific locations, including the change in conditions from the surface to the base of the litter profile.

Understanding the range of conditions in a shed is generally useful for describing the conditions throughout a meat chicken shed, but doesn't provide any specific values that can be related to the formation and emission of odorants (Section 2.5). A more detailed assessment of the litter conditions, especially surface conditions, was required.

During this investigation, litter conditions were quantified in meat chicken sheds and also in a laboratory based study, where birds were raised in a pen with a litter floor. In the laboratory study, stocking density and ventilation were different to the sheds and this contributed to some differences in litter conditions. The relationships between litter conditions and odour emissions are described in subsequent chapters.

# 6.2 Materials and methods

# 6.2.1 Litter collection from a meat chicken shed

Litter was collected from a meat chicken shed located in southeast Queensland (described in Section 4.2.1). Sampling methods were customised depending on the specific purpose for collecting the litter, which included quantifying:

- the range of moisture content within the shed
- spatial variation along the length of the shed
- changes in moisture content during a grow-out and across multiple grow-outs
- moisture content, pH and oxygen concentration through the litter profile, from the surface to the base of the litter (i.e. the shed floor) for a range of conditions.

The farm was comprise of five sheds that were all of similar design and construction (Table 5). All litter samples were collected from one shed during four grow-out periods (Table 9).

Grow- out	Period	Stocking number (# birds)	Stocking density (birds/m²)
А	19 April –12 June 2013	39150	19.05
В	25 June –19 August 2013	39960	19.45
С	28 August – 23 October 2013	39900	19.42
D	22 March –16 May 2014	39870	19.40

Table 9. Grow-out information and stocking den	sity
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During grow-outs A, B and D, litter was sub-sampled from trenches dug in the litter widthwise across the shed (described in Section 4.2.1). In summary, trenches were 75–100 mm wide and were half the shed width, extending from the centre of the shed to one side wall, which was randomly chosen. Trenches were spaced along the length of the shed (Table 10). Litter from trenches was placed in a container where it was mixed with a shovel before the sub-sample was collected. This type of sample was described as a 'mixture' or 'composite' litter sample. Along each trench, additional samples were collected and categorised according to the visual appearance of the litter surface, nominally 'wet' or 'dry and friable'. These additional samples provided extra detail about the range of litter moisture content throughout the shed. Litter was transported in sealed plastic bags and air-tight buckets for analysis.

During grow-out C, litter was only collected from specific locations using grab-sampling methods.

(Note: tunnel ventilation fans were 137 m from the front wall of the shed; brood curtain at 72 m						
Grow-out		A	В	D		
Sampling day	35	45, 52	15, 29, 43, 53	10, 17, 24, 31, 38, 45, 52		
<u>Trench</u>						
А	10.8	14.4	14.4	93.6		
В	32.4	43.2	43.2	108		
С	57.6	75.6	75.6	122.4		
D	79.2	100.8	100.8	(Note: Grow-out D litter only collected in brooding section, rear of the shed)		
Е	104.4	129.6	129.6			
F	129.6					

 
 Table 10.
 Position of litter sampling trenches within the meat chicken shed for growouts A, B and D (metres from the front shed wall)

#### **Bedding materials**

For Grow-out A, hardwood sawdust (*Eucalyptus spp.*) was used for bedding material at the start of the grow-out. During Grow-out B, hardwood sawdust (*Eucalyptus spp.*) was used for bedding material in most of the shed, but a small section of the shed floor was covered with different bedding materials, namely straw (lemongrass, finely cut and milled supplied by Animal Bedding Products, Tallebudgera Valley, Qld, Australia; provisional patent no. 2013904166) and pine shavings (Figure 45, *Pinus radiata*). During Grow-outs C and D, pine shavings (*Pinus radiata*) were used for bedding.



Figure 45. Small section of lemongrass straw and pine shavings bedding

# 6.2.1.1 Sub-sampling methods

Sub-samples of litter from each of the sampling trenches were sometimes combined to produce a 'shed average' litter sample. On other occasions, litter was collected by grab-sampling from particular locations because of the existence of a specific condition of interest (e.g. wet, cake or dry litter). The following sections describe some of the sample collection methods used.

# Sampling trenches

As described in Section 6.2.1, a trench (Figure 46) was dug in the litter widthways across the shed to facilitate collection of a mixed litter sample that represented 'average' litter conditions for that section of the shed. Where the litter was caked, a spade was used to make vertical cuts along the side of the trench. A trenching shovel was then used to excavate the material into a tub, where it was thoroughly mixed with the spade and then sub-sampled. Along the length of the trench, a grab-sample of 'dry friable' litter and 'wet' litter were also collected based on visual appearance and texture.



Figure 46. Sampling 'trench' use to collect litter samples (*left*); litter was mixed in a tub with a spade prior to sub-sampling (*right*)

#### Grab samples of dry and wet litter

Samples of dry and friable litter were collected using a hand-scoop. Samples were stored in a sealed plastic bag until required for analyses.

Samples of wet and caked litter needed to be cut from the litter using a sharp implement (Figure 47). Small samples of were able to be lifted out of the litter surface while medium-large samples required the surrounding litter to be removed to allow access (Figure 47).



Figure 47. Collecting small and medium sized cake samples. (*The caked surface and friable material underneath were distinctly different*)

A custom sample collection and transportation system was used to collect large samples of caked litter (Figure 48). This allowed caked litter, including the friable material underneath the cake, to be collected and transported back to the laboratory for analysis in a relatively undisturbed condition.



Figure 48. Collecting large cake sample in a custom sample tray (*left*), which was then sealed in a transportable box (*inset*) and transported to the laboratory for analysis (e.g. collecting odorants with using USEPA flux chamber) with minimal disturbance (*right*)

#### Sectioning the litter profile

Samples were collected from the surface, the bottom of the litter/cake or of the full litter profile (from surface to the floor) depending on the purpose for that sample. The friability of dry samples usually mean that they were well mixed from bird activity and layers within the litter were not well defined (Figure 49). To collect a sample from the base of the litter, the surface was first removed to prevent it from being mixed in.



Figure 49. Dry friable litter is well mixed from bird activity and layers are not well defined

Layers were more distinct in caked litter (Figure 50), allowing samples to be collected from the surface, middle and bottom of cake, and the friable material underneath the cake (Figure 51).



Figure 50. Layers of caked litter



Figure 51. Collecting litter samples from sections of the litter profile: Friable undercake material (*left*); bottom of the cake (*right*) from the sample in Figure 47; and the surface of the cake (*middle*) from the sample in Figure 48

# 6.2.2 Litter collection from a laboratory trial pen

A pen experiment was conducted within a laboratory setting at the University of New England (UNE, Armidale, NSW, Australia) to raise meat chickens in a pen to replicate conditions within a meat chicken shed but to provide greater opportunity to monitor and control litter conditions. This was to enable odour samples to be collected from the litter surface and related to the specific litter conditions. Litter was sampled from the specific

location where the odour samples were collected for the purposes of quantifying the moisture content, water activity, oxygen concentration and pH through the litter profile. The experiment commenced on 1 May 2015 when day-old chicks were placed in the pen and ended on 4 June 2015 when the birds were 34 days old. The experiment was approved by the UNE Animal Ethics Committee.

The pen (Figure 52) was 1.50 m wide and 3.05 m long (floor area 4.58 m<sup>2</sup>) and was stocked with 52, Ross 308 chickens (stocking density 11.35 birds/m<sup>2</sup>). At the start of the trial, the pen floor was covered with 50 mm of pine shavings (Hysorb, East Coast Woodshavings, Wacol, Australia).



Figure 52. Laboratory trial pen on day 13 (left) and day 34 (right) of the experiment

Feed and water were provided ad-libitum, with water supplied by nipple drinkers and feed provided in three phases: starter (0-10 d), grower (10-24 d) and finisher (24-35 d). All feeds were in crumble form to 10 d and in pellet form thereafter. The lighting program followed the recommendations for the breed (Aviagen Inc., 2014c).

Ventilation in the experimental room consisted of a wall-mounted exhaust fan that ran continuously. Air entered the room through a thermostatically controlled heat-exchanger that warmed the air as it entered the room. Additional heat was provided as required with by a portable electric heater and radiant heat lamps.

Litter conditions were measured approximately weekly on days 13–14, 19–20, 26–27 and 32–34. Litter samples were characterised as 'dry' or 'wet' by appearance, and further characterised as the 'surface' or 'base' of the litter profile.

Excreta samples were also collected including 'fresh' (collected immediately off the litter surface after being deposited by a bird) and 'aged' (particles that appeared to be excreta were selectively collected from the litter surface, but the length of time in the litter was unknown). The purpose of examining excreta samples was to quantify how excreta changed following contact with wet or dry litter compared to 'fresh' condition. Excreta collected from the dry friable litter was termed 'dry friable excreta'.

# 6.2.3 Methods to measure litter conditions

#### 6.2.3.1 Moisture content

Litter moisture content was determined gravimetrically (Eq. 26), after oven drying samples at 65 °C (model 8150, Contherm, Hutt City, New Zealand).Samples were weighed in aluminium trays with an analytical balance (model AB304-S, Mettler Toledo, Port Melbourne, Australia; or model AX324, OHAUS, Port Melbourne, Australia).

$$Moisture \ content = \frac{mass \ of \ water \ (kg)}{mass \ of \ water \ + mass \ of \ oven \ dried \ solids} \qquad \qquad \mathsf{Eq. 26}$$

# 6.2.3.2 рН

Litter and excreta pH was determined using a 1:10 solution with distilled water and pH electrode (model 90-P, TPS, Brendale, Australia; and model IJ44C electrode, IONODE, Tennyson, Australia). The 1:10 dilution was a modification of a published method using 1:5 dilution (Rayment and Lyons, 2011), due to high absorbency of litter materials there was inadequate solution for the pH electrode with 1:5 dilution.

Litter samples were not air dried prior to pH analysis (as is the method used for soil) and consequently some samples contained a significant amount of water (e.g. cake and excreta may contain 60–80% water by weight). Consequently, the amount of water in a sample was estimated, or determined by gravimetric moisture content analysis, prior to pH measurement (a fresh sample was used for the pH measurement and not the oven-dried sample used to determine moisture content).

#### 6.2.3.3 Litter temperature

Litter temperature was measured in the litter at the time of sample collection using a calibrated digital temperature probe (Figure 53, model DT2-1, Rototherm, UK, with 200 mm stainless steel stem). Qualitative surface temperature measurements were made with a thermal imaging camera (Figure 54) (Model F30S, NEC Avio Technologies, Japan). Thermal imagery was used to:

• observe spatial variability of litter surface temperature;

- observe temperature changes through the litter profile (by excavating the litter to expose the litter profile); and
- identify locations with non-uniform ventilation or cool spots where condensation or poor evaporation may affect litter conditions.



Figure 53. Using a thermometer to measure litter temperature



Figure 54. Example of a thermal image (*left*, including temperature scale) and comparable visible image (*right*). Note that the dark bedding was wet and this is why it was noticeably cooler than the pale coloured bedding

# 6.2.3.4 Air temperature and relative humidity

Air temperature and relative humidity were measured using a digital meter (VelociCalc model 9545, TSI Inc., Shoreview MN, USA).

Air temperature and relative humidity were recorded during Batch B at the commercial meat chicken farm and during the laboratory pen trial using data loggers (iButton model DS1923 Hygrochron for temperature and humidity; or DS1921 Thermochron for temperature only; Thermodata, Warnambol, Australia). These data loggers were installed either close to the litter to measure the air conditions above the litter, or outside the shed to measure ambient air conditions.

#### 6.2.3.5 Oxygen concentration

Oxygen (O<sub>2</sub>) concentration within the litter was measured using a portable fluorescence meter (Figure 55) (NeoFox-GT with 1.6 mm diameter FOXY-R oxygen Sensor Probe, Ocean Optics, Dunedin FL, USA).



Figure 55. Oxygen concentration measurement using a probe and accompanying temperature sensor in friable litter (*left*) and caked litter (*right*)

The oxygen sensor was calibrated before each use (two point calibration using ambient air with assumed 20.95%  $O_2$  and high purity Nitrogen with 0%  $O_2$ ). The probe was carefully inserted into the litter at a range of depths to measure changes in  $O_2$  concentration through the litter profile. Care was required to insert the probe without sidewards movement as this allowed air to penetrate the litter along with the probe, resulting in a false, high reading.

#### 6.2.3.6 Water activity

Water activity (A<sub>w</sub>) was measured using a water activity meter as described in Section 5.2.3. During the laboratory pen trial, the meter changed to an tuneable diode laser water activity meter (Figure 56) (AquaLab<sup>®</sup> model TDL, Decagon Devices Inc., Pullman, WA, USA—measurement range 0.030–1.000 A<sub>w</sub>, accuracy ±0.003 A<sub>w</sub>, repeatability ±0.001 A<sub>w</sub>).



Figure 56. Water activity meter showing the temperature controlled sample chamber (*right*) and a sample of friable litter)

#### 6.2.4 Statistical analysis

Table 11.

Moisture content and pH were initially analysed using linear mixed models (Patterson and Thompson, 1971), under the residual maximum likelihood (REML) framework in GenStat (VSN, 2016). The fixed effects were *Litter type, Sample type, Day* of the growout and '*Source*' (Table 11; *Litter types* and *Sample types* are defined in the following sections), and random effects were sheds and samples within sheds. The pronounced and significant interactions amongst these fixed effects led to the adoption of general linear models, with days being the continuous term and the discrete factors being the groups. Curvature of these relationships was tested using a second-degree polynomial for days, and where this was not-significant, the simpler linear form was adopted.

 Litter Type	Sample Type	Day (of the grow-ou
		•

Values use for fixed effects in REML analysis

Litter Type	Sample Type	Day (of the grow-out)	Source	
Mixture	Surface	0, 1,	shed	
Dry_friable	Base	9, 13, 14,		
Wet	Full profile	15, 17, 18, 19, 20,	pen	
Damp	Fresh	22, 24, 26,	(laboratory)	
Dry_cake	(excreta only)	29 ,31, 32, 33, 34, 35,		
Dry_friable_excreta		37, 38,		
Excreta		43, 45, 46		
		52, 53		

# Description of 'Litter Types'

<u>Mixture</u> (or '<u>Composite</u>') litter samples contained a mixture of wet and dry litter (including cake), collected in the sampling trenches or used to define the 'shed average'.

<u>Dry\_friable</u> litter was litter that visibly appeared to be dry and friable.

<u>Wet</u> litter was visibly wet and included both damp-friable litter or wet cake. Wet litter had greater than 40% moisture content; however, subsequent measurement of moisture content revealed that some of the *wet* samples had moisture content less than 40%, and these were re-classified as <u>damp</u>.

<u>Dry friable excreta</u> (Figure 57) was collected only during the laboratory pen trial. Sample of *dry\_friable\_excreta* were gathered by picking pieces of excreta out of the surface of *dry\_friable* litter. The exact length of time that this excreta was in the litter was unknown. The purpose of collecting these was to compare them with fresh *Excreta*.

<u>Excreta</u> (Figure 57) was collected only during the laboratory pen trial. Excreta was freshly deposited excreta, collected within 10 s of a bird excreting it onto the litter surface. Excreta was 'normal' in appearance.



Figure 57. Examples of *Excreta* and *Dry\_friable\_excreta* litter types used during data analysis.

# Description of 'Sample Types'

<u>Surface</u> samples were collected from close to the litter surface. For dry-friable samples, this meant the top 10–25 mm while for wet samples, that were usually caked, the surface was usually the top 5–10 mm.

<u>Base</u> samples were collected from the bottom of the litter profile. For dry friable samples, the surface layer was removed so that the bottom 10–25 mm of the litter could be collected. For wet (caked) samples, the surface cake was removed so that only the friable material underneath the cake was collected.

<u>Profile</u> samples were collected from grab-samples at specific locations. *Profile* samples were collected from the surface of the litter to the base and then mixed thoroughly to produce a homogeneous sample.

<u>Fresh</u> (term only used for *Excreta* litter type) samples were collected from the litter surface within 10 s of the bird excreting it.

# 6.3 Results and discussion

# 6.3.1 Moisture content spatial variability during a grow-out

Litter sampling methods enabled the spatial variability of moisture content in the commercial shed to be quantified during grow-outs A, B and D. Methods rapidly evolved because the original approach, which was to measure just the average moisture within the shed, did not provide the desired detail with respect to the full range of litter moisture content.

The average litter moisture content in each litter sampling trenches/rows is presented for grow-outs A, B and D in Figure 58, Figure 59 and Figure 60 respectively for multiple sampling days during each grow-out. The range of litter moisture content in each sampling trench, measured from grab-samples of visibly wet or dry litter, is illustrated using whiskers in these figures. The average values for the trenches show that litter moisture content varied along the length of the shed and moisture content fluctuated during the grow-out period. The back half of the shed, which is used as the brooding section at the start of each grow-out (72–137 m from the front wall of the shed), tended to be drier than the front half of the shed. It is hypothesised that the front half of the shed may have been wetter due to uneven airflow and/or use of evaporative cooling. Litter moisture content during grow-out D (Figure 60) was only measured in the back half of the shed. The values presented for grow-out D should not be considered to be the average moisture content for the entire shed.

A wide range of moisture content was measured in each trench on each day. In many cases, there was both very wet (60% moisture content) and dry (20% moisture content) in each section of the shed simultaneously. This is an important consideration if attempting to relate litter moisture content to odour emissions because different odour formation and emission processes are likely to dominate depending on the moisture content and other related physical properties such as caking. It is suggested that this may result in greater emissions or a more complex mixture of odorant than if there was a single litter condition.



Figure 58. Average moisture content in sampling rows A-E during grow-out A (rows A-F during on day 35) (*note*: whiskers indicate range of moisture content from grab samples of visibly wet and dry litter)



Figure 59. Average moisture content in sampling rows A-E during grow-out B (*note*: whiskers indicate range of moisture content from grab samples of visibly wet and dry litter)



Figure 60. Average moisture content in sampling rows A-C during grow-out D, which were in the back half of the shed (72–137 m from the front wall) (note: whiskers indicate range of moisture content from grab samples of visibly wet and dry litter)

#### 6.3.2 Moisture content variability across grow-outs

The mean moisture content for the litter collected from the trenches on each sampling day was calculated for grow-outs A, B and D (Figure 61). There was a general trend for average moisture content to change over the course of each grow-out, increasing until days 30–45. Previous research has shown that the litter moisture content may decrease after the first pickup, which occurs on about day 35, due to the reduction in stocking density (Dunlop et al., 2010). A slight reduction in average moisture content of Double the first pickup.

The average litter moisture content was observed to be higher during grow-outs A and B compared to grow-out D; however, the litter moisture content in grow-out D was only measured in the brooding section in the back half of the shed, which tended to be drier than the front half of the shed (Figure 58 and Figure 59).

The whiskers in Figure 61 show that a wide range of litter moisture content existed in the shed simultaneously and during the grow-out. This is an important consideration regarding odour emissions as explained in the previous section. Reporting only the average litter moisture content across the whole shed would not provide sufficient detail regarding the range of litter conditions, especially the existence of wet litter.





# 6.3.3 Observations of oxygen, pH and moisture content through the litter profile

Moisture content, pH and oxygen concentration were measured down through the litter profile. Changes in oxygen concentration were measured by progressively inserting the oxygen probe into the litter. Insertion of the probe was occasionally hampered by the presence of large bedding particles and at times it was difficult to achieve a stable reading because sidewards movement on the probe during insertion widened the hole allowing oxygen to enter the litter alongside the probe. When this occurred, it was necessary to withdraw the probe and re-start the measurement.

The combination of measurements through the litter profile were undertaken in wet and dry litter during the laboratory pen trial (Figure 62 and Figure 63 respectively) and on limited occasions in litter during grow-out D (Figure 64). These examples highlight the changes in moisture content, pH and oxygen concentration through the litter profile. In general, there was minimal change through the litter profile with dry friable litter; however, large changes in moisture content, pH and oxygen concentration were consistently observed in wet, caked litter. Moisture content was often lower at the base of the litter and pH was lowest at the surface and increased down through the litter profile. Oxygen concentration changed rapidly in heavily caked litter decreasing as low as 1.5% within millimetres of the surface. Oxygen concentrations increased to approximately 8% in the friable bedding material beneath the cake, even when cake extended for several metres from the sampling location. (Normal atmospheric values for oxygen concentration are approximately 20.95%.)



Figure 62. Profile of wet litter in the laboratory pen showing values for moisture content (MC), pH and oxygen concentration (O<sub>2</sub>)



Figure 63. Profile of dry friable litter in the laboratory pen showing values for moisture content (MC), pH and oxygen concentration (O<sub>2</sub>)



Figure 64. Profile of wet, caked litter in the shed showing values for moisture content (MC), pH and oxygen concentration (O<sub>2</sub>)

Measuring moisture content, pH and oxygen concentration through the litter profile was repeated at approximately weekly intervals during the laboratory pen trial (Figure 65). In dry litter, minimal changes were observed from the surface to bottom of the litter profile; however, pH was observed to increase gradually during the grow-out, and increased slightly with depth in the litter profile. Wet litter on the other hand began to display changes as early as three weeks into the grow-out. Under the caked surface that was developing, pH increased markedly. During weeks four and five, oxygen concentration was noticeably reduced within and underneath the cake; pH dropped on the litter surface and increased toward the base of the litter.

The observed changes in oxygen concentration are important from an odour emission perspective because anaerobic/anoxic conditions are known to support bacterial species that release low odour threshold and offensive odorants (e.g. reduced sulfur compounds). The high pH base and low pH surface may also be important for ammonia emissions because the acidic surface of wet litter may prevent ammonia emissions, resulting in low ammonia emissions from wet, caked litter surfaces (Miles et al., 2011a; Miles et al., 2011c). However, upon drying of the cake, increasing pH may then enable the trapped ammonia to be released.



Figure 65. Profiles of oxygen concentration (%), moisture content (%) and pH from the surface to the base of dry friable and wet litter during the laboratory pen trial (*note:* error bars indicate the range of measurements)

#### 6.3.4 Moisture content and pH data from shed and laboratory pen trial

Moisture content and pH data from grow-outs and the laboratory pen trial were compiled into a dataset (Appendix E). Data from all sampling days was grouped according to *litter types* and *sample types* using boxplots (Figure 66; where the bottom of the box is the 25th percentile, the top of the box is the 75th percentile, the line in the box is the median value, the whiskers represent the full extent of the data in each category and '*n*' value is the number of data points).



Figure 66. Moisture content and pH summary for different litter types (data combined from grow-outs A–D and the laboratory pen trial).

Separate box plots display the data for the commercial shed (Figure 67) and laboratory pen trial (Figure 68) because some differences in the data were anticipated due to differences in stocking density and ventilation (leading to different temperature and humidity conditions at the litter surface, Appendix F). Additionally, not all sample types were collected from each source.



Figure 67. Moisture content and pH summary for different litter types a commercial meat chicken shed only (data combined from grow-outs A–D)



Figure 68. Moisture content and pH summary for different litter types (data from laboratory pen trial only)

The range of litter moisture content measured in the shed was comparable with a previous study (Dunlop et al. (2011), Figure A. 16 in Appendix E); however, litter in the laboratory pen had a wider range of moisture content, including dry litter that was drier and wet litter that was wetter than was measured in the previous study.

The boxplots in Figure 66 to Figure 68 display the following:

• The moisture content was distinctly different between *dry* and *wet* litter samples, but only because some of the *wet* litter samples were re-classified as *damp* using a cut-off value of 40% moisture content.

- The pH of the damp litter samples appeared to be distinctly different to the wet litter samples, especially during the laboratory pen trial, despite these litter types initially being considered similar (based on visual appearance at collection).
- In the laboratory pen trial, the dry litter samples tended to be drier and the wet litter samples tended to be wetter compared to the commercial shed.
- The pH of the dry litter in the laboratory pen trial appeared to be lower than the dry litter in the commercial shed. It is suggested that this may be due to less manure (because of lower stocking density) in the laboratory trial pen. The pH of fresh bedding (day 0–1 of a grow-out) materials tended to be low (4.7–5.4; Appendix E).
- The pH of dry litter tended to be similar throughout the litter profile, but in the commercial shed was slightly higher at the base of the litter.
- The pH on the surface of wet litter was lower than in dry friable litter. This difference was most obvious in the commercial shed where the pH of dry litter was slightly higher than in the laboratory pen trial.
- The pH on the surface of wet litter was distinctly lower (4.8–7.5) than at the base of the litter (6.9–8.8).
- Excreta had the highest moisture content; however, the dry-friable excreta collected from the dry litter was much lower (i.e. excreta dries out when deposited in dry litter).

# 6.3.5 Statistical analysis of moisture content and pH

# 6.3.5.1 Moisture content

The statistical analysis showed that the relationships between *litter type*, *sample type*, *day* of the grow-out and *source* (i.e. commercial shed vs laboratory pen) were complex and there were significant two-way interactions including:

- *Day* by *Source* (*P*<0.001)
- Litter type by Source (P<0.001)
- Litter type by Day (P=0.003)
- Litter type by Sample type (P=0.020)

Differences in mean moisture content between litter types were anticipated due to litter samples being grouped according to visual appearance, which is related to moisture content.

Figure 69 shows the trends of moisture content during the grow-out for each litter type, separated by source (commercial shed or laboratory pen). (Equations for the trend-lines are in Appendix G.) The data was separated because of significant interactions between

*Source* and *Litter* type as well as the interaction between *Source* and *Day*. The moisture content of litter in the laboratory pens generally increased during the grow-out, but this may be due to:

- 1. The shorter grow-out period in the laboratory pens magnifying the slope of the trend lines; and
- 2. The single batch nature of the laboratory trial litter that started in very dry condition and absorbed moisture during the trial. This is in contrast to the commercial grow-out shed bedding, some of which started in relatively damp condition.



Figure 69. All litter and excreta samples— trends for moisture content during a growout for different litter types (dry friable, damp, wet, composite/mixture, dry cake and excreta) (*note*: dotted trend lines are for the pen trial data) Conditions at the litter surface are of interest because it is a principal location for odour emission due and is where the birds having most direct contact with the litter. Dry friable litter and wet litter had distinctly different moisture content throughout the grow-outs in the commercial sheds and laboratory trial pen (Figure 70). The full range of litter moisture content is not adequately quantified when collecting 'composite' samples of the complete litter profile (Figure 71).







Figure 71. Litter samples (full litter profile average)—relationships between moisture content and day of the grow-out for different litter types

Fresh excreta had the highest moisture content (Figure 71) and therefore must undergo substantial drying, either by evaporation or water being absorbed by the surrounding litter, for it to equalise in terms of water activity and moisture content to reach the low moisture content of the excreta that was found mixed in with the dry friable litter (Figure 69). This substantial water loss needs to be considered with respect to the emission of water soluble odorants.

# 6.3.5.2 Litter pH

Litter pH is an important consideration for gaseous emissions. It has previously been reported that ammonia is emitted when pH is greater than seven (Miles et al., 2008), and there will be a tendency for the emission of sulfur compounds when pH is low (Barth et al., 1984).

Statistical analysis showed that the relationships between *litter type*, *sample type*, *day* of the grow-out and litter *source* were complex and there were significant three-way interactions including:

- Litter type by Sample type by Day (P=0.026)
- Litter type by Source by Day (P=0.004)

There were also two-way interactions that showed stronger significance:

- Litter type by Day (P<0.001)
- Litter type by Sample type (P<0.001)
- *Day* by *Source* (*P*<0.001)
- Sample type by Source (P=0.001)
- Litter type by Source (P=0.024)

There was a trend for wet litter to have lower pH than dry litter (Figure 72), especially in the last half of the grow-out:

- dry and damp litter had pH in the range of 6.5–8.0;
- wet litter had pH in the range of 5.0–6.0;
- dry cake had pH in the range of 8.0–8.8; and
- composite litter samples had a wide pH range of 5.5–8.5 during the grow-out.

The lowest pH of all of the litter samples was measured in the surface of wet litter (Figure 72, with the exception of some fresh bedding samples). Wet, heavily caked litter has previously been observed to have low pH (Miles et al., 2008). In Figure 72, data were separated by *Source* (shed vs laboratory pen) because of the involvement of

the significant three-way and two-way interactions. (Equations for the trend-lines are in Appendix G.)





Trends in litter pH varied by *Litter type* (i.e. wet or dry friable) and *Sample type* (i.e. surface, base or mixture). This was most obvious when comparing the surface and base of wet and dry friable litter. With dry friable litter, pH was either constant or increasing during the grow-out (Figure 73, *bottom*). In contrast, the pH of wet litter tended to be constant or increasing at the base of the litter profile, but decreased at the surface during the grow-out (Figure 73, *top*). The pH at the surface or wet litter was



even lower than the pH of the fresh excreta being deposited onto it, which suggests that the pH decreased due to the conditions within the litter.

Figure 73. Litter pH data for surface and base of the litter: Wet litter (*top*) and dry friable litter (*bottom*)

# 6.3.6 Water activity of excreta and litter in the laboratory pen trial

Water activity of bedding, litter and excreta samples was routinely measured during the laboratory pen trial. Earlier experiments (discussed in Chapter 4) demonstrated that the water activity of litter decreased (for the same moisture content) during a grow-out as more manure was added. Data collected from the laboratory pen were sorted by week

(Figure 74) but a distinct reduction in water activity over the course of the grow-out was not observed as expected. It was hypothesised that the spread of water activity values (for a constant value of moisture content) was due to the sampling practice of collecting surface, base and excreta samples rather than homogenous samples representative of the overall litter profile.



Figure 74. Water activity of bedding, litter and excreta during each week of the laboratory pen trial

Data was re-categorised as either 'bedding' or 'excreta and litter surface' (Figure 75). Bedding samples were collected from the base of the litter profile and contained little or no excreta. By comparison the litter surface samples contained most of the excreta in the litter profile. For samples with moderate moisture content (15–40%), the water activity of the bedding samples was distinctly higher than the excreta and litter surface samples. Whereas there was minimal difference in water activity in samples with very low and very high moisture content. It is suggested that one practical outcome from this observation is that application of the exponential or Henderson equations described in Sections 5.3.2 and 5.3.3 respectively, may require a practical litter age to be used (e.g. 0 days for litter that contains little to no excreta and 56 days for excreta or heavily soiled litter) rather than simply using the day of the grow-out that the litter was collected (e.g. day 0–56).



Figure 75. Water activity of bedding, litter and excreta samples sorted as either bedding (no excreta) or litter/excreta samples from the laboratory pen trial

# 6.4 Summary

Litter was categorised as dry friable, wet or damp as a means of relating these conditions to odour emissions (to be discussed in subsequent chapters). Litter moisture content, pH, oxygen concentration and water activity were measured in a commercial shed and in a laboratory trial pen. Relationships between these measures of litter condition were found to be complex with significant interactions between litter type (e.g. wet or dry), sample type (e.g. litter surface or base or homogenised samples), day of the grow-out and source (whether it was collected at a commercial meat chicken shed or in the laboratory pen).

Litter moisture content varied spatially within a meat chicken shed, through the litter profile, during a grow-out and across multiple grow-outs. Composite samples did not adequately represent the conditions from any specific location on the litter, for example where an odour sample may be collected. Wet and dry litter were found to co-exist simultaneously within the commercial chicken shed and laboratory trial pen. It is suggested that measuring odour emissions from both wet and dry litter surfaces will be required to adequately describe the total emission from the shed.

Differences between wet and dry litter are likely to affect odour emissions (Chapter 2). The following points require consideration when relating litter conditions to odour emissions:

- Litter conditions change spatially and within the litter profile, especially with wet litter.
- Oxygen concentration within caked litter is very low, supporting anaerobic/anoxic conditions potentially promoting the growth of specific bacterial species. Low oxygen concentration is also a sign of restricted gaseous exchange. In friable litter, diffusion of oxygen into the litter appears to be unrestricted.
- Wet, caked conditions have low pH conditions on the litter surface and high pH conditions at the base of the litter. Due to assumed low gaseous exchange through the cake, it is likely that the surface conditions will dominate the emission mechanism for odour release from the litter.
- The practice of litter conditioning, which mixes the litter profile, is likely to introduce oxygen and enable gas diffusion from the litter particles at the base of the litter profile. It is hypothesised that litter conditioning will accelerate the release of gasses that were trapped deep in the litter profile, resulting in temporarily increased emissions and perhaps more odorous compounds compared to the caked surface.
- Dry friable litter is well mixed and is assumed to provide minor restriction to gaseous emissions. Therefore conditions at the base of the litter are likely to contribute to odour emissions from the surface.
- Fresh excreta contains a high percentage of water and has correspondingly high water activity. Water losses by evaporation into the air or by diffusion into the litter are likely to be rapid compared to other, drier litter conditions. It is hypothesised that water soluble odorants may be transferred with this water. Excreta needs to be examined as an odour source.

# Chapter 7. Odorant emissions from litter in a meat chicken shed

# 7.1 Introduction

Formation and emission of odorants were expected to be affected by litter conditions (Section 2.5). In particular, water availability (i.e. moisture content and water activity), pH, porosity and oxygen concentration within the litter were expected to affect the bio-chemical formation of odorants as well as molecular diffusion of these within the litter pores and from the litter surface into the turbulent air above the litter. In Chapter 6, litter in a meat chicken shed was found to have with a variety of moisture content, pH, and oxygen concentrations. Litter conditions varied spatially within the shed, during a grow-out and within the litter profile. Wet and dry litter were found to co-exist within the shed, often very close to each other. Wet litter was characterised by a wet surface (>40% moisture content) that was often caked, compacted, anaerobic/anoxic and acidic (pH 4.8–6.5). Conversely, dry litter was characterised by a relatively dry surface (10–30% moisture content) that was friable, aerobic and slightly acidic to alkaline (pH 6.5–8.5).

The experimental activities described in this chapter were undertaken to characterise the effect of litter conditions on odorant emissions, especially wet versus dry litter. The highly variable nature of litter conditions required focussing on very small areas of litter with distinct litter characteristics that could be measured rather than larger areas of litter that were more likely to contain a range of different conditions.

Two investigations were undertaken. Firstly, litter was collected from a meat chicken shed and transported to a laboratory where odorants were collected using a flux hood and then characterised and quantified using instrumental methods. Secondly, odorants were collected from undisturbed litter surfaces inside a meat chicken shed using a flux hood and then transported to the laboratory. Litter conditions were characterised at the odorant sampling site.

# 7.2 Materials and methods

### 7.2.1 Odorant and litter samples

Litter was collected using either a sampling trench method or grab-sampling described previously (Section 6.2.1.1). Litter samples were categorised by type and when they were collected during a grow-out (Table 12).

1					
Litter type	Number of samples	Grow- out	Day of the grow- out	Week of the grow-out	Litter collection method
Composite	8	Α, Β	15, 19, 29, 34, 43, 47, 53, 54	3, 5, 8	Grab-sample
Dry friable	9	A, B, D	18, 29, 32, 34, 43, 46, 47, 53, 54	3, 5, 8	Grab-sample
Cake	10	A, B, D	15, 18, 29, 32, 34, 43, 46, 47, 53, 54	3, 5, 8	Trench
Under cake	6	Α, Β	29, 34, 43, 47, 53, 54	5, 8	Grab-sample
Lemongrass*	4	В	15, 29, 43, 53	3, 5, 8	Trench
Pine*	4	В	15, 29, 43, 53	3, 5, 8	Trench
Dry cake	1	D	46	8	Grab-sample
Moist friable	2	D	18, 32	3, 5	Grab-sample

 Table 12.
 Summary of sampling activities for the collection of litter from meat chicken sheds

\*note: these litter types covered only a small section of the shed floor (Figure 45)

Litter sampling and analysis methods were described in Chapter 6. During grow-outs A and B, 6 L of litter was collected in the shed, sealed in individual plastic bags (Figure 76), and transported overnight to the UNSW Odour Laboratory for odorant emission measurement. A portion of these litter samples were retained for moisture content and pH analysis. During grow-out D, litter grab-samples were collected for moisture content and pH analysis from the odorant sampling site immediately following odorant collection.


Figure 76. Litter samples were sealed in plastic bags for transport to the laboratory (*left*) and spread in a tray ready for odorant collection using a flux hood

#### 7.2.2 Odorant collection

Odorants were collected from the litter surface with a dynamic flux hood as previously described (Pillai et al., 2012b) and carried out at room temperature (20–25 °C). In summary, flux hood sampling was conducted according to AS/NZS 4323.4:2009. The flux hood used for this study covered a litter surface area of 0.126 m<sup>2</sup>. During grow-outs A and B, litter that was transported to the UNSW Odour Laboratory was placed in a tray and levelled immediately prior to the flux hood was placed on the surface (Figure 76 and Figure 77). During grow-out D, the flux hood was placed directly on the litter surface in the meat chicken shed and care was taken to minimise any disturbance of the litter surface (Figure 78). The flux hood was purged with high purity nitrogen gas (BOC Gases, Sydney, Australia) at ambient temperature for 25 min at a flow rate of 5 L/min. To minimise contamination and the adsorption of odorous substances on the sampling equipment, only Teflon tube lines and stainless steel connectors were used. Care was taken to prevent the entry of surrounding air into the flux hood by sealing the hood border with litter material.

Two different sampling approaches were employed sequentially to collect the odorants for analysis. Firstly, VOC samples were collected in duplicate via sorption into Tenax TA sorbent tubes (Markes International, UK) (Figure 79). All sorbent tubes were conditioned and verified contaminant free prior to use. Samples were collected at a constant flow rate of 100 mL/min for 10 min (1 L sample volume) using a calibrated air sampling pump (SKC Inc., USA). Following VOC collection, VSC (volatile sulfur compounds) samples were collected in duplicate into Nalophan sample bags (1 L) using a lung sampler at a rate of 1 L/min. All VSC samples were analysed within 24 h of collection to reduce potential compound loss due to transformation, permeation through the bag, or adsorption onto the bag surface (Le et al., 2015).

During grow-out D, gas samples from the flux hood were also collected for odour analysis using dilution olfactometry according to AS/NZS 4323.3:2001. These odour samples were collected in the same manner as the VSC samples with the exception of using 30 L Nalophan sample bags (Figure 79). Samples were collected for 10 min at a flow rate of 2 L/min.



Figure 77. Flux hoods used to measure odorant emissions from litter samples at the laboratory



Figure 78. Using a flux hood to collect odorant samples from the litter surface in a meat chicken shed



Figure 79. Collection of odorant samples: VOC samples collected into sorbent tubes (*left*); and VSC and odour (for olfactometry) samples collected into Nalophan bags (*right*)

### 7.2.3 Analysis of odorants

Sivret et al. (2016) previously described the analysis of VOC samples using TD-GC-MS and Wang et al. (2015) previously described the analysis of VSC samples using TD-GC-SCD techniques.

#### 7.2.3.1 VOC analysis

VOC samples were thermally desorbed using a Unity thermal desorber (Markes International, UK) coupled with an Ultra automatic sampler (Markes International, UK). A general purpose graphitised carbon analyte focussing cold trap (U-T11GPC-2S, Markes International, UK) was used to collect the sample prior to injection into a gas chromatograph equipped with a mass spectrometer detector (7890N GC and 5975MSD, Agilent Technologies, USA). A DB-VRX column (30 m×0.25 mm×1.4 µm, Agilent Technologies, USA) was used for compound separation in the gas chromatograph, with a 1.8 mL/min helium carrier gas flow. The gas chromatograph column temperature was held at 50 °C for 2 min and then increased at 15 °C/min to 220 °C where it was held for 3 min. The mass spectrometer was operated in continuous scan mode (35-335 m/z) to maximise the range of VOCs identified. NIST02 and NIST11 libraries were used for spectra matching and compound identification. Gas phase TO-17 standard (from Air Liquide) was used for calibration and quantification of some compounds, and all other compounds were quantified based on their peak area and a toluene calibration factor.

#### 7.2.3.2 VSC analysis

VSC samples were connected to an air server (CIA 8, Markes International, UK) with Nafion dryer and thermal desorber (TD) (Series 2, Markes International, UK) and preconcentrated onto a specialised sulfur cold trap (U-T6SUL, Markes International, UK) prior to injection into a gas chromatograph equipped with a sulfur chemiluminescence detector (SCD) (7890N GC and 355 Sulfur Chemiluminescence Detector, Agilent Technologies, USA). A DB-VRX column (30 m×0.25 mm×1.4 µm, Agilent Technologies, USA) was used for compound separation, with a 1 mL/min helium carrier gas flow. The gas chromatograph column temperature was held at 37 °C for 3 min and increased at 15 °C/min to a maximum temperature of 225 °C where it was held for 2 min. VSC standards were used to confirm the identity of the sulfur peaks generated via retention time matching and to develop calibration curves to provide quantitative data (Wang et al., 2015).

H<sub>2</sub>S concentrations were measured using a calibrated Jerome 631-X Hydrogen Sulfide Analyzer (Arizona Instrument, USA).

## 7.2.3.3 Ammonia analysis

Ammonia concentration was determined using a nitrogen chemiluminescence detector (NCD) (255 NCD, Agilent Technologies) coupled as the second detector to the same TD-GC system used for detection of sulfur compounds.

#### 7.2.4 Calculation of odorant emission rates

Area source flux emission rates for odorants were calculated according to AS/NZS 4323.4:2009 (Eq. 27). One modification included the adjustment of flow rates and gas concentrations to standard conditions 20 °C and 101.325 kPa (according to (ISO-10780, VDI-3880 & EN-13725) instead of 0 °C as required by the AS/NZS Standard.

$$E = \frac{C.Q}{A}$$
Where:  
*E* is the area source emission rate (ng/m<sup>2</sup>/s)  
*C* is the odorant concentration (µg/m<sup>2</sup>, equivalent to ng/L)  
*Q* is the sweep air flow rate (m<sup>3</sup>/s)

A is the area enclosed by the chamber (m<sup>2</sup>)

Where required, concentrations expressed in PPB were converted to  $\mu g/m^3$  (Eq. 28).

 $C = \frac{C_{PPB} \times MW}{(R \times T \div P)}$ Eq. 28 (USEPA, 2016) Where: *C* is the odorant concentration (µg/m<sup>2</sup>, equivalent to ng/L) *C*<sub>PPB</sub> is the odorant concentration (ppb) *MW* is the molecular weight of the odorant (g/mol) *R* is the universal gas constant (8.3144 L.kPa.mol<sup>-1</sup>.K<sup>-1</sup>) *T* is the air temperature (K) *P* is the air pressure (kPa) The term (*R* × *T* ÷ *P*) is approximately 24.05 at 20 °C

#### 7.2.5 Calculation of odour activity values

Single compound odour activity values (OAV) were calculated (Eq. 29) (Parker et al., 2012). Total OAV was also calculated for selected groups of litter samples (Eq. 30; all litter samples; dry friable; wet). OTV values were selected from a single published set where available (Nagata, 2003), which is an approach used previously (Sivret et al., 2016) and recommended for benchmarking purposes. Other published OTV were used as required (Appendix A).

Eq. 27

$$OAV = \frac{C}{OTV}$$

Where: OAV is the odour activity value of individual compounds C is the odorant concentration ( $\mu$ g/m<sup>3</sup>) OTV is single compound odour threshold value ( $\mu$ g/m<sup>3</sup>)

$$OAV_{litter} = \sum OAV = \sum \frac{C}{OTV}$$

Eq. 30 (Capelli et al., 2013b)

Where:

 $OAV_{litter}$  is the sum of individual compound OAVs for a particular litter type OAV is the odour activity value of individual compounds C is the odorant concentration ( $\mu$ g/m<sup>3</sup>) OTV is single compound odour threshold value ( $\mu$ g/m<sup>3</sup>)

#### 7.2.6 Data analysis

Data were analysed using an unbalanced analysis of variance in Genstat (VSN, 2016). The fixed effects were treatment (*Litter type*) and time (*Week* of sampling), with their interaction being tested and omitted if not significant. Adjusted means and standard errors from this analysis are presented. Where the residual distributions showed skewness and heterogeneous variances, the log<sub>10</sub>-transformation was adopted to correct for these.

## 7.3 Results and discussion

#### 7.3.1 Odorant emission rates

Flux hood sampling followed by TD-GC-MS and TD-GC-SCD analysis allowed the emission rate of 61 odorants to be quantified during the experiment across a range of different litter types and conditions (Appendix H). The mean and range of emission rates (ng/m<sup>2</sup>/s) of odorants were calculated for all litter types and then specifically for dry friable litter and caked litter (Table 13 and Table 14).

The majority of these compounds were only able to be quantified for a few of the 45 litter type/condition combinations due to low concentration or weak match with the MS library where 70% match was considered the minimum threshold (Table A. 6 in Appendix H). Quantification of volatile sulfur compounds using TD-GC-SCD provided consistent measurement for the majority of these targeted compounds (Table A. 7).

Compound name	All litter types	Dry friable litter	Caked (wet) litter
Odour concentration (ou/m <sup>2</sup> /s)	1.1 [0.7–1.6]	0.9 [0.7–1.2]	1.3 [1.1–1.6]
Acids/Esters			
Acetic acid	1801 [3.5–5484]	3904 [3904–3904]	1809.9 [3.5–5484]
Acetic acid, methyl ester	41.6 [11.1–72]		72 [72–72]
Propanoic acid	173.4 [21–512.6]	21.0 [21.0-21.0]	255.5 [77.4–512.6]
2-methyl-propanoic acid	14.2	14.2	
Ethyl acetate	5009 [7.1–18805]		6773 [7.1–18805]
n-Propyl acetate	312.2 [17.5–765.5]		385.9 [45.2–765.5]
Butanoic acid, methyl ester	432.6 [13.3–1457]		722.7 [84.4–1457]
Butanoic acid, ethyl ester	1262.4 [16.2–4721]		1823 [16.2–4721]
Acetic acid, 1-methylpropyl ester	313.8 [44.1–645.7]		381.2 [89.2–645.7]
Propanoic acid, propyl ester	75.5 [8.6–310.9]		168 [25.1–310.9]
3-methyl butanoic acid	63.9 [12.3–115.4]	12.3	115.4
2-methyl butanoic acid	15.6	15.6	
Benzoic Acid	8.6 [7.2–9.9]	7.2 [7.2–7.2]	
Butanoic acid	1350 [12–7057]	108.7	2288 [214.4–7057]
Butanoic acid, propyl ester	373.9 [5.8–2924]		754.8 [5.8–2924]
Butanoic acid, butyl ester	57.1 [7.9–212.4]		78.4 [9.1–212.4]
Butanoic acid, 1-methylpropyl ester	411.3 [11./-1//3]		6/3 [19./-1//3]
<u>Alcohols</u>			05 7
Ethanol	53.7 [21.7-85.7]		85.7
1-propanoi	298.3 [4.9–11/3]	42 4 [27 4 57 4]	296.3 [31.1-554]
2-Butanol	2248 [2.6-48950]	42.1 [27.1–57.1]	207 [4.8-519.4]
I-Butanoi	2429 [8.2-26383]		4668 [61.2-26383]
2-methyl-3-buten-2-ol	319.7 EE 6 [22, 101,4]		
3-methyl-1-butanol	55.0[22-101.4]	1170 [1170 1170]	
Aldobydos	02 [0.2-117.8]	117.8 [117.8–117.8]	
Acetone	92 2 [4 7–243 1]	88 3 [5 7–184 9]	60 6 [18 2–102 9]
2-Butanone	1765 [/ 8_10999]	128 3 [16 6-268 5]	261 4 [6 1-850 6]
2 3-Butanedione	369[3-1269]	14 7 [3-30]	11 6 [10 3–12 8]
3-methyl-butanal	462 5 [7 9–1810]	14.7 [5 50]	611 5 [7 9–1810]
2-Pentanone	454 1 [13 8-2400]	163 8 [13 8-323 6]	318 3
2-Butanone, 3-hydroxy-	84.9 [4.1–241.6]	122.9 [4.1-241.6]	9
3-hvdroxy-3-methyl-2-butanone	46.2 [23.2–69.2]	46.2 [23.2-69.2]	J
Benzaldehvde	7.8 [5.1–10.5]	7.8 [5.1–10.5]	
Acetophenone	39	39	
Nonanal	5.9 [1.8-12.1]	7.0 [1.8-12.1]	
1,3-diphenyl-2-propen-1-one	9.1	9.1	
Hydrocarbons			
Pentane	82.2 [9.2–157.6]	9.2	143.9
Toluene	145.8 [4.5–1280]	439 [13.2–1280]	152.4 [5.4–299.4]
Benzene	1185 [28.5–4252]	71.4	
2-methyl-pentane	214.3 [5.3–735.8]	31.2	735.8
3-methyl-pentane	55.5 [8.4–117.7]	8.4	117.7
Hexane	612.5 [6.2–3483]	55.1 [6.2–104]	24.7
α-Pinene	31.5 [2.4–140.5]	50.2 [2.4–109.4]	26.6 [8–45.2]
β-pinene	5.6 [1.3–14.5]	3.1	1.3
Limonene	13.1 [5.6–21.4]		21.4
Decane	222.8 [4.1–441.5]	441.5	
2,2,4,6,6-pentamethyl-heptane	8.7 [6–12.8]	9.4 [6–12.8]	
Hexadecane	9.4 [7.9–10.8]	10.8	
Nitrogen compounds			
Trimethylamine	54.4 [3.9–97.8]		3.9
Sulfur compounds			
Dimethyl sulfide	106 [1.8–403.7]	69.6 [2.2–162.7]	156 [27.2–356.9]
Carbon disulfide	65.2 [31.1–99.3]		99.3
Dimethyl disulfide	151.7 [1.9–1823]	245.9 [1.9–1823]	286.5 [3.6–1646]
Dimethyl trisulfide	25 [2.7–100.5]	2.7	100.5

# Table 13.Mean and range of emission rates for odorants (ng/m²/s) quantified using<br/>TC-GC-MS (mean [minimum-maximum])

Compound name	All litter types	Dry friable litter	Caked (wet) litter
Hydrogen sulfide	20.1 [7.5–39.7]	23.7 [14.1–39.7]	10.9 [7.5–14.3]
Methyl mercaptan	71.5 [1.8–808.3]	35.4 [7.8–77.5]	155.8 [1.8–808.3]
Carbonyl sulfide	1848 [14.6–23104]	297.4 [20.3–2126]	140.2 [38.4–328.9]
Ethyl mercaptan	27.3 [4–96.2]		54.8 [22–96.2]
Dimethyl sulfide	1057 [1.9–3473]	136.7 [1.9–481.6]	1591 [3.7–3473]
Carbon disulfide	50.3 [0.5–604.5]	6.4 [1.5–13.5]	160.2 [3.4–604.5]
Diethyl sulfide	2.3 [0.7–3.6]		2.2 [0.7–3.6]
Dimethyl disulfide	112.2 [0.6–780]	14 [2.4–31]	97.5 [0.6–489.4]
Diethyl disulfide	3.7 [0.7–9.8]	4.3	4.9 [0.7–9.8]
Dimethyl trisulfide	0.2 [0.01–1.2]	0.04 [0.02-0.08]	0.2 [0.02–0.6]

# Table 14.Mean and range of emission rates of volatile sulfur compounds (ng/m²/s)<br/>quantified using TC-GC-SCD (mean [minimum-maximum])

Odorant emission rate data was log<sub>10</sub>-transformed and statistical analysis showed that the main effects, *Litter type* and *Week* of the grow-out, were significant with respect to litter moisture content and pH as well as the emission rate of some of the odorants (Table 15). There were no significant two-way interactions between the main effects.

	Week	Litter Type
Litter moisture content	0.097	< 0.001 **
Litter pH	0.003 **	< 0.001 **
<b>•</b> • • • • • • • • • • • •		
Odorant emission rates (ng/m²/s)		
Odour (ou/m²/s)	0.722	0.464
Hydrogen sulfide	0.361	0.283
Methyl mercaptan	0.291	0.237
Acetone	0.174	0.069
Acetic acid	0.935	0.888
Carbonyl sulfide	0.291	< 0.001 **
n-Propanol	0.950	0.723
Dimethyl sulfide (TD-GC-MS)	0.631	0.331
Dimethyl sulfide (TD-GC-SCD)	0.008 **	0.005 **
Ethyl mercaptan	0.014 *	0.079
2-Butanone (MEK)	0.003 **	0.435
Propanoic Acid	0.780	0.164
1-Butanol	0.538	0.978
2-Butanol	0.023 *	0.163
Carbon disulfide	0.029 *	0.011 *
2,3-Butanedione (Diacetyl)	0.966	0.381
2-Pentanone	0.940	0.172
Ethyl acetate	0.035 *	0.490
Butanoic acid	0.658	0.243
Toluene	0.747	0.830
Dimethyl disulfide	0.069	0.138
Butanoic acid, ethyl ester	0.248	0.506
Dimethyl trisulfide	0.467	0.665
Alpha pinene	0.725	0.533
Butanoic acid, 1-methylpropyl ester	-	0.981

#### Table 15. P-values for the main effects Week and Litter Type

*Note:* \*\* indicates (*P*<0.01); \* indicates (*P*<0.05)

Litter moisture content and pH showed similar trends to those seen in Chapter 6 (Figure 80). In particular:

- there were no significant changes in moisture content over the course of the grow-out (*P*>0.05), which may have been because the bedding material was not dry when placed in the shed and stayed relatively wet during the grow-outs.
- Litter pH reduced over the course of the grow-out and was different by litter type (*P*<0.01, Table 16).</li>



• Litter moisture content differed by litter type (*P*<0.01, Table 16).

Figure 80. Litter moisture content and pH during the grow-out (whiskers show standard errors)

Odorants that were significantly different by *Week* included dimethyl sulfide, ethyl mercaptan, 2-butanone, 2-butanol, carbon disulfide and ethyl acetate. In general, these compounds increased during the grow-out with the exception of 2-butanol, which decreased. Emission rates were lower during week 5 for 2-butanol, ethyl acetate and ethyl mercaptan (Figure 81).



Figure 81. Mean odorant emission rates that varied by *Week* (*P*<0.05) (whiskers show standard errors)

Significant differences were observed between some of the litter types (Table 16). Of greatest interest was the difference between dry friable litter and cake, because these types of litter are common in meat chicken sheds and can be used to define differences in litter management and litter conditions. By comparison:

- 'Composite' litter was a product of the litter sampling process rather than being a native form of litter in meat chicken sheds. Composite litter may be representative of litter conditions following litter conditioning.
- 'Dry cake' is a native form of litter in meat chicken sheds but is a secondary litter product because before being dry cake it must have first been 'cake'.
- 'Lemongrass straw' and 'pine litter' were small sections of litter placed in a meat chicken shed and surrounded by hardwood bedding. Because the hardwood bedding was wetter and cooler, bird density on the lemongrass straw and pine litter were greater than the surrounding litter. For this reason, the odorant emissions from these litter types should not be considered representative.
- 'Damp friable' litter, while initially classified this way had similar moisture content and pH to dry friable litter and consequently odorant emission rates were similar.
- 'Under-cake' is a native form of litter in meat chicken sheds but is capped by cake which reduces the contribution of any odorant emissions to the shed odour.

Comparing just dry friable litter and cake (Table 16), moisture content and pH were significantly different (P<0.01). Emission rates of carbonyl sulfide, dimethyl sulfide, and carbon disulfide were significantly greater from cake than dry friable litter (P<0.05). In particular, dimethyl sulfide and carbon disulfide emission rates were 13 and 9 times greater from cake than dry friable litter respectively.

Odour emission rates were found to be not significantly different between litter types; however, mean emission rates from wet litter were 37% greater than dry friable litter (1.29 compared to 0.94 ou/m<sup>2</sup>/s respectively). The non-significant difference was also despite the significant increase in the emission rate of most volatile sulfur compounds. The disparity in significant differences with odorant and odour emission rates requires further investigation.

Some differences were observed between odorant emission rates for different litter types (Table 13 and Table 14) despite the lack of statistically significant differences. Dry friable litter had many esters and alcohol compounds that were not detected. Also, apart from one high value for carbonyl sulfide, the emission rates of sulfide compounds were much lower from dry friable litter than caked litter. Wet litter, on the other hand, had several aldehyde and hydrocarbon compounds that were not detected. These observations agree with a previous study by Woodbury et al. (2015), which reported greater emission rates of volatile fatty acids and hydrocarbons from dry manure conditions, and greater sulfide emission rates from wet manure conditions.

Some of the compounds that were absent in wet litter, or had only low values compared to dry friable litter, were compounds that have low water solubility, especially aldehydes (2,3-butanedione, nonanal, 2-methyl-3-buten-2-ol, 2-ethyl-1-hexanol) and hydrocarbons (hexadecane, decane,  $\alpha$ - and  $\beta$ -pinene, hexane). With higher water evaporation rates expected from wet/caked litter compare to dry litter (Figure 32 in Section 4.3.3), the relatively low emission rates of these compounds may be related to their low water solubility.

				Litte	er type				
	Cake	Composite	Dry cake	Dry friable	Lemongrass straw	Damp friable	Pine litter	Under cake	
Moisture content (%)	50.5 <sup>f</sup>	37.7 <sup>bde</sup>	24.2 <sup>ab</sup>	21.8ª	43.4 <sup>ef</sup>	24.8 <sup>abc</sup>	41.8 <sup>e</sup>	30.9 <sup>bcd</sup>	**
рН	6.25 <sup>a</sup>	6.10 <sup>a</sup>	8.41 <sup>b</sup>	7.48 <sup>b</sup>	6.22 <sup>a</sup>	7.80 <sup>b</sup>	6.56 <sup>a</sup>	7.81 <sup>b</sup>	**
Odorant emission rates (log <sub>10</sub> ng/m²/s)									
Odour (ou/m²/s)	1.29	—	0.78	0.94	_	1.17	—	_	
Hydrogen sulfide	1.02		1.43	1.33	—	1.37		—	
Methyl mercaptan	1.65	1.51	0.77	1.36	1.92	0.96	1.85	1.29	
Acetone	1.58 <sup>abcd</sup>	2.14 <sup>ca</sup>	0.45 <sup>a</sup>	1.55 <sup>∞</sup>	2.47ª	0.91 <sup>ab</sup>	2.12 <sup>bca</sup>	1.75 <sup>0ca</sup>	
Acetic acid					_		_		ىلەرلە
Carbonyl sulfide	2.06 <sup>ab</sup>	2.74 <sup>bc</sup>	1.17 <sup>a</sup>	1.73 <sup>a</sup>	3.45 <sup>c</sup>	1.59 <sup>a</sup>	3.49 <sup>c</sup>	2.32 <sup>ab</sup>	**
n-Propanol Dimethyl sulfide	2.32 2.00	2.00 1.84	_	 1.28	1.81 2.04	** 0.36	2.33 2.04	2.50 1.16	
Dimethyl sulfide (TD-GC-SCD)	2.60 <sup>c</sup>	2.75°	_	1.47 <sup>ab</sup>	3.16 <sup>c</sup>	1.14 <sup>a</sup>	2.90 <sup>c</sup>	2.56 <sup>ac</sup>	**
Ethyl mercaptan	—	—	—	—	—	—	—	_	
2-Butanone (MEK)	2.09	1.96	_	1.85	2.55	—	2.75	2.72	
Propanoic acid		—	_	_	—	—	_	_	
1-Butanol	2.67	2.80	_	_	2.79	—	2.93	3.07	
2-Butanol	1.86 <sup>ab</sup>	2.04 <sup>abc</sup>	_	1.37 <sup>ab</sup>	1.68 <sup>ab</sup>	1.08ª	3.21 <sup>ac</sup>	2.51 <sup>abc</sup>	
Carbon disulfide	1.64 <sup>e</sup>	1.04 <sup>abcd</sup>	_	0.68 <sup>ab</sup>	1.63 <sup>de</sup>	0.30 <sup>a</sup>	1.42 <sup>acde</sup>	0.74 <sup>abc</sup>	*
2,3-Butanedione	1.06	1.36	_	1.05	2.04	1.04	1.35	1.90	
2-Pentanone	—	—	_	_	—	_	_	_	
Butanoic acid		—	_	_	—	—	—	_	
Ethyl acetate	3.36	2.34	_	_	3.30	_	3.01	_	
Toluene	1.48	1.23	_	1.95	1.37	_	1.47	1.29	
Dimethyl disulfide	1.92 <sup>b</sup>	1.41 <sup>ab</sup>	0.20 <sup>a</sup>	1.33 <sup>ab</sup>	1.40 <sup>ab</sup>	0.49 <sup>ab</sup>	1.90 <sup>b</sup>	1.22 <sup>ab</sup>	
Butanoic acid, ethyl ester	2.88	2.15	_	_	2.75	—	1.90	_	
Dimethyl trisulfide	1.90	—	_	0.50	1.22	—	1.03	1.10	
Alpha pinene	1.65	—	0.05	1.42	0.19	1.74	1.11	0.71	
Butanoic acid, 1- methylpropyl ester	—	_	_	_	—	_	_	_	

#### Table 16. Litter properties and emission rates from different Litter types

*Note*: Means in the same rows with different superscripts differ (*P*<0.05) \*\* indicates (*P*<0.01); \* indicates (*P*<0.05) (refer to Table 15 for P-values)

#### 7.3.2 Odour activity values

Odour threshold values (OTV) and odour character descriptions were compiled for the odorants (Table 17). Litter samples were grouped into three categories: 'All litter samples', 'Dry friable' and 'Wet/caked'. Odour activity values (OAV) were calculated for individual odorants (Figure 82) using the average, minimum and maximum odorant concentrations (Table 13 and Table 14).

Compound name	Odour character	OTV (µg/m³)
Ethanol	pleasant, alcoholic	640 <sup>5</sup>
Acetone	solvent, nail polish	99800 <sup>4</sup>
Trimethylamine	fishy, ammonia	1.1 <sup>7</sup>
Acetic acid	Vinegar	892 <sup>9</sup>
1-propanol	pleasant, alcoholic	231 <sup>4</sup>
2-Butanone	sweet, minty, acetone-like	737 <sup>8</sup>
Pentane	petrol-like	4130 4
Acetic acid, methyl ester	fruity, solvent, sweet	13900 <sup>1</sup>
Propanoic acid	pungent, rancid, cheesy	108 <sup>9</sup>
2-Butanol	strong, sweet	667 <sup>4</sup>
1-Butanol	solvent, sweet, banana	1485 <sup>9</sup>
Benzene	petrol-like	4500 <sup>8</sup>
2,3-Butanedione	sour, butter, rancid	0.2 4
3-methyl-butanal	malt, apple, rancid	7.8 <sup>9</sup>
2-Pentanone	acetone-like	38000 <sup>1</sup>
2-methyl-pentane	petrol-like	24700 <sup>4</sup>
3-methyl-pentane	petrol-like	31400 4
Hexane	petrol-like	5290 <sup>4</sup>
2-methyl-propanoic acid	butter-fat, sharp	5.4 <sup>4</sup>
Ethyl acetate	ether-like, fruity, alcoholic	3135 4
Butanoic acid	rancid, unpleasant	0.7 4
3-methyl-1-butanol	disagreeable	161 <sup>9</sup>
Toluene	solvent, fruity	1240 <sup>4</sup>
n-Propyl acetate	mild, fruity, pears	1002 4
Butanoic acid, methyl ester	apple-like	20 <sup>3</sup>
3-methyl butanoic acid	unpleasant, rancid, chees, body-odour	0.3 4
2-methyl butanoic acid	irritant, stench	7.8 <sup>9</sup>
Benzaldehyde	almond, onion, burnt	12.1 <sup>8</sup>
Acetophenone	pungent orange/jasmine blossom	19.7 <sup>1</sup>
1-Hexanol, 2-ethyl-	mild, floral, rose	400 5
a-Pinene	pine, turpentine	100 4
β-pinene	turpentine, woody	65 <sup>6</sup>
Limonene	lemon	212 4
Nonanal	orange-rose, dusty, goat	2.5 <sup>2</sup>
Hydrogen sulfide	rotten eggs	0.58 4
Methyl mercaptan	rotten cabbage	0.14 4
Carbonyl sulfide	sulfide	135 <sup>4</sup>
Ethyl mercaptan	natural gas	0.02 4
Dimethyl sulfide	rotten eggs/vegetables	7.6 <sup>4</sup>
Carbon disulfide	rotten	654 <sup>4</sup>
Diethyl sulfide	garlic, foul	0.12 4
Dimethyl disulfide	putrit, rotten garlic, rubber	8.5 <sup>4</sup>
Dimethyl trisulfide	pungent, garlic, metallic, onion	6.2 <sup>8</sup>

#### Table 17. Odour threshold values (OTV) and character of selected odorants

<sup>1</sup>INRS (2005); <sup>2</sup>Godayol et al. (2011); <sup>3</sup>Leyris et al. (2005); <sup>4</sup>Nagata (2003); <sup>5</sup>O'Neill and Phillips (1992); <sup>6</sup>Parcsi (2010); <sup>7</sup>Rosenfeld and Suffet (2004); <sup>8</sup>Ruth (1986); <sup>9</sup>Schiffman et al. (2001)



Figure 82. Odour activity value (OAV) for selected individual odorants (whiskers show the data range)

Ten odorants with the highest OAVs were determined for each litter category (Table 18). Butanoic acid, methyl mercaptan, ethyl mercaptan and 2,3-butanedione had the highest OAVs across the three litter categories. From the top-10 ranked compounds, OAVs were higher for dry friable litter compared to wet litter with 2,3-butanedione, hydrogen sulfide, acetic acid, nonanal and 2-methyl propanoic acid.

Ranked OAV*	All litter	Dry friable litter	Caked/wet litter
1	Butanoic Acid	Methyl mercaptan	Butanoic Acid
2	Ethyl mercaptan	Butanoic Acid	Ethyl mercaptan
3	Methyl Mercaptan	2,3-Butanedione	Methyl mercaptan
4	2,3-Butanedione	Hydrogen sulfide	3-Methylbutanoic acid
5	3-Methylbutanoic acid	3-Methylbutanoic acid	Dimethyl sulfide
6	Dimethyl sulfide	Dimethyl disulfide	3-Methylbutanal
7	3-Methylbutanal	Dimethyl sulfide	2,3-Butanedione
8	Trimethylamine	Acetic acid	Butanoic acid, methyl ester
9	Hydrogen sulfide	Nonanal	Dimethyl disulfide
10	Butanoic acid, methyl ester	2-Methylpropanoic acid	Hydrogen sulfide

 Table 18.
 Individual odorant OAVs in descending order for all litter samples, dry friable

 litter and cake/wet litter

\*Rank 1 has highest OAV

The total odour activity value for the three litter categories was then calculated from the individual odorant OAVs (Figure 83). OAV for wet litter was over 10 times greater than for dry litter, which gives a strong indication that wet litter was more odorous and may represent a higher risk for odour impacts.



Figure 83. Total OAV for litter samples (sum of individual odorant OAVs; whiskers show the data range)

## 7.4 Summary

Odorant emissions were measured from litter surfaces using a flux hood. Emission rates tended to increase over the course of the grow-out for some odorants. This was expected due to the accumulation of manure in the litter. Moisture content was also found to increase during the grow-out although the increase was not significant.

Three volatile sulfur compounds, namely carbonyl sulfide, dimethyl sulfide, and carbon disulfide, had significantly greater emission rates from caked litter compared to dry friable litter. Of these, dimethyl sulfide had the greatest increase and the highest odour activity value. It is suggested that the acidic and anaerobic conditions in the litter surface (Chapter 6) contributed to the higher emission rates of sulfides from the wet/cake litter, based on similar findings in previous studies (Woodbury et al., 2015).

Odour activity value was calculated for each of the odorants and it was found that butanoic acid, methyl mercaptan, ethyl mercaptan and 2,3-butanedione had the highest OAVs. Highest contributing odorants to total OAV were different for dry and caked litter. Of the odorants with highest ranking OAVs, dimethyl sulfide, 2,3-butanedione and 3-methylbutanal were found by Murphy et al. (2014) to be amongst the principal odorants for predicting odour concentration from meat chicken shed emissions. In contrast, butanoic acid, methyl mercaptan, ethyl mercaptan had the highest OAVs in this study of emissions from litter but were not ranked highly by Murphy et al. (2014).

Caked litter had higher total OAV than dry friable litter, which indicated that caked litter would be more odorous; however, odour emission rates (ou/m<sup>2</sup>/s) were not significantly different between the litter types. It is hypothesised that this may be due to small sample numbers.

In general there were limited conclusive findings from this experiment. One hypothesis was that the wide range of litter types and conditions limited the number of emission rates measured for each. From a practical perspective, it was challenging to identify odour sampling sites on the litter in a meat chicken shed because the exact conditions in terms of moisture content, pH and porosity were unknown at the time of sampling. The history and stratification of the litter conditions are also important parameters that need to be considered (Koerkamp and Groenestein, 2008). It was recommended that a more focussed approach be adopted to measure odorants from fewer but more distinct litter conditions under controlled conditions to allow the history of the litter to be quantified.

# Chapter 8. Odorant emissions from litter in a laboratory pen

# 8.1 Introduction

The measurement of odorants from litter in a meat chicken shed showed that litter conditions affected the emission rate of several odorants, especially volatile sulfur compounds (Chapter 7). A broad range of litter conditions were encountered during that on-farm study. It was expected that including a range of litter conditions would deliver a broad understanding of odorant emissions; however, data analysis was limited because some of the litter conditions were encountered only a few times and there was low detection frequency for some of the odorants from the different litter conditions. This chapter describes a study that was undertaken to address some of these shortcomings. Additionally, a proton transfer reaction time-of-flight mass spectrometer (PTR-TofMS) was used to complement VOC and VSC emission measurements with TD-GC-MS and TD-GC-SCD analyses.

The study described in this chapter involved establishing a meat-chicken pen, complete with a litter floor, inside a room so that conditions could be controlled and to facilitate regular measurement of odorant emissions and litter conditions. The objective was to characterise the effect of litter conditions on odorant emissions, especially wet versus dry litter. Within the small pen, distinct wet and dry litter characteristics developed and these enabled odorant emission rates to be compared.

# 8.2 Materials and methods

### 8.2.1 Laboratory trial pen

The laboratory trial pen was previously described (Section 6.2.2). In brief, the pen (Figure 52) was 1.50 m wide and 3.05 m long (floor area 4.58 m<sup>2</sup>) and was designed to replicate conditions within a meat chicken shed. It was stocked with 52 Ross 308 chickens (stocking density 11.35 birds/m<sup>2</sup>). At the start of the trial, the concrete pen floor was covered with 50 mm of pine shavings (Hysorb, East Coast Woodshavings, Wacol, Australia). The experimental room was ventilated with a wall-mounted exhaust fan that ran continuously. Air entered the room through a thermostatically controlled heat-exchanger that warmed the air. Additional heat was provided as required with by a

portable electric heater and radiant heat lamps. The experiment was conducted for 35 days with the approval of the UNE Animal Ethics Committee.

#### 8.2.2 Litter sampling

Litter samples for odorant emission measurement were collected from the trial pen and transferred to another room where odorants samples were collected. The full litter depth (from the surface to the concrete laboratory floor) was transferred into a shallow tray with minimal disturbance (Figure 84) and then covered with aluminium foil before being transferred. The foil was used to reduce odorant compounds in the air outside the pen room from diffusing into the litter prior to measuring odorant emissions.



Figure 84. Litter being collected from the pen and placed in a shallow tray before being covered with aluminium foil and transferred to another room for odorant sampling

Litter samples were collected for determination of moisture content, pH and water activity as described (Section 6.2.2). Conditions at the surface, within cake and at the base of the litter were individually determined so that the full litter profile could be described. Oxygen concentration profiles were measured in-situ in the pen as previously described (Section 6.2.3.5).

### 8.2.3 Odorant collection

Odorant emission rates were measured using a customised flux hood (Figure 85), which was smaller than the flux hood previously described (Section 7.2.2, i.e. designed

and operated according to AS/NZS 4323.4:2009). Thus, emission rates between this laboratory-based experiment and the shed trial were unlikely to be directly comparable but it was assumed that relative differences between litter types would be comparable when using the same area source enclosure (Smith and Watts, 1994; Zhang et al., 2002a).



Figure 85. Custom flux hood used for odorant sampling in the laboratory pen trial. Interior view (*left*) shows the inlet tube around the circumference that has three evenly spaced holes (arrows) and sample outlet in the centre. Exterior view (*right*) showing inlet and outlet tubes plus vent (arrow)

The small customised flux hood enabled smaller litter samples to be used and also reduced the equilibration time between placing the hood on the litter surface and commencing odorant sampling. Dimensions for the customised flux hood are summarised in Table 19. High purity nitrogen (Grade 5.0, Coregas, Yennora, NSW, Australia) was used for sweep-air at a flow rate of 500 ml/min. Sweep-air flow rate was controlled using a mass-flow controller (Model MC-1SLPM-D/5M, ALICAT SCIENTIFIC, Tucson, AZ, USA) that was configured to measure the flow rate at standardised temperature and pressure conditions (25 °C, 101.3 kPa). Before placing on a litter sample, the flux hood was placed on a stainless steel plate (Figure 85) and continuously flushed with nitrogen until very low concentrations of odorants were detected with the PTR-Tof-MS.

	Customised flux hood	AS/NZS 4323.4:2009 hood
Material	Stainless steel	Stainless steel and polycarbonate
Diameter (mm)	119	400
Height (mm)	68	280
Volume (L)	0.68	30.1
Sample surface area (m <sup>2</sup> )	0.011	0.126
Inlet line	3.2 mm Teflon tube	6.35 mm Teflon tube
Sample outlet line	3.2 mm stainless steel tube	6.35 mm stainless steel tube
Vent opening	60 mm length, 3.18 mm Teflon tube	vent hole, 15.7 mm, (Kienbusch, 1986)
Sweep air flushing rate (L/min)	0.5	5.0
Sample flow rate (L/min)	0.10–0.15	2.5 (maximum)
Equilibration time (min)	5 (Minimum. When used in conjunction with PTR-TofMS, operator was able to see when odorant concentrations stabilised within the hood)	24
Number of flushes during stabilising	3.7	4.0

# Table 19. Dimensions of the customised flux hood and AS/NZS 4323.4:2009 flux hood (Section 7.2.2)

The customised flux hood was used for collection of all odorant samples for TD-GC-MS and TD-GC-SCD analysis as well as direct analysis with the PTR-TofMS (Figure 86). VOC and VSC sample collection was previously described (Section 7.2.2). Sorbent tubes were connected directly to the outlet tube of the flux hood using a stainless steel T-piece and VSC sample bags were connected to the flux hood using a 30 cm long, 1/8" OD Teflon sample line (Swagelok, Melbourne, Vic, Australia). The sample inlet line for the PTR-TofMS was connected directly to the flux hood sample outlet.



Figure 86. Customised flux hood on a litter sample to collect odorant samples for TD-GC-MS (*top*), TD-GC-SCD (*middle*) and PTR-TofMS (*bottom*)

## 8.2.3.1 Odorant collection from excreta

Fresh excreta required additional preparation (Figure 87) because the surface area of undisturbed excreta was difficult to define and yet was expected to affect the emission rate of odorants. Fresh excreta were levelled to a thickness of approximately 5 mm on an aluminium foil surface and the dimensions of the sample were measured. The flux hood was then placed over the sample to collect the odour sample.



Figure 87. Odorant collection from fresh excreta: (*top*) fresh excreta as sampled from the litter surface; (*middle*) excreta levelled and measured to determine surface area; and (*bottom*) flux chamber sampling odorants for PTR-TofMS analysis

It was recognised that spreading the excreta changed the physical dimensions and characteristics of the excreta sample; however, it was considered necessary in order to

estimate the surface area, which would have been impossible to measure for undisturbed excreta given the complex shape. Observations of the trial pen and evidence of smaller excreta particles surrounding the fresh excreta (Figure 87, *top*) led to a belief that the excreta would naturally be spread and broken into many pieces, in which case the surface area of the excreta would change dynamically in the litter.

During calculations of the emission rate from excreta, the surface area of the excreta was considered the emission surface area rather than the area covered by the flux hood. Applying the measured emission rates from excreta to the litter surface within a poultry shed requires care because fresh excreta does not typically cover the entire floor area.

#### 8.2.4 Odorant analysis with TD-GC-MS and TD-GC-SCD

VOC and VSC samples were analysed with TD-GC-MS and TD-GC-SCD respectively as previously described (Section 7.2.3).

#### 8.2.5 Odorant analysis with PTR-TofMS

A proton transfer reaction time-of-flight mass spectrometer (PTR-TofMS, TOF1000, lonicon Analytik, Innsbruck, Austria) was used to measure the concentration of VOCs in the flux hood in real-time. The operation of PTR-TofMS to quantify volatile compounds has been previously described (Brilli et al., 2014; Cappellin et al., 2012; Klein et al., 2016). In summary, the PTR-TofMS was comprised of ion source coupled with a drift tube and a time-of-flight mass spectrometer that has high mass resolution. VOCs were detected in real-time through proton transfer reactions occurring between H3O+ ions produced from water vapour within the ion source and the sample gas that was injected into the drift tube. Compounds must have a proton affinity greater than that of water (691 kJ mol<sup>-1</sup>) for these reactions to occur. Some compounds including hydrogen sulfide have proton affinity only slightly higher than water (712 kJ mol<sup>-1</sup>), which makes them difficult to measure by PTR-MS due to the back reactions between H3S+ and water (Yao and Feilberg, 2015).

PTR-TofMS uses mass selectivity to separate compounds. Therefore, any protonated compounds with the same m/z were unable to be individually quantified. Consequently, data from the PTR-TofMS was analysed in terms of molecular masses (hereafter referred to as 'masses'), for which 'possible' VOCs or odorants could be assigned (Appendix I). Fragmentation occurs for many compounds even though protonation with H3O+ is considered a soft ionization technique. Fragmentation patterns are dependent

on the specific conditions in the PTR-TofMS drift tube and therefore previously observed fragmentation patterns (Ionicon, 2008) may not be transferable due to different instrument configuration. Fragmentation patterns were not determined during this study.

Instrument software (TOF2.0, Ionicon Analytik, Innsbruck, Austria) controlled the operating conditions and recorded mass spectral data. The drift tube was operated under controlled conditions of pressure (2.3 mbar), voltage (600 V) and temperature (drift tube and heated inlet temperatures were initially 80 °C and 130 °C but were changed to 90 °C and 120 °C respectively after week 3 of the grow-out on advice from the manufacturer). The resulting E/N was about 135 Td (E being the electric field strength and N the gas number density (Brilli et al., 2014)). Following proton transfer reactions, protonated ions from the drift tube were focussed into the time-of-flight mass spectrometer where they were separated according to their m/z ratio before being detected with a multichannel plate (MCP) and time-to-digital converter (TDC). The sampling time resolution of the TofMS allowed compounds with m/z less than 195 to be detected. Average mass spectra data were recorded every 10 seconds. The operator collected data until real-time concentration data appeared to reach steady-state (Appendix J).

The mass resolution, as well as the mass accuracy and the relative transmission efficiency, were routinely verified using a TO-14A aromatics gas standard mixture (Linde SPECTRA Environmental Gases, Alpha NJ, USA, 100 ppbV each in nitrogen).

#### 8.2.5.1 Determining odorant concentration with PTR-TofMS

Raw data from the PTR-TofMS were interpreted using *IONICON PTR-MS Viewer* software (version 3.1.0.31, Ionicon Analytik, Innsbruck, Austria) (Appendix J). This software was used to correct for mass-shifting of the mass spectra before being used to integrate the area under selected mass peaks. This process produced a continuous record of odorant concentration over time for selected masses (Figure 88). The concentration of each mass was recorded for emission rate calculations once the concentration values stabilised, which indicated that conditions within the customised flux hood had reached steady-state. Concentration of the masses were also recorded when the flux-hood was placed on a stainless steel surface (Figure 85) and designated as 'instrument background' concentrations, which were subtracted from the steady-state sample concentration values to account for contamination within the flux hood, sample lines or instrument.





Proton transfer rate constant, *k*, is used to calculate the concentration of gases in the PTR. A general value of *k* was used for all masses  $(2.0 \times 10^{-9})$  rather than using compound specific values. This introduces uncertainty into the measurement of absolute concentrations by potentially -50% to +100% based on published *k* values (Cappellin et al., 2010; Feilberg et al., 2010). Attempting to determine compound specific *k* values experimentally is difficult and can result in large errors (Cappellin et al., 2010), and was therefore not attempted. Also, theoretical values of *k* can be determined for some compounds but not all the poultry odorants included in this study. Therefore, for the purpose of this study (considered a screening study of a wide range of odorants), the general *k* value for all masses was considered appropriate to enable relative differences between litter materials to be investigated. The use of odorant concentrations measured by PTR-TofMS to calculate odour activity values was considered reasonable due to some single compound odour threshold values having published values that vary by orders of magnitude.

If the total concentration of VOCs (including other gases such as ammonia) entering the instrument exceeded the H3O+ ionization capacity then VOCs in the sample would not be completely protonated. When this happened, the operator would observe a drop in mass 21.02 (which is the third isotopic mass of the protonated water ion) and would dilute the sample gas. The PTR-TofMS was able to dilute samples using the same high-purity nitrogen gas that was used as the sweep air in the flux hood. When calculating the concentration of VOCs in a sample, the concentration measured by the PTR-TofMS was multiplied by the dilution factor thus providing the concentration of the odorants in the sample.

Odorants with similar protonated masses were resolved where possible using the multipeak analysis tool within the *PTR-MS Viewer* software (Figure 89).



Figure 89. Example of the multi-peak analysis tool in the *PTR-MS Viewer software* that was used to resolve peaks with similar protonated mass (61.028-green peak; 61.065-light blue peak). The dark blue trace was the counts per second (cps) measured by the PTR-TofMS and the red trace is the mathematical sum of the two peaks being analysed (61.028 + 61.065)

#### 8.2.6 Calculation of odorant emission rates

Area source flux emission rates for odorants were calculated as previously described (Section 7.2.4).

#### 8.2.7 Calculation of odour activity values

Single compound odour activity values were calculated as previously described (Section 7.2.5, but using values relevant for the customised flux hood: area 0.011 m<sup>2</sup> and sweep air flow rate 0.5 L/min). Odour activities were calculated for each of the protonated masses (measured by the PTR-TofMS) using the average, minimum and maximum odorant concentrations. As the PTR-TofMS was unable to distinguish individual odorants, the OTV assigned to each protonate mass was determined by calculating the geomean of the OTV for the possible compounds for that mass.

#### 8.2.8 Data analysis

Data analysis was previously described (Section 7.2.6). Data from GC-MS and PTR-TofMS were analysed separately. Data from the PTR-TofMS was analysed by molecular mass rather than individual compound names due to the instrument being unable to separate the contribution of compounds with the same mass.

Fixed effects included the *week* that samples were collected (weeks 2, 3, 4 and 5) *litter types* (described in Section 0, *n* value indicates the number of samples grouped into each type):

- dry friable (*n*=12)
- wet (usually caked) (*n*=12)
- normal excreta (*n=6*)
- wet excreta (*n*=1)
- caecal excreta (*n*=1)
- intermediate (damp friable litter between wet and dry friable) (*n*=1)
- 'mixed' wet (wet litter that was mixed to replicate emissions with litter disturbance such as litter conditioning (n=2)
- 'section' wet litter (the caked litter surface was separated friable material,
   flipped over and the flux hood was placed on the underside of the cake) (n=1).

With the exception of dry litter, wet litter and normal excreta, the remaining *types* were regarded as opportunistic samples. Limited sample numbers precluded these litter types from being analysed between litter *types* and *week* of the grow-out.

# 8.3 Results and discussion

Emission rates of volatile compounds from litter surfaces were measured using a customised flux hood combined with TD-GC-MS, TD-GC-SCD, TD-GC-NCD and PTR-TofMS analysis (GC results Appendix K; PTR-TofMS results Appendix L).

### 8.3.1 TD-GC-MS and TD-GC-SCD results

#### 8.3.1.1 Odorant emission rates

Insufficient sample concentration or weak match with the MS library (where 70% match was considered the minimum threshold) resulted in the detection frequency of individual odorants varying for 18 *Litter Type*/Week combinations when VOC and VSC samples were collected (Table A. 13 in Appendix K). The mean and range of emission rates (ng/m<sup>2</sup>/s) of odorants were calculated for all litter types and then specifically for

dry friable litter, caked litter and excreta (Table 20). No VSC samples were able to be shipped during week 2 of the grow-out (and therefore not collected), VSC concentrations were collected but were not able to be quantified with TD-GC-SCD during week 3 for reasons unknown and VSC samples were lost by the transport company during week 5 of the grow-out. Consequently, VSC concentrations were only available for week 4 of the grow-out.

Compound name	All litter types	Dry friable litter	Wet litter	Excreta
Acids/Esters				
Acetic acid	49.2 [5.9–177.2]	71.8 [8.8–177.2]	29.9 [5.9–80.6]	683.9 [20.7–1347]
Propanoic acid	53.5		53.5	
Ethyl acetate	23.2 [8–41.9]		23.2 [8-41.9]	
Butanoic acid	143.7 [18.9–507.8]	31 [18.9–45.2]	369.3 [230.8–507.8]	
Methyl isobutyrate	5.1 [1.8–8.3]		5.1 [1.8–8.3]	
Butanoic acid, methyl ester				
Isothiocyanic acid	6.8 [1.6–12.8]	1.6	7.7 [5.7–12.8]	
Propanoic acid, 2-methyl-,	22.4			
ethyl ester	23.4		23.4	
Butanoic acid, ethyl ester	16 [4.3–34]		16 [4.3–34]	1092.9
Hexanoic acid	9.5 [8.8–10.3]		9.5 [8.8–10.3]	
Benzoic acid	4.1 [1.5–9.5]	3 [1.5–4.9]	5.4 [1.6–9.5]	36.8 [8.8–64.8]
Methyl 3-hydroxybutyrate	13.2		13.2	
Ethyl 2-methylbutyrate	8.6		8.6	
Butanoic acid, propyl ester	5.6		5.6	
Butanoic acid, 1-	6.4		6.4	
methylpropyl ester				
Alashala				
<u>Alconois</u>	2.0	2.0		40.7
		3.0	20 0 [2 7 442 0]	40.7
	29.5 [0.0-113.0]	1.4 [0.6–2.1]	0 [4 4 44 4]	125.4
	9 [4.4–14.4]	00 4 [40 4 00 4]	9 [4.4–14.4]	18.2
	407.1 [0.3-2027]	20.4 [10.1–23.4]	956.7 [259.2-2027]	411.9[11.1-012.0]
	44 4 [44 0 00 4]		44 4 [44 0 00 4]	142.4
1-Butanoi	41.4 [11.9–92.4]		41.4 [11.9–92.4]	1013.2
3-methyl-1-butanol	18.9 [2.7–33.4]		18.9 [2.7–33.4]	450.0
2-metnyl-1-butanol	40,470,0,00,01	00.014.0.00.01	0.0.10.0.0.51	158.2
l etrahydrofurfuryl alcohol	13.4 [2.2–28.9]	20.2 [4.9–28.9]	8.8 [8.2–9.5]	
Aldenydes	24 0 [4 75 4]	42 2 [0 0 75 4]	46 [4 07 0]	404 7 [07 0 006 0]
Aceione 2 Butanana	31.0 [1-73.1]	43.2 [9.9-75.1]	760.9 [7.9, 4206]	101.7 [27.2 - 330.3]
2-Butanolie	303.5 [7.0-1200]	01.0 [20.2–90.0]	/09.0 [/.0-1200]	929.0 [40.4–1010] 512.2
2,3-Butanedione	90.1 [13.3–164]	131.7 [81.7–164]	40.4 [13.3–77.7]	513.3
2-Pentanone	2.8 [0.9–4.7]	3.2 [1.8–4.7]	3.3 [2.6–4]	54.2
3-methyl-butanal	3.8 [1.4–13.7]	2.7 [1.5–4.9]	6.2 [1.5–13.7]	00045
2-Butanone, 3-hydroxy-	423.5 [26.4–1667]	374.9 [131.1–592.3]	531.6 [26.4–1667]	2894.5
1-Hydroxy-2-pentanone	2.5		2.5	
Benzaldehyde	4.3 [2.7–7.5]	4.1 [2.8–7.5]	4.6 [3.9–5.7]	36 [10.1–61.8]
Acetophenone	6.1 [3.6–9]	5.3 [3.6–6.6]	7.1 [4.7–9]	53 [12.1–93.9]
3-Octanone	4 [1.4–8]	4.1 [3.3–4.9]	5.1 [2.1–8]	62.4
Nonanal	2.8 [1.1–5.1]	2.8 [1.1–5.1]		

# Table 20. Mean and range of emission rates for odorants (ng/m²/s) quantified using TC-GC-MS, TD-GC-SCD and Jerome meter (mean [minimum-maximum])

20	LUIIIIIUEU
	20

Compound name	All litter types	Dry friable litter	Wet litter	Excreta
Hydrocarbons				
Benzene	1.2 [0.4–1.7]	1.5 [1.2–1.7]	0.8 [0.4–1.4]	0.8
Toluene	6.6 [5.9–7.2]	7.2	5.9	4.4
Phenol	8.2 [5.7–10.7]	9.2 [6.5–10.7]	7.6 [5.7–10]	35.9 [7.7–64.2]
Hexanal	7.1	7.1		
Oxirane, 3-hydroxypropyl-	10.1		10.1	
Styrene	2.4 [1–5]	2.9 [1.8–5]	1.1	
p-xylene	2.4 [0.5-6.9]	4.0 [1.1–6.9]	1.1 [0.5–2.1]	
P-Cresol	1.7		1.7	
2,4,5-trimethyloxazole	13.2		13.2	
Octane	2.4 [1.4–5]	1.5	2.7 [1.4–5]	67.9
1-Hexanol, 2-ethyl-	3.2	3.2		
Paracymene	3.4		3.4	
Pyrazine, tetramethyl-	3.7		3.7	
α-Pinene	10.2 [3–41.7]	13.2 [3.2–41.7]	7.2 [3–12.9]	
Camphene	8.7	8.7		
Myrcene	2.9 [1–5.4]	1.9 [1–2.8]	3.9 [2.3–5.4]	
β-pinene	5.3 [2.2–15.4]	5.8 [2.2–15.4]	4.3 [2.6–5.9]	
Limonene	2.1 [1–6.2]	2.4 [1–6.2]	1.9 [1.1–2.7]	
.betaPhellandrene	2.3 [1–5.3]	2.6 [1.5–5.3]		
2-Thujene	2.3 [0.9–5.1]	1.3 [0.9–1.6]	3.9 [2.7–5.1]	
2-Pentylfuran	3.0	3.0		
Phthalic anhydride	2.9 [1.4–5.2]	2.2 [1.4–4]	3.8 [2–5.2]	28.7 [10.7–46.7]
Estragole	5.8 [1–15.7]	6.7 [3.6–15.7]	5.5 [1–12]	
6-[(Z)-1-Butenyl]-1,4- cycloheptadiene	3.4		3.4	
6-Butyl-1,4-cycloheptadiene	5.4		5.4	
Hexadecane	2.6		2.6	9.6
Nitrogan compounda				
Trimethylamine	80 5 [0 5-226 5]	99 9 10 5-226 51	49 4 [0 6-111 2]	1009
2.4 Pontadionanitrila	$21 \ 4 \ [2 \ 5 \ 42 \ 2]$	33.3 [0.3–220.3] 24 7 [2 5 43 2]		1003
2,4-r entadienentine Mothallyl cyapido	21.4 [2.3-43.2]	24.7 [2.3–43.2]	8 6 6 6 10 5	400.4
N-acetylethylenediamine	0.0 [0.0–10.3] ۸ ۵	1 0	0.0 [0.0-10.3]	
Ronzopitrilo	4.5	4.5	2 [1 9 2 2]	
Ammonia	1.7 [1-2.2]	882 / [63 2_2201]	2 [1.0-2.2] 1363 [1052_1675]	12/6 0
Ammonia	1170 [00.2-2201]	002.4 [00.2-2201]	1000 [1002-1070]	1240.5
Sulfur compounds				
Methyl mercaptan	161 [107.6–214.5]		161 [107.6–214.5]	
Dimethyl sulfide/ethyl	68 6 [47 6_00 8]		68 6 [47 6_00 8]	
mercaptan		<b>aa</b> -		
Dimethyl disulfide	33.1 [28.8–39.3]	28.8	34.6 [29.2–39.3]	
Dimethyl trisulfide	34.4		34.4	
Hydrogen sulfide	219.5 [19.3–611.9]	132.6 [19.3–472.8]	259.4 [28.8–611.9]	1039

Statistical analysis revealed significant (*P*<0.05) two-way interactions between the main effects, *Litter type* and *Week* of the grow-out for some of the odorants (Table 21) including 2-butanone, 2-butanol, 2,4-pentadienenitrile, benzene, 2,3-butanedione, acetoin, phenol, benzaldehyde, acetophenone, phthalic anhydride and estragole (OTV is unknown for Acetoin; OTV and odour character are unknown for 2,4-pentadienenitrile, phthalic anhydride and estragole). Interactions between *Litter Type* and *Week* for some

of these compounds are shown in Figure 90. (Due to data limitations, it was not possible to plot the interactions for all odorants.)

		Type.W	eek	Litter t	уре	Week	٢
	Litter Moisture Content	0.999		< 0.001	**	0.819	
	Water Activity	0.875		0.009	**	0.839	
	рН	0.088		0.573		0.386	
MW	VOC and VSC emission rates	(ng/m²/s)					
58.08	Acetone	0.295		0.254		0.760	
59.11	Trimethylamine			0.763		0.473	
60.05	Acetic acid	0.106		0.142		0.259	
60.10	n-Propanol			0.084		0.864	
72.11	2-Butanone (MEK)	< 0.001	**	< 0.001	**	< 0.001	**
74.12	1-Butanol			0.008	**	0.031	*
74.12	2-Butanol	0.002	**	< .001	**	< 0.001	**
78.11	Benzene	0.185		0.008	**	0.487	
79.10	2,4-Pentadienenitrile	0.013	*	0.010	*	0.202	
86.09	2,3-Butadione (Diacetyl)	0.198		0.003	**	0.075	
86.13	2-Pentanone			0.093			
86.13	3-Methyl-1-butanal	0.065		0.268		0.858	
88.11	Acetoin	0.040	*	0.022	*	0.019	*
88.11	Butanoic acid			0.036	*	0.565	
94.11	Phenol	0.008	**	0.005	**	0.241	
104.15	Styrene			0.277		0.849	
106.12	Benzaldehyde	0.001	**	< 0.001	**	< 0.001	**
106.17	p_Xylene	0.122		0.118		0.258	
120.15	Acetophenone	0.004	**	< 0.001	**	0.005	**
122.12	Benzoic acid	0.460		0.050		0.217	
128.21	3-Octanone			0.006	**	0.031	*
136.23	Alpha pinene	0.799		0.351		0.713	
136.23	Limonene	0.607		0.438		0.111	
148.12	Phthalic anhydride	0.272		< 0.001	**	0.013	*
148.20	Estragole	0.278		0.236		0.034	*
34.08	Hydrogen sulfide	0.143		0.087		0.119	
17.03	Ammonia			0.477		0.258	

Table 21.	P-values for two-way interaction Litter Type.Week and the main effects Week
	and Litter Type—TC-GC-MS, TD-GC-SCD and Jerome meter results

*Note:* \*\* indicates (*P*<0.01); \* indicates (*P*<0.05). Missing *P*-values indicates that there was insufficient data.



Figure 90. Selected VOC emissions from poultry litter by *Litter Type* and *Week* of a grow-out (measured with TD-GC-MS)

Emission rates tended to increase during the grow-out for 2-butanone, 2-butanol, benzene, 2,3-butanedione and acetoin, but were stable or decreased for the other compounds. Wet litter, compared to dry litter, had higher emission rates for 2-butanone, 2-butanol, acetone, benzaldehyde and phthalic anhydride, particularly towards the end of the grow-out. Emission rates for 2-butanone and 2-butanol were previously found to be significantly different by *Week* in a meat chicken shed (Section 7.3), and the trend for it to increase over time was observed in the current study. Additionally, this study also showed that these compounds were different by litter type, with wet litter having higher emission rates.

Fresh excreta generally had high emission rates compared to wet and dry litter for 2,3-butanedione, hydrogen sulfide, acetic acid and trimethylamine. This indicated the potential importance of fresh excreta as a source of odour, which has not previously been reported in the literature. The measured emission rates from excreta assumed that it was spread over the entire litter surface, which is not normally the case. Future research should focus on measuring odour emissions from fresh excreta, but in manner that is representative of the coverage and dynamic changes of excreta on the litter surface.

Data analysis did not reveal any significant interaction between sulfur compounds and *Litter Type* or *Week*. This was believed to be due to insufficient sample numbers for the reasons explained previously. This was unfortunate because *Litter type* had been found to significantly affect the emission rate of several sulfur compounds in meat chicken sheds (Section 7.3). Despite the lack of statistical significance, sulfide emission rates were greater from wet litter than dry litter.

Many alcohols, esters and sulfides were not detected in dry friable litter when compared to wet litter. This was similar to the mixtures of odorants detected from dry and wet litter in a meat chicken shed (Section 7.3). It is suggested that the detection of sulfide compounds from wet litter, in particular, was due to anaerobic conditions (Chapter 6), which have been reported to increase the emission rates of sulfides during manure decomposition (Woodbury et al., 2015).

#### 8.3.1.2 Odour activity values

Odour threshold values (OTV) and odour character descriptions were compiled for the odorants (Table 22). Litter samples were grouped into three categories: 'All litter samples', 'Dry friable litter' and 'Wet litter'. Excreta was also included. Odour activity values (OAV) were calculated for individual odorants (Figure 91) using the average, minimum and maximum odorant concentrations (Table 20).

Compound name	Odour character	OTV (µg/m³)
Ethanol	pleasant, alcoholic	640 <sup>5</sup>
Acetone	solvent, nail polish	99800 <sup>4</sup>
Trimethylamine	fishy, ammonia	1.1 <sup>7</sup>
Acetic acid	vinegar	892 <sup>9</sup>
Isopropyl Alcohol	pleasant, alcoholic	63904 <sup>4</sup>
1-propanol	pleasant, alcoholic	231 4
Isoprene	petrol-like	134 <sup>4</sup>
Isobutyraldehyde	pungent	1.04
2-Butanone	sweet, minty, acetone-like	737 <sup>8</sup>
Propanoic acid	pungent, rancid, cheesy	108 <sup>9</sup>
2-Butanol	strong, sweet	667 <sup>4</sup>
Isobutyl alcohol	sweet, musty	33 <sup>4</sup>
1-Butanol	solvent, sweet, banana	1485 <sup>9</sup>
Benzene	petrol-like	4500 <sup>8</sup>
2,3-Butanedione	sour, butter, rancid	0.184
2-Pentanone	acetone-like	38000 <sup>1</sup>
3-methyl-butanal	malt, apple, rancid	7.8 <sup>9</sup>
Ethyl acetate	ether-like, fruity, alcoholic	3135 <sup>4</sup>
Butanoic acid	rancid, unpleasant	0.74
3-methyl-1-butanol	disagreeable	161 <sup>9</sup>
2-methyl-1-butanol	sharp, sour	193 <sup>8</sup>
1-Pentanol	fusel-like, alcoholic	360 <sup>4</sup>
Toluene	solvent, fruity	1240 <sup>4</sup>
Phenol	medicinal, tarry	21.5 <sup>4</sup>
Methyl isobutyrate	N/A	7.9 <sup>4</sup>
Butanoic acid, methyl ester	apple-like	20 <sup>3</sup>
Styrene	floral, solventy, rubbery	149 <sup>4</sup>
Benzaldehyde	bitter-almond, onion, burnt	12.1 <sup>8</sup>
p-xylene	aromatic	252 <sup>4</sup>
P-Cresol	tarry, faecal	0.24 4
Octane	petrol-like	7940 <sup>4</sup>
Propanoic acid, 2-methyl-, ethyl ester	fruity, aromatic	0.1 4
Hexanoic acid	goat-like	2.9 <sup>4</sup>
Indole	Faecal	1.4 4
Acetophenone	pungent orange/jasmine blossom	19.7 <sup>1</sup>
3-Octanone	pungent	35.7 4
Butanoic acid, propyl ester	N/A	58.6 <sup>4</sup>
1-Hexanol, 2-ethyl-	mild, floral, rose	400 <sup>5</sup>
α-Pinene	pine, turpentine	1004
β-Pinene	turpentine, woody	65 <sup>6</sup>
Limonene	lemon	212 <sup>4</sup>
Nonanal	orange-rose, dusty, goat	2.5 <sup>2</sup>
Methyl mercaptan	Rotten cabbage	0.14 4
Dimethyl sulfide/ethyl mercaptan	rotten eggs/vegetables	7.64
Dimethyl disulfide	putrid, rotten garlic, rubber	8.5 <sup>4</sup>
Dimethyl Trisulfide	pungent, garlic, metallic, onion	6.2 <sup>8</sup>
Hydrogen sulfide	rotten eggs	0.64
Ammonia	pungent	1045 <sup>4</sup>

#### Table 22. Odour threshold values (OTV) and character of selected odorants

<sup>1</sup>INRS (2005); <sup>2</sup>Godayol et al. (2011); <sup>3</sup>Leyris et al. (2005); <sup>4</sup>Nagata (2003); <sup>5</sup>O'Neill and Phillips (1992); <sup>6</sup>Parcsi (2010); <sup>7</sup>Rosenfeld and Suffet (2004); <sup>8</sup>Ruth (1986); <sup>9</sup>Schiffman et al. (2001)



Figure 91. Odour activity value (OAV) for selected individual odorants for litter and excreta samples (whiskers show the data range)—TC-GC-MS, TD-GC-SCD and Jerome meter results

Ten odorants with the highest OAVs were determined for each litter category and excreta (Table 23). Methylmercaptan, 2,3-butanedione, hydrogen sulfide, butanoic acid and trimethylamine had the highest OAVs across the three litter categories and excreta. The highest ranking odorants differed slightly from the previous study (Section 7.3.2) with the inclusion of hydrogen sulfide and trimethylamine. Interestingly, dry friable litter and excreta shared the same top-four ranked odorants.

Ranked OAV*	All litter	Dry friable litter	Caked/wet litter	Excreta
1	Methylmercaptan	2,3-Butanedione	Methylmercaptan	2,3-Butanedione
2	2,3-Butanedione	Hydrogen sulfide	Butanoic acid	Hydrogen sulfide
3	Hydrogen sulfide	Trimethylamine	Hydrogen sulfide	Butanoic acid
4	Propanoic acid, 2- methyl-, ethyl ester	Butanoic acid	2,3-Butanedione	Trimethylamine
5	Butanoic acid	Dimethyl disulfide	Propanoic acid, 2- methyl-, ethyl ester	lsobutyraldehyde
6	Trimethylamine	Nonanal	Trimethylamine	Isobutyl alcohol
7	Dimethyl sulfide/ethyl mercaptan	Ammonia	Dimethyl sulfide/ethyl mercaptan	Benzaldehyde
8	<i>p</i> -Cresol	Phenol	<i>p</i> -Cresol	Acetophenone
9	Dimethyl trisulfide	3-methyl-butanal	Dimethyl trisulfide	3-Octanone
10	Dimethyl disulfide	Benzaldehyde	Dimethyl disulfide	Phenol

 Table 23.
 Individual odorant OAVs in descending order for all litter samples, dry friable litter, wet litter and excreta—TC-GC-MS, TD-GC-SCD and Jerome meter results

\*Rank 1 has highest OAV

Odour activity value for the three litter categories and excreta was then calculated from the individual odorant OAVs (Figure 92). OAV for wet litter was 2.4 times greater than for dry litter, which gave an indication that wet litter was more odorous. Wet litter also had a higher OAV than dry litter in the previous study (Section 7.3.2). Excreta had the highest OAV but caution needs to be applied in comparing excreta to litter samples due to the way that emission rates were measured and calculated. The OAV calculated for excreta assumed that it covered the entire litter surface, which is not usually the case.



Jerome meter results

#### 8.3.2 PTR-TofMS results

#### 8.3.2.1 Volatile compound emission rates

The mean and range of volatile compound emission rates (ng/m<sup>2</sup>/s) were calculated for all litter types, dry friable litter, wet caked litter and excreta (Table 24). Compounds were sorted by protonated masses because individual compounds were not able to be resolved (possible compounds corresponding with each protonated mass are listed in Appendix I).

Greatest emission rates (by protonated mass) from dry litter included 89.0597 (butanoic acid; acetoin), 61.028 (acetic acid) and 71.049 (methylvinylketone). For wet litter, greatest emission rates were associated with masses 73.065 (2-Butanal), 33.033 (Methanol) and 89.0597 (butanoic acid; acetoin). Mass 43 also registered high concentration readings by the PTR-TofMS; however, this mass tends to receive the fragments from the ionisation process and should not be considered an odorant compound.
protonated mass (H+)Dy literWet literExceta33.031122 (45.7-52.45)586 [06.6-1089]173.68 [31.6-32.65]887.5 [450.1-831]44.9888 [0-13.61]0.1 [0-0.3]5.6 [0.1-36.7]1.4 [0.3-2.8]42.03425 [0.1-1593]8.7 [0.1-34.9]1.6 5 [1.7-46.9]6 [0.8-10.4]43.018785.7 [75.5-4501]984.8 [75.5-4501]842.3 [127.6-2057]43.0041653 [10-115.6]632 [13.1-124.2]1159 [10-470.2]22.6 [14.8-575]43.004948.8 [85.4-4001]842.3 [127.6-2057]838 [15.1-223.2]1068 [123.2-23.2]45.034190.4 [13.1-527]58.8 [13.1-124.2]1068 [123.2-23.2]1058 [15.1-66.8]47.01315.6 [1.6-6.13]8.2 [12-15.6]16.6 [1.6-43.9]15.9 [13.7-28.1]47.01415.6 [1.6-6.13]8.2 [12-45.2]13.2 [13.2-27]13.8 [12-57]49.01111.2 [0.4-1397]12.2 [0.4-36.2]13.2 [13.2-27]14.8 [1.5-33.4]55.05413.8 4 [12-870]3.2 [10.5-73.2]120.8 [1.6-52.1]26.3 [14.3-143.4]55.05413.8 4 [12-871]13.4 [13.9-327.7]13.4 [12-43.5]1.1.6 [0.9-18.9]57.070119 [4.9-10.83]3.2 [10.5-73.2]120.8 [1.6-52.7]2.6 (1.4-74.4]59.0499.09-18.9]0.6 [1.4-13.6]1.1.6 [0.9-18.9]2.1.3 [0.4-36.9]60.0810.1.7 [13.4]1.2 [14.2-27]14.4 [1.2-47.9]1.3 [14.2-47.9]50.0413.9 [14.2-23.0]0.5 [11.7-49.3]1.0 [12.4-30.6]1.0.5 [11.7-49.7]60.0449 [0.9-18.9]0.	TOF				
$\begin{array}{                                    $	protonated	All litter	Dry litter	Wet litter	Excreta
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	mass (H+)				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	22 022	1192 [45 7 2245]		1726 9 [221 6 2246]	997 E [4E0 1 1921]
$ \begin{array}{l} 34.988 \\ 34.1039 \\ 34.17 \\ 34.$	33.055	1162 [43.7-3243]	580 [00.0-1098]	1/30.8 [331.0-3243]	887.5 [430.1-1851]
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	34.988	8 [0-136.1]	0.1 [0-0.3]	5.6 [0.1-36.7]	1.4 [0.3–2.8]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	41.039	342.1 [7.3–3448]	39.5 [10.3–68.4]	262 [7.3–1080.8]	128.5 [14.5–331.5]
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	42.034	25 [0.1–159.3]	8.7 [0.1–34.9]	16.9 [1.7–46.9]	6 [0.8–10.4]
$  \begin{array}{c} 43.064 \\ 43.064 \\ 43.064 \\ 43.06 \\ 94.88 \\ 45.4901 \\ 43.012 \\ 45.034 \\ 43.06 \\ 43.06 \\ 43.06 \\ 43.06 \\ 44.0191-526.71 \\ 55.081 \\ 43.012 \\ 57.072 \\ 45.034 \\ 43.013 \\ 15.6 \\ 11.6 \\ 47.013 \\ 15.6 \\ 11.6 \\ 11.272 \\ 41.33 \\ 11.272 \\ 41.33 \\ 11.272 \\ 41.33 \\ 11.272 \\ 41.33 \\ 11.272 \\ 41.33 \\ 11.272 \\ 41.31 \\ 42.112 \\ 42.11$	43.018	785.7 [75.5–4501]	779.4 [175.5–1400]	984.8 [75.5–4501]	842.3 [187.6–2057]
$  \begin{array}{c} 43.000 & 948. [85.4-4901] \\ 45.043 & 130.4 [91.3-6267] \\ 538 [255-122.6] \\ 45.065 & 7.3 [0-27.4] \\ 33 [0-14] & 7.6 [0.1-21.6] \\ 24.0 & 25.6 [2.3-26.3] \\ 47.013 & 15.6 [1.6-61] \\ 47.013 & 15.6 [1.6-61] \\ 47.013 & 15.6 [1.6-61] \\ 47.013 & 15.6 [1.6-61] \\ 47.013 & 15.6 [1.6-61] \\ 47.013 & 15.6 [1.6-61] \\ 47.013 & 15.6 [1.6-61] \\ 47.023 & 15.6 [1.6-71.6] \\ 14.2 & 15.7 & 12.3 [0.4-36.5] \\ 49.011 & 112.7 [0.4-1597] \\ 12.2 & 10.4-36.5] \\ 13.8 & [11.2-877] \\ 12.2 & 10.4-483] \\ 13.6 & [1.2-877] \\ 13.8 & [11.2-877] \\ 13.8 & [11.2-877] \\ 13.8 & [11.2-877] \\ 13.8 & [11.2-877] \\ 13.8 & [11.2-877] \\ 13.8 & [11.2-877] \\ 13.8 & [11.2-877] \\ 13.8 & [11.2-877] \\ 13.8 & [11.2-977] \\ 14.3 & [11.3-227.5] \\ 13.8 & [11.2-871] \\ 13.8 & [11.2-977] \\ 14.3 & [11.3-227.5] \\ 14.4 & [13.1-82367] \\ 25.5 & [11.2-8366] \\ 14.7 & [11.3-227.5] \\ 14.4 & [13.1-923.6] \\ 14.7 & [11.3-227.5] \\ 14.8 & [11.3-23.6] \\ 14.8$	43.054	163.5 [10–1152.6]	63.2 [15.5–128.2]	169.6 [10-470.2]	226.6 [34.8-575]
$  \begin{array}{c} + 6.04 & 130.4 \   9.1-26.7] & 59.8 \   10124.2] & 182.9 \   29.4-256.7] & 538 \   1027.6] \\ 60.05 & 7.3 \   0-27.4] & 3.3 \   0-44 \   15.6 \   1.6-6.13] & 3.2 \   3.1-15.6 \   1.6-6.14.3 & 9.15 \   15.7-23.8] \\ 47.049 & 19.13 \   1.1.3-1289 \   13.2 \   1.3-29.7] & 337 \   1.5-128.9 \   29.56 \   115.7-22.8] \\ 49.011 & 112.7 \   0.4-1597 \   12.3 \   0.4-36.5 \   31 \   12-48.3] & 14.8 \   15-33.4 \   35.6 \   1.6-7.1597 \   12.3 \   0.4-36.5 \   31 \   12-48.3] & 14.8 \   15-33.4 \   35.6 \   1.6-13.8 \   1.2-9.7] & 13.3 \   1.2-9.7] & 13.3 \   1.2-9.7] & 13.3 \   1.2-9.7] \\ 57.02 & 57. \   0.3-8.1 \   0.5.2 \   (0.4-53.2] & 132.5 \   1.86-374.6 \   14.7 \   123.7 \   125.7 \   126.7 \   124.7 \   127.7 \   13.7 \   127.7 \   14.4 \   1.2-13.6 \   11.5 \   1.5-233.6 \   14.9-43.31 \   14.9 \   1.2-7] & 13.3 \   1.2-9.7] & 13.3 \   1.2-9.7] & 13.4 \   1.4-9.1 \   13.4 \   1.4-31.5 \   11.7 \   13.4 \   1.5-233.6 \   1.5.7 \   11.7 \   13.4 \   1.5-233.6 \   1.5.7 \   11.7 \   13.4 \   1.5-233.6 \   1.5.7 \   11.7 \   13.7 \   1.5-233.6 \   1.5.7 \   11.7 \   1.5-233.6 \   1.5.7 \   1.5-233.6 \   1.5.7 \   1.5-233.6 \   1.5.7 \   1.5-233.6 \   1.5.7 \   1.5-233.6 \   1.5.7 \   1.5-233.6 \   1.5.7 \   1.5-233.6 \   1.5-4.6 \   1.5.7 \   1.5-233.6 \   1.5-233.6 \   1.5.7 \   1.5-233.6 \   1.5-233.6 \   1.5.7 \   1.5-233.6 \   1.5-233.6 \   1.5.7 \   1.5-233.6 \   1.5-233.7 \   1.5-233.6 \   1.5-233.6 \   1.5-233.6 \   1.5-233.6 \   1.5-233.6 \   1.5-233.6 \   1.5-233.6 \   1.5-233.6 \   1.5-233.7 \   1.5-233.6 \   1.5-233.7 \   1.5-233.6 \   1.5-233.7 \   1.5-233.6 \   1.5-233.7 \   1.5-233.6 \   1.5-233.7 \   1.5-233.6 \   1.5-233.7 \   1.5-233.7 \   1.5-233.7 \   1.5-233.7 \   1.5-233.7 \   1.5-233.7 \   1.5-233.7 \   1.5-233.7 \   1.5-$	43.000	948.8 [85.4-4901]	842.3 [217.8–1488]	1154 [85.4–4901.2]	1068 [222,3-2631]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	45 034	130 / [19 1_526 7]	59.8 [19.1_12/12]	182 9 [29 4-526 7]	538 [255_1220.6]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	45.054	7.2 [0.27.4]	2 2 [0 14]	7.6 [0.1, 21.6]	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	40.005	7.5 [0-27.4]	5.5 [0-14]	7.0 [0.1-21.0]	2.8 [0.0-0.8]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	47.013	15.6 [1.6-61.3]	8.2 [3.1–15.6]	16.6 [1.6–34.9]	15.9 [3.7-28.1]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	47.049	191.3 [1.3–1289]	13.2 [1.3–29.7]	337 [1.9–1289.2]	955.6 [154.7–2238]
55.054       138.4 [12-870]       32.2 [12-63.2]       132.5 [16.6-374.6]       142.7 [55.1-247.9]         57.030       1199 [4.9-10483]       32.6 [10.5-73.2]       1208.3 [4.9-5231]       26.2 [3.4-9-1143.4]         50.040       90.9-18.9]       6.9 [1.4-13.6]       11.6 [0.9-18.9]       26.3 [4.9-1143.4]         60.041       91.0-18.9]       6.9 [1.4-13.6]       11.6 [0.9-18.9]       21.3 [-0.4-36.9]         61.028       1034 [54-6432]       778.3 [98-1487.7]       133.4.5 [54-6432.4]       1709 [244-4068]         61.025       87.8 [3-53.3]       23.2 [2.9-91]       94.7 [7.5-229.6]       24.2 [11.1-90.8]         62.026       87.8 [3-3-34.4]       10.6 [3.7-19.3]       19 [8.4-34.4]       21.5 [7.6-73.2]         71.049       55.45 [28.6-3278]       592 [28.6-1321.4]       706.4 [53.9-3278.1]       23.8 [45.6-52.6]         75.050       33.2 [1.1-90.8]       52.6 [0.6.16.1-1977]       75.044       87.1 [7.3-60.5]       47.8 [8.9-289.5]         75.060       13.2 (0.1-71.9]       0.4 [0.1-13]       12.1 [0.3-31.3]       2.5 [0.2-6.2]         75.060       33.1 [0.1-24.5]       47 [1.1-7.9]       8.3 [1.5-54.5]       7 [2-21.1]         78.067       21.7 [0.2-23.1]       19.3 [1.2-253]       2.1 [0.2-6.6]       33.1 [0.1-15.1]         75.068 <td>49.011</td> <td>112.7 [0.4–1597]</td> <td>12.3 [0.4–36.5]</td> <td>83 [1.9–468.3]</td> <td>14.8 [1.5–33.4]</td>	49.011	112.7 [0.4–1597]	12.3 [0.4–36.5]	83 [1.9–468.3]	14.8 [1.5–33.4]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	55.054	138.4 [12–870]	32.2 [12–63.2]	132.5 [18.6–374.6]	142.7 [55.1–247.9]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	57.032	5.7 [0.3–18.1]	6.2 [0.6–13]	3.8 [1.2–9.7]	14.3 [2.1–43.5]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	57.070	1199 [4.9–10483]	32.6 [10.5–73.2]	1208.3 [4.9–5231]	262.3 [4.9–1143.4]
	59.049	368.6 [31.9-836.7]	414.6 [31.9-836.7]	295.5 [92.6-571.9]	467.9 [113.7–927.5]
$ \begin{array}{c} 0.0011 & 0.103 & 0.114 - 0.301 & 0.103 & 0.114 - 0.301 & 0.103$	60 044	9 [0 9–18 9]	69[14-136]	11.6 [0.9–18.9]	21 3 [-0 4-36 9]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	60.081	471 2 [1 5_2220]	225 5 [1.7 1214 6]	562 1 [1 5_2220 6]	105 0 [11 7_402 7]
0.1024 $1034$ $103$	61.039	471.3 [1.3-2330]	233.3 [1.7-1314.0]		1700 [244 4080]
b.10b5 $24.7 [1-87.4]$ $14.2 [5.9-35.7]$ $2b.4 [1-87.4]$ $30 [12.8-30.6]$ 68.050 $31.[0.3-6.6]$ $23 [0.3-5.8]$ $3.2 [1.1-5.6]$ $2.2 [0.8-4]$ 69.070 $14.8 [3.7-34.4]$ $10.6 [3.7-19.3]$ $19 [8.4-3.4]$ $21.5 [7.6-7.2.2]$ 71.049 $554.5 [28.6-3278]$ $592 [28.6-1321.4]$ $706.4 [53.9-3278.1]$ $238.4 [45.6-526.9]$ 73.055 $2723 [8.6-16375]$ $196.3 [8.6-562.5]$ $2785 [33.3-9958.5]$ $604.6 [16.1-1977]$ 75.044 $872 [7.3-604.5]$ $42.8 [9.1-95.6]$ $10.17 [7.3-381.3]$ $78.1 [8.9-289.5]$ 75.080 $13.2 [-0.1-7.1.9]$ $0.4 [-0.1-1.3]$ $12.1 [0.3-31.8]$ $25.[0.2-6.2]$ 79.054 $6.8 [1.7-54.5]$ $71 [2-21.1]$ $78.3 [8.6-191.6]$ $33.1 [1.9-152.4]$ 80.049 $77.3 [4.1-241.5]$ $96.3 [4.1-227.1]$ $59.3 [8.6-191.6]$ $33.1 [1.9-152.4]$ 81.070 $8.9 [0.7-33.8]$ $4.5 [0.6-8.5]$ $13 [2.4-31.9]$ $35.4 [8.8-77]$ 83.066 $3.1 [0-1.15]$ $14 [0-2.7]$ $3.7 [1.6-6.3]$ $33.1 [0.4-6.8]$ 83.086 $4.4 [0.4-18.8]$ $4.9 [0.4-18.8]$ $4.5 [0.5-15.6]$ $4.7 [2-6.4]$ 84.081 $2 [0.4-10]$ $1 [0.4-2.5]$ $1.9 [0.8-4]$ $1.1 [0.6-2.3]$ 87.044 $209.1 [16.2-895.6]$ $152.7 [15.2-50.1]$ $29.4 [8.0-99.1]$ $31.7 [11.5-10.6]$ 87.044 $209.1 [16.2-895.6]$ $152.7 [16.2-50.7]$ $29.4 [8.0-99.1]$ $31.7 [10.5-10.6]$ 87.044 $209.1 [16.2-895.6]$ $152.7 [16.2-80.7]$ $29.4 [8.0-99.1]$ $46.5.9 [43.4-132]$	61.028	1034 [54-6432]	//8.3 [98-1487./]	1334.5 [54-6432.4]	1709 [244-4089]
63.02687.8 $[3-53.3]$ 22.2 $[3-99.1]$ 94.7 $[7.5-22.6]$ 42.4 $[11.1-90.8]$ 68.0503.1 $[0.3-6.6]$ 2.3 $[0.3-5.8]$ 3.2 $[1.1-5.6]$ 2.2 $[0.8-4]$ 69.07014.8 $[3.7-34.4]$ 10.6 $[3.7-19.3]$ 19 $[8.4-34.4]$ 21.5 $[7.6-73.2]$ 71.049554.5 $[28.6-3278]$ 592 $[28.6-1321.4]$ 706.4 $[53.3-998.5]$ 04.6 $[16.1-1977]$ 75.06487.2 $[7.3-604.5]$ 42.8 $[9.1-95.6]$ 101.7 $[7.3-381.3]$ 2.5 $[0.2-6.2]$ 79.0546.8 $[1.1-54.5]$ 4.7 $[1.1-7.9]$ 8.3 $[1.5-54.5]$ 71.2-21.1]78.06721.7 $[0-129.7]$ 2.3 $[0-16.2]$ 19.4 $[3.2-53]$ 2.1 $[0.2-5.6]$ 80.0497.3 $[4.1-241.5]$ 96.3 $[4.1-227.1]$ 59.3 $[8.6-191.6]$ 33.1 $[1.5-15.2.4]$ 81.0708.9 $[0.1-34.3]$ 7.2 $[0.5-33.4]$ 6.8 $[1.7-24.2]$ 1 $[0-3.2]$ 82.0659.8 $[0.6-33.8]$ 4.5 $[0.6-8.5]$ 13 $[2.4-31.9]$ 35.4 $[9.8-77]$ 83.0603.1 $[0-11.5]$ 1.4 $[0-2.7]$ 3.7 $[1.6-6.3]$ 3.3 $[0.4-6.8]$ 83.0864.4 $[0.4-18.8]$ 4.9 $[0.4-18.8]$ 4.5 $[0.5-15.6]$ 4.7 $[2-6.4]$ 84.0812 $[0.4-10]$ 1 $[0.4-2.5]$ 1.9 $[0.8-4]$ 1.1 $[0.6-2.3]$ 85.06549.6 $[8.4-163.2]$ 65.2 $[9.5-137.8]$ 4.9 $[4.8-163.2]$ 17.5 $[5.9-50.4]$ 87.04420.2 $[1.6-395.6]$ 158.7 $[1.6-500.1]$ 29.4 $[74.3-895.6]$ 45.9 $[4.3+1.33]$ 87.08020.2 $[0.9-49.1]$ 18 $[0.9-43.7]$ 20 $[6.9-49.1]$ 3.1.7 $[1.5-15.9]$ 89.09641 $[0-339.9]$ 26.3 $[2-$	61.065	24.7[1-87.4]	14.2 [5.9–45.7]	26.4 [1-87.4]	30 [12.8–50.6]
68.0503.1 $[0.3-6.6]$ 2.3 $[0.3-5.8]$ 3.2 $[1.1-5.6]$ 2.2 $[0.8-4]$ 69.0701.4 $[3.7-34.4]$ 106 $[3.7-19.3]$ 19 $[8.4-34.4]$ 21.5 $[7.6-73.2]$ 71.049554.5 $[28.6-3278]$ 592 $[28.6-1321.4]$ 706.4 $[53.9-3278.1]$ 238.4 $[45.6-526.9]$ 73.0652723 $[8.6-16375]$ 196.3 $[8.6-562.5]$ 2785 $[53.3-998.5]$ 604.6 $[16.1-1977]$ 75.04487.2 $[7.3-604.5]$ 42.8 $[9.1-95.6]$ 101.7 $[7.3-381.3]$ 78.1 $[8.9-289.5]$ 75.08013.2 $[-0.1-71.9]$ 0.4 $[-0.1-1.3]$ 12.1 $[0.3-31.8]$ 2.5 $[0.2-6.2]$ 79.0546.8 $[1.1-54.5]$ 4.7 $[1.1-7.9]$ 8.3 $[1.5-54.5]$ 7 $[2-21.1]$ 78.6672.1.7 $[0-129.7]$ 2.3 $[0-16.2]$ 19.4 $[3.2-53]$ 2.1 $[0-2.5.6]$ 80.04977.3 $[4.1-241.5]$ 96.3 $[4.1-227.1]$ 59.3 $[8.6-191.6]$ 33.1 $[1.9-152.4]$ 81.0708.9 $[0-33.8]$ 4.5 $[0.6-8.5]$ 13 $[2.4-31.9]$ 35.4 $[9.8-77]$ 83.0663.1 $[0-11.5]$ 1.4 $[0-2.7]$ 3.7 $[1.6-6.3]$ 3.3 $[0.4-6.8]$ 83.0864.4 $[0.4-18.8]$ 4.9 $[0.4-18.8]$ 4.5 $[0.5-15.6]$ 4.7 $[2-6.4]$ 84.0812 $[0.4-10]$ 1 $[0.4-2.5]$ 1.9 $[0.8-4]$ 1.1 $[0.6-2.3]$ 85.06549.6 $[8.4-163.2]$ 17.5 $[5.9-50.4]$ 49.4 $[8.4-163.2]$ 17.5 $[5.9-50.4]$ 87.0800.2 $[0.9-49.1]$ 18 $[0.9-43.7]$ 20 $[6.9-49.1]$ 3.7 $[1.5-10.6]$ 87.04120.1 $[1.6-2895.6]$ 15.8 $7 [16.2-500.1]$ 29.4 $[7.4-3.895.6]$ 46.3 $9 [43.4-1333]$ 87.08010.0	63.026	87.8 [3–533.3]	23.2 [3–99.1]	94.7 [7.5–229.6]	42.4 [11.1–90.8]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	68.050	3.1 [0.3–6.6]	2.3 [0.3–5.8]	3.2 [1.1–5.6]	2.2 [0.8–4]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	69.070	14.8 [3.7–34.4]	10.6 [3.7–19.3]	19 [8.4–34.4]	21.5 [7.6–73.2]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	71.049	554.5 [28.6–3278]	592 [28.6–1321.4]	706.4 [53.9–3278.1]	238.4 [45.6–526.9]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	73.065	2723 [8.6–16375]	196.3 [8.6–562.5]	2785 [53.3–9958.5]	604.6 [16.1–1977]
75.08013.2 $[0.1-71.9]$ 0.4 $[0.1-1.3]$ 12.1 $[0.3-31.8]$ 2.5 $[0.2-6.2]$ 79.0546.8 $[1.1-64.5]$ 4.7 $[1.1-7.9]$ 8.3 $[1.5-64.5]$ 7 $[2-21.1]$ 78.96721.7 $[0-129.7]$ 2.3 $[0-16.2]$ 19.4 $[3.2-53]$ 2.1 $[0.2-5.6]$ 80.04977.3 $[4.1-241.5]$ 96.3 $[4.1-227.1]$ 59.3 $[8.6-191.6]$ 33.1 $[1.9-152.4]$ 81.0708.9 $[0.1-34.3]$ 7.2 $[0.5-33.4]$ 6.8 $[1.7-24.2]$ 1 $[0-3.2]$ 82.0659.8 $[0.6-33.3]$ 4.5 $[0.6-8.5]$ 13 $[2.4-31.9]$ 35.4 $[9.8-77]$ 83.0603.1 $[0-11.5]$ 1.4 $[0-2.7]$ 3.7 $[1.6-6.3]$ 3.3 $[0.4-6.8]$ 83.0864.4 $[0.4-18.8]$ 4.9 $[0.4-18.8]$ 4.5 $[0.5-15.6]$ 4.7 $[2-6.4]$ 84.0812 $[0.4-10]$ 1 $[0.4-2.5]$ 1.9 $[0.8-4]$ 1.1 $[0.6-2.3]$ 85.06549.6 $[8.4-163.2]$ 158.7 $[16.2-500.1]$ 294.3 $[74.3-895.6]$ 463.9 $[43.4-1383]$ 87.044209.1 $[16.2-895.6]$ 158.7 $[16.2-500.1]$ 294.3 $[74.3-895.6]$ 463.9 $[43.4-1383]$ 87.050100 $[6.7-57.9]$ 1.8 $[0.9-43.7]$ 20 $[6.9-49.1]$ 31.7 $[1.1.5-10.1.6]$ 87.1170.9 $[0.7-67.9]$ 8.6 $[0.7-20.3]$ 1.5 $[1.5-67.9]$ 7.3 $[2.2-19.2]$ 91.05810.9 $[0.7-67.9]$ 8.6 $[0.7-20.3]$ 1.5 $[1.5-67.9]$ 7.3 $[2.2-19.2]$ 93.0707.7 $[0.1-34.1]$ 2.4 $[0.1-9.3]$ 9.8 $[1.4-20.4]$ 2.7 $[0.5-77]$ 94.9987.9.9 $[0.2-669.9]$ 8.9 $[0.2-46.8]$ 51.4 $[3-116.6]$ 7 $[0.8-17.3]$ 95.0168.6 $[0.1-34.2]$ 7.6	75.044	87.2 [7.3-604.5]	42.8 [9.1–95.6]	101.7 [7.3–381.3]	78.1 [8.9–289.5]
79.0546.8 [1.1-54.3]4.7 [1.1-7.9]8.3 [1.5-54.5]7 [2-21.1]78.96721.7 [0-129.7]2.3 [0-16.2]19.4 [3.2-53]2.1 [0.2-5.6]80.04977.3 [4.1-241.5]96.3 [4.1-227.1]59.3 [8.6-191.6]33.1 [1.9-152.4]81.0708.9 [0.1-34.3]7.2 [0.5-33.4]6.8 [1.7-24.2]1 [0-3.2]82.0659.8 [0.6-33.8]4.5 [0.6-8.5]13 [2.4-31.9]35.4 [9.8-77]83.0603.1 [0-11.5]1.4 [0-2.7]3.7 [1.6-6.3]3.3 [0.4-6.8]83.0864.4 [0.4-18.8]4.9 [0.4-18.8]4.5 [0.5-15.6]4.7 [2-6.4]84.0812 [0.4-10]1 [0.4-2.5]1.9 [0.8-4]1.1 [0.6-2.3]85.06549.6 [8.4-163.2]15.5 [5.9-50.4]87.044209.1 [16.2-895.6]158.7 [16.2-500.1]294.3 [74.3-895.6]463.9 [43.4-1383]87.08020.2 [0.9-49.1]18 [0.9-43.7]20 [6.9-49.1]0.7 [-0.4-2.4]89.0601101 [68.7-5914]1058 [166.4-2367]1335 [80.9-5914]696 [98.8-1955]89.09641 [0-339.9]26.3 [9.3-52]65.4 [0-339.9]26 [5.7-52.4]91.058 10.9 [0.7-67.9]8.6 [0.7-20.3]15.1 [1.5-67.9]7.3 [2.2-19.2]93.0707.7 [0.1-34.1]2.4 (0.1-9.3]9.8 [1.6-20.4]2.7 [0.5-7]94.99879.9 [0.2-669.9]8.9 [0.2-46.8]51.4 [3-116.6]7 [0.8-17.3]95.04910.7 [0-90.4]3.8 [0-17.4]6.2 [1.2-11.6]5.6 [0.3-18.5]101.0607.6 [1.5-14.7]5.4 [1.5-7.9]9.3 [2.6-7.3]2.2 [0.4-6.1]101.0607.6	75.080	13.2 [-0.1–71.9]	0.4 [-0.1–1.3]	12.1 [0.3–31.8]	2.5[0.2-6.2]
78.96721.7 $[0-129.7]$ 2.3 $[0-16.2]$ 19.4 $[3.2-53]$ 2.1 $[0.2-5.6]$ 80.04977.3 $[4.1-241.5]$ 96.3 $[4.1-27.1]$ 59.3 $[8.6-191.6]$ 33.1 $[1.9-152.4]$ 81.0708.9 $[0.1-34.3]$ 7.2 $[0.5-33.4]$ 6.8 $[1.7-24.2]$ 1 $[0-3.2]$ 82.0659.8 $[0.6-33.8]$ 4.5 $[0.6-8.5]$ 13 $[2.4-31.9]$ 35.4 $[9.8-77]$ 83.0603.1 $[0-11.5]$ 1.4 $[0-2.7]$ 3.7 $[1.6-6.3]$ 3.3 $[0.4-6.8]$ 84.0812 $[0.4-10]$ 1 $[0.4-2.5]$ 1.9 $[0.8-4]$ 1.1 $[0.6-2.3]$ 85.06549.6 $[8.4-163.2]$ 65.2 $[9.5-137.8]$ 49.4 $[8.4-163.2]$ 17.5 $[5.9-50.4]$ 87.044209.1 $[16.2-895.6]$ 158.7 $[16.2-500.1]$ 294.3 $[74.3-895.6]$ 463.9 $[43.4-1383]$ 87.08020.2 $[0.9-49.1]$ 18 $[0.9-43.7]$ 20 $[6.9-49.1]$ 31.7 $[1.15-101.6]$ 87.1170.9 $[0.1-3.3]$ 0.7 $[0.2-2]$ 0.9 $[-0.1-3]$ 0.7 $[-0.4-2.4]$ 89.060110 $[68.7-5914]$ 1058 $[166.4-2367]$ 1335 $[80.9-5914]$ 696 $[98.8-1955]$ 99.0707.7 $[0.1-34.1]$ 2.4 $[0.1-9.3]$ 9.8 $[1.6-20.4]$ 2.7 $[0.5-72]$ 91.05810.9 $[0.7-67.9]$ 8.6 $[0.7-20.3]$ 15.1 $[1.5-67.9]$ 7.3 $[2.2-19.2]$ 93.0707.7 $[0.1-34.1]$ 2.4 $[0.1-9.3]$ 9.8 $[1.6-20.4]$ 2.7 $[0.5-73]$ 95.0168.6 $[0.1-34.2]$ 7.6 $[1.5-12.7]$ 8.4 $[0.1-19.2]$ 13.4 $[5.5-33.4]$ 95.0499.0 $[0.2-66.9]$ 8.9 $[0.2-46.8]$ 9.1 $[3.6-4.7]$ 5.1 $[0.1-9.6]$ 101.0607.6 $[1.5-14.7]$ 5.4 $[1$	79 054	6 8 [1 1–54 5]	4 7 [1 1–7 9]	8 3 [1 5–54 5]	7 [2-21 1]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	78.067	21.7 [0 - 120.7]	22[0-162]	10 4 [2 2_52]	21[02-56]
30.049 $77.5$ [4.7-24.1.3] $30.5$ [4.7-24.2] $35.3$ [1.7-24.2] $10-3.2$ ] $81.070$ $8.9$ [0.6-33.8] $4.5$ [0.6-8.5] $13$ [2.4-31.9] $35.4$ [1.9-12.4] $82.065$ $9.8$ [0.6-33.8] $4.5$ [0.6-8.5] $13$ [2.4-31.9] $35.4$ [9.8-77] $83.060$ $3.1$ [0-1.15] $1.4$ [0-2.7] $3.7$ [16-6.3] $3.3$ [0.4-6.8] $83.086$ $4.4$ [0.4-18.8] $4.9$ [0.4-18.8] $4.5$ [0.5-15.6] $4.7$ [2-6.4] $84.081$ $2$ [0.4-10] $1$ [0.4-2.5] $1.9$ [0.8-4] $1.1$ [0.6-2.3] $85.065$ $49.6$ [8.4-163.2] $65.2$ [9.5-137.8] $49.4$ [8.4-163.2] $17.5$ [5.9-50.4] $87.080$ $20.2$ [0.9-49.1] $18$ [0.9-43.7] $20$ [6.9-49.1] $31.7$ [11.5-101.6] $87.117$ $0.9$ [-0.1-3] $0.7$ [0.2-2] $0.9$ [-0.1-3] $0.7$ [-0.4-2.4] $89.060$ $1101$ [68.7-5914] $1058$ [166.4-2367] $1335$ [80.9-5914] $696$ [98.8-1955] $89.096$ $41$ [0-339.9] $26.3$ [9.3-52] $65.4$ [0-339.9] $26$ [5.7-52.4] $91.058$ $10.9$ [0.7-67.9] $8.6$ [0.7-20.3] $15.1$ [1.5-67.9] $7.3$ [2.2-19.2] $93.070$ $7.7$ [0.1-34.1] $2.4$ [0.1-9.3] $9.8$ [1.6-20.4] $2.7$ [0.5-7] $94.998$ $7.9$ [0.2-669.9] $8.9$ [0.2-46.8] $51.4$ [3-116.6] $7$ [0.8-17.3] $95.046$ $8.6$ [0.1-34.2] $7.6$ [1.5-12.7] $8.4$ [0.1-19.2] $13.4$ [5.5-33.4] $95.047$ $10.7$ [0.9-0.4] $3.8$ [0-17.4] $6.2$ [1.2-11.6] $5.6$ [0.3-18.5] $101.060$ $7.6$ [1.5-14.7]	80.040	77 2 [4 1 241 5]	2.5[0 10.2]	E0.2 [9.6, 101 6]	$2.1[0.2 \ 5.0]$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	81.070	77.5 [4.1-241.5]	90.5 [4.1-227.1]	59.5 [0.0-191.0]	35.1 [1.9–152.4]
$\begin{array}{llllllllllllllllllllllllllllllllllll$	81.070	8.9 [0.1–34.3]	7.2 [0.5-33.4]	6.8 [1.7-24.2]	1 [0-3.2]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	82.065	9.8 [0.6–33.8]	4.5 [0.6-8.5]	13 [2.4–31.9]	35.4 [9.8–77]
83.0864.4 $[0.4-18.8]$ 4.9 $[0.4-18.8]$ 4.5 $[0.5-15.6]$ 4.7 $[2-6.4]$ 84.0812 $[0.4-10]$ 1 $[0.4-2.5]$ 1.9 $[0.8-4]$ 1.1 $[0.6-2.3]$ 85.06549.6 $[8.4-163.2]$ 65.2 $[9.5-137.8]$ 49.4 $[8.4-163.2]$ 17.5 $[5.9-50.4]$ 87.044209.1 $[16.2-895.6]$ 158.7 $[16.2-500.1]$ 294.3 $[74.3-895.6]$ 463.9 $[43.4-1383]$ 87.08020.2 $[0.9-49.1]$ 18 $[0.9-43.7]$ 20 $[6.9-49.1]$ 31.7 $[11.5-101.6]$ 87.1170.9 $[-0.1-3]$ 0.7 $[0.2-2]$ 0.9 $[-0.1-3]$ 0.7 $[-0.4-2.4]$ 80.0601101 $[68.7-5914]$ 1058 $[166.4-2367]$ 1335 $[80.9-5914]$ 696 $[98.8-1955]$ 89.09641 $[0-339.9]$ 26.3 $[9.3-52]$ 65.4 $[0-339.9]$ 26 $[5.7-52.4]$ 91.05810.9 $[0.7-67.9]$ 8.6 $[0.7-20.3]$ 15.1 $[1.5-67.9]$ 7.3 $[2.2-19.2]$ 93.0707.7 $[0.1-34.1]$ 2.4 $[0.1-9.3]$ 9.8 $[1.6-20.4]$ 2.7 $[0.5-7]$ 94.99879.9 $[0.2-669.9]$ 8.9 $[0.2-46.8]$ 51.4 $[3-116.6]$ 7 $[0.8-17.3]$ 95.0168.6 $[0.1-34.2]$ 7.6 $[1.5-12.7]$ 8.4 $[0.1-19.2]$ 13.4 $[5.5-33.4]$ 95.04910.7 $[0-90.4]$ 3.8 $[0-17.4]$ 6.2 $[1.2-11.6]$ 5.6 $[0.3-18.5]$ 101.0607.6 $[1.5-14.7]$ 5.4 $(1.2-39.9)$ 49.2 $[3.3-183.2]$ 23.5 $[2.4-92.6]$ 103.07538.1 $[3.3-183.2]$ 20.1 $[4.2-39.9]$ 49.2 $[3.3-183.2]$ 23.5 $[2.4-92.6]$ 105.0704.4 $[0.4-13]$ 3.5 $[0.4-2.6]$ 3.7 $[1.4-5.3]$ 1.9 $[0.5-4.9]$ 107.0493.9 $[0.4-13.3]$ <td>83.060</td> <td>3.1 [0-11.5]</td> <td>1.4 [0-2.7]</td> <td>3.7 [1.6–6.3]</td> <td>3.3 [0.4–6.8]</td>	83.060	3.1 [0-11.5]	1.4 [0-2.7]	3.7 [1.6–6.3]	3.3 [0.4–6.8]
84.081 $2 [0.4-10]$ $1 [0.4-2.5]$ $1.9 [0.8-4]$ $1.1 [0.6-2.3]$ 85.06549.6 [8.4-163.2]65.2 [9.5-137.8]49.4 [8.4-163.2]17.5 [5.9-50.4]87.044209.1 [16.2-895.6]158.7 [16.2-500.1]294.3 [74.3-895.6]46.3.9 [43.4-1383]87.08020.2 [0.9-49.1]18 [0.9-43.7]20 [6.9-49.1]31.7 [11.5-101.6]87.1170.9 [-0.1-3.3]0.7 [0.2-2]0.9 [-0.1-3]0.7 [-0.4-2.4]89.0601101 [68.7-5914]1058 [166.4-2367]1335 [80.9-5914]696 [98.8-1955]80.09641 [0-339.9]26.3 [9.3-52]65.4 [0-339.9]26 [5.7-52.4]91.05810.9 [0.7-67.9]8.6 [0.7-20.3]15.1 [1.5-67.9]7.3 [2.2-19.2]93.0707.7 [0.1-34.1]2.4 [0.1-9.3]9.8 [1.6-20.4]2.7 [0.5-7]94.99879.9 [0.2-669.9]8.9 [0.2-46.8]51.4 [3-116.6]7 [0.8-17.3]95.0168.6 [0.1-34.2]7.6 [1.5-12.7]8.4 [0.1-19.2]13.4 [5.5-33.4]95.04910.7 [0-90.4]3.8 [0-17.4]6.2 [1.2-11.6]5.6 [0.3-18.5]101.0607.6 [1.5-14.7]5.4 [1.5-7.9]9.[3.6-14.7]5.1 [0.1-9.6]101.0963.2 [0.3-9.2]3 [0.5-9.2]2.5 [0.3-6.5]1.4 [0.2-2.9]103.07538.1 [3.3-183.2]20.1 [4.2-39.9]49.2 [3.3-183.2]23.5 [2.4-92.6]105.0704.4 (0.4-13]3.5 [0.4-12.6]3.7 [1.4-5.3]1.9 [0.5-4.9]107.0493.9 [0.4-13.3]2.5 [0.6-7.3]3.2 [0.4-6.1]2.7 [1.2-6.3]107.0867.2 [0.1-40.4]3.2 [0.	83.086	4.4 [0.4–18.8]	4.9 [0.4–18.8]	4.5 [0.5–15.6]	4.7 [2–6.4]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	84.081	2 [0.4–10]	1 [0.4–2.5]	1.9 [0.8–4]	1.1 [0.6–2.3]
87.044 $209.1$ $[16.2-895.6]$ $158.7$ $[16.2-500.1]$ $294.3$ $[74.3-895.6]$ $463.9$ $[43.4-1383]$ $87.080$ $20.2$ $[0.9-43.1]$ $18$ $[0.9-43.7]$ $20$ $[6.9-49.1]$ $31.7$ $[11.5-101.6]$ $87.117$ $0.9$ $[-0.1-3]$ $0.7$ $[0.2-2]$ $0.9$ $[-0.1-3]$ $0.7$ $[0.4-2.4]$ $89.060$ $1101$ $[68.7-5914]$ $1058$ $[166.4-2367]$ $1335$ $[80.9-5914]$ $696$ $[88.8-1955]$ $89.096$ $41$ $[0-339.9]$ $26.3$ $[9.3-52]$ $65.4$ $[0-339.9]$ $26$ $[5.7-52.4]$ $91.058$ $10.9$ $[0.7-67.9]$ $8.6$ $[0.7-20.3]$ $15.1$ $[1.5-67.9]$ $7.3$ $[2.2-19.2]$ $93.070$ $7.7$ $[0.1-34.1]$ $2.4$ $[0.1-9.3]$ $9.8$ $[1.6-20.4]$ $2.7$ $[0.5-7]$ $94.998$ $79.9$ $[0.2-669.9]$ $8.9$ $[0.2-46.8]$ $51.4$ $[-11.6.6]$ $7$ $[0.8-17.3]$ $95.049$ $10.7$ $[0-90.4]$ $3.8$ $[0-17.4]$ $6.2$ $[1.2-11.6]$ $5.6$ $[0.3-18.5]$ $101.060$ $7.6$ $[1.5-12.7]$ $8.4$ $[0.1-19.2]$ $13.4$ $[5.5-33.4]$ $95.049$ $10.7$ $[0-90.4]$ $3.8$ $[0-17.4]$ $6.2$ $[1.2-11.6]$ $5.6$ $[0.3-18.5]$ $101.060$ $7.6$ $[1.5-12.7]$ $5.4$ $[1.5-12.7]$ $9.4$ $[0.7-8]$ $23.5$ $[2.4-9.6]$ $101.060$ $7.6$ $[1.5-14.7]$ $5.4$	85.065	49.6 [8.4–163.2]	65.2 [9.5–137.8]	49.4 [8.4–163.2]	17.5 [5.9–50.4]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	87.044	209.1 [16.2–895.6]	158.7 [16.2–500.1]	294.3 [74.3–895.6]	463.9 [43.4–1383]
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	87.080	20.2 [0.9-49.1]	18 [0.9–43.7]	20 [6.9-49.1]	31.7 [11.5–101.6]
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	87.117	0.9 [-0.1–3.3]	0.7 [0.2–2]	0.9 [-0.1–3]	0.7 [-0.4–2.4]
89.09641 $[0-39.91]$ 26.3 $[9.3-52]$ 65.4 $[0-339.9]$ 26 $[5.7-52.4]$ 91.05810.9 $[0.7-67.9]$ 8.6 $[0.7-20.3]$ 15.1 $[1.5-67.9]$ 7.3 $[2.2-19.2]$ 93.0707.7 $[0.1-34.1]$ 2.4 $[0.1-9.3]$ 9.8 $[1.6-20.4]$ 2.7 $[0.5-7]$ 94.99879.9 $[0.2-669.9]$ 8.9 $[0.2-46.8]$ 51.4 $[3-116.6]$ 7 $[0.8-17.3]$ 95.0168.6 $[0.1-34.2]$ 7.6 $[1.5-12.7]$ 8.4 $[0.1-19.2]$ 13.4 $[5.5-33.4]$ 95.04910.7 $[0-90.4]$ 3.8 $[0-17.4]$ 6.2 $[1.2-11.6]$ 5.6 $[0.3-18.5]$ 101.0607.6 $[1.5-14.7]$ 5.4 $[1.5-7.9]$ 9 $[3.6-14.7]$ 5.1 $[0.1-9.6]$ 101.0963.2 $[0.3-9.2]$ 3 $[0.5-9.2]$ 2.5 $[0.3-6.5]$ 1.4 $[0.2-2.9]$ 103.07538.1 $[3.3-183.2]$ 20.1 $[4.2-39.9]$ 49.2 $[3.3-183.2]$ 23.5 $[2.4-92.6]$ 105.0704.4 $[0.4-13]$ 3.5 $[0.4-12.6]$ 3.7 $[1.4-5.3]$ 1.9 $[0.5-4.9]$ 107.0493.9 $[0.4-13.3]$ 2.5 $[0.6-7.3]$ 3.2 $[0.4-6.1]$ 2.7 $[1.2-6.3]$ 107.0867.2 $[0.1-40.4]$ 3.2 $[0.1-9.2]$ 3.3 $[0.4-8.2]$ 0.8 $[0.1-2.4]$ 109.0655.9 $[1.4-13.5]$ 4.7 $[1.4-12.6]$ 5.5 $[3.5-7]$ 3.4 $[0.7-8]$ 112.0761.2 $[0.1-4.7]$ 0.5 $[0.1-2.1]$ 1.2 $[0.3-3.3]$ 0.6 $[0.3-1.1]$ 112.120.5 $[0-5-7.4]$ 1.5 $[0-6-3.9]$ 2.9 $[1.8-4.4]$ 1.8 $[0.7-4.2]$ 113.0961.3 $[0-5.7]$ 0.8 $[0.2-1.9]$ 1.2 $[0-2.4]$ 0.7 $[0.3-0.9]$ 114.0307.5 $[0.6-19.5]$ 3.6 $[0.6-7.9]$ 1.5 $[2.7-19.5]$	89,060	1101 [68.7–5914]	1058 [166.4-2367]	1335 [80.9-5914]	696 [98.8–1955]
91.05810.9 [0.7-67.9]8.6 [0.7-20.3]15.1 [1.5-67.9]7.3 [2.2-19.2]93.0707.7 [0.1-34.1]2.4 [0.1-9.3]9.8 [1.6-20.4]2.7 [0.5-7]94.99879.9 [0.2-669.9]8.9 [0.2-46.8]51.4 [3-116.6]7 [0.8-17.3]95.0168.6 [0.1-34.2]7.6 [1.5-12.7]8.4 [0.1-19.2]13.4 [5.5-33.4]95.04910.7 [0-90.4]3.8 [0-17.4]6.2 [1.2-11.6]5.6 [0.3-18.5]101.0607.6 [1.5-14.7]5.4 [1.5-7.9]9 [3.6-14.7]5.1 [0.1-9.6]101.0963.2 [0.3-9.2]3 [0.5-9.2]2.5 [0.3-6.5]1.4 [0.2-2.9]103.07538.1 [3.3-183.2]20.1 [4.2-39.9]49.2 [3.3-183.2]23.5 [2.4-92.6]105.0704.4 [0.4-13]3.5 [0.4-12.6]3.7 [1.4-5.3]1.9 [0.5-4.9]107.0493.9 [0.4-13.3]2.5 [0.6-7.3]3.2 [0.4-6.1]2.7 [1.2-6.3]107.0867.2 [0.1-40.4]3.2 [0.1-9.2]3.3 [0.4-8.2]0.8 [0.1-2.4]109.0655.9 [1.4-13.5]4.7 [1.4-12.6]5.5 [3.5-7]3.4 [0.7-8]112.0761.2 [0.1-4.7]0.5 [0.1-2.1]1.2 [0.3-3.3]0.6 [0.3-1.1]112.1120.5 [0-2.5]0.2 [0-0.3]0.6 [0.1-1.1]1.4 [0.4-2.7]113.0602.5 [0.6-7.4]1.5 [0.6-3.9]2.9 [1.8-4.4]1.8 [0.7-4.2]113.0961.3 [0-5.7]0.8 [0.2-1.9]1.2 [0-2.4]0.7 [0.3-0.9]114.0307.5 [0.6-19.5]3.6 [0.6-7.9]11.5 [2.7-19.5]10.6 [2.4-36.5]115.0754 [0.6-10.9]1.9 [0.6-4.1]4.9 [1.8-7.6]2.6 [0.9-5.	89.096	41 [0-339 9]	26 3 [9 3-52]	65.4 [0-339.9]	26 [5 7–52 4]
93.03010.3 [0.7 0.7]0.0 [0.7 20.3]10.1 [1.6 -20.4]2.7 [0.2 -57]94.99879.9 [0.2 -669.9]8.9 [0.2 -46.8]51.4 [3 -116.6]7 [0.8 -17.3]95.0168.6 [0.1 - 34.2]7.6 [1.5 - 12.7]8.4 [0.1 - 19.2]13.4 [5.5 - 33.4]95.04910.7 [0 - 90.4]3.8 [0 - 17.4]6.2 [1.2 - 11.6]5.6 [0.3 - 18.5]101.0607.6 [1.5 - 14.7]5.4 [1.5 - 7.9]9 [3.6 - 14.7]5.1 [0.1 - 9.6]101.0963.2 [0.3 - 9.2]3 [0.5 - 9.2]2.5 [0.3 - 6.5]1.4 [0.2 - 2.9]103.07538.1 [3.3 - 183.2]20.1 [4.2 - 39.9]49.2 [3.3 - 183.2]23.5 [2.4 - 92.6]105.0704.4 [0.4 - 13]3.5 [0.4 - 12.6]3.7 [1.4 - 5.3]1.9 [0.5 - 4.9]107.0493.9 [0.4 - 13.3]2.5 [0.6 - 7.3]3.2 [0.4 - 6.1]2.7 [1.2 - 6.3]107.0867.2 [0.1 - 40.4]3.2 [0.1 - 9.2]3.3 [0.4 - 8.2]0.8 [0.1 - 2.4]109.0655.9 [1.4 - 13.5]4.7 [1.4 - 12.6]5.5 [3.5 - 7]3.4 [0.7 - 8]112.0761.2 [0.1 - 4.7]0.5 [0.1 - 2.1]1.2 [0.3 - 3.3]0.6 [0.3 - 1.1]112.1120.5 [0 - 2.5]0.2 [0 - 0.3]0.6 [0.1 - 1.1]1.4 [0.4 - 2.7]113.0602.5 [0.6 - 7.4]1.5 [0.6 - 7.9]1.2 [0 - 2.4]0.7 [0.3 - 0.9]114.0307.5 [0.6 - 19.5]3.6 [0.6 - 7.9]1.5 [2.7 - 19.5]10.6 [2.4 - 36.5]115.0754 [0.6 - 10.9]1.9 [0.6 - 4.1]4.9 [1.8 - 7.6]2.6 [0.9 - 5.4]115.123.2 [0 - 18.3]2.5 [0.2 - 8.1]2.5 [0.1 - 8.6]1 [	91 058	10 9 [0 7-67 9]	8 6 [0 7-20 3]	15 1 [1 5_67 9]	7 3 [2 2–19 2]
95.0707.7 $[0.1-34.1]$ 2.4 $[0.1-9.3]$ 5.8 $[1.0-20.4]$ 2.7 $[0.3-7]$ 94.99879.9 $[0.2-669.9]$ 8.9 $[0.2-46.8]$ 51.4 $[3-116.6]$ 7 $[0.8-17.3]$ 95.0168.6 $[0.1-34.2]$ 7.6 $[1.5-12.7]$ 8.4 $[0.1-19.2]$ 13.4 $[5.5-33.4]$ 95.04910.7 $[0-90.4]$ 3.8 $[0-17.4]$ 6.2 $[1.2-11.6]$ 5.6 $[0.3-18.5]$ 101.0607.6 $[1.5-14.7]$ 5.4 $[1.5-7.9]$ 9 $[3.6-14.7]$ 5.1 $[0.1-9.6]$ 101.0963.2 $[0.3-9.2]$ 3 $[0.5-9.2]$ 2.5 $[0.3-6.5]$ 1.4 $[0.2-2.9]$ 103.07538.1 $[3.3-183.2]$ 20.1 $[4.2-39.9]$ 49.2 $[3.3-183.2]$ 23.5 $[2.4-92.6]$ 105.0704.4 $[0.4-13]$ 3.5 $[0.4-12.6]$ 3.7 $[1.4-5.3]$ 1.9 $[0.5-4.9]$ 107.0493.9 $[0.4-13.3]$ 2.5 $[0.6-7.3]$ 3.2 $[0.4-6.1]$ 2.7 $[1.2-6.3]$ 107.0867.2 $[0.1-40.4]$ 3.2 $[0.1-9.2]$ 3.3 $[0.4-8.2]$ 0.8 $[0.1-2.4]$ 109.0655.9 $[1.4-13.5]$ 4.7 $[1.4-12.6]$ 5.5 $[3.5-7]$ 3.4 $[0.7-8]$ 112.0761.2 $[0.1-4.7]$ 0.5 $[0.1-2.1]$ 1.2 $[0.3-3.3]$ 0.6 $[0.3-1.1]$ 112.1120.5 $[0-2.5]$ 0.2 $[0-0.3]$ 0.6 $[0.1-1.1]$ 1.4 $[0.4-2.7]$ 113.0602.5 $[0.6-7.4]$ 1.5 $[0.6-3.9]$ 2.9 $[1.8-4.4]$ 1.8 $[0.7-4.2]$ 113.0961.3 $[0-5.7]$ 0.8 $[0.2-1.9]$ 1.2 $[0-2.4]$ 0.7 $[0.3-0.9]$ 114.0307.5 $[0.6-19.5]$ 3.6 $[0.6-7.9]$ 11.5 $[2.7-19.5]$ 10.6 $[2.4-36.5]$ 115.0754 $[0.6-10.9]$ 1.9 $[0.6-4.1]$ 4.9 $[1.8-7.6]$ <td>02 070</td> <td>77[01 241]</td> <td>24[01 02]</td> <td><math>0 \times [1 \times 20.4]</math></td> <td></td>	02 070	77[01 241]	24[01 02]	$0 \times [1 \times 20.4]$	
94.99879.9 $[0.2-669.9]$ 8.9 $[0.2-46.8]$ 51.4 $[3-116.6]$ 7 $[0.8-17.3]$ 95.0168.6 $[0.1-34.2]$ 7.6 $[1.5-12.7]$ 8.4 $[0.1-19.2]$ 13.4 $[5.5-33.4]$ 95.04910.7 $[0-90.4]$ 3.8 $[0-17.4]$ 6.2 $[1.2-11.6]$ 5.6 $[0.3-18.5]$ 101.0607.6 $[1.5-14.7]$ 5.4 $[1.5-7.9]$ 9 $[3.6-14.7]$ 5.1 $[0.1-9.6]$ 101.0963.2 $[0.3-9.2]$ 3 $[0.5-9.2]$ 2.5 $[0.3-6.5]$ 1.4 $[0.2-2.9]$ 103.07538.1 $[3.3-183.2]$ 20.1 $[4.2-39.9]$ 49.2 $[3.3-183.2]$ 23.5 $[2.4-92.6]$ 105.0704.4 $[0.4-13]$ 3.5 $[0.4-12.6]$ 3.7 $[1.4-5.3]$ 1.9 $[0.5-4.9]$ 107.0493.9 $[0.4-13.3]$ 2.5 $[0.6-7.3]$ 3.2 $[0.4-6.1]$ 2.7 $[1.2-6.3]$ 107.0867.2 $[0.1-40.4]$ 3.2 $[0.1-9.2]$ 3.3 $[0.4-8.2]$ 0.8 $[0.1-2.4]$ 109.0655.9 $[1.4-13.5]$ 4.7 $[1.4-12.6]$ 5.5 $[3.5-7]$ 3.4 $[0.7-8]$ 112.0761.2 $[0.1-4.7]$ 0.5 $[0.1-2.1]$ 1.2 $[0.3-3.3]$ 0.6 $[0.3-1.1]$ 112.1120.5 $[0-2.5]$ 0.2 $[0-0.3]$ 0.6 $[0.1-1.1]$ 1.4 $[0.4-2.7]$ 113.0602.5 $[0.6-7.4]$ 1.5 $[0.6-3.9]$ 2.9 $[1.8-4.4]$ 1.8 $[0.7-4.2]$ 113.0961.3 $[0-5.7]$ 0.8 $[0.2-1.9]$ 1.2 $[0-2.4]$ 0.7 $[0.3-0.9]$ 114.0307.5 $[0.6-19.5]$ 3.6 $[0.6-7.9]$ 1.5 $[2.7-19.5]$ 10.6 $[2.4-36.5]$ 115.0754 $[0.6-10.9]$ 1.9 $[0.6-4.1]$ 4.9 $[1.8-7.6]$ 2.6 $[0.9-5.4]$ 115.123.2 $[0-2-5.1]$ 0.2 $[0.2-0.2]$ 0.4 $[-0.2-1.6]$ <td>93.070</td> <td>7.7 [0.1-34.1]</td> <td>2.4 [0.1-9.3]</td> <td>9.8 [1.0-20.4]</td> <td>2.7 [0.5-7]</td>	93.070	7.7 [0.1-34.1]	2.4 [0.1-9.3]	9.8 [1.0-20.4]	2.7 [0.5-7]
95.0168.6 $[0.1-34.2]$ 7.6 $[1.5-12.7]$ 8.4 $[0.1-19.2]$ 13.4 $[5.5-33.4]$ 95.04910.7 $[0-90.4]$ 3.8 $[0-17.4]$ 6.2 $[1.2-11.6]$ 5.6 $[0.3-18.5]$ 101.0607.6 $[1.5-14.7]$ 5.4 $[1.5-7.9]$ 9 $[3.6-14.7]$ 5.1 $[0.1-9.6]$ 101.0963.2 $[0.3-9.2]$ 3 $[0.5-9.2]$ 2.5 $[0.3-6.5]$ 1.4 $[0.2-2.9]$ 103.07538.1 $[3.3-183.2]$ 20.1 $[4.2-39.9]$ 49.2 $[3.3-183.2]$ 23.5 $[2.4-92.6]$ 105.0704.4 $[0.4-13]$ 3.5 $[0.4-12.6]$ 3.7 $[1.4-5.3]$ 1.9 $[0.5-4.9]$ 107.0493.9 $[0.4-13.3]$ 2.5 $[0.6-7.3]$ 3.2 $[0.4-6.1]$ 2.7 $[1.2-6.3]$ 107.0867.2 $[0.1-40.4]$ 3.2 $[0.1-9.2]$ 3.3 $[0.4-8.2]$ 0.8 $[0.1-2.4]$ 109.0655.9 $[1.4-13.5]$ 4.7 $[1.4-12.6]$ 5.5 $[3.5-7]$ 3.4 $[0.7-8]$ 112.0761.2 $[0.1-4.7]$ 0.5 $[0.1-2.1]$ 1.2 $[0.3-3.3]$ 0.6 $[0.3-1.1]$ 112.1120.5 $[0-2.5]$ 0.2 $[0-0.3]$ 0.6 $[0.1-1.1]$ 1.4 $[0.4-2.7]$ 113.0602.5 $[0.6-7.4]$ 1.5 $[0.6-3.9]$ 2.9 $[1.8-4.4]$ 1.8 $[0.7-4.2]$ 113.0961.3 $[0-5.7]$ 0.8 $[0.2-1.9]$ 1.2 $[0-2.4]$ 0.7 $[0.3-0.9]$ 114.0307.5 $[0.6-10.9]$ 1.9 $[0.6-4.1]$ 4.9 $[1.8-7.6]$ 2.6 $[0.9-5.4]$ 115.0754 $[0.6-10.9]$ 1.9 $[0.6-4.1]$ 4.9 $[1.8-7.6]$ 2.6 $[0.9-5.4]$ 115.1123.2 $[0-18.3]$ 2.5 $[0.2-8.1]$ 2.5 $[0.1-8.6]$ 1 $[0.1-4.7]$ 115.1240.8 $[0.2-5.1]$ 0.2 $[0.2-0.2]$ 0.4 $[-0.2-1.6]$ 1.6	94.998	79.9 [0.2-669.9]	8.9 [0.2–46.8]	51.4 [3-116.6]	/[0.8-17.3]
95.04910.7 $[0-90.4]$ 3.8 $[0-17.4]$ 6.2 $[1.2-11.6]$ 5.6 $[0.3-18.5]$ 101.0607.6 $[1.5-14.7]$ 5.4 $[1.5-7.9]$ 9 $[3.6-14.7]$ 5.1 $[0.1-9.6]$ 101.0963.2 $[0.3-9.2]$ 3 $[0.5-9.2]$ 2.5 $[0.3-6.5]$ 1.4 $[0.2-2.9]$ 103.07538.1 $[3.3-183.2]$ 20.1 $[4.2-39.9]$ 49.2 $[3.3-183.2]$ 23.5 $[2.4-92.6]$ 105.0704.4 $[0.4-13]$ 3.5 $[0.4-12.6]$ 3.7 $[1.4-5.3]$ 1.9 $[0.5-4.9]$ 107.0493.9 $[0.4-13.3]$ 2.5 $[0.6-7.3]$ 3.2 $[0.4-6.1]$ 2.7 $[1.2-6.3]$ 107.0867.2 $[0.1-40.4]$ 3.2 $[0.1-9.2]$ 3.3 $[0.4-8.2]$ 0.8 $[0.1-2.4]$ 109.0655.9 $[1.4-13.5]$ 4.7 $[1.4-12.6]$ 5.5 $[3.5-7]$ 3.4 $[0.7-8]$ 112.0761.2 $[0.1-4.7]$ 0.5 $[0.1-2.1]$ 1.2 $[0.3-3.3]$ 0.6 $[0.3-1.1]$ 112.1120.5 $[0-2.5]$ 0.2 $[0-0.3]$ 0.6 $[0.1-1.1]$ 1.4 $[0.4-2.7]$ 113.0602.5 $[0.6-7.4]$ 1.5 $[0.6-3.9]$ 2.9 $[1.8-4.4]$ 1.8 $[0.7-4.2]$ 113.0961.3 $[0-5.7]$ 0.8 $[0.2-1.9]$ 1.2 $[0-2.4]$ 0.7 $[0.3-0.9]$ 114.0307.5 $[0.6-19.5]$ 3.6 $[0.6-7.9]$ 11.5 $[2.7-19.5]$ 10.6 $[2.4-36.5]$ 115.0754 $[0.6-10.9]$ 1.9 $[0.6-4.1]$ 4.9 $[1.8-7.6]$ 2.6 $[0.9-5.4]$ 115.1123.2 $[0-18.3]$ 2.5 $[0.2-8.1]$ 2.5 $[0.1-8.6]$ 1 $[0.1-4.7]$ 115.1480.8 $[0.2-5.1]$ 0.2 $[0.2-0.2]$ 0.4 $[-0.2-1.6]$ 11 $[0.1-4.7]$ 115.1480.8 $[0.2-5.1]$ 0.2 $[0.2-0.2]$ 0.4 $[-0.2-1.6]$ 1.8	95.016	8.6 [0.1–34.2]	7.6 [1.5–12.7]	8.4 [0.1–19.2]	13.4 [5.5–33.4]
101.060 $7.6 [1.5-14.7]$ $5.4 [1.5-7.9]$ $9 [3.6-14.7]$ $5.1 [0.1-9.6]$ $101.096$ $3.2 [0.3-9.2]$ $3 [0.5-9.2]$ $2.5 [0.3-6.5]$ $1.4 [0.2-2.9]$ $103.075$ $38.1 [3.3-183.2]$ $20.1 [4.2-39.9]$ $49.2 [3.3-183.2]$ $23.5 [2.4-92.6]$ $105.070$ $4.4 [0.4-13]$ $3.5 [0.4-12.6]$ $3.7 [1.4-5.3]$ $1.9 [0.5-4.9]$ $107.049$ $3.9 [0.4-13.3]$ $2.5 [0.6-7.3]$ $3.2 [0.4-6.1]$ $2.7 [1.2-6.3]$ $107.086$ $7.2 [0.1-40.4]$ $3.2 [0.1-9.2]$ $3.3 [0.4-8.2]$ $0.8 [0.1-2.4]$ $109.065$ $5.9 [1.4-13.5]$ $4.7 [1.4-12.6]$ $5.5 [3.5-7]$ $3.4 [0.7-8]$ $112.076$ $1.2 [0.1-4.7]$ $0.5 [0.1-2.1]$ $1.2 [0.3-3.3]$ $0.6 [0.3-1.1]$ $112.112$ $0.5 [0-2.5]$ $0.2 [0-0.3]$ $0.6 [0.1-1.1]$ $1.4 [0.4-2.7]$ $113.060$ $2.5 [0.6-7.4]$ $1.5 [0.6-3.9]$ $2.9 [1.8-4.4]$ $1.8 [0.7-4.2]$ $113.096$ $1.3 [0-5.7]$ $0.8 [0.2-1.9]$ $1.2 [0-2.4]$ $0.7 [0.3-0.9]$ $114.030$ $7.5 [0.6-19.5]$ $3.6 [0.6-7.9]$ $11.5 [2.7-19.5]$ $10.6 [2.4-36.5]$ $115.075$ $4 [0.6-10.9]$ $1.9 [0.6-4.1]$ $4.9 [1.8-7.6]$ $2.6 [0.9-5.4]$ $115.112$ $3.2 [0-18.3]$ $2.5 [0.2-8.1]$ $2.5 [0.1-8.6]$ $1[0.1-4.7]$ $115.148$ $0.8 [0.2-5.1]$ $0.2 [0.2-0.2]$ $0.4 [-0.2-1.6]$ $117.091$ $10.8 [0.7-76.8]$ $2 [0.7-3.8]$ $14.3 [1.7-76.8]$ $4.8 [0.3-14.5]$ $118.065$ $3.6 [0.3-19.5]$ $1.3 [0.3-2.9]$ $3.6 [1.1-10.2$	95.049	10.7 [0–90.4]	3.8 [0–17.4]	6.2 [1.2–11.6]	5.6 [0.3–18.5]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	101.060	7.6 [1.5–14.7]	5.4 [1.5–7.9]	9 [3.6–14.7]	5.1 [0.1–9.6]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	101.096	3.2 [0.3–9.2]	3 [0.5–9.2]	2.5 [0.3–6.5]	1.4 [0.2–2.9]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	103.075	38.1 [3.3–183.2]	20.1 [4.2–39.9]	49.2 [3.3–183.2]	23.5 [2.4–92.6]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	105.070	4.4 [0.4–13]	3.5 [0.4–12.6]	3.7 [1.4–5.3]	1.9 [0.5–4.9]
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	107.049	3.9 [0.4–13.3]	2.5 [0.6–7.3]	3.2 [0.4–6.1]	2.7 [1.2-6.3]
101/005         5.9 [1.4-13.5]         4.7 [1.4-12.6]         5.5 [3.5-7]         3.4 [0.7-8]           112.076         1.2 [0.1-4.7]         0.5 [0.1-2.1]         1.2 [0.3-3.3]         0.6 [0.3-1.1]           112.112         0.5 [0-2.5]         0.2 [0-0.3]         0.6 [0.1-1.1]         1.4 [0.4-2.7]           113.060         2.5 [0.6-7.4]         1.5 [0.6-3.9]         2.9 [1.8-4.4]         1.8 [0.7-4.2]           113.096         1.3 [0-5.7]         0.8 [0.2-1.9]         1.2 [0-2.4]         0.7 [0.3-0.9]           114.030         7.5 [0.6-19.5]         3.6 [0.6-7.9]         11.5 [2.7-19.5]         10.6 [2.4-36.5]           115.075         4 [0.6-10.9]         1.9 [0.6-4.1]         4.9 [1.8-7.6]         2.6 [0.9-5.4]           115.112         3.2 [0-18.3]         2.5 [0.2-8.1]         2.5 [0.1-8.6]         1 [0.1-4.7]           115.148         0.8 [-0.2-5.1]         0.2 [0.2-0.2]         0.4 [-0.2-1.6]         117.091           117.091         10.8 [0.7-76.8]         2 [0.7-3.8]         14.3 [1.7-76.8]         4.8 [0.3-14.5]           118.065         3.6 [0.3-19.5]         1.3 [0.3-2.9]         3.6 [1.1-10.2]         2.2 [0.5-5]	107.086	7.2 [0.1-40.4]	3.2 [0.1–9.2]	3.3 [0.4–8.2]	0.8[0.1-2.4]
100.003       1.0 [1.4 1.5]       1.7 [1.4 1.5]       1.5 [1.5 1]       1.5 [0.5 7]         112.076       1.2 [0.1-4.7]       0.5 [0.1-2.1]       1.2 [0.3-3.3]       0.6 [0.3-1.1]         112.112       0.5 [0-2.5]       0.2 [0-0.3]       0.6 [0.1-1.1]       1.4 [0.4-2.7]         113.060       2.5 [0.6-7.4]       1.5 [0.6-3.9]       2.9 [1.8-4.4]       1.8 [0.7-4.2]         113.096       1.3 [0-5.7]       0.8 [0.2-1.9]       1.2 [0-2.4]       0.7 [0.3-0.9]         114.030       7.5 [0.6-19.5]       3.6 [0.6-7.9]       11.5 [2.7-19.5]       10.6 [2.4-36.5]         115.075       4 [0.6-10.9]       1.9 [0.6-4.1]       4.9 [1.8-7.6]       2.6 [0.9-5.4]         115.112       3.2 [0-18.3]       2.5 [0.2-8.1]       2.5 [0.1-8.6]       1 [0.1-4.7]         115.148       0.8 [0.2-5.1]       0.2 [0.2-0.2]       0.4 [-0.2-1.6]       1         117.091       10.8 [0.7-76.8]       2 [0.7-3.8]       14.3 [1.7-76.8]       4.8 [0.3-14.5]         118.065       3.6 [0.3-19.5]       1.3 [0.3-2.9]       3.6 [1.1-10.2]       2.2 [0.5-5]	109.065	5 9 [1 4 - 13 5]	47[14-126]	5 5 [3 5-7]	3 4 [0 7-8]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	112.076	12[01 47]		12[0222]	$0 \in [0, 2, 1, 1]$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	112.0/0			1.2 [0.3-3.3]	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	112.112	0.5 [0-2.5]	0.2 [0-0.3]	0.0 [0.1–1.1]	1.4 [0.4–2.7]
113.096         1.3 [0-5.7]         0.8 [0.2-1.9]         1.2 [0-2.4]         0.7 [0.3-0.9]           114.030         7.5 [0.6-19.5]         3.6 [0.6-7.9]         11.5 [2.7-19.5]         10.6 [2.4-36.5]           115.075         4 [0.6-10.9]         1.9 [0.6-4.1]         4.9 [1.8-7.6]         2.6 [0.9-5.4]           115.112         3.2 [0-18.3]         2.5 [0.2-8.1]         2.5 [0.1-8.6]         1 [0.1-4.7]           115.148         0.8 [-0.2-5.1]         0.2 [0.2-0.2]         0.4 [-0.2-1.6]         117.091           117.091         10.8 [0.7-76.8]         2 [0.7-3.8]         14.3 [1.7-76.8]         4.8 [0.3-14.5]           118.065         3.6 [0.3-19.5]         1.3 [0.3-2.9]         3.6 [1.1-10.2]         2.2 [0.5-5]	113.060	2.5 [0.6-7.4]	1.5 [0.6-3.9]	2.9 [1.8–4.4]	1.8 [0.7-4.2]
114.030         7.5 [0.6–19.5]         3.6 [0.6–7.9]         11.5 [2.7–19.5]         10.6 [2.4–36.5]           115.075         4 [0.6–10.9]         1.9 [0.6–4.1]         4.9 [1.8–7.6]         2.6 [0.9–5.4]           115.112         3.2 [0–18.3]         2.5 [0.2–8.1]         2.5 [0.1–8.6]         1 [0.1–4.7]           115.148         0.8 [-0.2–5.1]         0.2 [0.2–0.2]         0.4 [-0.2–1.6]         117.091           117.091         10.8 [0.7–76.8]         2 [0.7–3.8]         14.3 [1.7–76.8]         4.8 [0.3–14.5]           118.065         3.6 [0.3–19.5]         1.3 [0.3–2.9]         3.6 [1.1–10.2]         2.2 [0.5–5]	113.096	1.3 [0–5.7]	0.8 [0.2–1.9]	1.2 [0-2.4]	0.7 [0.3–0.9]
115.075         4 [0.6–10.9]         1.9 [0.6–4.1]         4.9 [1.8–7.6]         2.6 [0.9–5.4]           115.112         3.2 [0–18.3]         2.5 [0.2–8.1]         2.5 [0.1–8.6]         1 [0.1–4.7]           115.148         0.8 [-0.2–5.1]         0.2 [0.2–0.2]         0.4 [-0.2–1.6]         1           117.091         10.8 [0.7–76.8]         2 [0.7–3.8]         14.3 [1.7–76.8]         4.8 [0.3–14.5]           118.065         3.6 [0.3–19.5]         1.3 [0.3–2.9]         3.6 [1.1–10.2]         2.2 [0.5–5]	114.030	7.5 [0.6–19.5]	3.6 [0.6–7.9]	11.5 [2.7–19.5]	10.6 [2.4–36.5]
115.112         3.2 [0-18.3]         2.5 [0.2-8.1]         2.5 [0.1-8.6]         1 [0.1-4.7]           115.148         0.8 [-0.2-5.1]         0.2 [0.2-0.2]         0.4 [-0.2-1.6]         1           117.091         10.8 [0.7-76.8]         2 [0.7-3.8]         14.3 [1.7-76.8]         4.8 [0.3-14.5]           118.065         3.6 [0.3-19.5]         1.3 [0.3-2.9]         3.6 [1.1-10.2]         2.2 [0.5-5]	115.075	4 [0.6–10.9]	1.9 [0.6–4.1]	4.9 [1.8–7.6]	2.6 [0.9–5.4]
115.1480.8 [-0.2–5.1]0.2 [0.2–0.2]0.4 [-0.2–1.6]117.09110.8 [0.7–76.8]2 [0.7–3.8]14.3 [1.7–76.8]4.8 [0.3–14.5]118.0653.6 [0.3–19.5]1.3 [0.3–2.9]3.6 [1.1–10.2]2.2 [0.5–5]	115.112	3.2 [0-18.3]	2.5 [0.2-8.1]	2.5 [0.1-8.6]	1 [0.1–4.7]
117.09110.8 [0.7–76.8]2 [0.7–3.8]14.3 [1.7–76.8]4.8 [0.3–14.5]118.0653.6 [0.3–19.5]1.3 [0.3–2.9]3.6 [1.1–10.2]2.2 [0.5–5]	115.148	0.8 [-0.2–5.1]	0.2 [0.2–0.2]	0.4 [-0.2–1.6]	
118.065 3.6 [0.3–19.5] 1.3 [0.3–2.9] 3.6 [1.1–10.2] 2.2 [0.5–5]	117.091	10.8 [0.7-76.8]	2 [0.7–3.8]	14.3 [1.7–76.8]	4.8 [0.3–14.5]
	118.065	3.6 [0.3-19.5]	1.3 [0.3–2.9]	3.6 [1.1–10.2]	2.2 [0.5–5]

# Table 24.Mean and range of emission rates (ng/m²/s) for compounds, categorised by<br/>mass, that were measured using PTR-TofMS (mean [minimum-maximum])

TOF				
protonated	All litter	Dry litter	Wet litter	Excreta
mass (H+)				
121.065	2.5 [0.5–5.1]	2.3 [0.5–5.1]	2.3 [1-4.4]	6.1 [0.3–16.4]
123.044	0.9 [0–3.9]	0.3 [0-0.8]	0.7 [0-1.6]	3.2 [0.3-8.7]
123.081	3.2 [1-7.2]	2.8 [1–7.2]	3.3 [2.1–6.3]	1.6 [0.3–4.7]
125.060	1.7 [0.5-3.4]	1.1 [0.5–2.1]	2.2 [1.1–3.4]	1.8 [0.9–4.6]
126.971	5.7 [0–34]	0.9 [0-4.5]	10.6 [2.1–34]	1.3 [0.1–2.5]
129.091	4.2 [0.4–14.5]	2.2 [0.4–4.3]	4.5 [1.9–9.4]	2 [0.8–6.1]
129.127	4.1 [0-14.3]	2.5 [0-6.6]	4.1 [1.3–13.1]	1.6 [0-8.3]
131.107	5.3 [0.4–22.9]	2.7 [0.4–7.7]	6.5 [1.9–22.9]	1.5 [0.1-4.1]
132.081	1.6 [0.1–7.3]	0.6 [0.1–1.9]	1.8 [0.5–3.5]	1.7 [1.1–2.7]
137.133	17.3 [2.8–49.2]	15 [3.3–49.2]	14.9 [2.8–38]	1.2 [0-2.5]
143.143	1.1 [0-5.5]	0.9 [0–3]	1.2 [0.1–5.5]	0.8 [0.1–2.1]
143.080	2.2 [0.6-7.5]	1.4 [0.6–2.2]	2.2 [0.8–4.7]	1.2 [0.5–2.4]
143.179	0.7 [0-4.6]	0.5 [0–0.8]	0.5 [0-1.1]	0.2 [0.1–0.2]
145.123	2 [0.3-8.8]	0.6 [0.3–1.7]	1.8 [0.5–5]	0.9 [0.3–2.5]
149.023	3.5 [0.7–17]	2.5 [1.1–5]	4.8 [0.7–17]	0.6 [0-1.3]
149.096	9.8 [1–53.8]	9.3 [3.6–19.8]	13 [1–53.8]	0.8 [0.1–2.8]
165.076	1.5 [0.1–7.4]	0.7 [0.1–3.4]	1.5 [0.3–3.1]	0.6 [0.2–1.3]
171.211	2.1 [0.1–11.6]	0.8 [0.1–2.8]	1.9 [0.6–4.1]	1.2 [0.5–2.9]

#### Table 24. Continued.

### 8.3.2.2 Using the PTR-TofMS for litter odour sampling

Using the PTR-TofMS in conjunction with the flux hood provided instant feedback on odorant concentrations within the flux hood. This was seen as an advantages over the use of sorption tubes and sample bags because it was possible to know when emissions from the litter surface had reached steady state. It was also possible to observe the concentration of odorants persisting in the flux hood after it was removed from the sample and placed on the stainless steel surface for flushing with high purity nitrogen prior to using on the following samples. Following wet and excreta samples in particular, the flux chamber occasionally required flushing for 30–60 minutes before some VOCs returned to low ppb concentrations (especially protonated masses 61.028, 47.013, 43.0).

Extremely high concentration of some samples required up to 90% dilution to keep the gas concentration with the instrument's range. The operator was able to increase the amount of dilution to enable valid sample measurement (rather than exceeding the ionization capacity).

Some of the challenges with using PTR-TofMS to analyse a broad range of VOCs included the detailed interpretation of the mass spectrum and inability to positively identify specific VOC compounds. Many of the odorants present in poultry odour have the same molecular weight as other odorants and when protonated will present as the same peak (protonated mass) in the mass spectrum. It is not possible to discriminate a broad number of compounds without customising the configuration of the instrument.

One option could have been to use additional reagent ions (NO+ and O2+) but this still would not have guaranteed discrimination between all compounds with the same mass. Additionally, the change between reagent ions requires a stabilisation period of several minutes, which extends the time required to analyse a sample. Some peaks in the mass spectrum were fragments of VOCs and with the wide range of compounds in poultry odour it was not possible to know if every peak was representing a VOC, percentage of a VOC or a fragment from the ionization process. As such, the outputs from the PTR-TofMS were interpreted in terms of protonated masses and the accompanying 'possible VOCs/odorants' (Appendix I) assigned to each protonated mass should be considered as a guide only.

### 8.3.2.3 Statistical analysis of PTR-TofMS results

At the conclusion of the laboratory pen trial, odour emissions from 37 *Litter Type* and *Week* combinations were analysed using PTR-TofMS. There was a significant two-way interaction between *Litter Type* and *Week* for pH (P<0.001) and a nearly significant interaction for moisture content (P=0.077). Both pH and moisture content were significantly affected by the main effects *Litter type* and *Week* (P<0.001). These interactions were similar to those found during the analysis of litter conditions from meat chicken sheds. Significant differences in moisture content and pH confirmed one of the objectives of the laboratory pen trial, which was to have distinct differences between dry and wet litter.

Emission rates (ng/m<sup>2</sup>/s) were calculated for each of the peaks in the mass spectrum (Appendix L). Statistical analysis showed that there were significant (P<0.05) two-way interactions between *Litter* Type and Week for 38% of the masses (Table 25). Furthermore, 77% of the masses were significantly different (P<0.05) by the main effect *Litter Type* and 61% were different by *Week*. This provided a clear indication that VOC emissions were different from wet litter compared to dry litter.

			Type.W	'eek	Litter Ty	/pe	Week	٢
		Litter Moisture Content	0.077		<0.001	**	<0.001	**
		Water Activity	0.257		<0.001	**	0.034	*
		рН	<0.001	**	0.002	**	0.015	*
<u>MW(H+)</u>	MW	Possible VOC/odorant con	npound					
33.033	32.026	Methanol	0.666		<0.001	**	0.009	**
34.988	33.988	Hydrogen Sulfide	0.469		<0.001	**	0.050	
41.039	40.031	Cyclopropene Propyne	0.010	*	<0.001	**	<0.001	**
42.034	41.027	Acetonitrile	0.019	*	<0.001	**	<0.001	**
43.000	42.011+ 42.047	Fragments of multiple compounds	<0.001	**	0.003	**	<0.001	**
45.034	44.026	Acetylaldehyde	0.060		<0.001	**	0.947	
46.065	45.058	Dimethylamine	0.169		<0.001	**	0.001	**
47.013	46.006	Formic Acid	0.181		0.018	*	0.194	
47.049	46.042	Ethanol	0.056		<0.001	**	0.065	
49.011	48.003	MethylMercaptan	0.721		0.002	**	0.009	**
55.054	54.047	(1,2- or 1,3-)Butadiene	0.012	*	<0.001	**	0.002	**
57.032	56.025	2-Propenal	0.028	*	0.045	*	0.286	
57.070	56.063	Butanol (M74); 2-Methyl-1-Propene	0.020	*	<0.001	**	<0.001	**
59.049	58.042	Acetone	0.297		0.709		<0.001	**
60.044	59.037	Acetamide	0.074		0.447		0.002	**
60.081	59.074	Trimethylamine	0.003	**	0.010	*	<0.001	**
61.028	60.021	Acetic Acid	0.005	**	0.036	*	0.006	**
61.065	60.058	n-Propanol; Ethylenediamine	0.014	*	0.020	*	0.018	*
63.026	62.019	DMS; Ethylmercaptan	0.296		<0.001	**	<0.001	**
68.050	67.042	Pyrrole	0.595		<0.001	**	<0.001	**
69.070	68.063	Isoprene	0.134		0.051		0.139	
71.049	70.042	Methylvinylketone	<0.001	**	0.003	**	<0.001	**
73.065	72.058	2-Butanone (MEK); Isobutyraldehyde; Butanal	0.055		<0.001	**	<0.001	**
75.044	74.037	Propanoic acid	0.005	**	0.089		0.015	*
75.080	74.073	Isobutyl alcohol n- and 2 Butanol (frag. to M57.070)	0.637		<0.001	**	0.003	**
79.054	78.047	Benzene	0.116		0.488		0.045	*
78.967	77.960	Possible sulfur compound	0.351		<0.001	**	0.058	
80.049	79.042	2,4-Pentadienenitrile	<0.001	**	0.002	**	0.003	**
81.070	80.063	1,3-Cyclohexadiene	0.008	**	<0.001	**	0.081	
82.065	81.058	Methallyl cyanide	0.628		<0.001	**	<0.001	**
83.060	82.053	3-Methyl-1H-Pyrazole	0.881		0.016	*	0.143	
83.086	82.078	Cyclohexane	<0.001	**	0.334		<0.001	**
84.081	83.074	Pentanitrile	0.993		<0.001	**	0.304	
85.065	84.058	3-Methyl-2-butenal	0.004	**	0.002	**	<0.001	**
87.044	86.037	2,3-Butanedione (Diacetyl)	0.057		0.015	*	<0.001	**

# Table 25. P-values for two-way interaction Litter Type.Week and the main effects Week and Litter Type—PTR-TofMS results

Note: \*\* indicates (P<0.01); \* indicates (P<0.05); MW(H+) is the protonated molecular weight measured by PTR-TofMS'; missing P-values indicates that there was insufficient data.

Table 25. continued	Tabl	e 25.	continued
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<u>MW(H+)</u>	MW	Possible VOC/odorant compound	Type.W	leek	Litter Ty	/pe	Weel	4
87.080	86.073	lso- & N- valeraldehyde	0.008	**	0.053		0.378	
87.117	86.110	Hexane	1.000		0.349		0.095	
89.060	88.052	Acetoin; Butanoic acid	<0.001	**	0.134		0.003	**
89.096	88.089	1- & 2-Pentanol (frag. to M43) 2- & 3-methyl-1-butanol (M43)	0.021	*	0.533		<0.001	**
91.058	90.050	Diethyl Sulfide	0.002	**	0.785		0.002	**
93.070	92.063	Toluene	0.927		<0.001	**	0.004	**
94.998	93.991	DMDS	0.838		<0.001	**	0.015	*
95.016	94.013	Dimethyl Sulfone	0.915		0.341		0.181	
95.049	94.042	Phenol	0.554		0.020	*	0.030	*
101.096	100.089	Hexanal	0.021	*	0.051		0.056	
103.075	102.068	Isovaleric acid; Valeric acid	0.013	*	0.096		0.007	**
105.070	104.063	Styrene	0.381		0.016	*	0.133	
107.049	106.042	Benzaldehyde	0.777		0.017	*	0.016	*
107.086	106.078	Xylene	0.040	*	<0.001	**	<0.001	**
109.065	108.058	P-Cresol; Benzyl alcohol	0.456		<0.001	**	0.191	
112.076	111.068	2,4,5-trimethyloxazole	0.068		<0.001	**	<0.001	**
112.112	111.105	Heptanonitrile	0.114		<0.001	**	0.054	
113.060	112.052	Sorbic Acid	0.229		0.002	**	0.811	
113.096	112.089	2-Heptanal	0.053		0.029	*	<0.001	**
114.030	113.030	Isothiocyanic Acid	0.245		<0.001	**	<0.001	**
115.075	114.068	Acids/Esters	0.949		<0.001	**	0.009	**
115.112	114.105	Heptanal	0.008	**	0.038	*	0.545	
115.148	114.141	Octane			0.964		0.467	
117.091	116.084	Hexanoic acid; Ethyl butyrate	0.069		<0.001	**	0.069	
118.065	117.058	Indole	0.521		<0.001	**	0.042	*
121.065	120.058	Acetophenone	<0.001	**	<0.001	**	<0.001	**
123.044	122.037	Benzoic Acid	0.056		<0.001	**	0.040	*
123.081	122.073	4-ethylphenol	0.249		<0.001	**	0.002	**
125.060	124.052	Guiacol	0.324		0.086		0.632	
126.971	125.963	DMTS	0.999		0.011	*	0.179	
129.091	128.008	Ethyl 2-methlybut-2-enoate; Ethyl 2-methyl-2-butenoate	0.184		<0.001	**	0.083	
129.127	128.120	3-Octanone	0.050		0.028	*	0.169	
131.107	130.099	Ethyl-2-methylbutyrate; Propyl butyrate	0.214		0.005	**	0.072	
132.081	131.074	Skatole	0.783		<0.001	**	<0.001	**
137.202	136.195	Tetramethyl pyrazine	0.034	*	<0.001	**	0.861	
137.133	136.125	Terpines; (alpha- & beta-pinene, limonene, camphene)	0.002	**	0.022	*	<0.001	**
143.143	142.136	Nonanal	0.426		0.010	*	0.570	
143.080	142.099	Esters	0.449		0.431		0.815	
143.179	142.172	Decane	0.449		0.431		0.815	
145.123	144.115	Butylbutyrate	0.373		<0.001	**	0.142	
149.023	148.016	Phthalic anhydride	0.002	**	<0.001	**	<0.001	**
149.096	148.089	Estragole	0.002	**	<0.001	**	<0.001	**
165.076	164.069	D-Fucose	<0.001	**	<0.001	**	<0.001	**
171.211	171.207	Dodecane	0.440		<0.001	**	<0.001	**

*Note:* \*\* indicates (P<0.01); \* indicates (P<0.05); MW(H+) is the protonated molecular weight measured by PTR-TofMS'; missing P-values indicates that there was insufficient data.

Some of these 'possible' odorants that correspond with the masses have been reported to contribute to poultry odour (Murphy et al., 2014). Emission rates of masses related to butanol; 2-butanone; 2,3-butanedione; acetoin; and 3-methyl-1-butanol tended to increase during the grow-out, especially after week 3 (Figure 93). Wet litter tended to have higher emission rates than dry litter, especially in week 5 of the grow-out, when emission rates from wet litter were 3–30 times greater than from dry litter.

Emission rates for masses corresponding with butanol, 2-butanone, 2,3-butanedione and acetoin showed similar trends between wet and dry litter, as well as trends over time during the grow-out, compared to the emission rates measured with TD-GC-MS methods (Figure 90). The magnitude of the emission rates was, however, commonly 0.5–1.0 orders of magnitude greater with the PTR-TofMS compared to TD-GC-MS. Higher measured emission rates may have been due to multiple compounds coinciding on the same mass (because compounds could not be individually quantified).



Figure 93. Emission rates of selected VOCs measured with PTR-TofMS that have previously been shown to contribute to poultry odour (Murphy et al., 2014). Possible odorants include: butanol (M56.0628); 2-butanone (M72.0575); 2,3-butanedione (M86.0368); acetoin (88.0524); and 3-methyl-1-butanol (M88.0888)

Emission rates of masses suspected to relate to trimethylamine, propanoic acid, isobutyl alcohol, 3-methylbutanal, hexanoic acid, indole, and skatole also tended to increase during the grow-out, especially after week 3 (Figure 94). Wet litter tended to have higher emission rates than dry litter, especially for isobutyl alcohol, indole and skatole.



Figure 94. Emission rates of selected VOCs measured with PTR-TofMS that have unpleasant character or low odour threshold value: Possible odorants include trimethylamine (M59.0735); propanoic acid (M74.0368); isobutyl alcohol (M74.0732); 3-methylbutanal (86.0732); hexanoic acid (M116.0637); indole (M117.0678); and skatole (M131.0735)

Masses suspected to relate to sulfides (Figure 95) had consistently higher emission rates from wet litter compared to dry litter (with the exception of diethyl sulfide during weeks 3 and 4 of the grow-out). Emission rates of sulfides increased during the grow-out. Dimethyl sulfide/ethyl mercaptan, dimethyl disulfide and dimethyl trisulfide, have previously been shown to relate to poultry odour concentration (Murphy et al., 2014) and the emission rates for masses relating to these compounds were consistently 3–30 times greater from wet litter compared to dry litter. It can be inferred that the higher emission rate for these compounds alone would contribute to increased odour emissions from wet litter compared to dry litter.



Figure 95. Emission rates of selected VSCs measured with PTR-TofMS that have previously been shown to contribute to poultry odour (Murphy et al., 2014), have unpleasant character and low odour threshold value (Appendix A). Possible odorants include: methylmercaptan (M48.0034); dimethyl sulfide/ethyl mercaptan (M62.0190); diethyl sulfide (M90.0503); dimethyl disulfide (M93.9911); isothicyanic acid (M113.0299); and dimethyl trisulfide (M125.9632)

### 8.3.2.4 Odour activity values

Odour threshold values (OTV) and odour character descriptions were compiled for compounds measured by the PTR-TofMS (Table 26). Litter samples were grouped into three categories: 'all litter samples', 'dry friable litter' and 'wet litter'. Excreta was also included. Odour activity values (OAV) were calculated for each of the protonated masses (Figure 96) using odorant concentrations (Table 24).

TOF protonated	Molecular	Possible compounds	Possible adour character	
mass (H+)	mass	Possible compounds	Possible odour character	010
33.0335	32.0262	Methanol	alcoholic	43000
34.9877	33.9877	Hydrogen Sulfide	rotten eggs	0.06
42.0338	41.0266	Acetonitrile	aromatic, sweet	22000
43.0542	42.0470	Propene: Pentanol	aromatic	22000
45.0335	44.0262	Acetylaldehyde	fruity, voghurt	2.7
46.0651	45.0578	Dimethylamine	ammona, fish-like	84
47.0491	46.0419	Ethanol	pleasant, alcoholic	640
49.0107	48.0034	MethylMercantan	Rotten cabbage	0.14
57 0320	56 0247	2-Propenal	coal-like	28000
57.0699	56.0628	Butanol: 2-Methyl-1-Propene	sweet musty: banana	320
59 0491	58 0419		solvent nail polish	99800
60 0808	59 0735	Trimethylamine	fishy ammonia	1 1
61 0284	60 0211		vinegar	802
61 06/8	60.0575	n-Pronanol: Ethylenediamine	nlessant alcoholic	231
62 0262	62 0100	Dimothyl sulfido: Ethylmorcantan	natural gas: rotton vogotablos	0.4
60.0600	68 0626	Isopropo	natural gas, rotteri vegetables	12/
72 0648	72 0575	1. 8. 2 Butanal: Isobutyraldobydo	solvent: pungent: rancid	125
75.0046	72.0373	I- & Z-Butanal, isobutylaidenyde	solvent, pungent, ranciu	100
75.0441	74.0508	Proparioic aciu		252
75.0804	74.0732		sweet, musty; banana	320
79.0542	78.0470	Benzene	petrol-like	4500
85.0648	84.0575	3-Methyl-2-Dutanai	chiorotorm	84000
87.0441	86.0368	2,3-Butanedione	sour, butter, rancid	0.2
87.0804	86.0732	2-Pentanone; Isovaleraldehyde	rancid; sour; butter; malt	147
87.1168	86.1096	Hexane	petrol-like	16009
89.0597	88.0524	Acetoin; Butanoic acid; Ethylacetate;	butter; mushroom; alcohol; rancid	22.7
89.0961	88.0888	1- & 2-Pentanol; 2- & 3-methyl-1-Butanol	disagreeable	161
91.0576	90.0503	Diethyl Sulfide	garlic, foul	0.12
93.0699	92.0626	Toluene	solventy	1240
94.9984	93.9911	DMDS	pungent, garlic, metallic	8.5
95.0491	94.0419	Phenol	medicinal, tarry	21.5
101.0597	100.0524	C5H8O2		3442
101.0961	100.0888	Hexanal	camphor	696
103.0754	102.0681	Methyl Butyrate; Methyl isobutyrate	apple, pears, rancid, cheesy	3.5
105.0699	104.0626	Styrene	aromatic	149
107.0492	106.0419	Benzaldehyde	almonds	12.1
107.0856	106.0783	Xylene	aromatic	252
109.0648	108.0575	P-Cresol, Benzyl alcohol	faecal, tarry	0.24
115.0754	114.0681	Acids/Esters		1897
115.1118	114.1045	Heptanal	rancid, citrus	14
115.1482	114.1409	Octane	petrol-like	7940
117.0910	116.0837	Hexanoic Acid; Ethyl butyrate	goat-like, fruity	7.1
118.0651	117.0578	Indole	faecal	1.4
121.0648	120.0575	Acetophenone	pungent, orange, jasmine	1283
123.0805	122.0732	4-ethylphenol	woody,medicinal	3.5
126.9705	125.9632	DMTS	pungent, garlic, metallic, onion	6.2
129.0910	128.0084	Ethyl 2-methyl-2-butenoate	n/a	812
129.1274	128.1201	3-Octanone	pungent	35.7
131.1067	130.0994	Ethyl-2-methylbutyrate; Propyl butyrate	mild, floral, rose	94
132.0808	131.0735	Skatole	Faecal	0.03
137.1325	136.1252	Terpines (alpha- & beta-pinene, limonene)	pine, woody, camphor	111
143.1431	142.1358	Nonanal	orange-rose, dusty	2.5
143.1795	142.1722	Decane	N/A	620
171.2108	171.2069	Dodecane	N/A	14000

## Table 26. Odour threshold values (OTV) and character of selected odorants used for PTR-TofMS results



Figure 96. Odour activity value (OAV) for selected protonated masses (PR-TofMS) in litter and excreta samples (whiskers show the data range)

Ten odorants with the highest OAVs were determined for each litter category and excreta (Table 27). Methyl mercaptan, 2,3-butanedione, butanoic acid, trimethylamine and dimethyl sulfide/ethyl mercaptan were the compounds possibly associated with the highest ranking OAVs. This selection of odorants was overall similar to the ranking of OAVs for odorants measured in meat chicken sheds (Section 7.3.2) and the results from TD-GC-MS and TD-GC-SCD (Section 8.3.1.2).

Ranked OAV*	All litter	Dry friable litter	Caked/wet litter	Excreta
1	87.044	87.044	87.044	87.044
	(2,3-butanedione)	(2,3-butanedione)	(2,3-butanedione)	(2,3-butanedione)
2	49.011	60.081	49.011	45.035
	(Methyl mercaptan)	(Trimethlamine)	(Methyl mercaptan)	(Acetylaldehyde)
3	60.081 (Trimethlamine)	49.011 (Methyl mercaptan)	60.081 (Trimethlamine)	63.026 (Dimethyl sulfide/ethyl mercaptan)
4	63.026 (Dimethyl sulfide/ethyl mercaptan)	91.058 (Diethyl sulfide)	63.026 (Dimethyl sulfide/ethyl mercaptan)	49.011 (Methyl mercaptan)
5	33.398 (Methanol)	63.026 (Dimethyl sulfide/ethyl mercaptan)	91.058 (Diethyl sulfide)	60.081 (Trimethlamine)
6	91.058	88.060	33.033	91.058
	(Diethyl sulfide)	(Butanoic acid)	(Methanol)	(Diethyl sulfide)
7	132.081	45.034	45.034	132.081
	(Skatole)	(Acetylaldehyde)	(Acetylaldehyde)	(Skatole)
8	89.060	132.081	132.081	89.060
	(Butanoic acid)	(Skatole)	(Skatole)	(Butanoic acid)
9	45.034	109.065	89.060	33.033
	(Acetylaldehyde)	( <i>p</i> -Cresol)	(Butanoic acid)	(Methanol)
10	109.065	103.075	109.065	109.065
	( <i>p</i> -Cresol)	(Isovaleric acid)	( <i>p</i> -Cresol)	( <i>p</i> -Cresol)

# Table 27. Individual masses with highest ranking OAVs for all litter samples, dry friable litter, wet litter and excreta (compound listed in bracket is a possible match to the listed protonated mass)—PTR-TofMS results

\*Rank 1 has highest OAV

Odour activity value for the three litter categories and excreta was then calculated from the individual OAVs (Figure 97). OAV for wet litter was 2.4 times greater than for dry litter, which gives an indication that wet litter was more odorous. This was the same ratio calculated from OAVs determined with TD-GC-MS and TD-GC-SCD (Section 8.3.1.2). Excreta had similar OAV to wet litter.



Figure 97. Total OAV for litter samples (sum of individual odorant OAVs; whiskers show the data range)—PTR-TofMS results

Some limitations needed to be considered regarding OAV calculations:

- There were some differences in the compounds analysed by the PTR-TofMS and TD-GC-MS/SCD, for example hydrogen sulfide was not measured by the PTR-TofMS.
- Assigning single compound OTVs to the PTR-TofMS results was complicated by the fact that the instrument could not resolve individual compounds with the same protonated mass.
- 3. The selection of available OTVs was limited and individual compound OTVs varied by orders of magnitude.
- 4. Summing individual compound OTVs assumed that there are no interactions between the compounds, which is unlikely (Ruth, 1986).

Nonetheless, many similarities were observed when comparing the contributions of individual compound OAVs to the total litter and excreta OAVs

### 8.4 Summary

Odour emission rates were measured from poultry litter in a laboratory pen trial with distinct wet and dry litter conditions. Odour emissions were measured with a customised flux hood and a combination of TD-GC-MS, TD-GC-SCD and PTR-TofMS.

TD-GC-MS analysis showed that emission rates were significantly different from wet litter compared to dry litter for nearly half of the odorants that were detected; however, the relationship between litter types changed for some of these compounds during the grow-out. Unfortunately, there was low detection frequency for some compounds, particularly sulfur compounds, which limited the ability to draw statistical conclusions.

PTR-TofMS was used to measure the concentration of VOCs in real-time from the flux hood. The real-time measurement capability ensured that valid measurements were measured for each litter sample and eliminated issues associated with odour sample storage and transportation. The PTR-TofMS was unable to resolve the concentration of individual odorants, instead odorant with the same protonated mass were added together and reported as 'masses'. Positive identification of odorants using TD-GC-MS provided some guidance as to which odorants were likely to correspond with the masses measured by the PTR-TofMS. Where comparisons could be made between TD-GC-MS and PTR-TofMS, there was similarity in terms of the relative differences between wet and dry litter and trends over time during the grow-out; however, the magnitude of emission rates measured with PTR-TofMS tended to be 0.5–1.0 orders of magnitude greater.

Emission rates for masses relating to sulfur compounds, as measured with PTR-TofMS, were almost always significantly greater from wet litter than dry litter. Emission rates for VOCs were also greater from wet litter compared to dry litter, especially after the third week of the grow-out. Many of these VSCs and VOCs have low odour threshold and unpleasant character (Appendix A), and have previously been used to predict the concentration of meat chicken shed odour (Murphy et al., 2014).

Odour activity values (OAVs) were calculated for each odorant and these were then summed to calculate the OAV for dry litter, wet litter and excreta. The odorants that made the greatest contribution to the calculated OAV for each litter type and excreta were found to be similar regardless of whether PTR-TofMS or TD-GC-MS/SCD were used. These odorants included 2,3-butanedione, methyl mercaptan, ethyl mercaptan, hydrogen sulfide, butanoic acid, trimethylamine and dimethyl sulfide. Summing the individual odorants for each litter type showed that wet litter had a higher OAV than dry litter, which is a strong indication that wet litter was more odorous. Excreta had similar or greater OAV than wet litter, which indicated that it may also be an important odour source.

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### **Chapter 9. Conclusions and recommendations**

### 9.1 Introduction

Litter conditions in meat chicken sheds are important for providing a healthy and comfortable environment for the birds and to regulate the emission of odours, which can impact on the surrounding community. The amount and availability of water in the litter is an important consideration it can affect litter friability, stickiness, compaction, pH, thermal insulation, oxygenation and microbial activity. This research study focussed on the water within litter by investigating the causes and consequences of 'wet litter'.

Aims of this study were to investigate how odour emissions from litter, in terms of chemical composition and emission rates, were affected by different litter conditions. This required assessing the variability of litter conditions spatially, temporally and through the litter depth. Focus was placed on measuring litter moisture content and pH. To improve understanding about the factors that affect litter conditions, especially moisture content, an additional aim was to estimate how much water is added to litter during a typical grow-out period, how much water is held by litter and how much water is evaporated by ventilation.

A method combining theoretical and empirical inputs was developed to estimate the amount of water being applied to litter during a grow-out. This was combined with experimental measurements of water holding capacity and evaporation rate to identify periods of the grow-out when managing litter moisture content would be challenging.

Litter sampling methods were refined during the course of this study. Initially, litter was collected using published methods to determine 'average' conditions; however, average litter conditions provided insufficient detail about the specific litter conditions that exist at the surface and through the depth of the litter. It is these specific litter conditions that are responsible for specific odour emissions. Measurements of moisture content, pH and oxygen concentration were conducted at different depths through the litter profile. The addition of manure during a grow-out was found to increase the water holding capacity of litter and reduced water activity, which is a measure of the availability of water within litter that affects friability and microbial growth.

The relationship between litter conditions and odorant emissions is complex and multifactorial. An in-depth literature review on the environmental conditions within meat chicken sheds, litter properties and odour diffusion mechanisms established a theoretical basis for relating gas transfer mechanisms to litter porosity, chemical concentration gradients, air turbulence (ventilation) and water availability. A list of more than 130 previously reported odorants associated with meat chicken production (Appendix A) also highlighted the complexity of meat chicken odour.

Odorant emissions were measured from a variety of litter conditions. Litter conditions were categorised according to appearance and physical properties; primarily as either 'dry friable' or 'wet' litter. Categorising litter was necessary to enable comparison with measured odorant emission rates. The emission rate of some odorants was found to be significantly affected by litter conditions (when litter was characterised as 'wet' or 'dry friable') and the length of the grow-out. In general, odorant emissions were found to increase during the grow-out. VOCs and VSCs with low odour thresholds and unpleasant character had significantly higher emission rates from wet litter than dry litter. Calculation of single compound odour activity values (OAV) showed which odorants made the greatest contribution to odour emission rates. Summing the OAVs for each litter type provided a strong indication that wet, caked litter was more odorous than dry friable litter.

### 9.2 Concise research summary

The objectives to estimate water added to litter and measure water holding capacity and water evaporation rates were successfully achieved. Quantifying the variability of litter properties was also successfully achieved and enabled the litter conditions to be related to odour emissions.

A method was developed to enable the amount of water being added to the litter from bird excretion and normal drinking spillage. It was estimated that 1.0–3.2 L/m<sup>2</sup>/day was being added to the litter.

The water holding capacity of bedding materials and litter were measured.

- Litter (containing manure) held more water than bedding materials for the same litter volume (e.g. litter held 2-5 times more water than pine shavings).
- Litter with finer bedding particles is denser and therefore held more water than the same bedding material with larger particles (e.g. sawdust vs shavings).

- Bedding/litter materials with greater bulk density held more water for the same value of moisture content.
- Compressibility of bedding materials made it difficult to reliably and repeatedly measure moisture content. Applying different methods produced different results.
- Methods to measure water holding capacity of bedding materials are not standardised and don't represent the condition of litter within chicken sheds.

Water evaporation rates were measured from litter.

- Evaporation rate was affected by litter moisture content and air velocity.
- Standardised evaporation rate when air speed was 2 m/s varied from 1 L/m<sup>2</sup>/day when litter had approximately 10% moisture content to over 10 L/m<sup>2</sup>/day when litter had 50% moisture content. At 0.5 m/s, the evaporation rate was approximately half as much.
- When litter was relatively dry (20–25% moisture content), evaporation rate was approximately 3 L/m<sup>2</sup>/day, which is potentially less than the amount of water that may be added to the litter. This indicates that maintaining dry litter at certain periods of grow-out may be difficult.
- Evaporation experiments were conducted at 25°C and 50% relative humidity. Theoretical and empirical methods enabled the evaporation rate of water from litter to be estimated at other temperature and relative humidity conditions.

Litter porosity was found to decrease during the grow-out presumably due to manure addition and comminuted bedding particles.

Water activity of litter and bedding materials were found to decrease over the course of a grow-out when comparing litter samples with the same moisture content. It is suggested, based on existing information, that water activity is an important measure of litter properties because high water activity:

- increases the opportunity for microbial growth in the litter, and consequently risks for disease, food safety and odour emissions.
- slows drying of fresh excreta by reducing the thermodynamic gradient that forces water molecules to move between excreta and litter.
- contributes to loss of friability and commencement of caking (especially at the litter surface).

Mechanisms contributing to the formation of friable vs caked litter were proposed based on observations and theories concerning litter cohesion, friability and considering excretion rates. Litter is a dynamic material and bird interaction with the litter is an essential element of litter management.

Litter conditions were found to vary spatially, temporally and within the litter profile. Litter sampling methods must be applied in a manner that provides more detail than average conditions. Wet litter was characterised by having a compacted or crusted surface, low pH at the surface and high pH at the base, and low oxygen concentration. When fresh excreta is added to the surface of wet litter, the compacted and cohesive surface prevents it from being incorporated and so a layer of manure forms on the surface. Dry friable litter, in comparison, had neutral to alkaline pH, and was a homogeneous mixture of excreta and bedding materials. When fresh excreta is added to the litter surface of dry friable litter, the excreta is rapidly dried and bird action breaks the excreta into smaller pieces that are worked into the litter.

Emission rates of some odorants (including VOCs and VSCs) were affected by litter conditions. Emission rates of several sulfur compounds, which have low odour threshold and unpleasant character, were found to be greater from wet litter compared to dry litter. Odorants including 2,3-butanedione, ethyl mercaptan, methyl mercaptan, hydrogen sulfide, butanoic acid, trimethylamine and dimethyl sulfide had the greatest single compound odour activity values (OAVs). Summing all of the OAVs for each litter type provided a strong indication that odour wet litter is more odorous than dry friable litter.

### 9.3 Future directions

### 9.3.1 Industry recommendations

Managing litter moisture content is paramount for good litter conditions and odour control. The causes of 'wet litter' are multifactorial, but ventilation management paramount. Minimum ventilation practices should be reviewed to ensure that sufficient water is evaporated daily from the litter based on the estimated quantity of water being added to the litter. Additionally, high relative humidity contributes to the litter surface becoming less friable, which then prevents incorporation of excreta. Future research should focus on technologies or strategies that reduce relative humidity at the litter surface.

Litter containing manure has higher water holding capacity and lower water activity than bedding materials, in other words more resistance to 'wet litter' and associated odour and chicken health concerns. Some sectors of the industry already reuse litter as bedding material in subsequent grow-outs. Wider adoption of litter re-use should be considered to take full advantage of the beneficial properties of litter from the start of each grow-out.

#### 9.3.2 Research recommendations

Real-time VOC concentration measurements functionality of the PTR-TofMS was found to be very useful when used in conjunction with a flux hood because it allowed the technician to identify when VOC emissions reached steady state. It also provided an indication about the degree of sample equipment contamination, with some compounds found to be more 'sticky' than others. It is recommended that practitioners using area source enclosures (wind tunnels and flux hoods) should consider the use of PTR-TofMS to improve knowledge about the dynamic nature of VOC concentrations the enclosure with an objective of optimising the sampling process.

There are many similarities between water activity and Henry's law regarding the establishment of equilibrium between a source (i.e. litter or water) and air for water vapour and chemical compounds respectively. Additionally, both phenomena are affected by temperature, turbulence, water/chemical concentrations, salts, organic matter. Future research should consider these similarities and investigate if water activity can be related to flux of water soluble compounds from porous materials, or liquids with reduced water activity (e.g. saline water).

Future research into poultry litter odour emissions should expressly consider fresh excreta as an odour source. The high moisture content of fresh excreta supports odour producing bacteria and the possibility for high water evaporation, which increases the potential for emission of water soluble odorants. Evaporation and odorant emissions would likely be accelerated as the excreta is broken down, smeared and spread on the surface of the litter by bird activity, but this requires further investigation.

### 9.4 Conclusions

The primary aims of this study were successfully achieved with the properties of poultry litter that contribute to odour emissions from meat chicken sheds in Australia being identified and quantified. Litter moisture content was identified as a key parameter because it affects the physical properties of litter (friability, pH, compaction, porosity,

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microbial activity). Experimental results also showed that water evaporation rates were greater from wetter litter. This is important because water evaporation rates have previously been reported to contribute to the emission rate of water soluble odorants, but also low water evaporation rates from drier litter may be insufficient to remove the quantity of water being added to the litter daily.

Litter properties were found to change during the a grow-out, with increased water holding capacity and lower water activity as manure accumulated in the litter. These changes are beneficial from the perspective of maintaining litter friability and reducing microbial growth in the litter. Industry can take advantage of these by re-using litter for multiple grow-outs.

Litter conditions varied spatially, temporally and through the litter profile when measured during in-shed and laboratory experiments. Wet litter was characterised by a compacted or crusted surface with low pH and low oxygen concentration. When fresh excreta was added to the surface of wet litter, it was observed that the compacted and cohesive surface prevented it from being incorporated and a layer of manure developed on the surface. Dry friable litter, in comparison, had neutral to alkaline pH and was a homogeneous mixture of fine excreta particles and bedding materials.

Odorant emission rates were successfully measured from a variety of litter conditions using flux hoods and a combination of TD-GC-MS (for VOCs), TD-GC-SCD (for VSCs) or PTR-TofMS methods. The emission rates for many odorants were different from wet litter than dry friable litter, but the relationships between litter conditions and odorant emission rates were complex and changed during the grow-out. Emission rates for selected sulfide compounds including dimethyl sulfide, dimethyl disulfide, carbonyl sulfide and carbon disulfide were found to be higher from wet litter. This finding was supported by measurements with the PTR-TofMS during a laboratory based trial, where measured VOC concentrations, suspected to be sulfides and other poultry odorants were found to be significantly higher from wet litter compared to dry friable litter. Calculation of single compound odour activity values (OAV) showed that 2,3-butanedione, methyl mercaptan, hydrogen sulfide, butanoic acid, trimethylamine and dimethyl sulfide made the greatest contribution to odour emission rates from litter and excreta. Summing the OAVs for each litter type provided a strong indication that wet, caked litter was more odorous than dry friable litter.

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Appendices

## Appendix A. List of poultry odorants

Selected odorants and other relevant compounds from meat chicken excreta, litter and/or housing (Dunlop et al., 2016a) Appendix A. Selected odorants and other relevant compounds from meat chicken excreta, litter and/or housing. Table includes identification information, chemical properties, odour thresholds and odour character.

n/a = 'not	available <sup>°</sup>													
Odorant	Alternative names	Molecular weight [32]	CAS No.[32]	Formula	Odour Character	Odour Threshold (min) (µg/m³)	Odour Threshold (max) (µg/m³)	Odour Threshold (min) (ppbv)	Odour Threshold (max) (ppbv)	Henry's constant at 25°C (M/atm) [32]	Log <sub>10</sub> Hcc at 25°C (dimension- less)	Vapour Pressure at 25°C (kPa) [32]	Water solubility at 25°C (mg/L)[30]	References (reported from meat chickens)
Acids and Esters														
Acetic acid	Ethanoic acid	60.052	64-19-7	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> or CH <sub>3</sub> COOH	Vinegar [44]	25 [33] (892) (1180) (2500 [41])	2.5 x 10 <sup>5</sup> [41] (1.0 x 10 <sup>4</sup> [33])	10.2 (363 [42]) (480 [16]) (1018)	1.02 × 10⁵ (4071)	6300	-5.19	2.	1,044,600	[17; 27; 48; 50; 55]; 'Poultry' litter [51]
Methylacetate	Acetic acid methyl ester; methyl acetate	74.0785	79-20-9	CH <sub>3</sub> OCOCH <sub>3</sub> or C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Fruity, solvent, sweet [53]; ether-like [5]	500 [33] (1.39 x 10 <sup>4</sup> )	5.5 x 10 <sup>5</sup> [33]	165 (4600 [16])	1.82 x 10⁵	9.133	-2.35	28.8	243500 (@20°C)	unpublished data
Propanoic acid	Propionic acid; Methyl acetic acid	74.0785	79-09-4	CH <sub>3</sub> CH <sub>2</sub> COOH or C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Pungent, disagreeable, rancid odour [5]; sour, mildly cheese-like [30]	84[41] (108) (485)	6.0 x 10 <sup>4</sup> [41]	27.7 (35.5 [42]) (160 [16])	1.98 x 10⁴	5950	-5.16	0.47 [30]	1,000,000	[48; 50; 55]
Ethyl acetate	Acetic acid ethyl ester; Ethylacetate; Ethyl ethanoate	88.1051	141-78-6	CH₃OCOC₂H₅ or C₄H₀O2	Ether-like, fruity [5]; fruity with a brandy note, reminiscent of pineapple [30]	600 [33] (3135) (3603) (9477)	1.8 × 10 <sup>5</sup> [33]	166.5 (870 [29]) (1000 [16]) (2630 [42])	5.0 × 10⁴	6.15	-2.18	12.6	80,100	[27; 55]
Butanoic acid	<i>n</i> -butyric acid; butyric acid	88.1051	107-92-6	C <sub>3</sub> H <sub>7</sub> C00H or C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	Unpleasant, rancid, obnoxious [30]	0.4 [33] (0.69) (3.6) (14))	4.2 x 10 <sup>4</sup> [33]	0.11 (0.19 [29]) (1.0 [16]) (3.9 [42])	1.17 × 10⁴	4700	-5.06	0.15	60,000	[17; 27; 48; 50; 55]; 'poultry' [33]
2-methyl-propanoic acid	Isobutyric acid; isobutanoic acid; 2- methylpropanoic acid	88.1051	79-31-2	(CH₃)₂C₂H₃COO H or C₄H₅O₂	Sharp, butter-fat-like odour, like butyric acid but not as unpleasant [30]	5 [33] (5.4) (70.3)	330 [33]	1.38 (1.5 [29]) (19.5 [42])	9.6	1100	-4.43	0.24 [30]	167,000 (@20°C)	[48; 50; 55]
n-propyl-acetate	Acetic acid, propyl ester	102.1317	109-60-4	CH <sub>3</sub> OCOC <sub>3</sub> H <del>,</del> or CH <sub>3</sub> COOCH <sub>2</sub> CH 2CH <sub>3</sub> or C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Mild fruity [5]; pleasant, odour of pears [30]	200 (1002) (2800)	7.0 × 10 <sup>4</sup>	48 (240 [29]) (670 [16])	1.68 × 10⁴	4.5	-2.04	4.78 [30]	18,900 (@20°C)	unpublished data
Butanoic acid, methyl ester	n-butyric acid, methyl ester; Methyl butyrate methyl butanoate	102.1317	623-42-7	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CO OCH <sub>3</sub> or C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Apple-like [30]	20 [21]	n/a	4 8.	n/a	4.8	-2.07	4.25	15,000	unpublished data
3-methylbutanoic acid	Isovaleric acid; Isobutylformic acid; 3 methylbutyric acid	102.1317	503-74-2	(CH <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> H <sub>3</sub> COO H or C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Unpleasant [36]; rancid- cheese [30]; body odour [22]	0.2 [33] (0.33) (2.5)	10.3 (6.9 [33])	0.05 (0.08 [29]) (0.6 [36])	2.5 [42] (1.65)	1200	-4.47	0.06 [30]	40,700 (@20°C)	[48; 50]

Odorant	Alternative names	Molecular	CAS	Formula	Odour Character	Odour Threshold	Odour	Odour	Odour	Henrv's	Log <sub>10</sub> Hcc	Vapour	Water	References
		weight	No.[32]			(min)	Threshold	Threshold	Threshold	constant at	at 25°C	Pressure at	solubility	(reported
		[32]				(raj/m³)	(max) (µg/m³)	(min) (ppbv)	(max) (ppbv)	25°C (M/atm) [32]	(dimension- less)	25°C (kPa) [32]	at 25°C (mg/L)[30]	from meat chickens)
2-methyl butanoic acid	2-methylbutyric acid	102.1317	116-53-0	C <sub>2</sub> H <sub>5</sub> CH(CH <sub>3</sub> )C OOH or C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Irritant, stench [42]	7.8	20 [33]	1.9 [42]	4.8	n/a	n/a	n/a	n/a	unpublished data
Pentanoic Acid	Valeric acid; n-pentanoic acid; n-valeric acid; propylacetic acid;1- butanecarboxylic acid	102.1317	109-52-4	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COO H or C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Unpleasant, similar to butyric acid [30]	0.16 (0.8 [33]) (20.0)	120 [33]	0.04 [29] (0.19) (4.8 [42])	28.7	2200	-4.73	0.026 [30]	24,000	[48; 50; 55]
Propanoic acid, propyl ester	Propionic acid, propyl ester; Propyl propionate	116.1583	106-36-5	CH <sub>3</sub> CH <sub>2</sub> COOCH 2CH <sub>3</sub> or C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	n/a	17.3	n/a	5.7[29]	n/a	2.6	-1.8	1.85	n/a	unpublished data
Butanoic acid, ethyl ester	n-butyric acid, ethyl ester; Ethyl butyrate	116.1583	105-54-4	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C(O )OC <sub>2</sub> H <sub>5</sub> or C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	Fruity odour with pineapple undernote [30]	n/a	n/a	n/a	n/a	2.8	-1.84	2.30	4900 (@20°C)	unpublished data
Hexanoic Acid	Caproic acid; n-Caproic acid; n-Hexanoic acid; Butylacetic acid	116.1583	142-62-1	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COO H or C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	Characteristic goat- like [30]	2.9 (20 [33])	520 [33] (59.8)	0.6 [29] (4.2)	109.5 (12.6 [42])	1300	-4.50	0.006 [30]	10,300	[48; 50; 55]
Benzoic acid	Benzenecarboxylic acid	122.1213	65-85-0	C <sub>6</sub> H <sub>5</sub> C00H or C7H <sub>6</sub> O <sub>2</sub>	Slight benzaldehyde odour (almonds), faint, pleasant [30]	n/a	n/a	n/a	n/a	14,000	-5.53	0.0001 [30]	3400	[48]
Butanoic acid, propyl ester	n-butyric acid, propyl ester; Propyl butyrate	130.1849	105-66-8	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CO OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> or C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	n/a	n/a	n/a	n/a	n/a	1.9	-1.67	0.79	n/a	unpublished data
Heptanoic acid	Enanthic acid; n- Heptanoic acid; Heptoic acid; Oenanthic acid	130.1849	111-14-8	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> COO H or C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	Disagreeable, rancid, tallow-like [30]	22 [33]	146.4 (33 [33])	4.1	27.5 [42] (6.2)	2965	-4.86	0.001 [30]	2820	[48; 50]
Butanoic acid, butyl ester	n-butyric acid, butyl ester; Butyl Butyrate	144.2114	109-21-7	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CO O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> or C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	unpublished data
Butanoic acid, 1- methylpropyl ester	butyric acid, sec-butyl ester; butanoic acid, 2- butyl ester	144.2114	819-97-6	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	unpublished data
Dimethyl itaconate	Butanedioic acid, methylene-, dimethyl ester;	158.1519	617-52-7	CH <sub>3</sub> O <sub>2</sub> CCH <sub>2</sub> C(= CH <sub>2</sub> )CO <sub>2</sub> CH <sub>3</sub> or C <sub>7</sub> H <sub>10</sub> O <sub>4</sub>	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[48]
Benzoic acid, 4-ethoxy- ,ethyl ester	Ethyl 4-ethoxybenzoate; Ethyl para- ethoxybenzoate	194.2271	23676-09-7	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.0 [39]	n/a	[27]

Odorant	Alternative names	Molacular	SAS	Formula	Odour Character	Odour Threehold	Odour	Odour	Odour	Hanry's		Vanour	Water	Rafarancae
		weight	No.[32]			(min)	Threshold	Threshold	Threshold	constant at	at 25°C	Pressure at	solubility	(reported
		[32]				(°m/gu)	(max) (µg/m³)	(min) (ppbv)	(max) (ppbv)	25°C (M/atm) [32]	(dimension- less)	25°C (kPa) [32]	at 25°C (mg/L)[30]	from meat chickens)
Diethyl-phthalate	Anozol; Phthalol; solvanol; Diethyl ester of Phthalic acid; Neantine	222.2372	84-66-2	C <sub>6</sub> H <sub>4</sub> -1,2- (CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> or C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	Very slight, aromatic, practically odourless[30]	n/a	n/a	n/a	n/a	1200	-4.47	0.0003 [30]	1080	[27]
Triethyl Citrate	Citric acid, triethyl ester; 1,2,3-propanetricarboxylic acid, 2-hydroxy-, triethyl ester	276.2830	77-93-0	HOC(COOC2H5) (CH2COOC2H5)2 or C12H20O7	n/a	n/a	n/a	n/a	n/a	2.6 x 10 <sup>5</sup> [39]	9. 9	0.0003	65,000	[48]
1-Octadecanesulfonyl chloride	Octadecane-1-sulphonyl chloride	353.0032	10147-41-8	C <sub>18</sub> H <sub>37</sub> CIO <sub>2</sub> S	n/a	n/a	n/a	n/a	n/a	n/a	n/a	3.18 × 10 <sup>-8</sup> [39]	n/a	[27]
Alcohols														
Methanol	Methyl alcohol; carbinol	32.0419	67-56-1	CH <sub>3</sub> OH or CH <sub>4</sub> O	Alcoholic, pungent [30]	3931 (4.3 x 10 <sup>4</sup> )	1.9 x 10 <sup>5</sup>	3000 [16] (3.3 × 10 <sup>4</sup> [29])	1.4 x 10 <sup>5</sup> [42]	220	-3.73	16.9	1,000,000	[17; 48]
Ethanol		46.068	64-17-5	CH <sub>3</sub> CH <sub>2</sub> OH or C <sub>2</sub> H <sub>6</sub> O	Mild, pleasant, wine-like (vinous), whisky-like, ethereal, [30]	640 [33]	1350 [33]	340	7.16 × 10 <sup>5</sup>	198	-3.68	7.8	1,000,000	[6; 17; 48]
i-Propanol	Isopropanol; Isopropyl alcohol; sec-Propyl alcohol; dimethylcarbinol; 2-Propanol	60.0950	67-63-0	(CH <sub>3</sub> ) <sub>2</sub> CHOH or C <sub>3</sub> H <sub>8</sub> O	Pleasant, mixture of ethanol and acetone [30]	3900 [33] (7840 [41]) (2.5 × 10 <sup>4</sup> ) (5.4 × 10 <sup>4</sup> )	5.4 x 10 <sup>6</sup> [33] (4.9 x 10 <sup>5</sup> [41]) (6.4 x 10 <sup>4</sup> )	1585 (3190) (1.02 × 10 <sup>4</sup> [42]) (2.2 × 10 <sup>4</sup> [16])	2.2 × 10 <sup>6</sup> (2.0 × 10 <sup>5</sup> ) (2.6 × 10 <sup>4</sup> [29])	125	-3.48	6.05 [30]	1,000,000	[6; 17]
1-propanol	Propyl alcohol; <i>n</i> -propyl alcohol; <i>n</i> -propanol; propanol	60.0950	71-23-8	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH or C <sub>3</sub> H <sub>8</sub> O	Alcohol-like [5]; similar to ethanol	75 [33] (231) (6390)	1.4 × 10 <sup>5</sup> [33]	30.5 (94 [29]) (2600 [16])	5.7 × 10 <sup>4</sup>	143.3	-3.54	2.81	1,000,000	[6; 48]; Poultry' litter [51]
2-butanol	sec-butanol; sec-butyl alcohol	74.1216	78-92-2	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>3</sub> or C4H <sub>10</sub> O	Strong pleasant [5]; wine like odour, sweet [30]	400 [33] (667) (7580)	8 × 10 <sup>4</sup> [33]	132 (220 [29]) (2500 [16])	2.64 × 10⁴	103.5	-3.40	2.43	181,000	[27]
1-butanol	<i>n</i> -butyl alcohol; n-butanol; butanol	74.123	71-36-3	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH or C₄H <sub>9</sub> OH	Solvent [34]; alcohol [19]; harsh fusel odour with banana (banana liqueur), amyl alcohol, sweet, rancid [30]	158 [33] (1485)	42,000 [33]	52.1 (490 [42])	13,854	125.0	-3.48	0.72	63,200	[6; 27; 28; 34; 48]
2-methyl-3-buten-2-ol	Dimethylvinylcarbinol; dimethylvinylmethanol	86.1323	115-18-4	CH <sub>2</sub> =CHC(CH <sub>3</sub> ) <sub>2</sub> OH or C <sub>5</sub> H <sub>10</sub> O	n/a	n/a	n/a	n/a	n/a	n/a	n/a	3.13 [30]	190,000 (@20°C)	unpublished data
3-methyl-1-butanol	Isoamyl alcohol; <i>i</i> - pentanol; isopentyl alcohol	88.148	123-51-3	C <sub>5</sub> H <sub>12</sub> O or (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH 2OH	Disagreeable [5]	80 [33] (3.6 × 10 <sup>4</sup> [41])	1.26 x 10 <sup>5</sup> [41] (161) (151)	22.19 (9985)	3.49 x 10 <sup>4</sup> (44.7 [42]) (42 [16])	70.9 [39]	-3.24	0.32 [30]	26,700	[27]

Alternative names	Molecular weight	· CAS No.[32]	Formula	Odour Character	Odour Threshold (min)	Odour Threshold	Odour Threshold	Odour Threshold	Henry's constant at	Log <sub>10</sub> Hcc at 25°C	Vapour Pressure at	Water solubility	References (reported
	[32]				(°m/gµ)	(max) (µg/m³)	(nim) (vdqq)	(max) (ppbv)	25°C (M/atm) [32]	(aimension- less)	25°С (КРа) [32]	at 25°C (mg/L)[30]	trom meat chickens)
nol; pentyl alcoh I alcohol, n-penty alcohol	iol, 88.1482 yl	71-41-0	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> OH or C <sub>5</sub> H <sub>12</sub> O	Fusel-like, mild [30]	360.5 (756 [41])	1658	100 [29] (209)	460 [16]	76	-3.27	0.29	22,000	[28]
icetone alcohol; Tyranton; ıyldimethylcarbin	116.1583 ol	123-42-2	(CH <sub>3</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> COCH <sub>3</sub> or C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	Faint, pleasant, minty [30]	1344 [41]	4.8 X 10 <sup>5</sup> [41]	282.9	1.01 X 10⁵	n/a	n/a	0.17	1,000,000	[27; 28]
/l glycol; Ethylene ol butyl ether; 2-n- butoxyethanol	118.1742	111-76-2	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OH or C <sub>6</sub> H <sub>14</sub> O <sub>2</sub>	Mild, ether-like, slightly rancid, pleasant, sweet [30]	208	483	43 [29]	100 [16]	625	-4.18	0.12 [30]	1,000,000	[28]
yl vinyl carbinol; 3- oxy-1-octene; Viny ol; Matsuica alcoh ushroom alcohol	- 128.2120 yl ol;	3391-86-4	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH(O H)CH=CH <sub>2</sub> or C <sub>8</sub> H <sub>16</sub> O	n/a	2.7 [27]	n/a	0.515	n/a	n/a	n/a	n/a	n/a	[27]
2-Ethylhexanol	130.2279	104-76-7	C₄H₅CH(C₂H₅)C H₂OH or C₅H₁₀0	Mild, oily, slightly floral odour reminiscent of rose [30]; musty [41]	400 [33]	734 [41]	75.1	137.8	n/a	n/a	0.02	880	[27; 28]
Ethanal	44.053	75-07-0	C₂H₄O or CH₃CHO	Fruity [44]; sweet fruity [8]; yoghurt, sweet burning [53]	0.2 [41] (2.7 [33])	4140 [41]	0.11 (1.5)	2397	4	-2.53	120	1,000,000	[17] ; 'Poultry' litter [51]; poultry [33]
2-propanone	58.079	67-64-1	(CH <sub>3</sub> ) <sub>2</sub> CO	Solvent, sweet [34]; nail polish	940 [33] (4.75 x 10 <sup>4</sup> [41]) (9.98 x 10 <sup>4</sup> )	1.61 × 10 <sup>6</sup> [41] (1.55 × 10 <sup>6</sup> [33]) (3.08 × 10 <sup>4</sup> )	58.1 (2.0 × 10 <sup>4</sup> ) (4.2 × 10 <sup>4</sup> [29])	6.79 x 10 <sup>5</sup> (6.53 x 10 <sup>5</sup> ) (1.3 x 10 <sup>4</sup> [16])	28.13	-2.84	32.8	1,000,000	[6; 17; 28; 34; 48]; 'Poultry' litter [51]
aldehyde; 1-butan: ıtyric aldehyde; <i>n</i> - anal; butylaldehyde	al; 72.1057	123-72-8	CH₃CH₂CH2CH O or C₄H₄O	Pungent, aldehyde odour [30]; sweet, rancid [41]	0.84 [33] (1.96 [29]) (13.6 [41]) (26.3)	2.6 × 10 <sup>4</sup> [41] (200 [33])	0.285 (0.67) (4.6) (8.9 [42])	9,000 (67.8)	<u>ග</u> ත	-2.37	14.8	71,000	[55]
ethyl ethyl ketone; butanone; MEK	72.106	78-93-3	C₂H₅COCH₃ or C₄H₅O	Sweet, minty [36]; acetone-like [5]	737.3 [41]	2.50 × 10 <sup>5</sup> [33] (1.48 × 10 <sup>5</sup> [41])	250	8.48 x 10 <sup>4</sup> (5.0 x 10 <sup>4</sup> )	50	-2.69	12.08 [30]	223,000	[6; 17; 27; 48; 55]; 'Poultry' litter [51]
Acetaldehyde, N- ıylhydrazone, AMFI 1-Ethylidene-2- methylhydrazine	72.1090 H;	17167-73-6	C <sub>3</sub> H <sub>6</sub> N <sub>2</sub>	n/a	n/a	n/a	n/a	n/a	n/a	n/a	4.8 [39]	n/a	[28]

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Odorant	Alternative names	weight	No.[32]	Formula	Odour Character	Odour Inresnoia (min)	Uaour Threshold	Uaour Threshold	Uaour Threshold	renry s constant at	Log <sub>10</sub> Hcc at 25°C	vapour Pressure at	water solubility	kererences (reported
		[32]				("mg/mg)	(max) (µg/m³)	(min) (ppbv)	(max) (ppbv)	25°C (M/atm) [32]	(dimension- less)	25°C (kPa) [32]	at 25°C (mg/L)[30]	from meat chickens)
2,3-butanedione	Diacetyl	86.089	431-03-8	CH <sub>3</sub> COCOCH <sub>3</sub> or C4H <sub>6</sub> O2	Butter, rancid, fat [34]; quinone, chlorine- like [30]; yoghurt, sour cream, sour milk [15]	0.007 [33] (0.18) (3.5 [41]) (5.0 [33]) (15.4)	88.0 [41] (26.0)	0.002 (0.05 [29]) (0.99) (1.42) (4.37 [40])	25.0 (7.39 [40])	65.50	-3.2	7.67	200 (@20°C)	[27; 34; 48]
3-methyl-butanal	Isovaleraldehyde; Isopenanal; Isovaleric aldehyde	86.132	590-86-3	C <sub>5</sub> H <sub>10</sub> O or (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH O	Malt, rancid [34]; apple- like, acrid [30]	1.6 [33] (7.8 [42])	8.1 [27]	0.45 (2.2)	2.3	2.46 [39]	-1.78	6.67 [30]	1400 (@20°C)	[27; 28; 34]
2-pentanone	Ethyl acetone; methyl propyl ketone	86.1323	107-87-9	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> or C <sub>5</sub> H <sub>10</sub> O	Acetone-like [5]	3.88 x 10 <sup>4</sup>	n/a	1.1 x 10 <sup>4</sup> [16]	n/a	12.37	-2.48	4.72 [30]	43,000	[48]
3-pentanone	Diethyl ketone; DEK; ethyl Ketone; Methacetone; 1,3- Dimethylacetone; Ethyl propionyl; pentan-3-one; Diethylcetone; Pentanone- 3	86.1323	96-22-0	C <sub>5</sub> H <sub>10</sub> O	Acetone-like [30]	1,090	n/a	310 [16]	n/a	50	-2.69	5.02 [30]	45,890	[48]
Pentanal	n- Valeraldehyde ; Valeraldehyde; n- Pentenal; valeric aldehyde; amyl aldehyde; Pentalaldehyde	86.1323	110-62-3	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CHO or C <sub>5</sub> H <sub>10</sub> O	Powerful, acrid, pungent [30]	1.44	31.7	0.41 [29]	9.0 [42]	6.6	-2.20	3.4 [30] (@20°C)	11,700	[27]
3-hydroxy-2-butanone	Acetoin; Dimethylketol; Acetyl-methyl-carbinol	88.105	513-86-0	C4H <sub>6</sub> O <sub>2</sub> or CH <sub>5</sub> COCH(OH) CH <sub>3</sub>	Mushroom, earth [34]; buttery; woody, yoghurt [30]; butter- like [42]	n/a	n/a	n/a	n/a	n/a	n/a	2.7 [30]	1,000,000	[27; 34; 48]
4-methyl-3-penten-2-one	Mesityl oxide; Isopropylidene-Acetone; Isobutenyl methyl ketone; isopropylideneacetone	98.1430	141-79-7	CH <sub>3</sub> ) <sub>2</sub> C=CHCOC H <sub>3</sub> or C <sub>6</sub> H <sub>10</sub> O	Spearmint, peppermint, honey-like [30]	68.8 [41]	1.0 × 10 <sup>5</sup> [41]	16.9	2.49 × 10 <sup>4</sup>	27.2 [39]	-2.82	1.46	28,900 @ 20°C	[28]
Hexanal	Caproaldehyde, Caproic aldehyde; n-hexanal	100.1589	66-25-1	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CHO or C <sub>6</sub> H <sub>12</sub> O	Fruity; green grass [30]; grassy [22]	n/a	n/a	n/a	n/a	6.9	-2.08	1.51	5640 (@30°C)	[6; 27; 28; 55]; Layer manure [22]
4-Methylpentan-2-one	Methyl isobutyl ketone MIK; MIBK;; isopropylacetone	100.1589	108-10-1	C <sub>6</sub> H <sub>12</sub> O or (CH <sub>3</sub> )2CHCH <sub>2</sub> C OCH <sub>3</sub>	Pleasant, ketonic, camphor [30]	410 [41] (696) (2200)	1.93 x 10 <sup>5</sup> [41]	100 (170 [29]) (537 [42])	4.7 × 10 <sup>4</sup>	2.4	-1.77	2.62	19,000	[48]
Benzaldehyde	Benzenecarbonal, benzoic aldehyde, phenylmethanal	106.1219	100-52-7	C <sub>6</sub> H <sub>5</sub> CH0 or C <sub>7</sub> H <sub>6</sub> O	Almond-like, oil of bitter almonds [30]; onion, burnt food [22]	0.8 [41]	182 [41]	0.184	42	ө Ю	-2.98	0.17	6950	[27; 28; 48; 55]; 'Poultry' litter[51]

Odorant	Alternative names	Molecular weight [32]	CAS No.[32]	Formula	Odour Character	Odour Threshold (min) (µg/m³)	Odour Threshold (max) (µg/m³)	Odour Threshold (min)	Odour Threshold (max) (ppbv)	Henry's constant at 25°C	Log <sub>10</sub> Hcc at 25°C (dimension-	Vapour Pressure at 25°C (kPa)	Water solubility at 25°C	References (reported from meat
2-n-Butylacrolein	2-methylene-hexanal; 2- Butylacrolein	112.1696	1070-66-2	C <sub>7</sub> H <sub>12</sub> O	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.89 [39]	n/a	[28]
Heptanal	Oenanthaldehyde	114.186	111-71-7	C,H₁4O or C6H₁3CHO	Rancid, citrus [34]; fatty, pungent, fruity [30]; green, soapy, stink bug, nuts [15]	6 [33] (14 [41])	260 [33] (93.2 [41])	1.3 (3.0)	55.7 (20.0)	3.50	-1.93	0.38 [30]	1250	[27; 28; 34; 55]
Acetophenone	Methyl phenyl ketone; acetylbenzene; 1- phenylethanone	120.1485	98-86-2	CH <sub>3</sub> COC <sub>6</sub> H <sub>5</sub> or C <sub>6</sub> H <sub>6</sub> O	Pungent odour of acacia, orange blossom or jasmine-like [30]; almond, sweet [41]	10 [33] (19.7) (835 [41]) (1500 [33])	2946 [41]	2.0 (4.0 [16]) (170) (305)	600	110	-3.43	0.05	6130	[27; 48; 55]
6-Methyl-5-hepten-2-one	Methylheptenone; Sulcatone	126.1962	110-93-0	(CH₃)₂C=CHCH₂ CH₂COCH₃ or C₅H₁₄O	Powerful, fatty, green, citrus [30]	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0 (insoluble)	[28]
Octanal	Caprylaldehyde; caprylic aldehyde	128.212	124-13-0	C <sub>8</sub> H <sub>16</sub> O or C <sub>7</sub> H <sub>15</sub> CHO	Green, citrus [34]; soapy, fatty, cardboard, metallic [15]	0.7 [11] (1.4 [11])	7.8 [33]	0.13 (0.27)	ר ני	2.00	-1.69	0.16 [30]	560	[28; 34]
2-ethyl-hexanal	Butylethylacetyaldehyde; 2-ethylhexaldehyde	128.2120	123-05-7	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(C <sub>2</sub> H <sub>5</sub> )CHO or C <sub>8</sub> H <sub>16</sub> O	Mild [30]	n/a	n/a	n/a	n/a	1.3 [39]	-0.51	0.27 [30]	700 (@20°C)	[27; 28]
3,5-dimethyl- benzaldehyde	m-Xylene-5- carboxaldehyde	134.1751	5779-95-3	(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO or C <sub>9</sub> H <sub>10</sub> O	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	unpublished data
2,5-Dimethyl- benzaldehyde	Isoxylaldehyde	134.1751	5779-94-2	(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO or C <sub>9</sub> H <sub>10</sub> O	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[27]
Nonanal	<i>n</i> -nonaldehyde; Perlargonaldehyde; nonyl aldehyde	142.2386	124-19-6	CH <sub>3</sub> (CH <sub>2</sub> )7CHO or C <sub>9</sub> H <sub>18</sub> O	Orange-rose odour, floral, waxy, green [30]; moldy-cellar-earthy, cardboard, fruity, dusty, goat stable, fatty, old chair/house [15]	0.3 [33] (1.0 [11]) (2.5 [11]) (13.0)	45 [33]	0.052 (0.172) (0.43) (2.24 [42])	7.74	6. 0.	-1.39	0.05	0 0	[27]
1,3-diphenyl-2-propen-1- one	Chalcone	208.2552	94-41-7	C <sub>6</sub> H <sub>5</sub> CH=CHCO C <sub>6</sub> H <sub>5</sub> or C <sub>15</sub> H <sub>12</sub> O	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	unpublished data

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Odorant	Alternative names	Molecular weight [32]	CAS No.[32]	Formula	Odour Character	0dour I hreshold (min) (µg/m³)	Odour Threshold (max) (µg/m³)	Odour Threshold (min) (ppbv)	Odour Threshold (max) (ppbv)	Henry's constant at 25°C (M/atm) [32]	Log <sub>10</sub> Hcc at 25°C (dimension- less)	vapour Pressure at 25°C (kPa) [32]	water solubility at 25°C (mg/L)[30]	Kererences (reported from meat chickens)
Fixed Gasses														
Ammonia		17.031	7664-41-7	۳	Ammonia, pungent [19];	26.6 [36] (1045)	37,800 [33]	38 (1500 [29])	5.43 x 10 <sup>4</sup>	67.8	-3.22	994.4	310,000– 480,000	[1; 2; 4; 9; 10; 13; 14; 18; 20; 23- 25; 31; 35; 37; 38; 46; 47; 52; 56; 57]
Hydrogen Sulfide		34.081	7783-06-4	H <sub>2</sub> S	Decaying vegetation[19]; Rotten eggs[26; 45];	0.2 [54] (0.6) (0.7 [41])	24.9 [49] (14 [41])	0.15 (0.41) (0.50)	17.9 (10.04)	0.10	-0.39	2032	insoluble	[49]
Sulfur dioxide	Sulphurous acid anhydride; sulphurous anhydride; SO <sub>2</sub> ;	64.0638	7446-09-5	O <sub>2</sub> S	Strong, suffocating, irritating, pungent [30]	870 [33] (1175 [41]) (2280)	3816	332 (448) (870 [29])	1.0 x 10 <sup>5</sup> [33]	1.33	-1.51	401.2	107,000 @ 21°C	[28]
Hydrocarbons														
Propene	Propylene; methylethylene	42.0797	115-07-1	CH <sub>3</sub> CH=CH <sub>2</sub> or C <sub>3</sub> H <sub>6</sub>	Aromatic [30, 41]	2.2 × 10 <sup>4</sup> (3.96 × 10 <sup>4</sup> [41]) (9.0 × 10 <sup>4</sup> )	1.3 × 10 <sup>5</sup> (1.16 × 10 <sup>5</sup> [41])	1.3 × 10 <sup>4</sup> [29] (2.3 × 10 <sup>4</sup> ) (5.2 × 10 <sup>4</sup> [42])	7.6 × 10 <sup>4</sup> [16] (6.7 × 10 <sup>4</sup> )	0.006	0.85	1160 [30]	200	[48]
2-Methyl-1-propene	Isobutylene; Isobutene; 1,1-Dimethylethylene; 2- Methylpropene	56.1063	115-11-7	(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub> or C4H <sub>8</sub>	Coal gas odour [30]	2.8 x 10⁴	4.58 × 10 <sup>4</sup> [41]	1.2 × 10 <sup>4</sup> [16]	2.0 × 10 <sup>4</sup>	0.0046	0.95	307.7 [30]	236	[48]
Chloroethane	Aethylis, Chlorethyl; Chlorene; Monochloroethane	64.514	75-00-3	C <sub>2</sub> H <sub>5</sub> Cl	Ethereal, pungent, ether-like [30]	n/a	n/a	n/a	n/a	0.084	-0.31	161 [39]	5680 (@20°C)	[48]
Cyclopentane	Pentamethylene	70.1329	287-92-3	C5H10	Mild, sweet [30]	n/a	n/a	n/a	n/a	0.006	0.8	42.3	156 [39]	[48]
Pentane	n-pentane	72.1488	109-66-0	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>3</sub> CH <sub>3</sub> or C <sub>5</sub> H <sub>12</sub>	Petrol-like [5]	4130 (6600 [41]) (1.18 × 10 <sup>6</sup> ) (3.5 × 10 <sup>5</sup> [33])	3 x 10 <sup>6</sup> [41]	1400 [29] (2236) (4.00 × 10 <sup>5</sup> [16]) (1.19 × 10 <sup>5</sup> )	1.02 × 10 <sup>6</sup>	0.0008	1.72	68.3	38	[27; 48] ; Poultry' litter [51]
Benzene		78.112	71-43-2	С°д	Sweet, solvent [34]; solventy [26]; aromatic, petrol-like [30]	1495 (4500 [41])	3.80 × 10 <sup>5</sup> [33] (2.7 × 10 <sup>5</sup> [41])	468 [16] (1408)	1.19 x 10 <sup>5</sup> (8.45 x 10 <sup>4</sup> )	0.17	-0.62	12.6	1790	[6; 27; 28; 34; 48]; Poultry' litter [51];
methylcyclopentane	Methyl-cyclopentane; methylpentamethylene	84.1595	96-37-7	C <sub>5</sub> H <sub>9</sub> CH <sub>3</sub> or C <sub>6</sub> H <sub>12</sub>	Petrol-like [30]	n/a	n/a	n/a	n/a	0.0028	1.16	18.3	42	[28]
Dichloromethane	Methylene chloride;	84.933	75-09-2	CH <sub>2</sub> Cl <sub>2</sub>	Chloroform-like, sweet, pleasant [30]	8.6 × 10 <sup>4</sup> (9.8 × 10 <sup>4</sup> )	5.6 x 10 <sup>5</sup>	2.5 x 10 <sup>4</sup> [16] (2.8 x 10 <sup>4</sup> [42])	1.6 x 10 <sup>5</sup> [29]	0.36	-0.94	57.2	13,000	[6; 48]

Odorant	Alternative names	Molecular weight [32]	CAS No.[32]	Formula	Odour Character	Odour Threshold (min) (µg/m³)	Odour Threshold (max) (µg/m³)	Odour Threshold (min) (ppbv)	Odour Threshold (max) (ppbv)	Henry's constant at 25°C (M/atm) [32]	Log <sub>10</sub> Hcc at 25°C (dimension- less)	Vapour Pressure at 25°C (kPa) [32]	Water solubility at 25°C (mg/L)[30]	References (reported from meat chickens)
Acetic acid, ethenyl ester	Vinyl acetate; acetic acid vinyl ester; Ethenyl acetate[30]	86.0892	108-05-4	CH <sub>3</sub> CO <sub>2</sub> CH=CH <sub>2</sub> or C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	Sweetish smelling (@ low conc.), sharp and irritating (@ high conc.) [30]	360 [41]	1760	102.2	500 [16]	1.7	-1.62	15.3	20,000 @ 20°C	[28]
3-Methyl-pentane	3-methylpentane	86.1745	96-14-0	$C_6H_{14}$	Petrol-like [5]	3.14 x 10 <sup>4</sup>	n/a	8900 [29]	n/a	0.0006	1.84	25.3	17.9	[9]
2-Methyl-pentane	2-methylpentane; isohexane	86.1754	107-83-5	(CH <sub>3</sub> ) <sub>2</sub> CHC <sub>3</sub> H <sub>7</sub> or C <sub>6</sub> H <sub>14</sub>	Petrol-like [5]	289[41]	2.47 x 10 <sup>4</sup>	81.9	7000 [29]	0.0006	1.83	28.2	4	[9]
Hexane	<i>n</i> -hexane	86.1754	110-54-3	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub> or C <sub>6</sub> H <sub>14</sub>	Petrol-like [5]	5290	2.8 × 10 <sup>5</sup> (2.3 × 10 <sup>5</sup> [33])	1500 [29]	8.0 x 10 <sup>4</sup> [16] (6.5 x 10 <sup>4</sup> )	0.0006	1.83	20.1	9.5	[27]
Toluene		92.138	108-88-3	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> or C7H <sub>8</sub>	Sweet, solvent [34]; strong, fruity [30]	600 [54]	5.9 × 10 <sup>5</sup> [54]	159	1.57 × 10 <sup>5</sup>	0.15	-0.56	æ r	526	[27; 28; 34; 48; 55]; 'Poultry' litter [51]
1,3,5-cycloheptatriene	Cycloheptatriene; Tropilidene	92.1384	544-25-2	C7H <sub>8</sub>	n/a	n/a	n/a	n/a	n/a	0.21	-0.71	3.13	n/a	[28]
Phenol	Carbolic acid	94.1112	108-95-2	C <sub>6</sub> H <sub>5</sub> OH or C <sub>6</sub> H <sub>6</sub> O	Phenolic [22]; medicinal, sweet [41]; sweet, tarry [30]	21.5 (178.6 [41])	2.2x10 <sup>4</sup> [41]	5.6 [29] (46.4)	5820	2900	-4.85	0.046[30]	82,400	[48; 50; 55]; Layer manure [22]
3-Methylhexane	2-ethylpentane; 2-ethyl- pentane; 3-Methyl-hexane	100.2019	589-34-4	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH( CH <sub>3</sub> or C <sub>7</sub> H <sub>16</sub>	Solvent odour [6]	3442	n/a	840 [29]	n/a	0.00042	1.99	n/a	4.95 [39]	[9]
3-hydroxy-3-methyl-2- butanone	dimethylacetylcarbinol	102.1317	115-22-0	(CH <sub>3</sub> ) <sub>2</sub> C(OH)CO CH <sub>3</sub> or C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	unpublished data
1,3,5,7-cyclooctatetraene	[8]-Annulene; cyclooctatetraene	104.1491	629-20-9	C <sub>8</sub> H <sub>8</sub>	n/a	n/a	n/a	n/a	n/a	n/a	n/a	1.05	n/a	[27]
Styrene	Vinylbenzene; Ethenylbenzene, Styrol, Phenylethylene, Cinnamene	104.1491	100-42-5	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub> or C <sub>8</sub> H <sub>8</sub>	Sweet, floral, aromatic, extremely penetrating [30]; solventy, rubbery [41]	149 (170) (430 [41])	8.6 × 10 <sup>5</sup> [41]	35 [29] (40 [16]) (101)	2.02 × 10 <sup>5</sup>	0.34	-0.91	0.85 [30]	300	[28]
Xylenes	Dimethyl benzene	106.1650	1330-20-7	C <sub>6</sub> H₄(CH <sub>3</sub> )₂ or C <sub>8</sub> H₁₀	n/a	304 (350 [33])	8.6 x 10 <sup>4</sup> [33]	70 [16] (80)	2.0 × 10⁴	0.14 [39]	-0.53 [39]	1.1 [39]	161 [39]	[9]
p-Xylene	p-methyltoluene; 1,4- dimethyl-benzene	106.1650	106-42-3	C <sub>6</sub> H₄(CH₃)₂ or C <sub>8</sub> H₁₀	Sweet, aromatic [30]	251.8 (304)	2127.6	58 [29] (70 [16])	490 [42]	0.14	-0.52	1.18	162	[27; 28]
1,3-dimethyl-benzene	m-Xylene	106.1650	108-38-3	C <sub>6</sub> H₄(CH <sub>3</sub> )₂ or C <sub>8</sub> H₁₀	Sweet, benzene-like, characteristic aromatic [30]	178	304	41 [29]	70 [16]	0.13	-0.50	1.11	161	[27]

Odorant	Alternative names	Molecular	CAS	Formula	Odour Character	Odour Threshold	Odour	Odour	Odour	Henry's	Log <sub>10</sub> Hcc	Vapour	Water	References
		weight	No.[32]			(min)	Threshold	Threshold	Threshold	constant at	at 25°C	Pressure at	solubility	(reported
		[32]				(-m/6rl)	(max) (µg/m <sup>-</sup> )	(vum)	(max) (ppov)	25 C (M/atm) [32]	(aimension- less)	zэ с (кга) [32]	ar 25 C (mg/L)[30]	rrom mear chickens)
Ethylbenzene	Ethylbenol; EB; Phenylethane	106.1650	100-41-4	C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub> or C <sub>8</sub> H <sub>10</sub>	Pungent, sweet, petrol- like [30]	12.5 (738) (8700 [41])	8.7 × 10 <sup>5</sup> [41]	2.88 [42] (170 [29]) (2003)	2.0 × 10 <sup>5</sup>	0.12	-0.47	1.28 [30]	169	[27; 28]
o-Xylene	1,2-Dimethyl -benzene; o- Dimethylbenzene; 2- Methyltoluene	106.165	95-47-6	C <sub>6</sub> H₄(CH₃)₂ or C <sub>8</sub> H₁₀	Sweet, aromatic [30]	304 (851 [42])	1650	70 [16] (196)	380 [29]	0.2	-0.69	0.88	178	[28]
4-methylphenol	p-Cresol; p-Tolyl alcohol	108.1378	106-44-5	CH₃C <sub>6</sub> H₄OH or C7H₃O	Phenolic, barnyard [22]; sweet, tarry [30]; Faecal [58]	0.239 (2.1 [58])	9.0 [58]	0.054 [29] (0.48)	(2.0)	1300	-4.50	0.015 [30]	21,400	[48; 50; 55]; Layer manure [22]
Benzyl alcohol	Benzenemethanol; phenylcarbinol	108.1378	100-51-6	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH or C <sub>7</sub> H <sub>8</sub> O	Faint aromatic [30]	n/a	n/a	n/a	n/a	0006	-5.34	0.013	42,900	[27]
Octane	n-Octane; Methylheptane	114.2285	111-65-9	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub> or C <sub>6</sub> H <sub>18</sub>	Petrol-like [30]	7940 (2.7 × 10 <sup>4</sup> ) (7.1 × 10 <sup>4</sup> [33]) (2.24 × 10 <sup>5</sup> )	(7.1 × 10 <sup>5</sup> [33])	1700 [29] (5750 [42]) (1.5 × 10 <sup>4</sup> ) (4.8 × 10 <sup>4</sup> [16])	(1.5 × 10⁵)	0.00034	2.08	1.88 [30]	0.66 [30]	[9]
2-Methylheptane	Dimethylhexane	114.2285	592-27-8	$(CH_3)_2CH(CH_2)_4$ $CH_3$ or $C_8H_{18}$	n/a	514	n/a	110 [29]	n/a	0.00027	2.18	6.8 [39]	0.0 [30]	[9]
3-Methylheptane	2-Ethylhexane	114.2285	589-81-1	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(C H <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub> or C <sub>8</sub> H <sub>18</sub>	n/a	2000	n/a	1500 [29]	n/a	0.00027	2.18	2.6 [39]	[66] 67.0	[9]
2,4-Dimethylhexane	2,4-dimethyl hexane	114.2285	589-43-5	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> or C <sub>8</sub> H <sub>18</sub>	n/a	n/a	n/a	n/a	n/a	0.00028	2.16	4.04	n/a	[9]
Trichloromethane	Chloroform; Formyl trichloride	119.378	67-66-3	CHCI <sub>3</sub>	Pleasant, etheric [30]	1.17 × 10 <sup>4</sup> (1.9 × 10 <sup>4</sup> ) (5.7 × 10 <sup>4</sup> ) (2.5 × 10 <sup>5</sup> [41])	1.0 × 10 <sup>6</sup> [41]	2400 [16] (3800 [29]) (1.17 × 10 <sup>4</sup> [42]) (5.12 × 10 <sup>4</sup> )	2.1 × 10 <sup>5</sup>	0.25	-0.92	25.8	7950	[48]
Propyl benzene	1-Phenylpropane; Phenylpropane; Isocumene; n- Propylbenzene	120.1916	103-65-1	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH 3 or C <sub>9</sub> H <sub>12</sub>	n/a	18.7	n/a	3.8 [29]	n/a	0.14	-0.53	0.45 [30]	23.4	[28]
Mesitylene	1,3,5-Trimethylbenzene; Trimethylbenzol	120.1916	108-67-8	$C_6H_3(CH_3)_3$ or $C_9H_{12}$	Peculiar, aromatic, sweet [30]	835	1131	170 [29]	230 [16]	0.16	-0.58	0.3 [30]	48.2	[28]
4-ethyl-phenol	p-Ethylphenol; Paraethylphenol	122.1644	123-07-9	C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> OH or C <sub>8</sub> H <sub>40</sub> O	Burnt, phenolic, medicinal [22]; powerful, woody-phenolic [30]; pungent [58]	3.5 [58]	10 [58]	0.7	0.	1290 [39]	4.5 C	0.005 [30]	4900	[48; 50]; Layer manure [22]

References (reported from meat chickens)	[27]; Layer manure [22]	[27]	[28]	[48]	[28; 34]	[34]	[6]; 'Poultry' litter [51]	[48]	[48]	unpublished data	[28]	[28]	[28]	[28]	[28]	[28]
Water solubility at 25°C (mg/L)[30]	18,700	31	0.22	1280 [39]	2.49	4.89	13.8	13.8	24.6	0.052	n/a	n/a	62	0.044	n/a	206
Vapour Pressure at 25°C (kPa) [32]	0.014	0.011 [30]	0.59 [30]	0.005 [39]	0.63 [30]	0.39	0.26	0.263 [30]	0.007 [30]	0.17 [30]	n/a	n/a	0.23 [30]	0.05 [30]	n/a	2.46 [30]
Log <sub>10</sub> Hcc at 25°C (dimension- less)	-4.34	-1.77	2.31	-4.33	1.08	-0.08	0.12	0.12	-1.72	2.47		2.36	-1.09	1.9	n/a	-0.15
Henry's constant at 25°C (M/atm) [32]	006	2.4	0.0002	877	0.003 [39]	0.05	0.03 [39]	0.031 [39]	2.1	0.00014	0.00018	0.00018	0.5	0.0005 [39]	n/a	0.058
Odour Threshold (max) (ppbv)	n/a	2.38 x 10⁴	6.5 x 10 <sup>5</sup> [29]	n/a	4130	n/a	n/a	38 [29]	50.0	(740 [16; 42])	n/a	n/a	3.0 x 10 <sup>5</sup>	1170 [42]	n/a	6.91 x 10 <sup>4</sup>
Odour Threshold (min) (ppbv)	n/a	84 [16] (286)	2200 (4.7 × 10 <sup>4</sup> [16])	n/a	377	1.17 × 10 <sup>4</sup>	1.8	8.	10.0	620 [29]	n/a	n/a	180 [16] (1.5 × 10 <sup>4</sup> )	870 [29]	n/a	4623 (2.7 × 10 <sup>4</sup> [16])
Odour Threshold (max) (µg/m³)	n/a	1.25 x 10 <sup>5</sup> [41]	3.4 x 10 <sup>6</sup> [41]	n/a	2.3 x 10 <sup>4</sup> [54]	n/a	n/a	211.7	290.5 [41]	4300	n/a	n/a	1.8 × 10 <sup>5</sup> [41]	7480	n/a	4.69 × 10⁵ [41]
Odour Threshold (min) (µg/m³)	n/a	440 (1500 [41])	1.15 × 10 <sup>4</sup> (2.47 × 10 <sup>5</sup> )	n/a	2100 [54]	65 [34]	10 [33]	10 [33]	58.1 [41]	3600	n/a	n/a	1082 (9.0 × 10 <sup>4</sup> [41])	5560	n/a	3.14 × 10 <sup>4</sup> [41] (1.83 × 10 <sup>5</sup> )
Odour Character	Burnt [22]; sweet, aromatic, slightly phenolic [30]	Mothballs [30]; tar like [41]	Petrol-like [30]	n/a	Pine [34]; turpentine	Earth, mushroom [34];Characte ristic turpentine odour, dry, woody, piney, resinous [30]	Pleasant, lemon-like [30]	Pleasant, lemon-like, citrus, penetrating, penetrating [30]	n/a	n/a	n/a	n/a	Mothball-like, penetrating [30]; mothballs [41]	n/a	n/a	Ether-like, mild, sweet, chloroform-like [30]; chlorinated solvent [41]
Formula	(CH₃O)C <sub>6</sub> H₄OH or C7H₃O2	C <sub>10</sub> H <sub>8</sub>	CH <sub>3</sub> (CH <sub>2</sub> )7CH <sub>3</sub> or C <sub>5</sub> H <sub>20</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H ₄OH or C <sub>9</sub> H <sub>12</sub> O	$C_{10}H_{16}$	C <sub>10</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>16</sub>	C11H10	$CH_3(CH_2)_8CH_3$ or $C_{10}H_{22}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH(C H <sub>3</sub> ) <sub>2</sub> or C <sub>10</sub> H <sub>22</sub>	C <sub>10</sub> H <sub>22</sub>	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CH <sub>3</sub> or C <sub>11</sub> H <sub>24</sub>	C <sub>11</sub> H <sub>24</sub>	CCI <sub>2</sub> =CCI <sub>2</sub> or C <sub>2</sub> CI <sub>4</sub>
CAS No.[32]	90-05-1	91-20-3	111-84-2	645-56-7	80-56-8	127-91-3	5989-27-5	138-86-3	91-57-6	124-18-5	871-83-0	2613-61-8	106-46-7	1120-21-4	2847-72-5	127-18-4
Molecular weight [32]	124.1372	128.1705	128.2551	136.1910	136.234	136.234	136.2340	136.2340	142.1971	142.2817	142.2817	142.2817	147.002	156.3083	156.3083	165.833
Alternative names	Guaiacol		n-nonane	P-propyl Phenol;	Alpha-pinene	Beta-pinene	Cyclohexane; Citrene; Carvene;	Dipentene; citrene; carvene;1-methyl-4-prop- 1-en-2-ylcyclohexene;	Methyl-2-naphthalene	<i>n</i> -Decane	Isoparaffin; iso-decane; 2- Methylnonane	2,4,6-Trimethylheptane	1,4-dichlorobenzene; p- Dichlorobenzene; Paradichlorobenzene	n-Undecane; Hendecane	4-Methyldecane	Ankilostin; Ethylene Tetrachloride; Perchlorethylene
Odorant	2-methoxy-phenol	Naphthalene	Nonane	4-propylphenol	α-pinene	β-pinene	D-Limonene	Limonene	2-Methyl naphthalene	Decane	2-Methyl-nonane	2,4,6-Trimethyl-heptane	1,4-dichloro-benzene	Undecane	4-Methyl-decane	Tetrachloroethylene

Odorant	Alternative names	Molecular weight [32]	CAS No.[32]	Formula	Odour Character	Odour Threshold (min) (µg/m³)	Odour Threshold (max) (µg/m³)	Odour Threshold (min) (ppbv)	Odour Threshold (max) (ppbv)	Henry's constant at 25°C (M/atm) [32]	Log <sub>10</sub> Hcc at 25°C (dimension- less)	Vapour Pressure at 25°C (kPa) [32]	Water solubility at 25°C (mg/L)[30]	References (reported from meat chickens)
2,2,4,6,6-pentamethyl- heptane	Permthyl 99A	170.3348	13475-82-6	C <sub>12</sub> H <sub>26</sub>	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[28]
Dodecane	n-Dodecane	170.3348	112-40-3	$CH_{3}(CH_{2})_{10}CH_{3}$ or $C_{12}H_{26}$	n/a	766	1.4 × 10 <sup>4</sup>	110 [29]	2040 [42]	0.00014	2.47	0.018 [30]	0.0037	[28; 48]
beta-Terpinyl acetate	B-Terpinal acetate; p-Menth-8-en-1-ol, acetate; Cyclohexanol, 1- methyl-4-(1- methylethenyl)-, acetate	196.286	10198-23-9	C <sub>12</sub> H <sub>20</sub> O <sub>2</sub>	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	'n/a	[28]
Hexadecane	<i>n</i> -hexadecane; cetane; n- cetane	226.4412	544-76-3	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> CH <sub>3</sub> or C <sub>16</sub> H <sub>34</sub>	n/a	n/a	n/a	n/a	n/a	0.0043	0.98	n/a	0.0000	unpublished data
2,2,4,4,6,8,8- Heptamethyl-nonane	Isocetane; HMN;	226.4412	4390-04-9	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> CH( CH <sub>3</sub> )CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub> or CH <sub>5</sub> H <sub>34</sub>	n/a	n/a	Ŋa	n/a	n/a	n/a	n/a	n/a	n/a	[27]
Amines														
Methylamine	MMA	31.057	74-89-5	CH <sub>5</sub> N or CH <sub>3</sub> NH <sub>2</sub>	Fishy [44]; ammonia-like [30]	1.2 [33] (25.2 [41]) (4065)	1.2 × 10 <sup>4</sup> [41] (6100 [33])	0.945 (19.8)	9450 (4802)	36	-2.94	353 [30]	1,250,000	unpublished data
Dimethylamine		45.084	124-40-3	(CH <sub>3</sub> ) <sub>2</sub> NH or C <sub>2</sub> H <sub>7</sub> N	Ammonia-like, fish-like [5]	84.6 [41]	86.7	45.8	47 [16]	31.0	-2.88	207	163,000 (@40°C)	unpublished data
Trimethylamine	ТМА	59.110	75-50-3	(CH <sub>3</sub> ) <sub>3</sub> N or C <sub>3</sub> H <sub>9</sub> N	Fishy [44]; cat urine [19]; fecal [22]	0.26 [33] (0.8 [41]) (1.064)	2100 [33]	0.11 (0.33) (0.44 [36])	898	9.5	-2.37	215 [30]	89,000 (@30°C)	[34]

Odorant	Alternative names	Molecular weight [32]	CAS No.[32]	Formula	Odour Character	Odour Threshold (min) (µg/m³)	Odour Threshold (max) (µg/m³)	Odour Threshold (min) (ppbv)	Odour Threshold (max) (ppbv)	Henry's constant at 25°C (M/atm) [32]	Log <sub>10</sub> Hcc at 25°C (dimension- less)	Vapour Pressure at 25°C (kPa) [32]	Water solubility at 25°C (mg/L)[30]	References (reported from meat chickens)
Nitrogen containing														
Acetonitrile	Cyanomethane; Ethanenitrile; Methyl Cyanide	41.0519	75-05-8	CH <sub>3</sub> CN or C <sub>2</sub> H <sub>3</sub> N	Aromatic, sweet, ethereal [30]	2.2 x 10 <sup>4</sup> (6.7 x 10 <sup>4</sup> ) (7.0 x 10 <sup>4</sup> [41])	1.64 × 10 <sup>5</sup>	1.3 x 10 <sup>4</sup> [29] (4.2 x 10 <sup>4</sup> [16]) (4.2 x 10 <sup>4</sup> )	9.8 x 10 <sup>4</sup> [42]	49	-3.08	11.8	1,000,000	[48]
Acetamide	Acetic acid amide; ethanamide; methanecarboxamide	59.0672	60-35-5	CH <sub>3</sub> CONH <sub>2</sub> or C <sub>2</sub> H <sub>5</sub> NO	Odourless or mousy [30]	n/a	n/a	n/a	n/a	2.3 x 10 <sup>5</sup> [39]	-6.74	0.005 [30]	2,250,000	[48]
2-Methyl-1H-pyrrole	2-methyl-pyrrole	81.1158	636-41-9	$C_5H_7N$	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[27]
4,5-dimethyloxazole		97.1152	20662-83-3	C <sub>5</sub> H <sub>7</sub> NO	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[48]
1-methyl-2-pyrrolidinone	M-Pyrol; N- methylpyrrolidione	99.1311	872-50-4	C <sub>5</sub> H <sub>9</sub> NO	Mild amine [30]	n/a	n/a	n/a	n/a	22,400 [39]	-5.74	0.05 [30]	1,000,000 [39]	[28]
Diisopropylamine	N-isopropyl-1-amino-2- methylethane	101.19	108-18-9	(CH <sub>3</sub> ) <sub>2</sub> CHNHCH( CH <sub>3</sub> ) <sub>2</sub> or C <sub>6</sub> H <sub>15</sub> N	Ammonia, fish-like [30]	520 [41] (7450)	3400 [41]	125.6 (1800 [16])	821.5	10.4 [39]	-2.41	79.4 [30]	110,000	[28]
Indole	Ketole;	117.1479	120-72-9	C <sub>8</sub> H <sub>7</sub> N	Faecal [58]	0.15 (1.4)	1.9[58]	0.032 [42] (0.30 [29])	0.40	1890	-4.67	0.0016 [30]	3560	[17; 48]
2,3,5-Trimethyl pyrazine	Trimethylpyrazine	122.1677	14667-55-1	$C_7H_{10}N_2$	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[48]
N-Butyl-1-butanamine	N-Dibutylamine;	129.2432	111-92-2	(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ) ) <sub>2</sub> NH or C <sub>8</sub> H <sub>19</sub> N	Ammonia like [30]; fishy, amine [41]	423[41]	2540[41]	80.1	481	11.0	-2.43	0.34 [30]	3500	[28]
Skatole	3-methyl-indole	131.1745	83-34-1	C <sub>9</sub> H <sub>9</sub> N	Barnyard [22]; perfume [41]; characteristic fecal (fecal at high concentration and pleasant/sweet at low concentration) [30]	4.0 x 10 <sup>-4</sup> [41] (0.03) (1.2 [11]) (3.02)	268 [41]	7.5x10 <sup>-5</sup> (0.006 [29]) (0.22) (0.56 [42])	20	n/a	n/a	0.0007 [30]	n/a	[17; 48]; Layer manure [22]; poultry [33]
N,N-dibutyl-formamide	DBF; Dibutylformamide	157.2533	761-65-9	HCON(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> or C <sub>9</sub> H <sub>19</sub> NO	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[27]

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Odorant	Alternative names	Molecular weicht	CAS No 1321	Formula	Odour Character	Odour Threshold (min)	Odour Threshold	Ddour Threshold	Odour Threshold	Henry's constant at	Log <sub>10</sub> Hcc at 25°C	Vapour Pressira af	Water solubility	Keterences (renorted
		[32]	[+c]·ou			(Em/gu)	(max) (µg/m³)	(min)	(max) (ppbv)	25°C	(dimension-	25°C (kPa)	at 25°C	from meat
							·	(vadd)		(M/atm) [32]	less)	[32]	(mg/L)[30]	cnickens)
Sulfur containing/Thiols														
Methanethiol	Methyl mercaptan; MM	48.107	74-93-1	CH <sub>3</sub> SH or CH <sub>4</sub> S	Rotten cabbage [36];	0.0003 [54] (0.04 [41]) (2.2 [49])	82 [41]	1.52 x 10 <sup>-4</sup> (0.02) (1.18)	41.67	0.31	-0.87	196.2	15,400	[17; 49]
Carbonyl sulfide		60.075	463-58-1	COS	Sulfide odour except when pure [30]	70 [54] (135 [49]) (654)	180 [54]	28.5 (55.1) (210 [29])	73.3	0.021	0.29	1254.8 [30]	1220	[17; 49]
Dimethyl sulfide	DMS	62.134	75-18-3	C <sub>2</sub> H <sub>6</sub> S or (CH <sub>3</sub> ) <sub>2</sub> S	Rotten eggs [19]; Rotten vegetable (cabbage, canned corn) [45]; wild radish [30]	0.3 [54] (2.5 [41]) (5.6 [49]) (7.6)	160 [54] (50.8 [41])	0.12 (1.0) (2.2) (3.0 [29])	63.0 (20.0)	0.55	13	60.0	22,000	[17; 27; 49; 55]
Ethanethiol	Ethyl mercaptan	62.134	75-08-1	C₂H₅SH or C₂H <sub>6</sub> S	Natural gas [44]; penetrating garlic-like, skunk-like	0.032 [41] (0.043 [54])	92 [41] (21 [54])	0.013 (0.017)	36.2 (8.264)	0.253	-0.79	70.3	15,603	[17]
Carbon disulfide	Methyl disulfide	76.141	75-15-0	CS2	Herbaceous, cabbage, sweet, vegetable [53]	24.3 [41] (70 [54]) (95.5 [42])	2.3 × 10 <sup>4</sup> [41] (296.4 [49]) (180 [54])	7.8 (22.5) (30.7)	7418 (95.2) (57.8)	0.055	-0.13	48.1	2160	[17; 28; 48; 49; 55]
1-propanethiol	Propyl mercaptan; n- propylmercaptan; propanethiol	76.161	107-03-9	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> SH or C <sub>3</sub> H <sub>8</sub> S	Onion [22]; offensive, characteristic cabbage odour[30]	0.04	3.9	0.013 [29]	1.26 [42]	0.25	-0.79	20.56	1900	[17]; Layer manure [22]
Diethyl sulfide	Ethyl sulfide; sulfodor; ethylthioethane	90.187	352-93-2	(C₂H₅)₂S or C₄H₁₀S	Garlic-like, ethereal [30]; Foul, garlicky [41]	0.122 (1.4 [33]) (4.5 [33])	17.7 [41]	0.033 [29] (0.38) (1.22)	4.8	0.56	-1.14	8.31	3130	unpublished data
Dimethyl sulfone	Methyl sulfone; Methylsulfonemethane; MSM; DMSO2	94.1328	67-71-0	(CH <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub> or C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> S	n/a	n/a	n/a	n/a	n/a	> 50,000	<ul><li>-6.09</li></ul>	n/a	n/a	[27; 48]
Dimethyl disulfide	DMD	94.199	624-92-0	CH <sub>3</sub> SSCH <sub>3</sub> or C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	Purification [12]; putrid [7]; rotten garlic [44]; smoke, burning, rubber [34]; rotten cabbage [45]; intense onion [30]	0.1 [41] (0.3 [11]) (1.1 [54]) (8.5) (47.5 [49])	346 [41] (78 [54])	0.03 (0.08) (0.29) (2.2 [29]) (12.3)	89.8 (20.2)	0.96	-1.37	α. ຕ	3000 [39]	[6; 17; 27; 28; 34; 48; 49; 55]
Tetrahydrothiophene 1,1- dioxide	Cyciic tetramethylene sulfone; Sulfolane;	120.170	126-33-0	C4H8O2S	Odourless [30]	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[48]
Diethyl disulfide	Ethyl disulfide	122.252	110-81-6	(C <sub>2</sub> H <sub>5</sub> S) <sub>2</sub> or C <sub>4</sub> H <sub>10</sub> S <sub>2</sub>		0.3 [33] (10)	19.5 [41]	0.06 (2.0 [29])	ດ. ຕໍ	0.56	-1.14	0.57	n/a	

Odorant	Alternative names	Molecular weight [32]	CAS No.[32]	Formula	Odour Character	Odour Threshold (min) (µg/m³)	Odour Threshold (max) (µg/m³)	Odour Threshold (min) (ppbv)	Odour Threshold (max) (ppbv)	Henry's constant at 25°C (M/atm) [32]	Log <sub>10</sub> Hcc at 25°C (dimension- less)	Vapour Pressure at 25°C (kPa) [32]	Water solubility at 25°C (ma/L)1301	References (reported from meat chickens)
Dimethyl trisulfide	DMTS	126.264	3658-80-8	C <sub>2</sub> H <sub>6</sub> S <sub>3</sub> or (CH <sub>3</sub> ) <sub>2</sub> S <sub>3</sub>	Metallic, sulfur, pungent [34]; garlicky [19]; onion [3]	0.06 [54] (6.2 [41]) (7.3 [33])	8.8 [49]	0.012 (1.2) (1.4)	1.7	n/a	n/a	0.15 [39]	2390 [39]	[27; 34; 49] [6; 17; 28]
Unclassified/Other														
Water vapour		18.0153	7732-18-5	H <sub>2</sub> O	Odourless					1785	-4.64	3.16		
2-methyl-,1-(1,1- dimethylethyl)-2-methyl- 1,3-propanediyl ester propanoic acid	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	'n/a	n/a	n/a	n/a	n/a	[27]
1,4-pentadiene	n/a	68.1170	591-93-5	CH <sub>2</sub> =CHCH <sub>2</sub> CH =CH or C <sub>5</sub> H <sub>8</sub>	n/a	n/a	n/a	n/a	n/a	0.0084	0.69	96.8	n/a	[28]
R-(-)-1,2-propanediol	(R)-(-)-Propylene glycol, (R)-(-)-Propylene glycerol	76.0944	4254-14-2	CH <sub>3</sub> CH(OH)CH <sub>2</sub> OH or C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>	n/a	n/a	n/a	n/a	n/a	n/a		0.011 [43] (@20°C)	n/a	[27]
6,7-Dimethyl-3H- isobenzofuran-1-one	n/a	162.1852	CID 583914 [30]	C <sub>10</sub> H <sub>10</sub> O <sub>2</sub>	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[27]
Diethyl ethylidenemalonate	Propanedioic acid, ethylidene- diethyl ester	186.2051	1462-12-0	CH <sub>3</sub> CH=C(CO <sub>2</sub> C ${}_{2}$ H <sub>5</sub> ) <sub>2</sub> or C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[48]
4,5,6,7- tetramethylphthalide	4,5,6,7-tetramethyl-2(3H)- Benzofuranone	190.238 [39]	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[27]
Hexamethylcyclotrisiloxan e		222.4618	541-05-9	C <sub>6</sub> H <sub>18</sub> O <sub>3</sub> Si <sub>3</sub>	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.58	n/a	[9]
Octamethylcyclotetrasilox ane		296.6158	556-67-2	$C_8H_{24}O_4Si_4$	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.14	0.005	[9]

[30] NCBI (; [31] Nicholson et al. (2004); [32] NIST (2013); [33] O'Neill and Phillips (1992); [34] Parcsi (2010); [35] Redwine et al. (2002); [36] Rosenfeld and Suffet (2004); [37] Roumeliotis et al. (2010); [38] Roumeliotis and Van Heyst (2008); al. (2008b); [51] Turan et al. (2009); [52] Ullman et al. (2004); [53] University of Reading (; [54] van Gemert (2003); [55] van Huffel et al. (2012); [56] Wathes et al. (1997); [57] Wheeler et al. (2009); [11] Godayol et al. (2011); [12] Gostelow et al. (2001); [13] Harper et al. (2010); [14] Hayes et al. (2006); [15] Hopfer et al. (2012); [16] INRS (2005); [17] Jiang and Sands (2000); [18] Lacey et al. (2004); [19] Lebrero et al. (2011); [20] [39] RSOC (2014); [40] Rumsey et al. (2012); [41] Ruth (1986); [42] Schiffman et al. (2001); [43] Sigma-Aldrich (2014); [44] Snyder (2013); [45] Suffet and Rosenfeld (2007); [46] Tasistro et al. (2007); [47] Topper et al. (2008); [48] Trabue et [1] Bejan et al. (2013); [2] Brewer and Costello (1999); [3] Cai et al. (2007); [4] Calvet et al. (2011); [5] CDC (2007); [6] Chang and Chen (2003); [7] CPCB (2008); [8] Decottignies et al. (2009); [9] Elliott and Collins (1982); [10] Fairchild et al. Liang et al. (2005); [23] Lin et al. (2012); [24] Miles et al. (2011a); [25] Miles et al. (2008); [26] Muñoz et al. (2010); [27] Murphy et al. (2014); [28] Murphy et al. (2012); [29] Nagata (2003);

## References

al. (2010); [49] Trabue et al. (2008a); [50] Trabue et Leonard et al. (1984); [21] Leyris et al. (2005); [22] (2006); [58] Zahn et al. (2001)



Figure A. 1. Graphical summary of odour thresholds (OTV) for selected compounds

0.0

-5.0

-4.0

-3.0

-2.0

-1.0

1.0

Log<sub>10</sub> OTV (ppb)

2.0

3.0

4.0

5.0

6.0

7.0

Figure A. 2. Graphical summary of Henry's Law constants for selected compounds. Classifications for dependence on gas phase, gas/liquid phase or liquid phase turbulence derived from (Hudson and Ayoko, 2008b)











## Appendix B. Litter microbiota

Selected odorant producing bacterial genera and fungi reported to exist in meat chicken lower gastro-intestinal tract and litter (Dunlop et al., 2016a)

Odorants produced by organism           Organic acids; 3-hydroxy-2-butanone and dimethyl disulfide <sup>16</sup> Organic acids; 3-hydroxy-2-butanone and dimethyl disulfide <sup>16</sup> 3-hydroxy-2-butanone and dimethyl disulfide <sup>16</sup> , 2-butanol, 2,3-butanedione, hexanone, methylallyl acetate, 2,6-dimethyl-3-butyric, valetic, carpotic society, iso-butylamine, iso-butylamine, iso-butylamine, iso-butylamine, iso-butylamine, iso-amylamine, iso-amylamine, iso-amylamine, dipropyl- and dibutyl-amine <sup>2,*</sup> amines, ammonia and volatile amines <sup>2,*</sup> methyl-, ethyl-, propyl-, butyl-, anyl-, iso-butyl-, iso-amyl-, hexyl-, dipropyl- and dibutyl-amine <sup>2,*</sup> ammonia and indole <sup>6</sup> Formic, acetic, propionic, butyric; iso-butyric, valetic, carpotic iso-valetic and iso-caproic acids; indoles and phenols <sup>2,*</sup> , addroxy-2-butanone and ammonia         Amines and ammonia           Termic, acetic, propionic, butyric; so-butyric, valetic, carpotic iso-valetic and iso-caproic acids; indoles and phenols <sup>2,*</sup> , addroxy-2-butanone and amethyl disulfide <sup>17</sup> Farty acids, aldehydes, alcohols, volatile alphatic acids (C <sub>2</sub> -C <sub>1</sub> ), sulfur compounds <sup>18</sup> , methyl-, ethyl-, propyl- phenols <sup>2,*</sup> , addroxy-2-butanone and dimethyl disulfide, methyl-mercaptan           Reduced sulfates including Carbonyl sulfide, Carbon disulfide, methyl-mercaptan, ethyl-mercaptan         2,3-butanedione and disulfide, methyl-mercaptan, ethyl-mercaptan           Reduced sulfates including Carbonyl sulfide, Carbon disulfide, methyl-mercaptan, ethyl-teraptan         2,3-butanedione and 2,3-butanediol <sup>17</sup> Reduced sulfates including Carbonyl sulfide, indopyl-mercaptan', ethyl-teraptan         2,3-butanedione and 2,3-butanediol <sup>17</sup> Reduced sulfates inclu	<b>Description of preferred conditions</b> <sup>7</sup> Facultative anaerobic conditions <sup>7</sup> Min. water activity 0.93–0.95 <sup>13</sup> pH 5–8.5 <sup>20</sup> ; 25–45 °C <sup>20</sup> ; Anaerobic conditions <sup>20</sup> pH 5–8.5 <sup>20</sup> ; 15–69 °C <sup>20</sup> ; Most strains do not tolerate oxygen <sup>20</sup> , Min. water activity 0.93–0.97 <sup>13</sup> Resistant to desiccation and starvation <sup>7</sup> ; Anaerobic conditions <sup>9</sup> Anaerobic conditions <sup>9</sup> Anaerobic conditions <sup>9</sup> Anaerobic conditions <sup>9</sup> Anaerobic conditions <sup>9</sup> Anaerobic conditions <sup>9</sup> Anaerobic conditions <sup>9</sup> Some strains are obligate anaerobes <sup>14</sup>	(reported in Litter Litter 17, 7 17, 7, 9 17, 7, 9 17, 7, 9 17, 7, 9 9 1, 3 1, 3 7 7	References           meat ch meat ch intestinal tract           11, 2, 8, 18           11, 15, 2, 21, 14, 8, 18           11, 2, 10, 18           11, 21, 14, 8           11, 21, 14, 8           11, 2, 14, 18           11, 21, 14, 13           11, 21, 14, 13           11, 21, 14, 13           11, 21, 14, 13           11, 21, 14, 13           11, 15, 21, 3           11, 15, 21, 3           11, 15, 21, 3	
	Resistant to lower pH conditions/	3, 17, 7, 9	14 0 10	
Ecrimic control control but with order $20$ , $2.2$ but and $2.2$ but and $2.2$ but and $12.2$ but on $2.2$			41 1E 01	
Indole <sup>6</sup>			8	
Butyric acid and other short chain fatty acids <sup>14</sup>	Some strains are obligate anaerobes <sup>14</sup>		11, 2, 14, 18	
Formic, acetic, propionic, butyric; iso-butyric, valeric, caproic, iso-valeric and iso-caproic acids; indoles and phenols <sup>20</sup> ; methyl-, ethyl-, propyl-, butyl-, amyl-, iso-butyl-, iso-amyl-, hexyl-, dipropyl- and dibutyl-amine <sup>12</sup>	pH 6.5–7.5 <sup>20</sup> ; 20–45 °C <sup>20</sup> ; Anaerobic conditions <sup>20</sup>	7	11, 2, 21, 8, 10, 18	
Formic, acetic, propionic and butyric acids; indoles and phenols <sup>20,</sup> methyl-, ethyl-, propyl-, butyl-, amyl-, iso-butyl-, iso-amyl-, hexyl-, dipropyl- and dibutyl-amine <sup>12</sup> , indole and phenols <sup>6</sup>	Min. water activity 0.95 <sup>13</sup>	1, 3	11, 21, 14, 8	
2,3-Butanedione and 2,3-Butanediol $^{17}$		<b>0</b>	11, 2, 8	
Reduced sulfates including Carbonyl sulfide, Carbon disulfide, methyl-mercaptan, ethyl-mercaptan and propyl-mercaptan <sup>6</sup>	Anaerobic conditions <sup>6</sup>		11	
Reduced sulfates including Carbonyl sulfide, Carbon disulfide, methyl-mercaptan, ethyl-mercaptan and propyl-mercaptan <sup>6</sup>	Anaerobic conditions <sup>9</sup>	თ		
Fatty acids, aldehydes, alcohols, volatile aliphatic acids (C <sub>2</sub> -C <sub>11</sub> ), sulfur compounds <sup>19</sup> ; methyl-, ethyl-, propyl-, butyl-, amyl-, iso-butyl-, iso-amyl-, hexyl-, dipropyl- and dibutyl-amine <sup>12</sup>	Resistant to desiccation and starvation <sup>7</sup> ; Anaerobic conditions <sup>9</sup>	17, 7, 9	15	
Formic, acetic, propionic, butyric; iso-butyric, valeric, caproic, iso-valeric and iso-caproic acids; indoles and phenols <sup>20</sup> ; 3-hydroxy-2-butanone and dimethyl disulfide <sup>16</sup> , dimethylamine, ethylamine, 1,4-diaminobutane <sup>12</sup> ; skatole, indole and phenols <sup>6</sup>	pH $6.5-7^{20}$ ; 15–69 °C <sup>20</sup> ; Most strains do not tolerate oxygen <sup>20</sup> , Min. water activity 0.93–0.97 <sup>13</sup>	1, 9	11, 2, 10, 21, 14, 8, 18	
Dimethyl trisulfide <sup>17</sup>		17, 7, 9	15	
Amines and ammonia <sup>6</sup>			21, 8, 10	
Formic, acetic, propionic, butyric; iso-butyric, valeric, caproic, iso-valeric and iso-caproic acids; ammonia and volatile amines <sup>20</sup> , methyl-, ethyl-, propyl-, butyl-, amyl-, iso-butyl-, iso-amyl-, hexyl-, dipropyl- and dibutyl-amine <sup>12</sup> ; amines, ammonia and indole <sup>6</sup>	pH 5–8.5 <sup>20;</sup> 25–45 °C <sup>20;</sup> Anaerobic conditions <sup>20</sup>		11, 15, 2, 21, 14, 8, 18	
3-hydroxy-2-butanone and dimethyl disulfide <sup>16</sup> ; 2-butanol, 2,3-butanedione, hexanone, methylallyl acetate, 2,6-dimethyl-3-heptanone <sup>17</sup> ; sulfur compounds <sup>19</sup> ; propylamine, iso-butylamine, amylamine, iso-amylamine, diaminoethane <sup>12</sup> ; indole <sup>6</sup>	Min. water activity 0.93–0.95 <sup>13</sup>	1, 3, 17, 9	11, 2, 8, 18	
Organic acids; 3-hydroxy-2-butanone and dimethyl disulfide <sup>16</sup>	Facultative anaerobic conditions <sup>7</sup>	17, 7		
		Litter	Excreta or intestinal tract	
Odorants produced by organism	Description of preferred conditions	(reported in ickens)	References meat ch	
Organism (Genus)	References meat ch	(reported in iickens)	Description of preferred conditions	Odorants produced by organism
--	---	---	--	---
	Excreta or intestinal tract	Litter		
Megasphaera	15		pH 7.4–8.0 <sup>20</sup> ; 25–40 °C <sup>20</sup> ; Anaerobic conditions <sup>20</sup>	Formic, acetic, propionic, butyric; iso-butyric, valeric, caproic, iso-valeric and iso-caproic acids; volatile sulfur containing compounds <sup>20</sup>
Peptostreptococcus	10		pH 6–8 <sup>20</sup> ; 25–45 °C <sup>20</sup> ; Anaerobic conditions <sup>20</sup>	Formic, acetic, propionic, butyric; iso-butyric, valeric, caproic, iso-valeric and iso-caproic acids; amnonia and volatile amines <sup>20</sup>
Propionibacterium	21		pH 6.5–7.5 <sup>20</sup> ; 30–37 °C <sup>20</sup> ; Anaerobic but tolerate oxygen <sup>20</sup>	Formic, acetic, propionic, butyric; iso-butyric, valeric, caproic, iso-valeric and iso-caproic acids; indole <sup>6</sup> indole <sup>6</sup>
Proteus	21			2,3-Butanedione, 3-hydroxy-2-butanone, 3-methyl-1-butanol, dimethyl disulfide <sup>16</sup> , methyl-, ethyl-, propyl-, butyl-, amyl-, iso-butyl-, iso-amyl-, hexyl-, dipropyl- and dibutyl-amine, 3-methylbutylamine, 2-phenylethylamine <sup>12</sup> ; indole <sup>6</sup>
Pseudomonas	11, 21		Some species are capable of aerobic respiration <sup>21</sup>	methyl-, ethyl-, propyl-, butyl-, amyl-, iso-butyl-, iso-amyl-, hexyl-, dipropyl- and dibutyl-amine <sup>12</sup>
Salmonella	5, 11	1, 5	Min. water activity 0.92–0.95 <sup>13</sup>	Hydrogen sulfide <sup>5</sup>
Shigella	11			Indole <sup>6</sup>
Staphylococcus		3, 17, 7, 9	Facultative anaerobe and tolerates dry and salty conditions $^7$ ; Min. water activity 0.86 $^{13}$	Dimethyl disulfide, acetone <sup>16</sup> ; fatty acids, aldehydes, alcohols <sup>19</sup> ; sulfur compounds <sup>19</sup> ; methyl-, ethyl-, propyl-, butyl-, amyl-, iso-butyl-, iso-amyl-, hexyl-, dipropyl- and dibutyl-amine <sup>12</sup>
Streptococcus	11, 8	3, 7	pH 4–9.6 <sup>20</sup> ; 15–45 °C <sup>20;</sup> Oxygen tolerant <sup>20</sup> ; facultative anaerobe <sup>7</sup>	Formic, acetic, propionic and butyric acids; ammonia and volatile amines <sup>20</sup> , methyl-, ethyl-, propyl-, butyl-, amyl-, iso-butyl-, iso-amyl-, hexyl-, dipropyl- and dibutyl-amine <sup>12</sup> , amines <sup>6</sup>
Fungi				
Aspergillus		1, 17	Min. water activity 0.76–0.83 <sup>13</sup>	1,10-dimethyl1,9-decanol; 3,octanone; nerodiol; 2-octen-1-ol; 1-octen-3-ol and phenylethyl alcohols <sup>17</sup>
Penicillium		17	Min. water activity 0.79–0.87 <sup>13</sup>	1,10-dimethyl1,9-decanol; 3,octanone; nerodiol; 2-octen-1-ol; 1-octen-3-ol and phenylethyl alcohols <sup>17</sup>
Eurotium		17	Min. water activity 0.70-0.71 <sup>4</sup>	1,10-dimethyl1,9-decanol; 3,octanone; nerodiol; 2-octen-1-ol; 1-octen-3-ol and phenylethyl alcohols <sup>17</sup>
[1] Bolan et al. (20 <sup>°</sup> [8] Lu et al. (2003a al. (2011); [15] Vid⁄ [21] Zhu et al. (200	10); [2] Choi ( ); [9] Lu et al enska et al. (; 2)	et al. (2014); . (2003b); [1( 2014); [16] M	[3] Fries et al. (2005); [4] Fontana (20 0] Mead (1989); [11] Singh et al. (201 <sup>,</sup> Vadud (2011); [17] Wadud et al. (2012	07); [5] Kizil et al. (2015); [6] Le et al. (2005a); [7] Lovanh et al. (2007); 4); [12] Spoelstra (1980); [13] Taoukis and Richardson (2007); [14] Torok et !); [18] Wei et al. (2013); [19] Wood and Kelly (2010); [20] Zhu et al. (1999);

Organism (Genus)	References (reported i	n meat chickens)	Description of preferred conditions
	Excreta or lower intestinal tract	Litter	
Achromobacter	8		
Acinetobacter	11	3, 17	
Aerococcus		3, 17, 9	
Alcaligenes	8	9	
Alistipes	11. 2. 14	-	
Anaerostipes	18		
Aquamicrobium		9	
Arthrobacter		1. 7. 9	Resistant to desiccation and starvation <sup>7</sup>
Blautia	11, 2, 18	1 1 -	
Bordetella	,_,	9	
Brachvbacterium		17.7.9	
Butvrivibrio	18	, , -	
Campylobacter	8	1	Min. water activity 0.98 <sup>13</sup>
Cellulomonas		9	,
Citrobacter	11		
Denitrobacter		9	
Enterobacter	11		
Erysipelothrix	2		
Facklamia		17, 7, 9	
Flavobacterium	8	3	
Gallibacterium	14		
Gemmiger	10, 21		
Geobacter		9	
Georgenia		9	
Globicatella		9	Anaerobic conditions <sup>9</sup>
Hespellia	18		
Haemophillus	11		
Jeotgalicoccus		17, 7	
Klebsiella	11		
Listeria	11	1, 3	Min. water activity 0.92–0.94 <sup>13</sup>
Lysobacter		9	-
Megamonas	18		
Moraxella		3	
Nosocomilcoccus		17	
Ochrobacterium	8		
Oscillibacter	2		
Parabacteriodes	11, 18		
Paracoccus		9	
Pediococcus		3, 9	
Prevotella	11, 15		
Pseudoflavonifractor	11		
Roseburia	18		
Ruminococcus	11, 15, 21, 14, 8,	7 9	
Rammococcus	18	1, 5	
Salinicoccus		17, 7, 9	
Sphingobacterium		17, 9	
Stenotrophomonas		9	
Subdoligranulum	11, 2		
Tetragenococcus	2		
Trichococcus		17, 9	
Vagococcus		9	
Veillonella	11, 18		• • • • • • • • • • • • • • • • • • • •
Vibrio	11	4 <del>7</del> -	Min. water activity 0.9413
Virgibacillus		17, 7	
Weisella	8		
Xanthomonas		9	
Yania		17	
Yersinia	11		Min. water activity 0.9513

## Appendix B.2 Extended list of bacterial genera reported to exist in meat chicken lower gastro-intestinal tract and litter but information regarding odorant production was not found (refer to footnotes for references)

[1] Bolan et al. (2010); [2] Choi et al. (2014); [3] Fries et al. (2005); [4] Fontana (2007); [5] Kizil et al. (2015); [6] Le et al. (2005); [7] Lovanh et al. (2007); [8] Lu et al. (2003a); [9] Lu et al. (2003b); [10] Mead (1989); [11] Singh et al. (2014); [12] Spoelstra (1980); [13] Taoukis and Richardson (2007); [14] Torok et al. (2011); [15] Videnska et al. (2014); [16] Wadud (2011); [17] Wadud et al. (2012); [18] Wei et al. (2013); [19] Wood and Kelly (2010); [20] Zhu et al. (1999); [21] Zhu et al. (2002)

## Appendix C. Spreadsheet used to calculate water additions to litter

### Appendix C. Screenshot of the spreadsheet used to calculate the amount of water added daily to litter from bird excretion and normal drinking spillage

This spreadsheet estimates the amout of water applied to the litter from bird excretion Prepared by Mark Dunlop, DAF Qld (last updated 16 May 2016)



41	2676	95	210	21.0	93.81	0.98	1.76	368	8.3	100%	66%	30
42	2771	95	212	21.2	94.93	0.98	1.76	372	8.7	100%	66%	31
43	2865	95	215	21.5	96.04	0.98	1.76	376	9.1	100%	66%	32
44	2958	93	217	21.7	97.16	0.98	1.76	381	9.5	100%	66%	33
45	3051	93	220	22.0	98.28	0.98	1.76	385	9.8	100%	66%	34
46	3143	92	222	22.2	99.40	0.98	1.76	390	10.2	100%	66%	35
47	3234	91	224	22.4	100.30	0.98	1.76	393	10.6	100%	44%	24
48	3324	90	226	22.6	101.19	0.98	1.76	397	11.0	100%	44%	25
49	3413	89	229	22.9	102.31	0.98	1.76	401	11.4	100%	44%	26
50	3502	89	230	23.0	102.99	0.98	1.76	404	11.8	100%	44%	26
51	3589	87	231	23.1	103.43	0.98	1.76	405	12.2	100%	44%	27
52	3675	87	232	23.2	103.88	0.98	1.76	407	12.6	100%	44%	27
53	3760	85	233	23.3	104.33	0.98	1.76	409	13.1	100%	44%	28
54	3844	84	234	23.4	104.78	0.98	1.76	411	13.5	100%	44%	29
55	3927	83	235	23.5	105.22	0.98	1.76	412	13.9	100%	44%	29
56	4010	83	236	23.6	105.45	0.98	1.76	413	14.3	100%	44%	30
Average			141		63			255				
Maximum	L		236		105			413				35.8
Minimum			13		5			32				

92.91

0.98

364

1.76

8.0

100%

66%

29

20.8

40

2581

96

208

Batch average water:feed ratio (days 1-42) 1.85

Batch average water:feed ratio (days 1-56) 1.81

Appendix C. (*Continued*) Screenshot of the spreadsheet used to calculate the amount of water added daily to litter from bird excretion and normal drinking spillage

					Whole shed e	estimates				Exc	retion estimator		
					Floor area (m <sup>2</sup> )	1584							
					Flock size	26928			Assumed exc	reta density (g/L	or kg/m³)	900	
									Assumed vol	ume reduction w	th drying	70%	
	Water deposit	ed to litter	Water ava	ailable for		Estimated	Water deposi	ted to litter					
	per square	emetre	respiration a	nd excretion	Estimated	cumulative	pers	ned					
					daily shed	shed			Estimated	Cumulative	Estimated		mm
	Daily	Cumulative	Daily (L/day)	Cumulative	drinking water	drinking	Daily (L/day)	Cumulative	manure	manure	manure	Daily excretion	depth
_	(L/day/m²)	(L/m²)		(L)		water		(L)	deposition	deposition per	deposition kg	over shed floor	after
Day	Fer (1)		(1) 11						per bird (g)	bird (kg)	per m <sup>2</sup> per day	(mm)	drying
0	Eq. (1)		(drinking + ree	ed + metabolic									
1	0 517	0.5	819	819	873	873	410	410	17	0.02	0.6	0.6	0.2
2	0.641	1.2	1015	1834	1,074	1,947	508	917	21	0.04	0.7	0.8	0.2
3	0.777	1.9	1230	3065	1,275	3,222	615	1,532	26	0.03	0.9	1.0	0.3
4	0.895	2.8	1417	4482	1,477	4,699	709	2,241	30	0.06	1.0	1.1	0.3
5	1.013	3.8	1604	6086	1,678	6,377	802	3,043	34	0.03	1.1	1.3	0.4
6	1.125	5.0	1781	7867	1,880	8,257	891	3,934	37	0.07	1.3	1.4	0.4
7	0.941	5.9	1968	9835	2,081	10,338	984	4,918	41	0.04	1.0	1.2	0.3
8	1.059	7.0	2214	12050	2,316	12,654	1107	6,025	47	0.09	1.2	1.3	0.4
9 10	1.198	0.2 9.5	2504	17323	2,018	15,272	1252	8 662	53	0.05	1.4	1.5	0.5
10	1.324	10.8	3003	20326	3 081	21,214	1501	10 163	65	0.06	1.5	1.7	0.5
12	1.358	12.1	3227	23553	3,290	24,503	1614	11,777	71	0.14	1.6	1.0	0.5
13	1.453	13.6	3451	27005	3,489	27,993	1726	13,502	77	0.08	1.7	1.9	0.6
14	1.555	15.1	3695	30700	3,710	31,703	1847	15,350	83	0.16	1.9	2.1	0.6
15	1.238	16.4	3922	34622	3,925	35,628	1961	17,311	89	0.09	1.5	1.7	0.5
16	1.319	17.7	4179	38801	4,161	39,789	2090	19,400	96	0.19	1.6	1.8	0.5
17	1.399	19.1	4432	43233	4,393	44,183	2216	21,616	103	0.10	1.8	1.9	0.6
18	1.484	20.6	4701	47933	4,623	48,806	2350	23,967	111	0.21	1.9	2.1	0.6
19 20	1.505	22.1	4959 5210	52892	4,852	53,058	2480	26,446	118	0.12	2.0	2.2	0.7
20	1 733	25.5	5489	63600	5 313	64 054	2003	23,033	133	0.24	2.1	2.4	0.7
22	1.829	27.3	5795	69395	5,573	69,626	2897	34,697	133	0.28	2.3	2.7	0.8
23	1.927	29.3	6103	75498	5,835	75,462	3052	37,749	151	0.15	2.6	2.8	0.9
24	2.031	31.3	6435	81933	6,102	81,563	3218	40,967	161	0.31	2.7	3.0	0.9
25	2.150	33.4	6812	88745	6,373	87,936	3406	44,373	170	0.17	2.9	3.2	1.0
26	2.259	35.7	7156	95901	6,649	94,585	3578	47,951	180	0.35	3.1	3.4	1.0
27	2.356	38.1	7465	103366	6,907	101,493	3732	51,683	189	0.19	3.2	3.6	1.1
28	2.468	40.5	7819	111185	7,194	108,687	3910	55,592	200	0.39	3.4	3.8	1.1
29 30	2.579	45.1	8502	119554	7,480	173 932	4085	59,077 63 978	210	0.21	3.0	4.0	1.2
31	2.790	48.6	8840	136696	8.036	131.968	4420	68.348	229	0.43	3.9	4.3	1.2
32	2.891	51.5	9158	145854	8,294	140,262	4579	72,927	238	0.47	4.0	4.5	1.3
33	3.002	54.5	9511	155365	8,577	148,839	4756	77,682	248	0.25	4.2	4.7	1.4
34	3.114	57.6	9864	165229	8,861	157,700	4932	82,615	259	0.51	4.4	4.9	1.5
35	3.218	60.8	10196	175425	9,121	166,821	5098	87,712	268	0.27	4.6	5.1	1.5
36	2.165	63.0	6860	182285	6,129	172,950	3430	91,143	274	0.54	3.1	3.4	1.0
37	2.198	65.2	6962	189247	6,207	179,157	3481	94,624	279	0.28	3.1	3.5	1.0
38 30	2.236	67.4 69.7	7085	196333	6,301	185,457	3543	98,166 101 760	284	0.56	3.2	3.5	1.1 1 1
40	2.306	72.0	7304	210824	6 472	198 308	3652	105,412	203	0.29	3.2 २ २	3.0	1.1
41	2.333	74.3	7392	218216	6,534	204,842	3696	109,108	298	0.30	3.3	3.7	1.1
42	2.368	76.7	7501	225717	6,612	211,455	3750	112,858	304	0.60	3.4	3.8	1.1
43	2.400	79.1	7603	233320	6,690	218,145	3801	116,660	308	0.31	3.5	3.8	1.2
44	2.438	81.5	7724	241044	6,768	224,914	3862	120,522	314	0.62	3.5	3.9	1.2
45	2.470	84.0	7826	248870	6,846	231,760	3913	124,435	319	0.32	3.6	4.0	1.2
46	2.507	86.5	7941	256811	6,924	238,684	3970	128,405	325	0.64	3.6	4.0	1.2
47	1.691	88.2	5357	262168	4,658	243,342	26/8	131,084	330	0.33	2.5	2.7	0.8
40 29	1.711	91.6	5496	2073083	4,099	240,042	2710	135,794	34	0.00	2.3	2.0	0.8
50	1.749	93.4	5541	278625	4.783	257.576	2771	139.312	343	0.68	2.6	2.9	0.9
51	1.762	95.1	5581	284206	4,803	262,379	2791	142,103	347	0.35	2.6	2.9	0.9
52	1.772	96.9	5612	289818	4,824	267,203	2806	144,909	349	0.70	2.6	2.9	0.9
53	1.784	98.7	5652	295470	4,845	272,048	2826	147,735	352	0.35	2.6	2.9	0.9
54	1.795	100.5	5688	301158	4,866	276,914	2844	150,579	355	0.71	2.7	3.0	0.9
55	1.807	102.3	5723	306881	4,887	281,800	2862	153,441	358	0.36	2.7	3.0	0.9
56	1.812	104.1	5741	312623	4,897	286,697	2871	156,311	360	0.72	2.7	3.0	0.9
Average	1.9				5120		2791		Total manure	depth for the ba	tch	157 9	
Maximum	3.2	104.1			9121	286697	5098	156311	Total depth a	fter drying		10.1.5	47.4
Minimum	0.5				873		410						

## Appendix D. Preliminary investigations and method development for water holding capacity and drying rate of litter

Bedding and litter water holding capacity, moisture content at saturation and evaporation rates (Dunlop, 2014)

## Appendix D. Preliminary investigations and method development for water holding capacity and drying rate of litter

#### **D.1** Introduction

A series of activities were undertaken to develop methods for measuring:

- litter water holding capacity
- drying rate
- moisture content at saturation.

This section describes some of the activities and what was learnt about litter and the methods required to assess litter properties. These measures of litter water content and drying were reported in the literature (Bilgili et al., 2009; Miles et al., 2011b; Reed and McCartney, 1970). Data for a wide range of bedding materials was not comprehensive.

The primary purpose of these activities was to evaluate methods for measuring litter water properties and drying rate. At the conclusion of the experiment, a number of practical and fundamental problems were identified with the methods. As such, the data was not analysed for statistical significance between treatments; however, some of the data collected was very useful and therefore presented. Experimental methods were changed as a result of these experiments, with the results of subsequent tests presented in Chapter 4.

#### **D.2 Methods and materials**

#### **D.2.1** Bedding material acquisition

Bedding materials were acquired from meat chicken farms in 'as delivered' condition (Figure A. 5):

- Hardwood sawdust
- Pine shavings (East Coast Woodshavings, Wacol Qld)
- Pine sawdust
- Peanut shells
- Mixed softwood shavings (suspected to include pine and meranti)
- Lemongrass straw (novel material not currently used commercially for bedding, supplied by Animal Bedding Products, Tallebudgera Valley, Qld, Australia; provisional patent no. 2013904166)
- Cypress pine sawdust
- Rice hulls

- Chopped sugarcane trash
- Sand (washed river sand).



Figure A. 5. Selected bedding materials acquired for testing: *Top, L–R*: hardwood sawdust, pine shavings, pine sawdust. *Middle L–R*: peanut shells, mixed softwood shavings, lemongrass straw. *Bottom L–R*: Cypress sawdust, rice hulls, sand.

#### D.2.2 Litter and cake sample collection

Litter samples were collected from a tunnel ventilated shed stocked with approximately 39,000 Ross 308 meat chickens. Litter was collected on day 35 of the grow-out (23 May 2013). The shed had a floor area of 2,055 m<sup>2</sup> resulting in an initial stocking density of 19 birds/m<sup>2</sup>. Hardwood sawdust was used at the start of the batch to a depth of 5 cm. Part shed brooding was used, with day-old chicks being restricted to 50% of the floor area (the brooding section) before being allowed access to more of the shed.

Litter used for analysis was sub-sampled from the brooding section (so all litter collected on a sampling day had a similar opportunity for manure accumulation). Litter was collected from three trenches dug in the litter widthwise across the shed Figure A.

6. Trenches were 75–100 mm wide and were equally spaced along the length of the brooding section. The length of each trench was half the shed width, extending from the centre of the shed to one side wall, which was randomly chosen. Litter from all three trenches was placed in a container where it was mixed with a shovel before the sub-sample was collected. Litter was transported in a sealed 20 L bucket for analysis.

Cake was collected by cutting out a section (Figure A. 7) and transporting it in a sealed zip-lock sample bag.

Litter and cake samples were stored at 4 °C until being analysed.



Figure A. 6. Litter collection 'trench' extending from the centre of the shed to the wall. Litter was mixed and sub-sampled from the black tub.



Figure A. 7. Cake collected to assess moisture holding capacity and drying rate

#### **D.2.3** Moisture content at saturation

Selected bedding materials (pine shavings, pine sawdust, softwood shavings, hardwood sawdust, hardwood shavings, peanut shells, rice hulls, sugarcane trash, lemongrass straw and sand were placed in a 10 L bucket and water was added to cover the material. Materials were allowed to soak in water for 24 h.

After soaking, the water was drained away and a sample (approximately 100 g) was placed in a pre-weighed aluminium dish. Samples were dried at 65 °C until constant weight was achieved. The moisture content was calculated.

#### D.2.4 Dry bulk density

AS 3743—2003 (Appendix B method) (Standards Australia, 2003) was used to determine the dry bulk density of the materials. The methods described in the Standard enabled the bedding materials to be compacted in a repeatable manner to obtain a known volume of the material in the sampling apparatus (Figure 25). The litter sample was then dried at 65 °C to determine the dry mass. Density was then calculated by dividing the mass by the volume of the sample.

#### D.2.5 Drying rate

Bedding, litter and cake samples were placed into pre-weighed plastic sample jars (25, 50 and 75 mm deep and 41 mm diameter). Each sample and jar combination was prepared in triplicate (each material had 3 jars 25 mm deep, 50 mm deep and 75 mm deep). Bedding samples were soaked for 24 h prior to putting in the sample jars. The cake material was put in the oven in as-received condition (previous activities with cake demonstrated that cake is not able to be wet-up without it dissolving and losing its structure). Jars were over-filled and then the side of the jar was tapped 5 times allowing the litter to settle into the jar. Any excess was carefully scraped off the top, leaving the litter sample level with the top of the jar. Cake samples were prepared by cutting a piece of cake to neatly fit the sample jars (Figure A. 8). Each jar was weighed and placed in a randomly determined position on aluminium trays (Figure A. 9). A 50 mm deep sample jar filled with water was also added to each tray as a reference material.



Figure A. 8. Cutting cake to fit the sample jars



Figure A. 9. Samples in jars prepared on trays for drying rate trial

The trays holding the sample jars were placed in a temperature and humidity controlled chamber (Figure A.10, described in Section 4.2.3) using at 30°C and 50% relative humidity. Samples were removed (one tray at a time) and weighed every 3 hours for the first 9 hours, then every 5-7 hours for the next 24 hours and then occasionally until the experiment was concluded after 70 hours. Samples were then dried at 65°C until they reached constant weight. For some of the 75 mm deep samples, this took approximately one week.



Figure A.10. Sample trays in the temperature and humidity controlled cabinet

#### D.3 Results and discussion

#### **D.3.1** Porosity

The porosity of bedding and litter materials is summaries in Table A. 1. Measuring the porosity of cake could not be attempted using this method. Previous attempts to increase the moisture content of cake demonstrated that cake had no obvious saturation point because the fine particle simply liquefied.

Bedding/litter material	Air filled porosity
Pine shavings	74.9%
Lemongrass straw	60.4%
Softwood shavings	56.9%
Hardwood shavings	54.1%
Peanut shells	53.2%
Rice Hulls	51.4%
Sugarcane trash	42.2%
Hardwood sawdust	34.5%
Friable litter	16.7%
Washed sand	5.1%

## Table A. 1. Air filled porosity of selected bedding and litter materials.

#### D.3.2 Moisture content at saturation and dry bulk density

The dry bulk density and moisture content of the bedding materials at saturation point (the point at which free water stops draining from the pores) was measured for a selection of bedding and litter materials (Table A. 2).

The moisture content at the point of saturation is not very useful because litter is never saturated when in use in a meat chicken shed. Using the dry bulk density and water holding capacity data, the amount of water contained in litter samples at 10–60% moisture content was calculated Table A. 2. These figures should be considered approximate only because the volume and compaction of litter materials changes as moisture content changes (litter particles swell but the litter compacts more easily as moisture content increases). These calculated values demonstrate that at 'normal' litter moisture content (20–30%), litter materials hold very little water. The 1–3 L/m<sup>2</sup>/day being added to the litter by bird excretion (Chapter 3) is sufficient to increase the litter moisture content by 20–30% moisture content in a single day (assuming no drying).

The measured moisture content at saturation values and litter water holding capacity (L/m<sup>2</sup>, assuming 50 mm depth and L/m<sup>3</sup>) measured in this study were combined with literature values (Table A. 3). The 'saturation' moisture content for cake was measured in this study. The 'saturation' point was a matter of judgment by the researcher, who increased added water to a sample of cake until it started to become liquid.

## Table A. 2. Comparison between moisture content and litres of water per square metre of litter (L/m<sup>2</sup>) (Dunlop, 2014)

(Assuming starting litter depth 50mm air dried materials with moisture content 5–10%, except for hardwood shavings (13%) and friable litter (23%). Note that final volume will be greater due to expansion when moisture is added.)

		Friable litter	Hardwood sawdust	Hardwood shavings	Pine sawdust	Pine shavings	Mixed softwood shavings	Lemongrass straw	Sugarcane trash chopped	Peanut shells	Rice hulls	Washed sand
Litte dens	r dry bulk ity (kg/m³)	483	335	138	172	97	95	104	103	113	135	1397
Sa moist	iturated ure content	67%	67%	72%	71%	77%	71%	81%	79%	72%	62%	18%
oť	10%	2.7	1.9	0.8	1.0	0.5	0.5	0.6	0.6	0.6	0.7	7.8
Ľ J	15%	4.3	3.0	1.2	1.5	0.9	0.8	0.9	0.9	1.0	1.2	12.3
per itter	20%	6.0	4.2	1.7	2.1	1.2	1.2	1.3	1.3	1.4	1.7	
ent   ep li	30%	10.3	7.2	3.0	3.7	2.1	2.0	2.2	2.2	2.4	2.9	
onte dee	40%	16.1	11.2	4.6	5.7	3.2	3.2	3.5	3.4	3.8	4.5	
n c	50%	24.1	16.8	6.9	8.6	4.8	4.7	5.2	5.1	5.6	6.7	
Vate 50r	60%	36.2	25.2	10.4	12.9	7.3	7.1	7.8	7.7	8.5	10.1	
5	Saturated	48.4	34.5	17.7	21.4	16.0	11.7	21.7	19.3	14.7	10.9	15.8

## Table A. 3.Moisture content and water holding capacity for bedding and litter<br/>materials (Dunlop, 2014).

(Data from experimental measurements and literature (Bilgili et al., 2009; Miles et al., 2011b; Reed and McCartney, 1970). Mass of dry material was based on air dried materials with moisture content 5–10%, except for hardwood shavings (13%) and friable litter 23%). Note that final volume will be greater due to expansion when moisture is added.)

Bedding/litter material	Dry Density	Saturated moisture Content	Water holding capacity per m <sup>2</sup> (starting with 50mm depth of air dried litter)	Water holding capacity per m <sup>3</sup> (starting with 1 m <sup>3</sup> air dry litter)
	(kg/m³)	(%)	(L/m²)	(L/m³)
rice hulls	115-135	50-62	6-11	118-218
pine bark	191	55	12	234
peanut hulls	96-116	67-72	10-15	199-294
pine shaving	96-128	63-80	8-16	156-320
pine bark and chips	171	60	13	255
softwood shavings	95-112	65-75	12-15	234-304
hardwood shavings	138	72-72	11-18	224-354
pine chips	170	65	16	316
sand (river sand)	1342	12-20	16-17	316-342
lemongrass straw (chopped and milled)	104	77-81	12-22	230-434
sugarcane trash chopped	103	79-80	15-19	296-386
cypress sawdust	166	69	19	372
clay	575	41	20	397
pine sawdust	172-211	66-71	20-21	402-428
corn cobs	211	67	21	429
hardwood sawdust	304-335	60-67	19-35	380-690
friable litter (35 day old)	483	67-69	28-48	562-968
cake	639	77	45	

#### D.3.3 Rate of drying

Initial moisture content of the samples (Figure A. 11) were similar to the *saturated moisture content* values in Table A. 3 with the exception of cake, which had a moisture content of 50% (in other words, the cake wasn't 'saturated' like the litter samples). The moisture content of cake was not able to be increased for reasons explained in the previous sections.



Figure A. 11. Moisture content (%, wet basis) of selected bedding and litter materials during the drying experiment

Despite the lower moisture content of the cake material, it still contained a greater quantity of water when calculated on a square metre basis ( $L/m^2$ ) (Figure A. 12).



Figure A. 12. Water content of selected bedding and litter samples (L/m<sup>2</sup>)

The rate of water loss (standardised to L/m²/day, assuming 50mm deep sample) was measured for each sample and sample depth. This was plotted against time (Figure A.

13, selected results for 50 mm deep samples). Evaporation rates were greatest after the first three hours of drying. Subsequently the drying rate reduced as water became less available at the litter surface the resistance of water movement through the litter pores had a more dominant effect (compared to water, which had constant drying rate due to un-restricted evaporation. The drying rate of cake was only 25–50% as much as the bedding and litter materials. Some of this may be due to the lower initial moisture content, but most of it is more likely due to restricted movement of water molecules due to low porosity.



Figure A. 13. Water loss from 50 mm deep samples

Sample depth had minimal effect on the initial drying rate of the litter samples (data not presented). Over time, the 25 mm deep samples had a lower drying rate and the 75 mm deep samples had a greater drying rate than the 50 mm deep samples. This is due to water becoming unavailable much more quickly in the 25 mm deep samples (less total water volume). In contrast, the 75 mm deep samples had the greatest quantity of water and therefore sustained a higher rate of water loss for longer. This was similar to the trends observed by Ghaly and MacDonald (2012). A drying front was visible in the sample jars (Figure A. 14). This drying front was a clear demonstration that a difference in moisture content from the surface to the base of the litter can develop due to all drying occurring from the surface.

A further issue that was identified was the shrinking of cake in the sample jars as it dried Figure A. 15. This increased the exposed surface are of the sample creating a greater surface for moisture to be emitted. In some other samples, the cake cracked through the centre of the sample.



Figure A. 14. Drying front visible in the sample jars as water evaporated from the surface



Figure A. 15. Gap formed between the cake and the jar as the cake dried and shrunk

#### **D.4 Summary and recommendations**

The experimental activities to measure water holding capacity and drying rate of litter provided a great deal of knowledge about methods to measure these properties and about the litter itself.

#### **D.4.1** Experimental methods

- Methods used to measure litter porosity and dry bulk density create conditions that are not representative of conditions within a meat chicken shed. *No better method was identified.*
- The air velocity during the drying experiment was unknown and unable to be controlled. *Future experiments must enable control of air velocity to enable the drying conditions to be reported.*
- When litter material is kept wet for several days, mould and fungi develop. The changes to litter properties with these changes are unknown.
- Drying rate and presumably gas emission rates change as the surface changes.
- Repeated weighing of the samples affects the drying rate. By opening the temperature and humidity controlled cabinet:
  - Control of conditions within the cabinet is temporarily lost.
  - The rate of drying changes as samples are removed and then returned to the cabinet (there is a delay in returning to the original evaporation rate).
  - It took approximately an hour to weigh all of the samples at each weighing.
     Early in the experiment, this meant that the cabinet was closed for about 2 hours and then intermittently opened for an hour.

For the previous two dot points, the following method changes were recommended:

- Use less samples. Litter in sheds is usually 50 mm deep, so test only with this sample depth.
- Measure only after the first 3 hours because litter is not still in the shed due to bird movement. Litter at the surface is more likely to be 'freshly exposed'.
- Measure evaporation rate only for litter samples collected during a grow-out as data for bedding materials has limited value (explanation in the following section).

#### D.4.2 Litter materials

- Data about bedding materials was interesting, but the difference between the bedding materials (bedding only) and litter (bedding + manure) demonstrated that the addition of manure changed the properties of the litter. *All future experiments would need to measure litter properties during a grow-out.*
- Cake is a challenging material to work with:
  - It is difficult to wet
  - o It has no definable upper limit of wetness
  - o It is difficult to fit into sample containers
  - o When it shrinks, the geometry of the cake changes
  - Litter cracks, changing the surface are for emission
  - Air filled porosity is unable to be measured because the pores are not open to water ingress or for draining free water.
- Bedding materials that have 'shavings' particles have lower bulk density and higher porosity than finer particles (sawdust). Shavings hold less water but dry more quickly.
- Measuring from saturated has limited value because litter is not saturated in a meat chicken shed. Estimating the moisture content as the litter dries is not going to give accurate values for the litter surface due to the drying front. *It is recommended to prepare the litter at multiple moisture content values to assess the effect of moisture content on initial drying rate.*
- There is no one measure for the wetness of litter:
  - Moisture content (wet basis) is sensitive to changes in dry bulk density, which occurs with different bedding materials and accumulation of manure
  - Litres of water per square meter (L/m<sup>2</sup>) enables comparison of water addition and evaporation, but is sensitive to changes in litter volume due to compaction.

It is recommended to continue to measure litter wetness in multiple ways and to investigate alternative measures for the wetness of litter.

## Appendix E. Litter moisture content, pH, water activity and temperature dataset

Litter samples were collected from commercial farm (growouts A-D) or during a laboratory pen trial

Date	Day	Grow- out	Sample number	Original description	Litter type	Sample Description	Complete description	Litter Temperature	Moisture content	Hd	Water activity
19/04/2013	1	A	133	Fresh shavings	Dry_friable	Base	Dry_friable_Base		39.7	4.9	
7/05/2013	19	A	134	19 day litter from brood section	Dry_friable	Profile	Dry_friable_Profile		30.9	6.5	
22/05/2013	34	A	135	Bulk sample (shed Average)	Mixture	Profile	Mixture_Profile		43.5	5.6	
22/05/2013	34	A	136	Whole Cake	Wet	Surface	Wet_Surface		56.6	5.6	
22/05/2013	34	A	137	Bottom of cake	Wet	Middle	Wet_Middle		54.2	5.8	
22/05/2013	34	A	138	Friable material under cake	Damp	Base	Damp_Base		27.9	8.1	
22/05/2013	34	A	139	Top of cake	Wet	Surface	Wet_Surface		55.2	5.1	
22/05/2013	34	A	140	Row D Dry floor material (approx 1 m from wet sample)	Dry_friable	Profile	Dry_friable_Profile		25.2	7.5	
23/05/2013	35	A	141	Row A	Mixture	Profile	Mixture_Profile		36.5	6.3	
23/05/2013	35	A	142	Row B	Mixture	Profile	Mixture_Profile		41.7	5.8	
23/05/2013	35	A	143	Row C	Mixture	Profile	Mixture_Profile		44.9	5.7	
23/05/2013	35	A	144	Row D	Mixture	Profile	Mixture_Profile		39.8	5.9	
23/05/2013	35	A	145	Row E	Mixture	Profile	Mixture_Profile		29.9	7.0	
23/05/2013	35	A	146	Row F	Mixture	Profile	Mixture_Profile		33.3	6.7	
23/05/2013	35	A	147	Row D - Wet litter (cake + under cake)	Wet	Profile	Wet_Profile		47.2	5.9	
23/05/2013	35	A	148	Row D Dry floor material (approx 1 m from wet sample)	Dry_friable	Profile	Dry_friable_Profile		23.4	7.5	
2/06/2013	45	A	149	Row A Bulk	Mixture	Profile	Mixture_Profile		32.9	6.9	
2/06/2013	45	A	150	Row A dry	Dry_friable	Surface	Dry_friable_Surface		22.7	7.7	
2/06/2013	45	A	151	Row A Cake	Wet	Surface	Wet_Surface		52.9	5.6	
2/06/2013	45	A	152	Row B Bulk	Mixture	Profile	Mixture_Profile		51.7	5.5	
2/06/2013	45	A	153	Row B dry	Dry_friable	Surface	Dry_friable_Surface		22.3	7.6	
2/06/2013	45	A	154	Row B Cake	Wet	Surface	Wet_Surface		59.3	5.2	
2/06/2013	45	A	155	Row C Bulk	Mixture	Profile	Mixture_Profile		48.0	6.0	
2/06/2013	45	A	156	Row C dry	Dry_friable	Surface	Dry_friable_Surface		23.0	7.9	
2/06/2013	45	A	157	Row C Cake	Wet	Surface	Wet_Surface		51.2	5.4	
2/06/2013	45	A	158	Row D Bulk	Mixture	Profile	Mixture_Profile		33.7	7.6	
2/06/2013	45	A	159	Row D dry	Dry_friable	Surface	Dry_friable_Surface		19.4	7.3	
2/06/2013	45	A	160	Row D Cake	Wet	Surface	Wet_Surface		45.7	6.5	
2/06/2013	45	A	161	Row E Bulk	Mixture	Profile	Mixture_Profile		26.3	7.9	
2/06/2013	45	A	162	Row E dry	Dry_friable	Surface	Dry_friable_Surface		20.5	7.5	
2/06/2013	45	A	163	Row E Cake	Damp	Surface	Damp_Surface		33.2	7.7	
2/06/2013	45	A	164	ROW B UNSW CAKE	Wet	Surface	Wet_Surface		58.4	5.4	
2/06/2013	45	A	165	ROW B UNSW UNDER CAKE	Damp	Base	Damp_Base		31.2	7.9	
9/06/2013	52	A	166	Row A Bulk	Mixture	Profile	Mixture_Profile		31.1	7.1	
9/06/2013	52	A	167	Row A dry	Dry_friable	Surface	Dry_friable_Surface		23.2	7.4	
9/06/2013	52	A	168	Row A Cake	Wet	Surface	Wet_Surface		51.3	6.1	

Dataset of litter samples: Moisture content, pH, water activity and temperature Appendix E.

ay (	- more	ample number	Original description	Litter type	oample Description	<b>Complete description</b>	Lemperature	Moisture content	Нд	water activity
A		169	Row B Bulk	Mixture	Profile	Mixture_Profile	•	50.1	6.0	
A		170	Row B dry	Dry_friable	Surface	Dry_friable_Surface		22.8	7.4	
۷		171	Row B Cake	Wet	Surface	Wet_Surface		59.6	5.3	
۷		172	Row C Bulk	Mixture	Profile	Mixture_Profile		52.8	5.5	
۷		173	Row C dry	Dry_friable	Surface	Dry_friable_Surface		24.4	7.9	
۷		174	Row C Cake	Wet	Surface	Wet_Surface		55.8	5.4	
٩		175	Row D Bulk	Mixture	Profile	Mixture_Profile		25.6	7.9	
٩		176	Row D dry	Dry_friable	Surface	Dry_friable_Surface		22.0	7.3	
۷		177	Row D Cake	damp	Surface	damp_Surface		37.4	7.9	
۷		178	Row E Bulk	Mixture	Profile	Mixture_Profile		32.7	7.8	
۷		179	Row E dry	Dry_friable	Surface	Dry_friable_Surface		19.1	7.3	
۷		180	Row E Cake	Wet	Surface	Wet_Surface		40.1	7.6	
۷		181	Row C CAKE	Wet	Surface	Wet_Surface		51.4	5.3	
۷		182	ROW C Under Cake	Wet	Base	Wet_Base		43.6	7.9	
۷		183	ROW B UNSW CAKE	Wet	Surface	Wet_Surface		59.7	5.2	
۷		184	ROW B UNSW UNDER CAKE	Damp	Base	Damp_Base		29.3	7.1	
В		006	Hardwood sawdust in Brood section (Row C)	Damp	Profile	Damp_Profile		37.5	4.7	
В		007	Hardwood sawdust in Non-brood section (Row B)	Damp	Profile	Damp_Profile		37.9	4.6	
В		008	LGF	Dry_friable	Profile	Dry_friable_Profile		17.4	5.4	
ш		600	Pine Shaving (Hysorb)	Dry_friable	Profile	Dry_friable_Profile		12.9	5.4	
-	~	010	SURFACE Non-Brood hardwood	Dry_friable	Surface	Dry_friable_Surface		28.5	7.0	
ш	~	011	Non-brood Hardwood	Damp	Profile	Damp_Profile		35.7	5.3	
æ	_	012	LGF Non-caked	Dry_friable	Profile	Dry_friable_Profile		31.9	6.8	
В		013	LGF cake Profile Full depth	Wet	Profile	Wet_Profile		56.6	6.2	
ш		014	LGF Cake	Wet	Surface	Wet_Surface		66.6	6.3	
ш		015	LGF Under Cake	Damp	Base	Damp_Base		25.5	8.4	
ш		016	Hysorb Non-caked	Wet	Profile	Wet_Profile		40.3	6.5	
ш	~	017	Hysorb Cake Profile Full depth	Wet	Profile	Wet_Profile		54.6	7.1	
В		018	Hysorb Cake	Wet	Surface	Wet_Surface		60.0	6.4	
В		019	Hysorb Under Cake	Damp	Base	Damp_Base		25.8	7.6	
В		020	Hardwood Non-Cake	Damp	Profile	Damp_Profile		30.3	7.1	
В		021	Hardwood Cake Profile full depth	Wet	Profile	Wet_Profile		41.1	7.4	
В		022	Hardwood Under Cake	Damp	Base	Damp_Base		35.1	5.4	
в		023	Row A Bulk	Mixture	Profile	Mixture_Profile		20.8	7.0	
В		024	Row A wet	Dry_friable	Surface	Dry_friable_Surface		17.5	5.9	
В		025	Row A dry	Dry_friable	Surface	Dry_friable_Surface		20.7	5.8	
В		026	Row B bulk	Mixture	Profile	Mixture_Profile		49.0	6.3	
в		027	Row B wet	Wet	Surface	Wet_Surface		54.1	6.9	

028         Row B dry         Dry_friable         Surface           023         Row C bulk         Mixture         Profile           033         Row C bulk         Mixture         Profile           033         Row D wet         Dry_friable         Surface           033         Row D wet         Dry_friable         Surface           033         Row E wet         Dry_friable         Surface           034         Row E wet         Dry_friable         Surface           035         Row E wet         Dry_friable         Surface           033         Row E wet         Dry_friable         Surface           034         Row E wet         Dry_friable         Surface           033         Row E wet         Dry_friable         Surface           034         LGF bulk         Mixture         Profile           041         LGF uk         Wet         Surface           043         Hardwood - wet + cake         Dry_friable         Surface           044         Hysorb - Wet         Wet         Surface           044         Hysorb - Wet + cake         Dry_friable         Surface           045         LGF - Wet + cake         Dry_friable         Surface<	Description		Temperature c	ontent	activity
29     Row C bulk     Mixture     Profile       30     Row C dry     Dyy friable     Surface       31     Row D ukt     Dyy friable     Surface       32     Row D ukt     Dyy friable     Surface       33     Row D ukt     Dyy friable     Surface       34     Row E bulk     Mixture     Profile       35     Row E bulk     Mixture     Profile       36     Row E bulk     Mixture     Profile       37     Row E Dry     Dry friable     Surface       38     Row E Dry     Mixture     Profile       39     LGF bulk     Mixture     Profile       39     LGF bulk     Mixture     Profile       40     LGF under Cake     Dry friable     Surface       41     Hysorb bulk     Mixture     Profile       42     LGF under Cake     Dry friable     Surface       43     Hysorb - Wet + cake     Dry friable     Surface       44     Hysorb - Wet + cake     Dry friable     Surface       45     LGF under Cake     Dry friable     Surface       46     LGF under Cake     Dry friable     Surface       47     Hysorb - Wet     Surface     Surface       48     Hy	ble Surface	Dry_friable_Surface		24.9 7.3	
330     Row C wet     Damp     Surface       331     Row D bulk     Dry_friable     Surface       332     Row D dry     Dry_friable     Surface       333     Row D dry     Dry_friable     Surface       335     Row D dry     Dry_friable     Surface       335     Row E Dry     Dry_friable     Surface       335     Row E Dry     Dry_friable     Surface       336     Row E Dry     Wet     Dry_friable     Surface       339     LGF bulk     Witture     Profile     Surface       331     Row B CAKE - for UNSW     Wet     Surface     Profile       333     Row B CAKE - for UNSW     Wet     Surface     Profile       334     Hardwood - wet + cake     Dry_friable     Surface       335     Hysorb UR     Mixture     Profile       345     LGF - wet     Dry_friable     Surface       345     LGF - Wet     Dry_friable     Surface       345     LGF - Dry     Dry_friable     Surface       346     LGF - Dry     Dry_friable     Surface       347     Hysorb - Dry     Dry_friable     Surface       348     Row A - Bulk     Mixture     Profile       349     Row B	e Profile	Mixture_Profile		35.9 7.5	
031     Row C dry     Dry Iriable     Surface       032     Row D bulk     Mixture     Profile       033     Row D bulk     Mixture     Profile       034     Row E bulk     Mixture     Profile       035     Row E bulk     Mixture     Profile       036     Row E bulk     Mixture     Profile       037     Row E bulk     Mixture     Profile       038     Row E bulk     Mixture     Profile       039     LGF bulk     Mixture     Profile       040     LGF dee     Dry Iriable     Surface       041     Hardwood - wet - cake     Dry Iriable     Surface       042     Hardwood - wet - cake     Dry Iriable     Surface       043     Hardwood - wet - cake     Dry Iriable     Surface       044     Hardwood - wet - cake     Dry Iriable     Surface       045     LGF - Dry     Mixture     Profile       046     LGF - Dry     Dry Iriable     Surface       047     Hysorb - Dry     Dry Iriable     Surface       048     Row A - Bulk     Mixture     Profile       050     Row E - Bulk     Mixture     Surface       051     Row C - Dry     Dry Iriable     Surface <tr< td=""><td>Surface</td><td>Damp_Surface</td><td></td><td>30.2 7.4</td><td></td></tr<>	Surface	Damp_Surface		30.2 7.4	
032     Row D bulk     Mixture     Profie       033     Row D dry     Dry_friable     Surface       034     Row E bulk     Mixture     Profie       035     Row E bulk     Mixture     Profie       036     Row E bulk     Mixture     Profie       037     Row E bulk     Mixture     Profie       038     Row E bulk     Wet     Surface       039     LGF bulk     Witture     Profie       041     LGF bulk     Mixture     Surface       042     Hardwood - wet + cake     Dyy_friable     Surface       043     Hardwood - bry     Wet     Surface       044     Hardwood - bry     Dyy_friable     Surface       045     Hardwood - bry     Dyy_friable     Surface       046     Hysorb bulk     Diy_friable     Surface       047     Hysorb - Dry     Dry_friable     Surface       048     Hysorb - Dry     Dry_friable     Surface       049     Row A - Dry     Mixture     Surface       051     Row A - Dry     Mixture     Surface       052     Row B - Duk     Mixture     Surface       053     Row C - Dry     Mixture     Surface       053     Row C - Dry	ble Surface	Dry_friable_Surface		23.1 7.2	
033     Row D ury     Dry_friable     Surface       034     Row E bulk     Dry_friable     Surface       035     Row E bulk     Dry_friable     Surface       036     Row E bulk     Dry_friable     Surface       037     Row E bulk     Dry_friable     Surface       038     Row E bry     Wet     Surface       039     LGF bulk     Wrt     Surface       040     LGF bulk     Mixture     Profile       041     LGF bulk     Mixture     Profile       042     LGF bulk     Wrt     Surface       043     Hardwood - wet + cake     Dry_friable     Surface       044     LGF - Wet     Dry_friable     Surface       045     LGF - Wet     Dry_friable     Surface       046     LGF - Wet     Dry_friable     Surface       045     LGF - Wet     Dry_friable     Surface       046     LGF - Dry     Dry_friable     Surface       046     LGF - Dry     Dry_friable     Surface       047     Hysorb - Dry     Mixture     Surface       048     Bulk     Mixture     Surface       051     Row A - Bulk     Mixture     Surface       052     Row B - Dry <t< td=""><td>e Profile</td><td>Mixture_Profile</td><td></td><td>28.7 7.2</td><td></td></t<>	e Profile	Mixture_Profile		28.7 7.2	
034     Row D dry     Dry_friable     Surface       035     Row E bulk     Mixture     Profile       036     Row E bulk     Mixture     Profile       037     Row E bulk     Mixture     Profile       038     Row E bulk     Mixture     Profile       039     Row E bulk     Wet     Surface       039     LGF bulk     Wixture     Profile       040     LGF under Cake     Dry_friable     Surface       041     LGF under Cake     Dry_friable     Surface       042     Hardwood - Dry     Mixture     Profile       043     Hardwood - Dry     Dry_friable     Surface       044     Hardwood - Dry     Wet     Surface       045     LGF - Wet + cake     Wet     Surface       046     HGF - Wet + cake     Dry_friable     Surface       047     Hysorb - Wet + cake     Dry_friable     Surface       048     Hord - Dry     Dry_friable     Surface       049     Row A - Wet     Dry_friable     Surface       043     Row A - Wet     Dry_friable     Surface       044     Row A - Bulk     Mixture     Surface       055     Row B - Bulk     Mixture     Surface       0	ble Surface	Dry_friable_Surface		26.3 6.7	
035         Row E bulk         Mixture         Profile           036         Row E wet         Dy, friable         Surface           037         Row E or         Dy, friable         Surface           038         Row E or         Wet         Surface           040         LGF bulk         Mixture         Profile           041         LGF under Cake         Dy, friable         Surface           042         LGF under Cake         Dy, friable         Surface           043         Hardwood - wet + cake         Dy, friable         Surface           044         Hysorb bulk         Nixture         Profile           045         LGF - Wet + cake         Dy, friable         Surface           045         Hysorb - Wet + cake         Dy, friable         Surface           046         Hysorb - Wet + cake         Dy, friable         Surface           045         Row A - Bulk         Mixture         Profile         Surface           045         Row B - Bulk         Mixture         Profile         Surface           046         Row A - Dry         Dry, friable         Surface         Surface           055         Row B - Bulk         Mixture         Surface         Su	ble Surface	Dry_friable_Surface		21.6 6.9	
036         Row E wet         Dry_friable         Surface           033         Row E Dry         Dry_friable         Surface           033         LGF Aulk         Mixture         Profile           040         LGF Lunder Cake         Dry_friable         Surface           041         Hysorb bulk         Mixture         Profile           043         Hardwood - wet + cake         Dry_friable         Surface           044         Hysorb bulk         Mixture         Surface           045         LGF - Wet + cake         Dry_friable         Surface           045         LGF - Wet + cake         Dry_friable         Surface           045         Hysorb - Dry         Wet         Surface           046         Hysorb - Dry         Wet         Surface           047         Hysorb - Dry         Wet         Surface           046         Hysorb - Dry         Mixture         Surface           047         Hysorb - Dry         Met         Surface           048         Not         Dry_friable         Surface           050         Row A - Dry         Myture         Surface           053         Row A - Dry         Myture         Surface <td>e Profile</td> <td>Mixture_Profile</td> <td></td> <td>31.7 7.4</td> <td></td>	e Profile	Mixture_Profile		31.7 7.4	
037     Row E Dry     Dry friable     Surface       038     LGF bulk     Mixture     Profile       039     LGF bulk     Mixture     Profile       040     LGF uder Cake     Wet     Surface       041     Hysorb bulk     Mixture     Profile       042     Hysorb bulk     Mixture     Profile       043     Hardwood - wet + cake     Dry friable     Base       044     Hardwood - bry     Wet     Surface       045     LGF - Wet + cake     Dry friable     Base       046     LGF - Wet + cake     Dry friable     Surface       047     Hysorb - Dry     Dry friable     Surface       048     Hysorb - Dry     Mixture     Profile       049     Row A - Bulk     Mixture     Surface       050     Row A - Dry     Mixture     Surface       051     Row A - Dry     Mixture     Surface       052     Row A - Dry     Myth     Surface       053     Row A - Dry     Myth     Surface       055     Row A - Dry     Myth     Surface       055     Row A - Dry     Myth     Surface       055     Row B - Mixture     Dry friable     Surface       055     Row C - Bu	ble Surface	Dry_friable_Surface		24.2 7.0	
038         Row B CAKE - for UNSW         Wet         Surface           039         LGF bulk         Mixture         Profile           041         LGF under Cake         Dny_friable         Base           042         Hysorb bulk         Mixture         Profile           043         Hardwood - bry         Damp         Surface           044         Hysorb bulk         Dny_friable         Base           045         LGF - Wet + cake         Dny_friable         Surface           045         Hysorb - Wet + cake         Dny_friable         Surface           043         Hardwood - Dry         Wet         Surface           044         Hysorb - Wet + cake         Dny_friable         Surface           045         Hysorb - Wet + cake         Dny_friable         Surface           046         Hysorb - Wet         Dny_friable         Surface           055         Row A - Bulk         Mixture         Profile           056         Row A - Wet         Dny_friable         Surface           055         Row A - Bulk         Mixture         Surface           056         Row B - UK         Mixture         Surface           057         Row A - Bulk         Mixtur	ble Surface	Dry_friable_Surface		22.7 7.0	
039     LGF bulk     Mixture     Profile       040     LGF cake     DNy friable     Base       041     LGF under Cake     Dny friable     Base       042     Hysorb bulk     Mixture     Profile       043     Hardwood - bry     Wet     Bare       044     LGF - Wet + cake     Dny friable     Surface       045     LGF - Wet + cake     Dny friable     Surface       046     Hysorb - Wet     Wet     Surface       047     Hysorb - Wet + cake     Dny friable     Surface       048     Hysorb - Dry     Dny friable     Surface       049     Row A - Bulk     Mixture     Surface       050     Row A - Bulk     Mixture     Surface       051     Row B - Ury     Dny friable     Surface       052     Row B - Ury     Dny friable     Surface       053     Row A - Bulk     Mixture     Surface       054     Row A - Bulk     Mixture     Surface       055     Row B - Dry     Dny friable     Surface       055     Row B - Dry     Dny friable     Surface       055     Row C - Bulk     Mixture     Surface       056     Row C - Dry     Dny friable     Surface       <	Surface	Wet_Surface		60.3 6.9	
040     LGF Cake     Wet     Surface       041     LGF under Cake     Dry friable     Base       042     Hysorb bulk     Mixture     Profile       043     Hysorb bulk     Mixture     Profile       044     Hardwood - wet + cake     Damp     Surface       045     LGF - Wet + cake     Dry friable     Surface       046     LGF - Wet + cake     Dry friable     Surface       047     Hysorb - Dry     Wet     Surface       048     Hysorb - Dry     Wet     Surface       049     Row A - Bulk     Mixture     Profile       050     Row A - Bulk     Mixture     Surface       051     Row A - Bulk     Mixture     Surface       052     Row B - Bulk     Mixture     Surface       053     Row B - Bulk     Mixture     Surface       054     Row B - Bulk     Mixture     Surface       055     Row D - Wet     Dry friable     Surface       056     Row C - Bulk     Mixture     Surface       055     Row D - Wet     Dry friable     Surface       056     Row C - Dry     Dry friable     Surface       057     Row C - Bulk     Mixture     Surface       058	e Profile	Mixture_Profile		41.4 6.7	
041     LGF under Cake     Dyy friable     Base       042     Hysorb bulk     Mixture     Profile       043     Hardwood - wet + cake     Damp     Surface       044     Hardwood - Dry     Wet     Surface       045     LGF - Wet + cake     Dyy friable     Surface       046     LGF - Wet + cake     Dyy friable     Surface       047     Hysorb - Dry     Wet     Surface       048     Hysorb - Dry     Nvet     Surface       049     Row A - Bulk     Mixture     Profile       050     Row A - Dry     Dry friable     Surface       051     Row A - Dry     Mixture     Profile       052     Row B - Wet     Mixture     Surface       053     Row B - Wet     Mixture     Surface       054     Row C - Bulk     Mixture     Surface       055     Row C - Wet     Dry friable     Surface       056     Row D - Bulk     Mixture     Surface       057     Row C - Bulk     Mixture     Surface       058     Row C - Bulk     Mixture     Surface       059     Row E - Wet     Damp     Surface       051     Row E - Wet     Damp     Surface       053     Ro	Surface	Wet_Surface		54.6 7.3	
042     Hysorb bulk     Mixture     Profile       043     Hardwood - wet + cake     Damp     Surface       044     Hardwood - Dry     Wet     Surface       045     LGF - Wet + cake     Dwet     Surface       046     LGF - Wet + cake     Dry_friable     Surface       047     Hysorb - Wet + cake     Dry_friable     Surface       048     Hysorb - Wet + cake     Dry_friable     Surface       049     Row A - Bulk     Mixture     Profile       050     Row A - Wet     Dry_friable     Surface       051     Row A - Wet     Dry_friable     Surface       052     Row B - Bulk     Mixture     Profile       053     Row B - Bulk     Mixture     Surface       054     Row C - Bulk     Mixture     Surface       055     Row B - Dry     Mixture     Surface       055     Row C - Dry     Mixture     Surface       055     Row D - Dry     Mixture     Surface       051     Row C - Dry     Mixture     Surface       052     Row D - Dry     Mixture     Surface       055     Row D - Dry     Mixture     Surface       056     Row E - Wet     Mixture     Surface	ble Base	Dry_friable_Base		29.7 6.6	
043     Hardwood - wet + cake     Damp     Surface       044     LGF - Wet + cake     Dry_friable     Surface       045     LGF - Wet + cake     Wet     Surface       046     LGF - Wet + cake     Dry_friable     Surface       047     Hysorb - Wet + cake     Dry_friable     Surface       048     Hysorb - Wet + cake     Dry_friable     Surface       049     Hysorb - Dry     Dry_friable     Surface       050     Row A - Bulk     Mixture     Profile       051     Row A - Wet     Wet     Surface       052     Row B - Ukt     Mixture     Profile       053     Row B - Wet     Mixture     Profile       054     Row B - Wet     Mixture     Surface       055     Row B - Wet     Mixture     Surface       055     Row B - Wet     Dry_friable     Surface       055     Row C - Dry     Dry_friable     Surface       056     Row C - Dry     Dry_friable     Surface       057     Row C - Dry     Dry_friable     Surface       058     Row C - Dry     Dry_friable     Surface       059     Row C - Dry     Dry_friable     Surface       051     Row C - Dry     Dry_friable     Surfa	e Profile	Mixture_Profile		39.0 7.4	
04Hardwood - Dry LGF - Wet + cakeDry_friableSurface045LGF - Wet + cakeWetSurface047Hysorb - Wet + cakeNetSurface048Hysorb - Wet + cakeNetSurface049Hysorb - DryNixtureSurface049Hysorb - DryNixtureSurface050Row A - BulkMixtureSurface051Row A - BulkNixtureSurface052Row A - DryDry_friableSurface053Row B - UktNixtureSurface054Row B - UktNixtureSurface055Row B - UktNixtureSurface056Row C - DryDry_friableSurface057Row C - DryDry_friableSurface058Row D - DryDry_friableSurface059Row D - DryDry_friableSurface060Row D - DryDry_friableSurface061Row E - BulkNixtureSurface063Row E - DryDry_friableSurface064LGF - WetDry_friableSurface065LGF - WetDry_friableSurface066LGF - WetDry_friableSurface066LGF - WetDry_friableSurface066LGF - WetDry_friableSurface066LGF - WetDry_friableSurface066LGF - WetDry_friableSurface066LGF - WetDry_friable <t< td=""><td>Surface</td><td>Damp_Surface</td><td></td><td>39.7 7.0</td><td></td></t<>	Surface	Damp_Surface		39.7 7.0	
045     LGF - Wet + cake     Wet     Surface       046     LGF - Dry     Mixtue     Surface       047     Hysorb - Wet + cake     Wet     Surface       048     Hysorb - Dry     Mixtue     Surface       049     Row A - Bulk     Mixture     Surface       050     Row A - Wet     Wet     Surface       051     Row A - Ury     Dry_friable     Surface       052     Row A - Ury     Dry_friable     Surface       053     Row A - Ury     Dry_friable     Surface       053     Row B - Ury     Dry_friable     Surface       054     Row B - Ury     Dry_friable     Surface       055     Row B - Ury     Dry_friable     Surface       055     Row C - Bulk     Mixture     Profile       055     Row C - Dry     Dry_friable     Surface       056     Row C - Dry     Dry_friable     Surface       057     Row E - Bulk     Mixture     Surface       060     Row E - Wet     Dry_friable     Surface       053     Row D - Dry     Dry_friable     Surface       064     Row E - Wet     Dry_friable     Surface       063     Row E - Wet     Dry_friable     Surface	ble Surface	Dry_friable_Surface		22.2 6.9	
046     LGF - Dry     Dry_friable     Surface       047     Hysorb - Wet + cake     Wet     Surface       048     Hysorb - Dry     Wet     Surface       049     Row A - Bulk     Mixture     Profile       050     Row A - Wet     Wet     Surface       051     Row A - Wet     Wet     Surface       052     Row A - Dry     Dry_friable     Surface       053     Row B - Wet     Wet     Surface       054     Row B - Wet     Wet     Surface       055     Row B - Wet     Mixture     Profile       056     Row C - Bulk     Mixture     Surface       055     Row C - Bulk     Mixture     Surface       056     Row C - Dry     Dry_friable     Surface       057     Row C - Dry     Dry_friable     Surface       058     Row C - Dry     Dry_friable     Surface       050     Row E - Bulk     Mixture     Surface       060     Row E - Wet     Dry_friable     Surface       061     Row E - Wet     Dry_friable     Surface       063     Row E - Wet     Dry_friable     Surface       064     LGF - Wet     Wet     Surface       065     LGF - Wet	Surface	Wet_Surface		51.6 6.7	
047     Hysorb - Wet + cake     Wet     Surface       048     Hysorb - Dry     Dry_friable     Surface       049     Row A - Bulk     Mixture     Profile       050     Row A - Wet     Dry_friable     Surface       051     Row A - Wet     Dry_friable     Surface       052     Row B - Bulk     Wet     Surface       053     Row B - Bulk     Wet     Surface       054     Row B - Wet     Dry_friable     Surface       055     Row B - Wet     Dry_friable     Surface       054     Row B - Wet     Dry_friable     Surface       055     Row C - Bulk     Wet     Surface       056     Row C - Wet     Dry_friable     Surface       057     Row C - Dry     Dry_friable     Surface       058     Row C - Dry     Dry_friable     Surface       059     Row D - Bulk     Mixture     Surface       060     Row E - Urck     Dry_friable     Surface       061     Row E - Urck     Dry_friable     Surface       063     Row E - Urck     Dry_friable     Surface       064     LGF - Wet     Dry_friable     Surface       065     LGF - Wet     Dry_friable     Surface	ble Surface	Dry_friable_Surface		23.4 7.3	
048     Hysorb - Dry     Dry_friable     Surface       049     Row A - Bulk     Mixture     Profile       050     Row A - Wet     Surface     Surface       051     Row A - Uvet     Dry_friable     Surface       052     Row B - Bulk     Wet     Surface       053     Row B - Bulk     Wet     Surface       054     Row B - Bulk     Wet     Surface       055     Row B - Bulk     Wet     Surface       054     Row B - Bulk     Wet     Surface       055     Row B - Bulk     Wet     Surface       054     Row B - Bulk     Wet     Surface       055     Row C - Bulk     Wet     Surface       056     Row C - Wet     Dry_friable     Surface       057     Row C - Dry     Dry_friable     Surface       058     Row D - Bulk     Mixture     Surface       059     Row D - Wet     Dry_friable     Surface       060     Row E - Unit     Mixture     Surface       061     Row E - Unit     Mixture     Surface       063     Row E - Unit     Mixture     Surface       064     LGF - Wet     Mixture     Surface       065     LGF - Wet     Mixture<	Surface	Wet_Surface		53.4 6.6	
049     Row A - Bulk     Mixture     Profile       050     Row A - Wet     Surface       051     Row A - Ury     Wet     Surface       052     Row B - Bulk     Wet     Surface       053     Row B - Wet     Dry_friable     Surface       054     Row B - Wet     Wet     Surface       055     Row B - Wet     Wet     Surface       056     Row B - Wet     Wet     Surface       057     Row C - Bulk     Wet     Surface       056     Row C - Wet     Dry_friable     Surface       057     Row C - Wet     Dry_friable     Surface       058     Row C - Wet     Dry_friable     Surface       057     Row C - Wet     Dry_friable     Surface       058     Row D - Wet     Dry_friable     Surface       060     Row D - Wet     Dry_friable     Surface       061     Row E - Wet     Dry_friable     Surface       063     Row E - Wet     Dry_friable     Surface       064     LGF - Wet     Dry_friable     Surface       065     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture	ble Surface	Dry_friable_Surface		22.1 7.4	
050     Row A - Wet     Surface       051     Row A - Dry     Mixture     Surface       052     Row B - Bulk     Mixture     Profile       053     Row B - Wet     Dry_friable     Surface       054     Row B - Dry     Mixture     Profile       055     Row B - Dry     Mixture     Surface       056     Row C - Bulk     Wet     Surface       057     Row C - Wet     Dry_friable     Surface       058     Row C - Wet     Dry_friable     Surface       057     Row C - Wet     Dry_friable     Surface       058     Row C - Wet     Dry_friable     Surface       050     Row C - Wet     Dry_friable     Surface       053     Row D - Bulk     Mixture     Profile       054     Row D - Wet     Damp     Surface       061     Row E - Ury     Dry_friable     Surface       063     Row E - Ury     Dry_friable     Surface       064     LGF - Wet     Mixture     Surface       065     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture     Surface	e Profile	Mixture_Profile		37.7 6.4	
051     Row A - Dry     Dry_friable     Surface       052     Row B - Bulk     Mixture     Profile       053     Row B - Wet     Wet     Surface       054     Row B - Dry     Mixture     Profile       055     Row B - Dry     Mixture     Profile       056     Row C - Bulk     Wet     Surface       057     Row C - Wet     Dry_friable     Surface       058     Row C - Wet     Dry_friable     Surface       057     Row C - Wet     Dry_friable     Surface       058     Row C - Dry     Dry_friable     Surface       057     Row C - Wet     Dry_friable     Surface       058     Row D - Wet     Dry_friable     Surface       050     Row D - Wet     Dry_friable     Surface       061     Row E - Urt     Dry_friable     Surface       063     Row E - Dry     Dry_friable     Surface       064     LGF - Wet     Mixture     Profile       065     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture     Surface	Surface	Wet_Surface		54.5	
052     Row B - Bulk     Mixture     Profile       053     Row B - Wet     Wet     Surface       054     Row B - Dry     Mixture     Profile       055     Row C - Bulk     Wet     Surface       056     Row C - Wet     Nixture     Profile       057     Row C - Wet     Dry_friable     Surface       058     Row C - Dry     Dry_friable     Surface       057     Row C - Dry     Dry_friable     Surface       058     Row D - Bulk     Mixture     Profile       059     Row D - Wet     Damp     Surface       060     Row D - Wet     Damp     Surface       061     Row E - Bulk     Mixture     Profile       063     Row E - Wet     Dry_friable     Surface       063     Row E - Dry     Dry_friable     Surface       064     LGF - Wet     Wet     Surface       065     LGF - Wet     Mixture     Profile       066     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture     Surface	ble Surface	Dry_friable_Surface		24.0 7.3	
053     Row B - Wet     Wet     Surface       054     Row B - Dry     Dry_friable     Surface       055     Row C - Bulk     Mixture     Profile       056     Row C - Wet     Surface     Surface       057     Row C - Dry     Dry_friable     Surface       058     Row C - Dry     Dry_friable     Surface       057     Row D - Bulk     Wixture     Profile       058     Row D - Bulk     Mixture     Surface       059     Row D - Wet     Damp     Surface       060     Row D - Wet     Damp     Surface       061     Row E - Bulk     Mixture     Profile       063     Row E - Wet     Dry_friable     Surface       063     Row E - Dry     Dry_friable     Surface       064     LGF - Wet     Wet     Surface       065     LGF - Wet     Mixture     Profile       066     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture     Surface	e Profile	Mixture_Profile		38.7 5.7	
054     Row B- Dry     Dry_friable     Surface       055     Row C - Bulk     Mixture     Profile       056     Row C - Wet     Surface       057     Row C - Dry     Dry_friable     Surface       058     Row D - Bulk     Wet     Surface       059     Row D - Bulk     Mixture     Profile       059     Row D - Wet     Dry_friable     Surface       060     Row D - Wet     Damp     Surface       061     Row D - Wet     Damp     Surface       063     Row E - Wet     Dry_friable     Surface       063     Row E - Wet     Wixture     Profile       064     Cake (Row B)     Wet     Surface       065     LGF - Wet     Mixture     Profile       066     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture     Surface	Surface	Wet_Surface		45.5	
055     Row C - Bulk     Mixture     Profile       056     Row C - Wet     Surface       057     Row C - Wet     Surface       058     Row C - Dry     Dry_friable     Surface       059     Row D - Wet     Dry_friable     Surface       050     Row D - Wet     Dry_friable     Surface       050     Row D - Wet     Dry_friable     Surface       060     Row D - Wet     Dry_friable     Surface       061     Row E - Bulk     Mixture     Profile       062     Row E - Wet     Dry_friable     Surface       063     Row E - Dry     Dry_friable     Surface       064     Cake (Row B)     Wet     Surface       065     LGF - Bulk     Mixture     Profile       066     LGF - Wet     Dry_friable     Surface       066     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture     Surface       066     LGF - Wet     Mixture     Surface	ble Surface	Dry_friable_Surface		23.5 7.3	
056     Row C - Wet     Surface       057     Row C - Dry     Dry_friable     Surface       058     Row D - Bulk     Mixture     Profile       059     Row D - Wet     Dry_friable     Surface       050     Row D - Wet     Dry_friable     Surface       060     Row D - Dry     Dry_friable     Surface       061     Row E - Bulk     Mixture     Profile       062     Row E - Wet     Dry_friable     Surface       063     Row E - Dry     Dry_friable     Surface       064     Cake (Row B)     Wet     Surface       065     LGF - Bulk     Mixture     Profile       066     LGF - Wet     Dry_friable     Surface       065     LGF - Wet     Dry_friable     Surface	e Profile	Mixture_Profile		49.2 6.4	
057     Row C - Dry     Dry_friable     Surface       058     Row D - Bulk     Mixture     Profile       059     Row D - Wet     Damp     Surface       060     Row D - Wet     Dry_friable     Surface       061     Row E - Bulk     Mixture     Profile       062     Row E - Wet     Dry_friable     Surface       063     Row E - Wet     Dry_friable     Surface       064     Cake (Row B)     Wet     Surface       065     LGF - Bulk     Mixture     Profile       066     LGF - Wet     Dry_friable     Surface       065     LGF - Wet     Dry_friable     Surface       066     LGF - Wet     Wet     Surface       066     LGF - Wet     Dry_friable     Surface	Surface	Wet_Surface		51.3	
058     Row D - Bulk     Mixture     Profile       059     Row D - Wet     Damp     Surface       060     Row D - Dry     Dry_friable     Surface       061     Row E - Bulk     Mixture     Profile       062     Row E - Wet     Dry_friable     Surface       063     Row E - Dry     Dry_friable     Surface       064     Cake (Row B)     Wet     Surface       065     LGF - Bulk     Mixture     Profile       066     LGF - Wet     Dry_friable     Surface       065     LGF - Wet     Wet     Surface       066     LGF - Wet     Wet     Surface	ble Surface	Dry_friable_Surface		25.3 7.1	
059         Row D - Wet         Damp         Surface           060         Row D - Dry         Dry_friable         Surface           061         Row E - Bulk         Dry_friable         Surface           062         Row E - Wet         Wet         Surface           063         Row E - Dry         Dry_friable         Surface           064         Cake (Row B)         Wet         Surface           065         LGF - Bulk         Mixture         Profile           066         LGF - Wet         Surface         Surface           066         LGF - Wet         Wet         Surface           066         LGF - Wet         Wet         Surface	e Profile	Mixture_Profile		27.3 7.8	
060         Row D - Dry         Dry_friable         Surface           061         Row E - Bulk         Mixture         Profile         Surface           062         Row E - Wet         Wet         Surface         Profile           063         Row E - Dry         Dry_friable         Surface         Surface           064         Cake (Row B)         Wet         Surface         Surface           065         LGF - Bulk         Mixture         Surface         Surface           065         LGF - Wet         Wet         Surface         Surface           066         LGF - Wet         Wet         Surface         Surface           066         LGF - Wet         Wet         Surface         Surface	Surface	Damp_Surface		26.3	
061         Row E - Bulk         Mixture         Profile           062         Row E - Wet         Wet         Surface           063         Row E - Dry         Dry_friable         Surface           064         Cake (Row B)         Wet         Surface           065         LGF - Bulk         Mixture         Profile           066         LGF - Wet         Wet         Surface           066         LGF - Wet         Wet         Surface	ble Surface	Dry_friable_Surface		28.5 7.7	
062         Row E - Wet         Surface           063         Row E - Dry         Dry_friable         Surface           064         Cake (Row B)         Wet         Surface           065         LGF - Bulk         Mixture         Profile           066         LGF - Wet         Out         Surface	e Profile	Mixture_Profile		35.4 7.9	
063     Row E - Dry     Dry_friable     Surface       064     Cake (Row B)     Wet     Surface       065     LGF - Bulk     Mixture     Profile       066     LGF - Wet     Wet     Surface	Surface	Wet_Surface		44.1	
064     Cake (Row B)     Wet     Surface       065     LGF - Bulk     Mixture     Profile       066     LGF - Wet     Wet     Surface       067     LGF Due     Due Final     Surface	ble Surface	Dry_friable_Surface		29.5 7.4	
065 LGF - Bulk Mixture Profile 066 LGF - Wet Surface 067 LGE Day Ficialo Surface	Surface	Wet_Surface		45.6 6.5	
066 LGF - Wet Wet Surface	e Profile	Mixture_Profile		37.5 6.6	
067 Day fisioklo Curforo	Surface	Wet_Surface		53.6	
טס/ רטר - טוא אין אין אין אין אין אין אין אין אין אי	ble Surface	Dry_friable_Surface		22.0 7.1	

Water activity																																								
Hq	7.3		7.3	6.3	4.9	6.3	6.3	7.2	7.3	6.5		7.5	5.6		7.0	6.3		6.8	7.7		7.1	7.5		7.1	5.1	7.6	5.8		7.1	6.2		7.2	6.4		6.9	5.9		7.2	6.0	
Moisture content	34.4	42.8	23.5	42.5	63.0	47.5	48.9	37.0	25.6	38.0	53.7	20.7	50.2	61.5	18.9	47.8	51.6	22.8	32.3	45.5	18.8	29.3	46.0	20.0	62.5	31.4	46.1	58.8	26.8	50.6	56.2	20.8	37.7	49.9	18.6	49.5	58.1	28.4	44.4	54.4
Litter Temperature	-																																							
Complete description	Mixture Profile	Wet_Surface	Dry_friable_Surface	Mixture_Profile	Wet_Surface	Mixture_Profile	Mixture_Profile	Damp_Base	Dry_friable_Surface	Mixture_Profile	Wet_Surface	Dry_friable_Surface	Wet_Surface	Damp_Base	Mixture_Profile	Wet_Surface	Dry_friable_Surface	Mixture_Profile	Wet_Surface																					
Sample Description	Profile	Surface	Surface	Profile	Surface	Profile	Profile	Base	Surface	Profile	Surface	Surface	Surface	Base	Profile	Surface	Surface	Profile	Surface																					
Litter type	Mixture	Wet	Dry_friable	Mixture	Wet	Mixture	Mixture	Damp	Dry_friable	Mixture	Wet	Dry_friable	Wet	Damp	Mixture	Wet	Dry_friable	Mixture	Wet																					
Original description	Pine - Bulk	Pine - Wet	Pine - Dry	Hardwood bulk	Hardwood Cake (Row B)	Pine Bulk	LGF Bulk	Under Cake (Row B_)	Dry - near Feeder	Row A Bulk	Row A Wet	Row A Dry	Row B Bulk	Row B Wet	Row B Dry	Row C Bulk	Row C Wet	Row C Dry	Row D Bulk	Row D Wet	Row D Dry	Row E Bulk	Row E Wet	Row E Dry	Cake Row B	Under Cake (Row B_)	LGF Bulk	LGF Wet	LGF Dry	Pine Bulk	Pine Wet	Pine Dry	Row A Bulk	Row A Wet	Row A Dry	Row B Bulk	Row B Wet	Row B Dry	Row C Bulk	Row C Wet
Sample number	068	690	070	071	072	073	074	075	076	077	078	079	080	081	082	083	084	085	086	087	088	089	060	091	092	093	094	095	960	2007	860	660	100	101	102	103	104	105	106	107
Grow- out	в	в	В	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	в	В
Day	29	29	29	37	37	37	37	37	37	43	43	43	43	43	43	43	43	43	43	43	43	43	43	43	43	43	43	43	43	43	43	43	53	53	53	53	53	53	53	53
Date	23/07/2013	23/07/2013	23/07/2013	31/07/2013	31/07/2013	31/07/2013	31/07/2013	31/07/2013	31/07/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	6/08/2013	16/08/2013	16/08/2013	16/08/2013	16/08/2013	16/08/2013	16/08/2013	16/08/2013	16/08/2013

כ	, YB	out	number	Original description	Litter type	Description	Complete description	Temperature	content	Hđ	activity
55	3	в	108	Row C Dry	Dry_friable	Surface	Dry_friable_Surface	•	22.7	6.1	
5	3	в	109	Row D Bulk	Mixture	Profile	Mixture_Profile		27.7	6.1	
5	3	в	110	Row D Wet	Wet	Surface	Wet_Surface		44.0		
5	ю	в	111	Row D Dry	Dry_friable	Surface	Dry_friable_Surface		18.0	7.0	
Ъ.	3	в	112	Row E Bulk	Mixture	Profile	Mixture_Profile		27.9	8.3	
Ъ.	3	в	113	Row E Wet	Damp	Surface	Damp_Surface		32.0		
5	e	в	114	Row E Dry	Dry_friable	Surface	Dry_friable_Surface		34.6	7.3	
5	e	в	115	Cake Row B	Wet	Surface	Wet_Surface		44.0	4.9	
5:	e	в	116	Under Cake (Row B_)	Wet	Base	Wet_Base		42.8	7.0	
5:	e	в	117	LGF Bulk	Mixture	Profile	Mixture_Profile		47.3	6.1	
5:	3	в	118	LGF Wet	Wet	Surface	Wet_Surface		52.5		
5:	e	в	119	LGF Dry	Dry_friable	Surface	Dry_friable_Surface		17.7	6.8	
5:	3	В	120	Pine Bulk	Mixture	Profile	Mixture_Profile		41.7	6.0	
5:	e	в	121	Pine Wet	Wet	Surface	Wet_Surface		50.1		
5:	ŝ	в	122	Pine Dry	Dry_friable	Surface	Dry_friable_Surface		19.6	6.9	
3 2(	0	υ	123	Wet Cake	Wet	Surface	Wet_Surface		44.2	7.8	
3 2(	0	υ	124	Under Cake	Damp	Base	Damp_Base		23.3	8.0	
3 2(	0	υ	125	Friable Litter	Dry_friable	Surface	Dry_friable_Surface		22.0	6.9	
3 2(	0	υ	126	Bulk	Mixture	Profile	Mixture_Profile		31.9	7.6	
M	7	υ	128	Wet Cake	Wet	Surface	Wet_Surface		51.6	5.3	
Μ	7	υ	129	Dry Cake	Dry_cake	Surface	Dry_cake_Surface		34.1	8.1	
Μ	7	υ	130	Under Cake	Wet	Base	Wet_Base		41.9	7.5	
 	7	υ	131	Friable Litter	Dry_friable	Profile	Dry_friable_Profile		20.3	7.2	
1	7	D	201	Transect A Composite sample	Mixture	Profile	Mixture_Profile		24.8		
1.	7	۵	202	Transect A Wet sample	Damp	Surface	Damp_Surface		38.9		
1	7	D	203	Transect A Dry sample	Dry_friable	Surface	Dry_friable_Surface		16.4		
1.	7	۵	204	Transect B Composite sample	Mixture	Profile	Mixture_Profile		28.9		
1	7	۵	205	Transect B Wet sample	Damp	Surface	Damp_Surface		29.6		
1	7	۵	206	Transect B Dry sample	Dry_friable	Surface	Dry_friable_Surface		21.9		
1	7	D	207	Transect C Composite sample	Mixture	Profile	Mixture_Profile		26.2		
1.	7	۵	208	Transect C Wet sample	Damp	Surface	Damp_Surface		33.2		
1.	7	۵	209	Transect C Dry sample	Dry_friable	Surface	Dry_friable_Surface		23.2		
1.	7	۵	210	Bulk sample composite transects A - C	Mixture	Profile	Mixture_Profile		24.8	8.8	
15	8	۵	211	Dry litter - Flux chamber used to measure gases	Dry_friable	Surface	Dry_friable_Surface		17.9	7.8	
15	80	۵	212	damp litter - (sample cultivated 2 days prior)	Dry_friable	Surface	Dry_friable_Surface		20.2	8.1	
15	∞	D	213	damp litter with crust - (sample cultivated 2 days prior)	Dry_cake	Surface	Dry_cake_Surface		28.9	8.7	
1 24	4	۵	214	Transect A Composite sample	Mixture	Profile	Mixture_Profile		26.1		

ay Grow- Sample out number O	out number 0	oumber 0	Ō	riginal description	Litter type	sample Description	<b>Complete description</b>	Litter Temperature	ivioisture content	Ηd	water activity
24 D 215 Transect A Wet sample	D 215 Transect A Wet sample	215 Transect A Wet sample	Transect A Wet sample		Wet	Surface	Wet_Surface		46.3		
24 D 216 Transect A Dry sample	D 216 Transect A Dry sample	216 Transect A Dry sample	Transect A Dry sample		Dry_friable	Surface	Dry_friable_Surface		21.3		
24 D 217 Transect B Composite sample	D 217 Transect B Composite sample	217 Transect B Composite sample	Transect B Composite sample		Mixture	Profile	Mixture_Profile		23.5		
24 D 218 Transect B Wet sample	D 218 Transect B Wet sample	218 Transect B Wet sample	Transect B Wet sample		Damp	Surface	Damp_Surface		31.5		
24 D 219 Transect B Dry sample	D 219 Transect B Dry sample	219 Transect B Dry sample	Transect B Dry sample		Dry_friable	Surface	Dry_friable_Surface		18.3		
24 D 220 Transect C Composite sample	D 220 Transect C Composite sample	220 Transect C Composite sample	Transect C Composite sample		Mixture	Profile	Mixture_Profile		24.8		
24 D 221 Transect C Wet sample	D 221 Transect C Wet sample	221 Transect C Wet sample	Transect C Wet sample		Wet	Surface	Wet_Surface		46.8		
24 D 222 Transect C Dry sample	D 222 Transect C Dry sample	222 Transect C Dry sample	Transect C Dry sample		Dry_friable	Surface	Dry_friable_Surface		16.2		
24 D 223 Bulk sample composite transects A - C	D 223 Bulk sample composite transects A - C	223 Bulk sample composite transects A - C	Bulk sample composite transects A - C		Mixture	Profile	Mixture_Profile		26.2	8.5	
31 D 224 Transect A Composite sample	D 224 Transect A Composite sample	224 Transect A Composite sample	Transect A Composite sample		Mixture	Profile	Mixture_Profile		32.1		
31 D 225 Transect A Wet sample	D 225 Transect A Wet sample	225 Transect A Wet sample	Transect A Wet sample		Damp	Surface	Damp_Surface		31.2		
31 D 226 Transect A Dry sample	D 226 Transect A Dry sample	226 Transect A Dry sample	Transect A Dry sample		Dry_friable	Surface	Dry_friable_Surface		26.3		
31 D 227 Transect B Composite sample	D 227 Transect B Composite sample	227 Transect B Composite sample	Transect B Composite sample		Mixture	Profile	Mixture_Profile		34.1		
31 D 228 Transect B Wet sample	D 228 Transect B Wet sample	228 Transect B Wet sample	Transect B Wet sample		Damp	Surface	Damp_Surface		29.8		
31 D 229 Transect B Dry sample [	D 229 Transect B Dry sample I	229 Transect B Dry sample	Transect B Dry sample	_	Dry_friable	Surface	Dry_friable_Surface		26.7		
31 D 230 Transect C Composite sample	D 230 Transect C Composite sample	230 Transect C Composite sample	Transect C Composite sample		Mixture	Profile	Mixture_Profile		32.4		
31 D 231 Transect C Wet sample	D 231 Transect C Wet sample	231 Transect C Wet sample	Transect C Wet sample		Damp	Surface	Damp_Surface		28.2		
31 D 232 Transect C Dry sample Dr	D 232 Transect C Dry sample Dr	232 Transect C Dry sample Dr	Transect C Dry sample Dr	Ď	y_friable	Surface	Dry_friable_Surface		21.0		
31 D 233 Bulk sample composite transects A - C N	D 233 Bulk sample composite transects A - C N	233 Bulk sample composite transects A - C N	Bulk sample composite transects A - C N	2	1 ixture	Profile	Mixture_Profile		26.3	8.5	
32 D 234 Dry litter - Flux chamber used to measure Dr gases	D 234 Dry litter - Flux chamber used to measure Dr gases	234 Dry litter - Flux chamber used to measure Dr gases	Dry litter - Flux chamber used to measure Brease	D	y_friable	Surface	Dry_friable_Surface		16.7	8.0	
32 D 235 damp litter - (sample cultivated 2 days Dry	D 235 damp litter - (sample cultivated 2 days Dry prior)	235 damp litter - (sample cultivated 2 days Dry	damp litter - (sample cultivated 2 days Dry prior)	D	/_friable	Surface	Dry_friable_Surface		23.1	8.5	
32 D 236 damp litter with crust - (sample cultivated 2 days prior)	D 236 damp litter with crust - (sample cultivated 2 days prior)	236 damp litter with crust - (sample cultivated 2 days prior)	damp litter with crust - (sample cultivated 2 days prior)		Damp	Surface	Damp_Surface		37.3	8.5	
34 D 247 Door cake top	D 247 Door cake top	247 Door cake top	Door cake top		Wet	Surface	Wet_Surface		48.5	5.2	
34 D 248 door cake middle	D 248 door cake middle	248 door cake middle	door cake middle		Wet	Middle	Wet_Middle		51.9	5.6	
34 D 249 door cake bottom	D 249 door cake bottom	249 door cake bottom	door cake bottom		Wet	Base	Wet_Base		50.6	6.9	
34 D 250 door cake undercake	D 250 door cake undercake	250 door cake undercake	door cake undercake		Wet	Base	Wet_Base		42.2	7.6	
34 D 251 door cake (Full cake profile no undercake)	D 251 door cake (Full cake profile no undercake)	251 door cake (Full cake profile no undercake)	door cake (Full cake profile no undercake)		Wet	profile	Wet_profile		53.2	7.5	
34 D 252 Middle shed cake - top	D 252 Middle shed cake - top	252 Middle shed cake - top	Middle shed cake - top		Wet	Surface	Wet_Surface		46.1	6.8	
34 D 253 Middle shed cake - middle	D 253 Middle shed cake - middle	253 Middle shed cake - middle	Middle shed cake - middle		Wet	Middle	Wet_Middle		47.5	7.5	
34 D 254 Middle shed cake - bottom	D 254 Middle shed cake - bottom	254 Middle shed cake - bottom	Middle shed cake - bottom		Wet	Middle	Wet_Middle		44.5	8.7	
34 D 255 Middle shed cake - undercake	D 255 Middle shed cake - undercake	255 Middle shed cake - undercake	Middle shed cake - undercake	_	Jamp	Base	Damp_Base		24.3	8.8	
34 D 256 Dry cake - top D	D 256 Dry cake - top D	256 Dry cake - top D	Dry cake - top D		ry_cake	Surface	Dry_cake_Surface		36.4	7.3	
34 D 257 Dry cake - bottom [	D 257 Dry cake - bottom E	257 Dry cake - bottom	Dry cake - bottom		Dry_cake	Middle	Dry_cake_Middle		31.9	8.7	
34 D 258 Dry cake - undercake	D 258 Dry cake - undercake	258 Dry cake - undercake	Dry cake - undercake		Dry_cake	Base	Dry_cake_Base		25.0	8.9	
34 D 259 Friable litter near fans - top D	D 259 Friable litter near fans - top D	259 Friable litter near fans - top D	Friable litter near fans - top		ry_friable	Surface	Dry_friable_Surface		25.1	7.4	
34 D 260 Friable litter near fans - bottom	D 260 Friable litter near fans - bottom	260 Friable litter near fans - bottom	Friable litter near fans - bottom		Dry_friable	Base	Dry_friable_Base		25.1	8.3	

Water activity																														
Hq	7.4	8.1										8.4											5.5	6.8	7.0	7.7	8.0	5.9	7.7	8.2
Moisture content	18.8	14.4	35.1	52.0	18.8	32.0	29.5	19.4	25.3	37.4	27.9	30.1	28.3	42.9	17.0	31.4	46.5	17.3	26.4	49.7	19.5	26.4	51.0	55.0	36.0	26.0	26.7	49.5	22.5	20.1
Litter Temperature																														
Complete description	Dry_friable_Surface	Dry_friable_Surface	Mixture_Profile	Wet_Surface	Dry_friable_Surface	Mixture_Profile	Damp_Surface	Dry_friable_Surface	Mixture_Profile	Damp_Surface	Dry_friable_Surface	Mixture_Profile	Mixture_Profile	Wet_Surface	Dry_friable_Surface	Mixture_Profile	Wet_Surface	Dry_friable_Surface	Mixture_Profile	Wet_Surface	Dry_friable_Surface	Mixture_Profile	Wet_Surface	Wet_Middle	Damp_Base	Dry_friable_Surface	Dry_cake_Surface	Wet_Surface	Dry_friable_Surface	Dry_friable_Base
Sample Description	Surface	Surface	Profile	Surface	Surface	Profile	Surface	Surface	Profile	Surface	Surface	Profile	Profile	Surface	Surface	Profile	Surface	Surface	Profile	Surface	Surface	Profile	Surface	Middle	Base	Surface	Surface	Surface	Surface	Base
Litter type	Dry_friable	Dry_friable	Mixture	Wet	Dry_friable	Mixture	Damp	Dry_friable	Mixture	Damp	Dry_friable	Mixture	Mixture	Wet	Dry_friable	Mixture	Wet	Dry_friable	Mixture	Wet	Dry_friable	Mixture	Wet	Wet	Damp	Dry_friable	Dry_cake	Wet	Dry_friable	Dry_friable
Original description	Friable litter under drinker near mid shed migration fence	Friable litter under drinker near mid shed migration fence	Transect A Composite sample	Transect A Wet sample	Transect A Dry sample	Transect B Composite sample	Transect B Wet sample	Transect B Dry sample	Transect C Composite sample	Transect C Wet sample	Transect C Dry sample	Bulk sample composite transects A - C	Transect A Composite sample	Transect A Wet sample	Transect A Dry sample	Transect B Composite sample	Transect B Wet sample	Transect B Dry sample	Transect C Composite sample	Transect C Wet sample	Transect C Dry sample	Bulk sample composite transects A - C	Cake - top of cake - collected 5/5/2014 in big tray for pH and O2	Cake - bottom of cake - collected 5/5/2014 in big tray for pH and O2	Cake - under cake - collected 5/5/2014 in big tray for pH and O2	Dry litter - Flux chamber used to measure gases	Dry cake/crust - flux chamber used to measure gases	Wet cake - flux chamber used to measure gases	Dry litter - surface - Flux chamber used to measure gases	Dry litter - bottom - Flux chamber used to measure gases
Sample number	261	262	237	238	239	240	241	242	243	244	245	246	263	264	265	266	267	268	269	270	271	272	284	285	286	274	275	276	277	278
Grow- out	D	۵	۵	۵	۵	۵	۵	D	D	۵	۵	۵	۵	۵	۵	۵	۵	۵	۵	۵	۵	۵	Δ	D	۵	۵	D	D	D	۵
Day	34	34	38	38	38	38	38	38	38	38	38	38	45	45	45	45	45	45	45	45	45	45	45	45	45	46	46	46	46	46
Date	24/04/2014	24/04/2014	28/04/2014	28/04/2014	28/04/2014	28/04/2014	28/04/2014	28/04/2014	28/04/2014	28/04/2014	28/04/2014	28/04/2014	5/05/2014	5/05/2014	5/05/2014	5/05/2014	5/05/2014	5/05/2014	5/05/2014	5/05/2014	5/05/2014	5/05/2014	5/05/2014	5/05/2014	5/05/2014	6/05/2014	6/05/2014	6/05/2014	6/05/2014	6/05/2014

Date	Dау	Grow- out	Sample number	Original description	Litter type	Sample Description	Complete description	Litter Temperature	Moisture content	Hq	Water activity
6/05/2014	46	D	279	Dry cake/crust - flux chamber used to measure gases	Dry_cake	Surface	Dry_cake_Surface		40.0	7.9	
6/05/2014	46	۵	280	Dry cake/crust - under cake - flux chamber used to measure gases	Dry_cake	Middle	Dry_cake_Middle		22.3	8.4	
6/05/2014	46	۵	281	Wet cake - top of cake - flux chamber used to measure gases	Wet	Surface	Wet_Surface		50.9	5.4	
6/05/2014	46	۵	282	Wet cake - bottom of cake - flux chamber used to measure gases	Wet	Middle	Wet_Middle		55.1	6.1	
6/05/2014	46	۵	283	Wet cake - under cake - flux chamber used to measure gases	Damp	Base	Damp_Base		36.1	6.8	
12/05/2014	52	D	287	Transect B Composite sample	Mixture	Profile	Mixture_Profile		27.5		
12/05/2014	52	۵	288	Transect B Wet sample	Wet	Surface	Wet_Surface		41.0		
12/05/2014	52	۵	289	Transect B Dry sample	Dry_friable	Surface	Dry_friable_Surface		15.1		
12/05/2014	52	۵	290	Transect C Composite sample	Mixture	Profile	Mixture_Profile		27.5		
12/05/2014	52	۵	291	Transect C Wet sample	Damp	Surface	Damp_Surface		37.1		
12/05/2014	52	۵	292	Transect C Dry sample	Dry_friable	Surface	Dry_friable_Surface		15.1		
12/05/2014	52	۵	293	Bulk sample composite transects A - C	Mixture	Profile	Mixture_Profile		36.1	8.6	
12/05/2014	52	۵	294	Transect A Composite sample	Mixture	Profile	Mixture_Profile		33.2		
12/05/2014	52	۵	295	Transect A Wet sample	Wet	Surface	Wet_Surface		50.9		
12/05/2014	52	۵	296	Transect A Dry sample	Dry_friable	Surface	Dry_friable_Surface		14.1		
14/05/2015	13	PEN	PEN 1	Dry friable - bedding material	Dry_friable	Base	Dry_friable_Base		6.5	5.5	0.351
14/05/2015	13	PEN	PEN 2	Dry friable - mostly excreta	Dry_friable_excreta	Surface	Dry_friable_excreta_Surface		36.6	6.0	0.879
14/05/2015	13	PEN	PEN 3	Wet litter - bedding material	Damp	Base	Damp_Base		17.4	5.7	0.982
14/05/2015	13	PEN	PEN 4	Wet Litter - Excreta	Wet	Surface	Wet_Surface		42.3	6.5	0.969
14/05/2015	13	PEN	PEN 5	Dry Litter - Surface condition	Dry_friable	Surface	Dry_friable_Surface		7.0	5.9	0.491
14/05/2015	13	PEN	PEN 6	Wet Litter - Surface condition	Damp	Surface	Damp_Surface		18.3	6.1	0.878
14/05/2015	13	PEN	PEN 7		Excreta	Accumulation	Excreta_Accumulation		63.7	5.9	0.987
14/05/2015	13	PEN	PEN 8		Excreta	Accumulation	Excreta_Accumulation		72.8	6.8	0.979
15/05/2015	14	PEN	PEN 9	Dry Litter - Bedding	Dry_friable	Base	Dry_friable_Base		5.4	6.0	
15/05/2015	14	PEN	PEN 10	Dry Litter - Excreta	Dry_friable_excreta	Surface	Dry_friable_excreta_Surface		25.8	6.0	
15/05/2015	14	PEN	PEN 11	Dry Litter - Surface condition	Dry_friable	Surface	Dry_friable_Surface		7.6	6.2	
15/05/2015	14	PEN	PEN 12	Wet Litter - Bedding	Damp	Base	Damp_Base		36.1	6.0	
15/05/2015	14	PEN	PEN 13	Wet Litter - Excreta	Wet	Surface	Wet_Surface		54.6	6.0	
15/05/2015	14	PEN	PEN 14	Wet Litter - Surface condition	Wet	Surface	Wet_Surface		43.5	6.4	
15/05/2015	14	PEN	<b>PEN 15</b>	Dry Litter - Bedding	Dry_friable	Base	Dry_friable_Base	25	8.8	5.8	
15/05/2015	14	PEN	PEN 16	Dry Litter - Excreta	Dry_friable_excreta	Surface	Dry_friable_excreta_Surface	25	25.3	6.1	
15/05/2015	14	PEN	PEN 17	Dry Litter - Surface condition	Dry_friable	Surface	Dry_friable_Surface	25	22.4	6.0	
15/05/2015	14	PEN	PEN 18	Wet Litter - Bedding	damp	Base	damp_Base	23	22.6	6.3	
15/05/2015	14	PEN	PEN 19	Wet Litter - Excreta	Wet	Surface	Wet_Surface	23	67.7	5.7	
15/05/2015	14	PEN	PEN 20	Wet Litter - Surface condition	Damp	Surface	Damp_Surface	23	31.3	5.9	

Water	(			0.997								0.976							0.987							0.990
Hd	6.3	6.3	7.1	5.3	5.7	6.7	7.4	5.1	5.3	7.9	8.8	6.0	7.8	8.5	5.1	6.3	7.6	8.8	5.3	6.6	6.7	5.5	7.8	8.8	8.7	5.4
Moisture	19.3	36.7	20.5	72.7	80.0	21.7	20.7	64.6	69.4	69.3	33.6	79.0	28.1	37.3	67.5	6.99	58.2	23.5	76.8	16.7	18.1	59.3	62.1	50.9	65.2	76.2
Litter Temnerature	25.5	25.5	25.5	25.5		24.3	24.3	24.2	24.9	25.6	25.6		26.2	26.2	24.2	24.9	25.6	25.6		25.3	25.3	25.55	25.55	25.55	25.55	
<b>Complete description</b>	Dry_friable_Surface	Dry_friable_excreta_Surface	Dry_friable_Base	Excreta_Fresh_normal	Excreta_Fresh_normal	Dry_friable_Surface	Dry_friable_Base	Wet_Surface	Wet_Middle	Wet_Base	Damp_Base	Excreta_Fresh_normal	Dry_friable_Surface	Dry_friable_Base	Wet_Surface	Wet_Middle	Wet_Base	Damp_Base	Excreta_Fresh_normal	Dry_friable_Surface	Dry_friable_Base	Wet_Surface	Wet_Middle	Wet_Base	Wet_Base	Excreta_Fresh_normal
Sample Descrintion	Surface	Surface	Base	Fresh_normal	Fresh_normal	Surface	Base	Surface	Middle	Base	Base	Fresh_normal	Surface	Base	Surface	Middle	Base	Base	Fresh_normal	Surface	Base	Surface	Middle	Base	Base	Fresh_normal
Litter type	Dry_friable	Dry_friable_excreta	Dry_friable	Excreta	Excreta	Dry_friable	Dry_friable	Wet	Wet	Wet	Damp	Excreta	Dry_friable	Dry_friable	Wet	Wet	Wet	Damp	Excreta	Dry_friable	Dry_friable	Wet	Wet	Wet	Wet	Excreta
<b>Original description</b>	Dry Litter - Surface condition	Dry Litter - Excreta	Dry Litter - Bedding	Fresh Excreta	Fresh Excreta	Dry Litter - Surface condition	Dry Litter - Bedding	Wet Litter - Surface condition	Wet litter - Bottom of cake	Wet Litter - Bedding	Wet Litter - Bedding at base	Fresh Excreta	Dry Litter - Surface condition	Dry Litter - Bedding	Wet Litter - Surface condition	Wet litter - Bottom of cake	Wet Litter - Bedding	Wet Litter - Bedding at base	Fresh Excreta	Dry Litter - Surface condition	Dry Litter - Bedding	Wet Litter - Surface condition	Wet litter - Bottom of cake	Wet Litter - Bedding	Wet Litter - Bedding at base	Fresh Excreta
Sample	PEN 61	PEN 62	PEN 63	PEN 64	PEN 66	PEN 67	PEN 68	PEN 70	PEN 71	PEN 72	PEN 73	PEN 74	PEN 75	PEN 76	PEN 77	PEN 78	PEN 79	PEN 80	PEN 81	PEN 82	PEN 83	PEN 84	PEN 85	PEN 86	PEN 87	PEN 89
Grow-	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN	PEN
Day	27	27	27	27	32	33	33	33	33	33	33	33	33	33	33	33	33	33	33	34	34	34	34	34	34	34
Date	28/05/2015	28/05/2015	28/05/2015	28/05/2015	2/06/2015	3/06/2015	3/06/2015	3/06/2015	3/06/2015	3/06/2015	3/06/2015	3/06/2015	3/06/2015	3/06/2015	3/06/2015	3/06/2015	3/06/2015	3/06/2015	3/06/2015	4/06/2015	4/06/2015	4/06/2015	4/06/2015	4/06/2015	4/06/2015	4/06/2015



Data from previous study (Dunlop et. al., 2011)



# Appendix F. Air temperature and relative humidity logging records

Air temperature and relative humidity above the litter in a commercial meat chicken shed (grow-out B, described in Section 6.2.1) and during a laboratory pen trial (described in Section 6.2.2)


Figure A. 17. Air temperature and relative humidity above the litter surface in a commercial meat chicken shed (grow-out B, described in Section 6.2.1)



Figure A. 18. Air temperature and relative humidity above the litter surface in a laboratory trial pen (described in Section 6.2.2)

## Appendix G. Linear regression parameters for litter moisture content and pH

Litter samples were collected from commercial farm (grow-outs A-D) or during a laboratory pen trial (PEN)

Including: Table A. 4. Moisture content linear regression parameters Table A. 5. pH linear regression parameters

	Mixed full	depth profile	Litter	surface	Base of	the litter
	Slope	Intercept	Slope	Intercept	Slope	Intercept
Litter from commercial rearing sheds						
Mixed litter	0.169	29.35	_	_	_	_
Dry friable	0.119	20.84	-0.04	23.18	-0.408	38.44
Damp	_	_	0.053	31.39	0.129	26.13
Wet	0.077	47.49	-0.076	54.77	-0.12	49.33
Dry cake	_	_	0.142	28.09	_	_
Excreta (fresh)	_	_	_	_	_	_
Excreta (in dry litter)	_	_	_	_	_	_
Litter from PEN trial						
Mixed litter	_	_	_	_	_	_
Dry friable	_	_	0.399	9.44	0.925	-5.28
Damp	_	_	13.003	-150.61	0.205	24.55
Wet	_	_	0.41	49.88	-0.12	104.23
Dry cake	_	-	—	—	—	—
Excreta (fresh)	_	_	-0.079	79.86	—	—
Excreta (in dry litter)	_	_	0.354	24.28	_	_

## Table A. 4. Moisture content linear regression parameters

## Table A. 5. pH linear regression parameters

	Mixed full o	depth profile			Litter	surface
	Slope	Intercept	Slope	Intercept	Slope	Intercept
Litter from commercial rearing sheds						
Mixed litter	-0.0172	7.462	_	_	_	-
Dry friable	0.0515	5.614	0.0054	7.066	0.0765	5.165
Damp	_	_	0.0169	7.138	0.0013	7.451
Wet	-0.0048	6.851	-0.0337	7.174	0.0067	7.101
Dry cake	_	—	-0.0229	8.828	_	_
Excreta (fresh)	_	—	_	_	_	_
Excreta (in dry litter)	_	_	_	_	_	_
Litter from pen trial						
Mixed litter	_	_	_	_	_	_
Dry friable	_	_	0.0517	5.238	0.0927	4.38
Damp	_	_	-0.2001	8.738	0.1292	4.838
Wet	_	_	-0.031	7.07	0.0329	7.181
Dry cake	_	_	_	_	_	_
Excreta (fresh)	-	—	-0.0618	7.56	—	-
Excreta (in dry litter)	_	—	0.0422	5.45	_	_

## Appendix H. Dataset of odorant emissions and litter conditions from a meat chicken shed

Collected from commercial meat chicken farm. For Growouts A and B, litter was transported to a laboratory for odorant emission rate measurement while for grow-out D, odorant emission rates were measured from undisturbed litter in the shed.

## Including:

Table A. b. VOUS quantilied using TD-GU-IM	Table A. 6.	VOCs quantified	l using TD-GC-MS
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- Table A. 7. VSCs detected using TD-GC-SCD
- Table A. 8. VOCs identified using TD-GC-MS
- Table A. 9. Dataset of odorant emission rates (ng/m²/s;measured with TD-GC-MS) and litter conditions
- Table A. 10. Dataset of reduced sulfur compound emission rates (ng/m<sup>2</sup>/s; measured with TD-GC-SCD)

Molecular	Formula	Compound name	Other name	CAS	Detection
weight	00.110.0	Eth an al		number	trequency
46.0684	C2 H6 O	Ethanol		64-17-5	4%
58.0791	C3 H6 O	Acetone		67-64-1	53%
59.1103	C3 H9 N	Irimethylamine	IMA	75-50-3	9%
60.0520	C2 H4 O2	Acetic acid		64-19-7	18%
60.0950	C3 H8 O	1-propanol	Propyl alcohol	71-23-8	47%
62.1340	C2 H6 S	Dimethyl Sulfide	DMS	75-18-3	49%
72.1057	C4 H8 O	Tetrahydro-furan		109-99-9	2%
72.1057	C4 H8 O	2-Butanone	Methyl ethyl ketone (MEK)	78-93-3	58%
72.1488	C5 H12	Pentane	<i>n</i> -pentane	109-66-0	13%
74.0785	C3 H6 O2	Acetic acid, methyl ester	Methylacetate	79-20-9	4%
74.0785	C3 H6 O2	Propanoic acid	Methyl acetic acid	79-09-4	18%
74.1216	C4 H10 O	2-Butanol	sec-butyl-alcohol	78-92-2	71%
74.1216	C4 H10 O	1-Butanol	<i>n-</i> butanol	71-36-3	47%
76.1410	C S2	Carbon disulfide	Methyl disulfide	75-15-0	4%
78.1118	C6 H6	Benzene		71-43-2	11%
86.0892	C4 H6 O2	2,3-Butanedione	diacetyl	431-03-8	31%
86.1323	C5 H10 O	3-methyl-butanal	Butanal, 3-methyl-	590-86-3	9%
86.1323	C5 H10 O	2-methyl-3-buten-2-ol	Dimethylvinylcarbinol	115-18-4	2%
86.1323	C5 H10 O	2-Pentanone	Methyl propyl ketone	107-87-9	20%
86.1754	C6 H14	2-methyl-pentane	isohexane	107-83-5	11%
86.1754	C6 H14	3-methyl-pentane		96-14-0	11%
86.1754	C6 H14	Hexane	<i>n</i> -hexane	110-54-3	16%
88.1051	C4 H8 O2	2-methyl-propanoic acid	Isobutyric acid	79-31-2	2%
88.1051	C4 H8 O2	Ethyl acetate	Acetic acid, ethyl ester	141-78-6	24%
88.1051	C4 H8 O2	2-Butanone, 3-hydroxy-	Acetoin	513-86-0	7%
88.1051	C4 H8 O2	Butanoic acid	Butyric Acid	107-92-6	38%
88.1482	C5 H12 O	3-methyl-1-butanol	1-Butanol, 3-methyl-	123-51-3	7%
92.1384	C7 H8	Toluene		108-88-3	40%
94.1990	C2 H6 S2	Dimethyl Disulfide		624-92-0	87%
96.1513	C2 H6 F2 Si	Difluorodimethyl-silane		353-66-2	0%
102.1317	C5 H10 O2	<i>n</i> -Propyl acetate	Acetic acid, propyl ester	109-60-4	11%
102.1317	C5 H10 O2	Butanoic acid, methyl ester	Methyl butyrate	623-42-7	18%
102.1317	C5 H10 O2	3-hydroxy-3-methyl-2-butanone	3-Methylacetoin	115-22-0	4%
102.1317	C5 H10 O2	3-methyl butanoic acid	Isovaleric Acid	503-74-2	4%
102.1317	C5 H10 O2	2-methyl butanoic acid	Methylethylacetic acid	116-53-0	2%
106.1219	C7 H6 O	Benzaldehvde	, ,	100-52-7	4%
116.1583	C6 H12 O2	Butanoic acid, ethyl ester	Ethvl butvrate	105-54-4	29%
116.1583	C6 H12 O2	Acetic acid, 1-methylpropyl ester	sec-Butyl-acetate	105-46-4	11%
116.1583	C6 H12 O2	Propanoic acid, propyl ester	n-Propyl propionate	106-36-5	11%
120.1485	C8 H8 O	Acetophenone	Methyl phenyl ketone	98-86-2	2%
122,1213	C7 H6 O2	Benzoic Acid		65-85-0	4%
126,2640	C2 H6 S3	Dimethyl Trisulfide	DMTS	3658-80-8	24%
130,1849	C7 H14 O2	Butanoic acid, propyl ester	<i>n</i> -Propyl butyrate	105-66-8	22%
130 2279	C8 H18 O	1-Hexanol 2-ethyl-	2-Ethyl-1-hexanol	104-76-7	4%
134 1751	C9 H10 O	Benzaldehyde 3 5-dimethyl-		5779-95-3	2%
136 2340	C10 H16	a-Pinene		80-56-8	31%
136 2340	C10 H16	ß-pipepe		127-91-3	9%
136 2340	C10 H16	Limonene		138-86-3	7%
142 2386	C9 H18 O	Nonanal		124-19-6	7%
142 2817	C10 H22	Nonana Necene		124-19-0	1%
111 0111	C8 H16 O2	Butanoic acid butul actor	n-Butyl-butyroto	100.21 7	
144.2114 144.2114	C8 H16 O2	Butanoic acid 1-methylpropyl actor	sec-Butyl-butyrate	810-07-6	1170 22%
170 22/0	C12 L26	2.2.4.6.6 poptamethyl bostone	366-Dulyi-Dulyiale	12/75 00 0	22 /0 00/
208 2552		2,2,4,0,0-peritametryi-hepiane	Chalcona	01 11 7	3% 20/
200.2002			Chaicone	54-41-1	∠70 10/
220.4412	C10 H34	nexadecane		544-76-3	4%

## Table A. 6. VOCs quantified using TD-GC-MS

Molecular weight	Formula	Compound name	Other name	CAS number	Detection frequency
34.0809	H2 S	Hydrogen sulfide	H2S	7783-06-4	20%
48.1076	C H4 S	Methyl mercaptan	MM, Methanethiol	74-93-1	93%
60.0750	COS	Carbonyl sulfide	COS	463-58-1	89%
62.1340	C2 H6 S	Ethyl mercaptan	Ethanethiol	75-08-1	27%
62.1340	C2 H6 S	Dimethyl sulfide	DMS	75-18-3	96%
76.1410	C S2	Carbon disulfide		75-15-0	84%
90.1870	C4 H10 S	Diethyl sulfide		352-93-2	11%
94.1990	C2 H6 S2	Dimethyl disulfide		624-92-0	96%
122.2520	C4 H10 S2	Diethyl disulfide		110-81-6	22%
126.2640	C2 H6 S3	Dimethyl Trisulfide	DMTS	3658-80-8	78%

Table A. 7. VSCs detected using TD-GC-SCD

 Table A. 8. VOCs identified using TD-GC-MS but with inadequate match with the MS library for quantification

Molecular weight	Formula	Compound name	Other name	CAS number	Detection frequency
72.1057	C4 H8 O	Butanal	Butyraldehyde	123-72-8	0%
72.1488	C5 H12	2-methyl-butane	iso-Pentane	78-78-4	0%
84.1595	C6 H12	Cyclohexane		110-82-7	0%
100.2019	C7 H16	3-methyl-hexane		589-34-4	0%
102.1317	C5 H10 O2	Pentanoic acid	Valeric acid	109-52-4	0%
106.1650	C8 H10	Ethylbenzene		100-41-4	0%
106.1650	C8 H10	p-Xylene		106-42-3	0%
120.1916	C9 H12	1-ethyl-3-methyl-benzene	m-ethyltoluene	620-14-4	0%
120.1916	C9 H12	1,3,5-trimethyl-benzene	Mesitylene	108-67-8	0%
134.2182	C10 H14	1-methyl-4-(1-methylethyl)-benzene	p-Cymene	99-87-6	0%
136.2340	C10 H16	Camphene		79-92-5	0%
137.3680	C CI3 F	Trichloromonofluoromethane		75-69-4	0%

ND=no data - sample not analysed or lost, N	IA=not analysed; E	Manks values III	Litter	Dav of			loisture	Idtori						imethvl	etrahvdro-	2-		Acetic acid.
Sample Index	Batch Sample	Description	collection Date <u>c</u>	the jrow-out	Week	Bedding material	content pH (%)	Odour (ou/m²/s)	Ethanol	Acetone Tri	methylamine Acetic	acid 1-pr	opanol	sulfide	furan	butanone	Pentane	methyl ester
Batch A - Day 0 - Fresh_bedding	A Fresh	n_bedding	22/05/13	0	- 0	Hardwood	39.7 4.91							226.1			82.8	
Batch A - Day 19 - Composite	A	mposite	7/05/13	19	3	Hardwood	30.9 6.50					Ň	30.4				73.5	
Batch A - Day 34 - Composite	A	mposite	22/05/13	34	5	Hardwood	43.5 5.66							32.0			157.6	
Batch A - Day 34 - Dry_friable	A Dry	/_friable	22/05/13	34	5	Hardwood	25.5 7.59							109.7			9.2	
Batch A - Day 34 - Cake	Ā	Cake	22/05/13	34	5	Hardwood	56.6 5.83					ũ	J6.1	137.5				
Batch A - Day 34 - Under_cake	A Unc	ter_cake	22/05/13	34	5	Hardwood	27.9 8.17			24.7						84.1	26.2	
Batch A - Day 47 - Composite	A	mposite	4/06/13	47	8	Hardwood	38.5 6.06			157.2								
Batch A - Day 47 - Dry_friable	A Dry	/_friable	4/06/13	47	8	Hardwood	21.6 7.55			146.3				5.5				
Batch A - Day 47 - Cake	A	Cake	4/06/13	47	8	Hardwood	58.4 5.44			102.9	5484	4.	36.2	27.2				
Batch A - Day 47 - Under_cake	A Una	ter_cake	4/06/13	47	8	Hardwood	31.2 7.94			219.0								
Batch A - Day 54 - Composite	A	mposite	11/06/16	54	8	Hardwood	38.4 6.06					õ	39.6	186.8		13.4		
Batch A - Day 54 - Dry_friable	A Dry	/_friable	11/06/16	54	8	Hardwood	22.3 7.42			92.1				135.2		172.6		
Batch A - Day 54 - Cake	A	Cake	11/06/16	54	8	Hardwood	59.7 5.19				3.5	(1)	1.1	356.9		850.6		
Batch A - Day 54 - Under_cake	A Una	ter_cake	11/06/16	54	8	Hardwood	29.3 7.07			119.1						8433.7		
Batch B - Day 15 - Composite	B	mposite	9/07/13	15	3	Hardwood	33.2 6.44		21.7	78.7		U	7.9	41.8		57.3		
Batch B - Day 15 - Cake	В	Cake	9/07/13	15	3	Hardwood	60.3 ND		85.7		299.	1	54.0	217.2			143.9	72.0
Batch B - Day 15 - Lemongrass Litter	B Lemon	grass_Litter	9/07/13	15	3 L(	emongrass	41.4 6.68			119.7	92.0	-	15.4			96.3		
Batch B - Day 15 - Pine_Litter	B	ie_Litter	9/07/13	15	3 Pii	ne shavings	39.0 6.96			30.7	97.8					4.8		11.1
Batch B - Day 29 - Composite	B	mposite	23/07/13	29	5	Hardwood	37.7 6.22			100.2			4.0	82.8		78.7		
Batch B - Day 29 - Dry friable	B	r friable	23/07/13	29	5	Hardwood	26.2 7.32			130.4						268.5		
Batch B - Day 29 - Cake	. Э Ш	Cake	23/07/13	29	5	Hardwood	45.6 6.50				3.9		6.0	41.1		173.7		
Batch B - Day 29 - Under cake	B	ler cake	23/07/13	00		Hardwood				13.4	2	,		37.6		30.4		
Batch B - Dav 29 - Lemondrass Litter		orass Litter	23/07/13	5		amondrass	37.5 6.55			152 5		÷	7 66	30.1		7.6		
Batch R - Dav 20 - Dine 1 itter		a litter	23/07/13	2 00	л с Ц	un shavinds	34.4 7.29			115.1	24.0	-		85 Q		314.0		
Batch B - Day 43 - Fille_Eliter	ے <u>-</u> م م	moneite	6/08/13	13	 	Jardwood	30 F 6 10				0.14		0	0.00		r F		
Datch D Dov 42 - Composite		riipusite friabla	0/00/13	₽ ¢	0 0	Jordwood				0101			0.+	7 631		107		
Datch D - Uay 43 - Uly_IIIable	בֿ ם ם	V_IIIable ≏aba	6/00/13	5 ć	0 0	Lardwood Jardwood	20.7 C.04			104.9		Ŧ	2 01	107.1		101.4		
balcri b - Day 43 - Cake		Cake	0/00/13 0/00/13	5 5	0 0		11.0 0.20						09.0	C L				
Batch B - Day 43 - Under_cake	ОПС В	aer_cake	6/08/13	43	 	Hardwood	31.4 7.64					4	50.4 2.0	5.6 		2054.1		
Batch B - Day 43 - Lemongrass_Litter	B Lemon	grass_Litter	6/08/13	43	ت 8	emongrass	46.1 5.81				644.		0.8	403.7		3056.3		
Batch B - Day 43 - Pine_Litter	B	ne_Litter	6/08/13	43	8	ne shavings	50.6 6.18						7.9			5259.1		
Batch B - Day 53 - Composite	Ö	mposite	16/08/13	53	8	Hardwood	37.4 6.18				815.	6	49.1			941.7		
Batch B - Day 53 - Dry_friable	BDry	/_friable	16/08/13	53	8	Hardwood	22.5 6.65			129.4	3904	2						
Batch B - Day 53 - Cake	۵	Cake	16/08/13	53	8	Hardwood	44.0 4.91				19.6	4	51.5					
Batch B - Day 53 - Under_cake	B Unc	ter_cake	16/08/13	53	8	Hardwood	42.8 7.00			243.1		÷	54.3			6794.5		
Batch B - Day 53 - Lemongrass_Litter	B Lemon	grass_Litter	16/08/13	53	8 8	emongrass	47.3 6.09						0.8			5975.1		
Batch B - Day 53 - Pine_Litter	B	ie_Litter	16/08/13	53	8 Pii	ne shavings	41.7 6.04						73.6			10999.8		
Batch D - Day 18 - Dry_friable	D	/_friable	8/04/14	18	3 Pii	ne shavings	17.9 7.83	0.94		11.5						76.2		
Batch D - Day 18 - Moist_friable	D Mois	st_friable	8/04/14	18	3 Pii	ne shavings	20.2 8.14	1.12										
Batch D - Day 18 - Cake	٥	Cake	8/04/14	18	3 Pii	he shavings	28.9 8.70	1.09							20.0	6.1		
Batch D - Day 18 - Shed Air	D	hed Air	8/04/14	18	3 Pii	he shavings	24.8 8.79	3.24										
Batch D - Day 32 - Cake	۵	Cake	22/04/14	32	5 Pil	he shavings	37.3 8.49	1.2		18.2						15.2		
Batch D - Day 32 - Moist friable	D Mois	st friable	22/04/14	32	5 Pii	ne shavings	23.1 8.49	1.2		4.7				1.8				
Batch D - Day 32 - Dry friable	Drv	r friable	22/04/14	32	5 Pil	he shavings	16.7 8.02	1.2		6.2				2.2				
Batch D - Day 32 - Shed_Air	, n D	hed_Air	22/04/14	32	5 Pii	ne shavings	26.3 8.49	8.73			210.	2						
Batch D - Day 46 - Cake	0	Cake	6/05/14	46	8 Pii	ne shavings	49.5 5.89	1.58			3243	۲.						
Batch D - Day 46 - Dry_cake	D	y_cake	6/05/14	46	8 Pii	ne shavings	26.7 8.01	0.79		6.5								
Batch D - Day 46 - Dry_friable	D	/_friable	6/05/14	46	8 Pii	ne shavings	26.0 7.72	0.68		5.7				2.7		16.6		
Batch D - Day 46 - Shed_Air	D	hed_Air	6/05/14	46	8 Pii	ne shavings	26.4 8.33	7.7		127.5	1059	.2						

## Table A. 9. Dataset of odorant emission rates ( $ng/m^2/s$ ; measured with TD-GC-MS) and litter conditions

Emission rate values adjusted to standard conditions 20°C, 101.3 kPa — ISO-10780, VDI-3880 & EN-13725 ND=no data - sample not analysed or lost; NA=not analysed; Blanks values indicate that odorants were below

Table A. 9. continued																		
Sample Index	Propanoic acid	2-butanol	1-butanol	Carbon disulfide	Benzene <sub>k</sub>	2,3- utanedione	3-methyl- butanal	2-methyl-3- 2-pentanor buten-2-ol	le 2-methyl- pentane	3- methyl- pentane	Hexane	2-methyl- Ethy propanoic aceta acid	l 3-hydroxy- te 2-butanone	Butanoic acid	3-methyl- 1-butanol	Toluene	Dimethyl <sup>I</sup> disulfide	Difluorodi methyl- silane
Batch A - Day 0 - Fresh bedding					4252.4				256.6	53.4	66.6					702.3		
Batch A - Day 19 - Composite		8.1			1538.1				42.4	88.5	537.7					21.7	9.1	
Batch A - Dav 34 - Composite		66.1			28.5						3483.1					38.9	2.8	
Batch A - Day 34 - Dry friable		)			71.4				31.2	8.4	104.0					1280.3	6.7	
Batch A - Day 34 – Cake		44.4	26383.4									7.1		744.2			107.4	
Batch A - Day 34 - Under_cake	93.7	35.4			36.2				5.3	9.6	65.3					4.5	23.9	
Batch A - Day 47 - Composite		194.1	8.2			77.4								12.0			824.6	
Batch A - Day 47 - Dry_friable		57.1															1823.7	
Batch A - Day 47 - Cake		514.0	283.6									554.(	0	7057.5			187.8	
Batch A - Day 47 - Under_cake		88.5	1627.8					568.9						35.7	43.5		23.1	
Batch A - Day 54 - Composite		620.8	1366.8														7.7	
Batch A - Day 54 - Dry_friable								323.6									72.9	
Batch A - Day 54 - Cake	107.2	483.8	5487.2									2368.	~	297.6			74.1	
Batch A - Day 54 - Under_cake		537.9				7.77		49.6									74.6	
Batch B - Day 15 - Composite		48950.1				7.2						49.6			101.4	19.2		
Batch B - Day 15 - Cake		519.4	61.2						735.8	117.7	24.7	2694.	0			299.4	11.6	
Batch B - Day 15 - Lemongrass_Litter		86.5	666.3			97.3		319.7							22.0		5.7	
Batch B - Day 15 - Pine_Litter																	65.9	
Batch B - Day 29 - Composite		76.7	2852.4					2400.0								16.6	12.4	
Batch B - Day 29 - Dry_friable								119.6			6.2					23.5		
Batch B - Day 29 - Cake		7.5	85.1													5.4	3.6	
Batch B - Day 29 - Under_cake		40.6														8.0	27.6	
Batch B - Day 29 - Lemongrass_Litter		64.3	616.3			126.9										12.4	16.5	
Batch B - Day 29 - Pine_Litter		55.8				20.8										25.4	25.2	
Batch B - Day 43 - Composite	80.8	107.0	1996.5									1233.	4	28.0		0	159.8	
Batch B - Day 43 - Dry_friable		27.1				11.2		198.4								13.2	10.1	
Batch B - Day 43 - Cake	325.0	22.9	170.2	99.3								16208	9.	3254.6			178.6	
Batch B - Day 43 - Under_cake		1887.0	3764.8	31.1										44.4		56.0	9.7	
Batch B - Day 43 - Lemongrass_Litter		459.1	895.2											67.4		33.5	20.4	
Batch B - Day 43 - Pine_Litter		6947.6	721.9									7496.	4	258.2		25.3	90.5	
Batch B - Day 53 - Composite	169.3	6.1	2561.9											1236.6			21.8	
Batch B - Day 53 - Dry_friable	21.0											14.2	4.1	108.7			10.3	
Batch B - Day 53 - Cake	77.4	59.2	202.5									18805	œ.	2161.7			82.6	
Batch B - Day 53 - Under_cake		3327.4	176.5					94.9						151.6		38.7	6.9	
Batch B - Day 53 - Lemongrass_Litter		6.1	293.1									4851.	<b>о</b> .	3902.9			99.1	
Batch B - Day 53 - Pine_Litter		6642.5	788.1									833.		3374.2			127.4	
Batch D - Day 18 - Dry_friable						30.0											1.9	
Batch D - Day 18 - Moist_triable						21.5												
Batch D - Day 18 - Cake						12.8	16.7											
Batch D - Day 18 - Shed_Air						0	i I											
Batch D - Day 32 - Cake		4.8				10.3	7.9	318.3					9.0				1645.9	
Batch D - Day 32 - Moist_friable		2.6				5.7	15.3										2.0	
Batch D - Day 32 - Dry_friable						14.7		13.8					241.6				25.2	
Batch D - Day 32 - Shed_Air		51.2				500.6	52.4										71.9	
Batch D - Day 46 - Cake	512.6						1809.9							214.4			(	
Batch U - Day 46 - Ury_cake						c											2.X	
Batch U - Uay 40 - Ury_IIIaule Dototh D - Dou 46 - Shod Air						0.C											7.01 2.10	с <i>с</i> 2
םמוכון ע - עמץ 40 - טוופע_מו																	04.0	7.20

Sample Index	n-propyl- acetate	Butanoic acid, methyl ester	3-hydroxy-   3-methyl-2- butanone	3-methyl butanoic acid	2-methyl butanoic acid	Benzaldehyde	Butanoic acid, ethyl ester	Acetic acid, 1- methylpropyl ester	Propanoic acid, propyl ester	Acetophenone	Benzoic acid	Dimethyl trisulfide	Butanoic acid, propyl ester	2-ethyl-1- 3,5-dimet hexanol benzaldel	thyl- α- hyde piner	β- ie pinene	D-Limonene
Batch A - Day 0 - Fresh_bedding Batch A - Day 19 - Commosite											00						
Batch A - Day 34 - Composite											2						
Batch A - Day 34 - Dry_friable										39.0	7.2						
Batch A - Day 34 - Cake							2828.6	89.2									
batch A - Day 34 - Under_cake Batch A - Dav 47 - Composite																	
Batch A - Day 47 - Dry_friable												2.7					
Batch A - Day 47 - Cake		421.5		115.4			1568.2	374.5					35.7				
Batch A - Day 47 - Under_cake												20.7					
Batch A - Day 54 - Composite Potch A - Dov 64 - Drv frichlo						207											
Batch A - Dav 54 - Cake	192.1	84.4				0.01	131.2		310.9				53.6				
Batch A - Day 54 - Under_cake												14.4					
Batch B - Day 15 - Composite																	
Batch B - Day 15 - Cake	45.2						16.2										
Batch B - Day 15 - Lemongrass_Litter												4.7					5.6
Batch B - Day 15 - Pine_Litter Patch B - Day 20 - Comments												31.9			9.1		
batch B - Day 23 - Composite Batch B - Day 29 - Dry friahle						л 1											
Batch B - Day 29 - Cake						-						100.5					
Batch B - Day 29 - Under_cake												15.9					
Batch B - Day 29 - Lemongrass_Litter												67.3					
Batch B - Day 29 - Pine_Litter												4.2			4.4		
Batch B - Day 43 - Composite	17.5	13.3					50.2	44.1	19.9				18.1				
batch B - Day 43 - Dry_triable Batch B - Dav 43 - Cake	765.5	7 7 70	23.2				3463.6	415 G	25.1				5 8				
Batch B - Day 43 - Under cake	2						0		-			7.5	0		15.9		
Batch B - Day 43 - Lemongrass_Litter							949.3		12.9				11.2		4.8		
Batch B - Day 43 - Pine_Litter		200.5					264.2		8.6				25.3		8.6		
Batch B - Day 53 - Composite							1232.8						138.2				
Batch B - Day 53 - Dry_friable Batch B - Dav 53 - Cake	540.8	1457.1	69.2	12.3	15.6		4721.4	645.7					2924.0				
Batch B - Day 53 - Under_cake												5.7					
Batch B - Day 53 - Lemongrass_Litter		210.8					1079.5						169.0				12.2
Batch B - Day 53 - Pine_Litter		145.3					75.9						358.0		140.	ю	
Batch D - Day 18 - Dry_friable															38.6		
batch D - Day 18 - Moist_friable Batch D - Day 18 - Cake															0.8 0.8		
Batch D - Day 18 - Shed Air																	
Batch D - Day 32 - Cake							29.6								45.2	1.3	21.4
Batch D - Day 32 - Moist_friable														6.2 1.6	15.5	3.7	
Batch D - Day 32 - Dry_friable														117.8	2.4	c	
Batch D - Day 32 - Sileu_All Batch D - Day 46 - Cake															000	7	
Batch D - Day 46 - Dry cake															3.5	14.5	
Batch D - Day 46 - Dry_friable															109.	4 3.1	
Batch D - Day 46 - Shed_Air															47.5		

Table A. 9. continued

ample Index	Nonanal	Decane	Butanoic acid, butyl ester	Butanoic acid, 1- methylpropyl ester	2,2,4,6,6-pentamethyl- heptane	1,3-deiphenyl-2- propen-1-one	Hexadecane
atch A - Day 0 - Fresh_bedding							
atch A - Day 19 - Composite							
iatch A - Uay 34 - Composite atch A - Day 34 - Dry frishle							
atch A - Dav 34 - Dry_mane atch A - Dav 34 - Cake				19.7			
atch A - Day 34 - Under_cake							
atch A - Day 47 - Composite							
iatch A - Day 47 - Dry_friable							
atch A - Day 47 - Cake			212.4	797.4			
iatch A - Day 47 - Under_cake							
iatch A - Day 54 - Composite							
iatch A - Day 54 - Dry_friable					12.8	9.1	
iatch A - Day 54 - Cake			9.1	1772.9			
atch A - Day 54 - Under_cake							
iatch B - Day 15 - Composite					7.2		
iatch B - Day 15 - Cake							
atch B - Day 15 - Lemongrass_Litter							7.9
atch B - Day 15 - Pine_Litter					8.7		
atch B - Day 29 - Composite							
atch B - Day 29 - Dry_friable		441.5			6.0		
atch B - Day 29 - Cake							
atch B - Day 29 - Under_cake							
atch B - Day 29 - Lemongrass_Litter							
atch B - Day 29 - Pine_Litter							
iatch B - Day 43 - Composite				555.0			
atch B - Day 43 - Dry_friable							
iatch B - Day 43 - Cake			13.8	49.9			
atch B - Day 43 - Under_cake							
atch B - Day 43 - Lemongrass_Litter							
iatch B - Day 43 - Pine_Litter				27.0			
atch B - Day 53 - Composite				132.8			
atch B - Day 53 - Dry_friable							
atch B - Day 53 - Cake				725.0			
atch B - Day 53 - Under_cake		4.1					
atch B - Day 53 - Lemongrass_Litter			42.0	11.7			
iatch B - Day 53 - Pine_Litter			7.9	21.1			
iatch D - Day 18 - Dry_friable							
iatch D - Day 18 - Moist_friable							
iatch D - Day 18 - Cake							
iatch D - Day 18 - Shed_Air							
alcii U - Day 32 - Cane	0						
atch U - Day 32 - Moist_friable	3.6						
atch D - Day 32 - Dry_Iriable	0. 0						10.0
atch D - Day 32 - Sheq_Air	4.70						
atch D - Day 46 - Cake							
atcii U - Day 40 - Diy_cane atch D - Day 46 - Dry frichlo	7 C 7						
atch D - Dav 46 - Shed Air							

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kPa — ISO-1( ks values indi	0780, VDI-3880 8 cate that odorant	& EN-13725 s were below de	stection limit or	r inadequate h	MS match			
Methyl mercaptan	Carbonyl sulfide	Ethyl mercaptan	Dimethyl sulfide	Carbon disulfide	Diethyl sulfide	Dimethyl disulfide	Diethyl disulfide	Dimethyl trisulfide
Ð	QN	Ŋ	QN	QN	QN	QN	QN	QN
15.5	40.8		6.8	1.5		32.3		0.0
37.5	23.4		308.0	2.1		21.0		0.0
58.1			275.5	3.3		15.8		0.0
15.8 3.6			1085.1 107 8	5.8 ≁	0.7	9.0 0 3	0.7	0.0
0.0 15.5	452.9		647.2	t 13		171		
55.4	35.7		50.8	1.5		28.2		0.0
15.4	64.7		1995.8	29.9		5.7		0.0
8.2	18.5		44.1	0.5		39.8		0.3
49.0	2910.4	7.6	1933.2	18.0		34.4		0.1
77.5	24.2		481.6	13.5		31.0	4.3	0.1
38.1	82.3	96.2	3473.0	209.8	3.6	41.7	2.1	0.1
31.6	30.3		1832.5	14.9		544.2	3.0	1.2
10.8	416.4		380.9	12.9		6.7		0.0
233.4	116.0		1442.4	6.0		9.1		0.1
127.8	671.4		169.0	10.8		365.5		0.6
41.1	3091.6 		147.6	38.8		146.5		0.3
71.0	5209.7	4.0	1610.3	22.5		40.4		0.1
7.01	2126.0		42.5	0.0		2.4		0.0
132.2	130.0 1662 E	160	2218.9	4.2.4 0.01		489.4 115.6		0.0
0.45	0.2021	C.CI	2.1042 0 7001	44.0 0 1 0		0.01		
9.4.9 90.9	1.2020.U	0.7	1006.2	31.U 7.27		192.U 664.0		4. C
75.0	1225.1	10.2	1962 0	30.0		81.3		0.0
30.7	69.8	1	288.4	7.8		19.3		0.0
808.3	328.9	22.0	2766.8	379.3		107.6	6.9	0.2
135.7	285.1	18.1	2888.5	27.5	2.3	780.0		0.7
86.8	1891.5	19.7	2805.7	53.9	2.1	232.4		0.3
242.8	170.3	45.1	2880.8	73.8		224.7		0.3
30.1	1901.5		1091.5	17.9		55.3	2.5	0.2
30.3	39.0		84.5	8.9		15.7		0.1
151.2	281.0	46.1	2901.9	604.5		210.6	9.8	0.3
21.9	2645.9		5/1.6	9.7	L C	29.3	1. 1 4. 0	0.1
21.9	23103.9	00.9	571.6	0.161	0.7	29.3	0.0	2.0
2	27.8	AN	2.3	3.1	٩N	5.1	NA	NA
1.9	20.5	AN	3.8		ΝA	1.6	NA	NA
1.8	73.7	AN	6.3	3.4	ΝA	0.6	NA	AN
	342.3	AN		45.3	ΝA		NA	AN
6.1	38.4	NA	14.8		ΝA	3.5	NA	NA
19.4	65.1	AN	7.7	1.4	ΝA	18.4	NA	AN
12.3	36.7	NA	1.9		ΝA	5.3	NA	AN
		AN 2			AN 2		NA	AA I
		AN	3.7		AN 2		AN	AN
7.9	14.6	AN 2	č		₹ Z	Э.1	AN 2	AN 3
۷.۵	20.3	AN A	4.7		₹ Z	Q.D	AN A	AN A
		NA			ΨN		NA	NA

Table A. 10.Dataset of reduced su	ilfur compou	pun
Emission rate values adjusted to standard co ND=no data - sample not analysed or lost; N	nditions 20°C, 1 A=not analysed;	01.3 Blan
Sample Index	H2S (ng/	L)
Batch A - Day 0 - Fresh_bedding		
Batch A - Day 19 - Composite		
Batch A - Day 34 - Composite Batch A - Dav 34 - Drv friable		
Batch A - Day 34 - Cake		
Batch A - Day 34 - Under_cake		
Batch A - Day 47 - Composite		
Batch A - Day 47 - Dry_triable Batch Δ - Dav 47 - Cake		
Batch A - Day 47 - Under_cake		
Batch A - Day 54 - Composite		
Batch A - Day 54 - Dry_friable		
Batch A - Day 54 - Cake		
Batch B - Day 54 - Under_cake Batch B - Dav 15 - Composite		
Batch B - Day 15 - Cake		
Batch B - Day 15 - Lemongrass_Litter		
Batch B - Day 15 - Pine_Litter		
Batch B - Day 29 - Composite		
Batch B - Day 29 - Dry_friable		
Batch B - Day 29 - Cake		
Batch B - Day 29 - Unuer_cave Batch B - Day 29 - Lemongrass Titter		
Batch B - Day 29 - Pine_Litter		
Batch B - Day 43 - Composite		
Batch B - Day 43 - Dry_friable		
Batch B - Day 43 - Cake		
Batch B - Day 43 - Under_cake		
Batch B - Day 43 - Lemongrass_Litter Batch B - Day 43 - Dine I itter		
Batch B - Day 53 - Composite		
Batch B - Day 53 - Dry_friable		
Batch B - Day 53 - Cake		
Batch B - Day 53 - Under_cake		
Batch B - Day 53 - Lemongrass_Litter		
Batch D - Day 33 - FINE_LINE Batch D - Day 18 - Dry friable	14.1	
Batch D - Day 18 - Moist_friable	15.8	
Batch D - Day 18 - Cake	14.3	
Batch D - Day 18 - Shed_Air	100.7	
Batch D - Day 32 - Cake	7.5	
Batch D - Day 32 - Moist_friable	24.6	
Batch D - Day 32 - Dry_friable Batch D - Day 32 - Shod Air	17.3	
Batch D - Day 46 - Cake	10.8	
Batch D - Day 46 - Dry_cake	37.1	
Batch D - Day 46 - Dry_friable	39.7	
Batch D - Day 46 - Shed_Air	450.1	

## Appendix I. PTR-TofMS—Index of protonated molecular masses and likely/possible compounds

TOF protonated (H+) mass	Molecular weight	Formula	Possible compounds
33 0335	32 0262	CH4O	Methanol
3/ 9880	33 9877	H2S	Hydrogen sulfide
41 0386	40 0313	C3H4	Cyclopropene
41.0500	40.0515	Conte	Pronyne
12 0338	41 0266	C2H3N	Acetonitrile
42.0550	42.0106	C2H2O	Ketene
45.0170	42.0100	021120	Multiple fragments
12 0512	42 0470	СЗНЕ	Dronene
43.0342	42.0470	CSITO	Pentapol (M88)
13 0000	12 0000		M13 (combined
45.0000	44 0262	C2H4O	
45.0555	44.0202	C2H7N	Dimethylamine
40.0051	45.0578	CH2O2	Eormic acid
47.0128	40.0000	C11202	Ethanol
47.0491	40.0419		Mothylmorcantan
55 0542	54 0470	C/H6	(1.2  or  1.3  )Butadiene
57.0220	56 0247	C2H4O	2 Propopal
57.0520	56.0247		Putanol (M74)
57.0055	50.0028	04118	2 Motbul 1 propopo
E0.0401	E9 0410	C21160	Acotono
59.0491	50.0419		Acetonie
60.0444	59.0571		Trimethylamine
61.0394	59.0755	COLINO	
01.0284	60.0211 60.0E7E		ACELIC ACIU
01.0048	00.0575		II-Propanoi
62 0262	62.0100	CZHONZ	Dimothyl cylfide
03.0203	62.0190	C2H05	Diffectivit suffice
69.0405	67.0422	CALIEN	Ethymercaptan
60.0495	67.0422		Pyrrole
71 0401	70.0410		Isopiene
71.0491	70.0419		Methylathylketone
75.0040	72.0373	C4H6U	
			Butanal
75 0441	74.0269	C2116O2	Buldiidi
75.0441	74.0500		Propanoic aciu
75.0604	74.0752	C4H100	n and 2 Butanal (fragments to MEZ 060)
70.0542	79.0470	CELLE	n- and 2 Butanoi (Iraginents to M57.009)
79.0542	78.0470		(Unknown sulfur compound)
70.9071	77.9596		(Unknown sunur compound)
80.0495	79.0422		2,4-Pentadienenthie
01.0099	80.0020 91.0E70		1,5-Cyclonexadiene
82.0051	81.0579 82.0E21		2 Mothyl 1H Dyrazolo
03.0004	02.0331		Cycloboxano
83.0855	82.0783 82.072E		Cyclonexane
04.0000 95.0649	05.0755 04.0E7E	CELINO	2 Mathyl 2 butanal
03.0040	84.0373	C3H6O2	Disastul
87.0441	80.0308		Diacetyi
87.0804	80.0732	CONTOO	Z-Pentanone
07 11 00	06 1006	001114	Isovaleraldenyde
87.1168	86.1096	C6H14	Hexane
89.0597	ōð.U524	C4H8UZ	ACETOIN Butanaia asid
			Butanoic ació
00.0064	00 0000	CE1120	2-metnyl-1,3-aloxolane
03.020T	88.088	C3H12U	$L^{-} \propto 2$ -remandly (see W43)
			2- & 3-Wethyl-1-Dutanol (See W43)

## Table A. 11. Index of protonated molecular masses and likely/possible compounds with PTR-TofMS

TOF protonated	Molecular	Formula	Possible VOCs/odorants
(H+) mass	weight		
91.0576	90.0503		Diethyl sulfide
93.0699	92.0626	C7H8	Toluene
94.9984	93.9911	C2H6S2	Dimethyl disulfide
95.0161	94.0127	C2H6O2S	Dimethyl sulfone
95.0491	94.0419	C6H6O	Phenol
101.0597	100.0524	C5H802	
101.0961	100.0888	C6H12O	Hexanal
103.0754	102.0681	C5H10O2	Isovaleric acid
20010701	101.0001	00112002	Valeric acid
105.0699	104.0626	C8H8	Styrene
107.0492	106.0419	C7H6O	Benzaldehyde
107 0856	106 0783	C8H10	Xvlene
109.0648	108.0575	C7H8O	P-Cresol
105.0010	100.0375	0/1100	Benzyl alcohol
112 0757	111 0684	Сенаои	2 4 5-trimethyloxazole
112.0737	111.0004	C7H13N	Hentanonitrile
112.1121	112 0524	C6H8O2	Sorbic acid
113.0961	112.0324	C7H12O	2-Hentanal
115.0501	112.0000	0/1120	Cyclohentanone
11/ 0300	112 0200	C5H7NS	Isothiocyanic acid
114.0300	114.0691	C6H10O2	Assorted acids/osters
115.0754	114.0081	C7H14O	Hontanal
115.1110	114.1045	C9U19	Octano
117.0010	114.1409	C6H12O2	Hovanois asid
117.0910	110.0657	0001202	Ethyl isobutyrato
			Ethyl butyrate
119 0651	117 0579		
121 0649	120.0575		Acetophonono
121.0048	120.0373	C01180	Renzoic acid
123.0441	122.0500	C7H0U2	Belizoic aciu
125.0605	122.0732	C011100	4-ethyphenol
125.0597	124.0524	C7H6U2	Dimothyl triculfido (DMTS)
120.9705	123.9052	C2H035	Ethyl 2 mothybut 2 anosto
129.0910	120.0004	C/H1202	Ethyl 2 methyl 2 byteneste
120 1274	120 1201	C9U16O	2 Ostanono
129.1274	128.1201		3-Octanone
151.1007	150.0994	C/H1402	Ethyl-2-methylbutylate
122 0000	121 0725	COLION	Propyi butyrate
132.0808	131.0735	CIOUIC	Skalole
137.1325	130.1252	CIUHIO	(alpha & bata pinana
142 1421	142 1250	011100	limonene, campnene, myrcene)
143.1431	142.1358	C9H180	Nonanai
143.0800	142.0994		Esters
143.1795	142.1/22	0014600	Decane
145.1228	144.1150	C8H16O2	Butanoic acia, 1-methylpropyl ester
149.0233	148.0160	C8H4U3	Prithalic annydride
149.0961	148.0888	C10H12O	Estragole
165.0758	164.0685	C6H12O5	D-Fucose
1/1.2108	170.2035	C12H26	Dodecane

Table A. 11. continued

## Appendix J. Screen-shot of IONICON PTR-MS Viewer software

This software was used to interpret raw PTR-TofMS data.

The top half of the screen displays the mass spectrum data for individual samples.

The bottom half of the screen shows the concentration (ppb) of individual masses (operator selected) over the course of a sample collection. The operator then selected a portion of the sample, typically where the sample concentration was stable (e.g. cycles 40-50 with each cycle representing 10 seconds) to define the steady state concentration for that sample. Steady-state concentration values were recorded for data analysis. Instrument background concentration data was recorded when no sample was being analysed (e.g. cycles 1-12) and concentration values were subtracted from the sample concentration.



Figure A. 19. Screen-shot of IONICON PTR-MS Viewer software

## Appendix K. Dataset of odorant emissions and litter conditions from a laboratory pen (TD-GC-MS and TD-GC-SCD)

## Including:

- Table A. 12. VOCs quantified using TD-GC-MS
- Table A. 13. VSCs detected using TD-GC-SCD and Ammonia detected with TD-GC-NCD
- Table A. 14. VOCs quantified using TD-GC-MS one or fewer times; or VOCs with inadequate match with the MS library for quantification
- Table A. 15. VOC emission rates (ng/m<sup>2</sup>/s) from a laboratory pen trial: gas concentrations measured using TD-GC-MS
- Table A. 16. VSC and ammonia emission rates (ng/m²/s) from a laboratory pen trial: gas concentrations measured using TD-GC-SCD and TD-GC-NCD

Molecular weight	Formula	Compound name	Other name	CAS number	Detection frequency
46.068	C2 H6 O	Ethanol		64-17-5	11%
58.079	C3 H6 O	Acetone		67-64-1	72%
59.110	C3 H9 N	Trimethylamine	ТМА	75-50-3	67%
60.052	C2 H4 O2	Acetic acid		64-19-7	89%
60.095	C3 H8 O	Isopropyl alcohol		67-63-0	22%
60.095	C3 H8 O	1-propanol	Propyl alcohol	71-23-8	61%
72.106	C4 H8 O	2-Butanone	Methyl ethyl ketone (MEK)	78-93-3	83%
74.079	C3 H6 O2	Propanoic acid	Methyl acetic acid	79-09-4	11%
74.122	C4 H10 O	2-Butanol	sec-butyl-alcohol	78-92-2	78%
74.122	C4 H10 O	1-Butanol	n-butanol	71-36-3	44%
78.112	C6 H6	Benzene		71-43-2	67%
79.100	C5 H5 N	2,4-Pentadienenitrile		1615-70-9	61%
81.116	C5 H7 N	Methallyl cyanide		4786-19-0	11%
86.089	C4 H6 O2	2,3-Butanedione	Diacetyl	431-03-8	67%
86.132	C5 H10 O	2-Pentanone	Methyl propyl ketone	107-87-9	39%
86.133	C5 H10 O	3-methyl-butanal	Butanal, 3-methyl-	590-86-3	61%
88.105	C4 H8 O2	Ethylacetate	Acetic acid, ethyl ester	141-78-6	17%
88.105	C4 H8 O2	2-Butanone, 3-hydroxy-	Acetoin	513-86-0	78%
88.105	C4 H8 O2	Butanoic acid	Butyric acid	107-92-6	44%
88.148	C5 H12 O	3-methyl-1-butanol	1-Butanol. 3-methyl-	123-51-3	33%
92.138	C7 H8	Toluene		108-88-3	22%
94.111	C6 H6 O	Phenol		108-95-2	78%
102.132	C5 H10 O2	Methyl isobutyrate		547-63-7	11%
102.132	C5 H10 O2	Tetrahvdrofurfurvl alcohol		97-99-4	33%
103.121	C7 H5 N	Benzonitrile			28%
104.149	C8 H8	Styrene		100-42-5	50%
106.122	C7 H6 O	Benzaldehyde		100-52-7	100%
106.165	C8 H10	p-xylene		106-42-3	44%
108.138	C7 H8 O	P-cresol		106-44-5	17%
113.181	C5 H7 N S	Isothiocyanic acid		3386-97-8	39%
114.229	C8 H18	Octane		111-65-9	28%
116.158	C6 H12 O2	Ethyl butyrate		105-54-4	28%
116.158	C6 H12 O2	Hexanoic acid		142-62-1	11%
120.149	C8 H8 O	Acetophenone	Methyl phenyl ketone	98-86-2	100%
122.121	C7 H6 O2	Benzoic Acid		65-85-0	94%
128.169	C7 H12 O2	Ethyl 2-methylbut-2-enoate		5837-78-5	11%
128.212	C8 H16 O	3-Octanone		106-68-3	44%
130.185	C7 H14 O2	Butanoic acid, propyl ester	n-Propyl butyrate	105-66-8	11%
136.234	C10 H16	α-Pinene		80-56-8	78%
136.234	C10 H16	Myrcene		123-35-3	22%
136.234	C10 H16	β-pinene		127-91-3	50%
136.234	C10 H16	Limonene		138-86-3	56%
136.234	C10 H16	β-phellandrene		555-10-2	28%
136.234	C10 H16	2-thujene		28634-89-1	33%
142.239	C9 H18 O	Nonanal		124-19-6	17%
144.211	C8 H16 O2	Butanoic acid, 1-methylpropyl ester	sec-Butyl-butyrate	819-97-6	11%
148.116	C8 H4 O3	Phthalic anhydride		85-44-9	94%
148.202	C10 H12 O	Estragole		140-67-0	61%
226.441	C16 H34	Hexadecane		544-76-3	11%
299.754	C16 H14 CI N3 O	CGS-17867A		71239-15-1	11%

## Table A. 12. VOCs quantified using TD-GC-MS

Molecular weight	Formula	Compound name	Other name	CAS number	Detection frequency
34.0809	H2S	Hydrogen sulfide	H2S	7783-06-4	11%
48.1076	C H4 S	Methyl mercaptan	MM, Methanethiol	74-93-1	17%
62.1340	C2 H6 S	Dimethyl sulfide	DMS	75-18-3	22%
94.1990	C2 H6 S2	Dimethyl disulfide		624-92-0	6%
126.2640	C2 H6 S3	Dimethyl Trisulfide	DMTS	3658-80-8	78%
17.03052	NH3	Ammonia		7664-41-7	44%

Table A. 13. VSCs detected using TD-GC-SCD and Ammonia detected with TD-GC-NCD

## Table A. 14.VOCs quantified using TD-GC-MS one or fewer times; or VOCs with<br/>inadequate match with the MS library for quantification

Molecular weight	Formula	Compound name	Other name	CAS number	Detection frequency
68.117	C5 H8	Isoprene		78-79-5	6%
72.106	C4 H8 O	Isobutyraldehyde		78-84-2	6%
74.122	C4 H10 O	Isobutyl alcohol		78-83-1	6%
84.116	C5 H8 O	3-Methyl-2-butenal		107-86-8	6%
88.105	C4 H8 O2	2-Methyl-1,3-dioxolane		497-26-7	0
88.148	C5 H12 O	2-Pentanol		6032-29-7	6%
88.148	C5 H12 O	1-Butanol, 2-methyl-		137-32-6	6%
88.148	C5 H12 O	1-Pentanol		71-41-0	6%
100.159	C6 H12 O	Hexanal		66-25-1	6%
100.202	C7 H16	Heptane		142-82-5	0
102.132	C5 H10 O2	Butanoic acid, methyl ester	Methyl butyrate	623-42-7	6%
102.132	C5 H10 O2	1-Hydroxy-2-pentanone		64502-89-2	6%
102.132	C5 H10 O2	Oxirane, 3-hydroxypropyl-		21915-56-0	6%
102.135	C4 H10 N2 O	N-acetylethylenediamine		1001-53-2	6%
108.138	C7 H8 O	Benzyl alcohol		100-51-6	6%
111.142	C6 H9 N O	2,4,5-trimethyloxazole		20662-84-4	6%
116.158	C6 H12 O2	Propanoic acid, 2-methyl-, ethyl ester	Ethyl isobutyrate	97-62-1	6%
117.148	C8 H7 N	Indole		120-72-9	6%
118.131	C5 H10 O3	Methyl 3-hydroxybutyrate		1487-49-6	6%
119.378	C H Cl3	Chloroform	Trichloromethane	67-66-3	0
128.169	C7 H12 O2	Ethyl 2-methyl-2-butenoate		55514-48-2	6%
130.185	C7 H14 O2	Ethyl 2-methylbutyrate		7452-79-1	6%
130.228	C8 H18 O	1-Hexanol, 2-ethyl-	2-Ethyl-1-hexanol	104-76-7	6%
134.175	C9 H10 O	Benzaldehyde, 3,5-dimethyl-		5779-95-3	6%
134.218	C10 H14	Paracymene		99-87-6	6%
136.194	C8 H12 N2	Pyrazine, tetramethyl-		1124-11-4	6%
136.234	C10 H16	Camphene		79-92-5	6%
138.207	C9 H14 O	2-Pentylfuran		3777-69-3	6%
142.282	C10 H22	Decane		124-18-5	0
148.245	C11 H16	6-[(Z)-1-Butenyl]-1,4-cycloheptadiene		33156-93-3	6%
150.261	C11 H18	6-Butyl-1,4-cycloheptadiene		22735-58-6	6%
164.156	C6 H12 O5	D-fucose		3615-37-0	6%
170.335	C12 H26	Decane, 3,7-dimethyl-		17312-54-8	0
170.335	C12 H26	Dodecane		112-40-3	0

Note: Emission rates were not calculated for compounds unable to be quantified

		ä	Equiv	alent litter		Moisture					, iii		cito Curron		1,3						1 00000	
٩	Sample group ID	Replicate <sup>Bi</sup> a <sub>£</sub>	rd sampr çe Tabl	e r IN-101005 ID ( le A. 18)	Week	content (%)	Aw	pH Ter	mp	ianol Acc	stone Irif	ietnyl- Ac 1ine a	etic Isopre cid Alcol	opyi 1-Prc hol 1-Prc	panol Butad 2-me	liene, Prop thyl- 2-me	anal, 2. thyl- 2.	-Butanone	Propanoic acid	2-Butanol	1-Propanol, 2-methyl-	1-Butanol
1	Week_3_Dry Litter	1	6	8	3	18.1	0.809 (	5.09 23	.2 2	.97 9	.88	17	7.23	0.	79			20.66				
2	Week_3_Wet Litter	1	6	11	ŝ	61.4	. 9960.0	7.21 27.	.5	1	3.88 11	1.20 5.	86					7.81				
£	Week_3_Normal Excreta	1	6	14	с	71.6	0.983 (	5.44 2.	5	33	6.32 10	18.97 134	7.11 78.1	17 12	5.44 43.	63 28.	.78	1818.87		812.63	142.41	1013.21
4	Week_4_Dry Litter	1 2	9	17	4	13.1	0.733 (	5.15 24	.2	54	1.16 6.	3.81 75	1.26					21.16		19.31		
ъ	Week_4_Dry Litter	2 2	9	18	4	25.9	0.84 (	5.85 24	с. Э	31	5.70 22	6.52 8.	80					20.22				
9	Week_4_intermediate litter	1 2	7	20	4	38.8	0.958 (	5.72 26	1.2	25	5.83 12	7.53						57.67		6.31		
7	Week_4_Wet Litter	1 2	9	21	4	65.4	0.981 (	5.89 23	8.	2.	7.81 6	3.72 15	14.4	11 34	.65			864.19		407.29		11.94
8	Week_4_Wet Litter	2	6	22	4	69.7	0.988	5.41 23	77	2	1.51 1.	i.11 80	0.63 8.1	0 11	3.79			410.18		256.14		15.53
6	Week_4_Wet Litter	3 2	7	23	4	51.4	0.943	7.31 27	.5	0	.95 (	.55 5.	86 4.4	0 3.	68			979.59		239.15		
10	Week_4_Normal Excreta	1 2	7	24	4	72.7	0.997	5.27 2.	5 4	7.74 2.7	7.16	2C	0.66					40.36		11.09		
11	Week_5_Dry Litter	1	3	25	5	21.7	0.822	6.7 24		41	68	62	.42	2.	08			84.63		20.57		
12	Week_5_Dry Litter	2 3.	3	26	ъ	28.1	0.915 ;	7.75 26	1.2	42	10 10	8.75 14	.59					67.26		18.11		
13	Week_5_Dry Litter	т т	4	27	ъ	16.7	0.755 6	5.58 25	e.	75	5.05 C	48 85	1.29					95.47		23.39		
14	Week 5 Wet Litter	1 3.	3	28	Ŋ	64.6	0.971	5.06 24	.2			33	.60	25	.07			1150.67		2027.46		36.25
15	Week 5 Wet Litter	2	3	29	5	67.5	0.982	5.08 24	2			34	.94	19	.91				53.49			51.08
16	Week 5 Wet Litter	τ τ	4	30	ß	59.3	0.966	5.53 25.	55			30	.33	35	.64			1206.48		1853.23		92.36
17	Week 5 Wet Litter Mixed	2	4	36	Ŋ	69.2	9.988	5.29 25.	9		1	.80 12	.19	104	1.21				58.27	2130.63		354.67
18	Week 5 Caecal excreta	. 4	· ~	37	i n	86.6	0.993 6	5.11 21	۲.		12	02.0		316	.15					125.05		551.85
₽	Sample group ID	Benzene	2,4- Pentadiene <sup>.</sup> nitrile	Methallyl cyanide	2-Butena 3-methyl	l, 2,3-  - Butaned	lione Pe	2- intanone	3-methyl- butanal	Ethyl acetate	Acetoin	Butanoic acid	2-Pentanol	1-Butanol 3-methyl-	, 1-Butanol, 2-methyl-	1-Pentanc	l Toluen	lonahd at	Hexanal	Propanoic acid, 2-methyl , methyl ester	Butanoic acid, methyl	1-Hydroxy-2- pentanone
-	Week 3 Dry Litter	1.45	2.49			81.9	9		4.87		369.11	45.20					7.22	6.50	7.08		COLCI	
2	Week 3 Wet Litter	0.42	20.06			13.3	2		1.46		26.44			2.72				6.35				
m	Week_3_Normal Excreta		488.43		54.54	513.2	2	54.24			2894.50	1092.90			158.16			64.23				
4	Week_4_Dry Litter	1.27	42.28			158.5	35		2.19		446.76	31.36						10.48				
S	Week_4_Dry Litter	1.17	31.23			81.7	2		1.51		131.11							10.66				
9	Week_4_intermediate litter	0.54	29.78			38.7	ņ	0.88	1.35		66.92							8.44				
7	Week_4_Wet Litter		8.89	6.60		7.77	ŝ	4.03	7.36	8.02	197.54			20.69				10.03		8.33		
∞	Week_4_Wet Litter	1.35		10.53		37.8	2		13.71	19.69				14.05			5.94	7.26				
6	Week_4_Wet Litter	0.55	6.75			32.6	5	2.62	2.18		116.03							5.66		1.84		2.52
10	Week_4_Normal Excreta	0.77					Ċ		00								4.40	7.65				
1,		1.68	12.17			14/	77	10	2.09		435.54	28.40										
12	Week_5_Dry Litter	1.56	43.18			163.5	Lf i	4.65 1.80	2.24		274.55	10 01										
1 7 7		П.00	10.8D			1.0CL	/0	1.8U	2.03		942.29 212.29	18.87 220 70										
Т 4	Week_5_W et Litter										410.05 17	230.78		23.00				6 07				
16	Week 5 Wet Litter									11 90	765 97	507 76		33 11				20.0 1 / D				
17	Week 5 Wet Litter Mixed							14.55		4 F. J.O	10.001	364.59	15.37	14.00				74.64			8,56	
	MONT E Caeral averate	12 05						2						1		80.98	20.05	10.22			2	

Table	e A. 15. continued																			
₽	Sample group ID	2-Furan- methanol, tetrahydro-	Oxirane, 3- hydroxy- propyl-	N-acetyl- ethylene- diamine	Benzo- nitrile	Styrene	Benz- aldehyde	p- ¢ylene A	Benzyl Vicohol	Phenol, 4- methyl-	Oxazole, trimethyl-	1-butene, 4-isothio- cyanato-	P Octane	rropanoic acid, 2- methyl-, ethyl ester	Butanoic acid, ethyl ester	Hexanoic acid	Indole	Butanoic acid, 3-hydroxy-, methyl ester	Acetophenone	Benzoic Acid
1	Week_3_Dry Litter	28.85				2.97	7.46	1.11										•	6.63	4.56
2	Week_3_Wet Litter	8.16				1.05	5.30	2.06					1.53						8.16	5.93
m	Week_3_Normal Excreta						61.81		30.00				67.87						93.93	64.84
4	Week_4_Dry Litter	26.84				5.00	5.00	3.97											5.99	2.33
ы С	Week_4_Dry Litter	4.88				1.79	3.58						1.51						6.16	4.88
9	Week_4_intermediate litter	2.16			0.95	1.01	2.70	1.35											3.78	2.97
7	Week_4_Wet Litter	9.51	10.14		1.94		4.48	0.69				12.78		23.40	4.27				8.96	7.50
∞	Week_4_Wet Litter				1.76		4.63					7.83	5.00						6.62	3.14
б,	Week_4_Wet Litter						4.02	0.48		1.70		5.66	1.43						6.88	4.70
10	Week_4_Normal Excreta						10.14												12.05	8.80
11	Week_5_Dry Litter					1.88	2.76												3.63	1.82
12	Week_5_Dry Litter					1.76	3.05	6.92				1.63							4.99	2.71
13	Week_5_Dry Litter			4.91		3.70	2.83												4.25	1.52
14	Week_5_Wet Litter						4.33					6.53			12.62	8.80			5.98	1.58
15	Week_5_Wet Litter				2.24		3.93				13.16	5.70			12.99				4.65	
16	Week 5 Wet Litter						5.68					7.43			33.96	10.27		13.15	8.42	9.45
17	Week 5 Wet Litter Mixed				3.22	4.45	6.57	20.47		4.90					28.41		6.13		12.97	8.56
28	Week 5 Caecal excreta						32.08			18.49									39.15	14.14
9							75.00			01-01									67.00	F 7.F 7
Table	e A. 15. continued																			
₽	Sample group ID	Ethyl tiglate	2-Butanoic d, 2-methyl-, sthvl ester	3- Octanone	Butanoic 2-mthyl-, ester	acid, <sup>B</sup> l ethyl p	utanoic acid, ıropyl ester	1-Hexar 2-ethy	ıol, Benz  - 3,5-ı	aldehyde, dimethyl-	Benzene, 1- methyl-4-(1- methvlethvl)-	Pyrazine tetrameth	t, Alp Iyl- pine	ha Camphene ene	β-Myrcene	β-Pinene	Limonene	β- e Phell- andrene	Bicyclo[3.1.0]hex-2- ene, 4-methyl-1-(1- methylethyl)-	Furan, 2- pentyl-
⊣	Week 3 Dry Litter												11.(	65	1.04	3.66	6.19	5.29		3.04
2	Week 3 Wet Litter			8.02							3.35		12.	70		5.93	2.65		2.72	
ŝ	Week_3_Normal Excreta			62.42																
4	Week_4_Dry Litter												10.1	51		4.35	1.92	1.85	1.57	
S	Week_4_Dry Litter			3.30				3.16					5.2	56	2.75	3.10	1.27	1.51	1.31	
9	Week_4_intermediate litter			1.42									9.7	2		4.79	1.15	1.01		
2	Week_4_Wet Litter	6.60			8.64								12.3	88	5.42		1.08		5.14	
~ ~	Week_4_Wet Litter	1.69											3.0	14						
ъć	Week_4_Wet Litter			2.11									5.7	9		2.59				
1 F	Week_4_NOTITIAL EXCIELA			70 C									с с	2			101			
11	Week_2_Dry Litter			4 77									. LA	57 8 68		15 43	1.04 2.68	1 83		
13	Week 5 Drv Litter			4.94										24		2.22	1.24	i	0.86	
14	Week_5_Wet Litter																			
15	Week_5_Wet Litter											3.66	5.2	6	2.31					
16	Week_5_Wet Litter						5.61						3.5	99						
1/	Week_5_Wet_Litter_Mixed		5.79				18.90			0.89			33.1	04		13.93	3.66		2.05	

÷ _	Phthalic anhydride	Estragole	6-[(Z)-1- Butenyl]-1,4- cycloheptadiene	6-Butyl-1,4- cycloheptadiene	D- Fucose	Hexadecane	CGS-17867A
	4.01	15.72					
	5.09	12.00	3.42	5.44			7.05
	46.66						
	2.26	6.44					23.76
	2.41	6.19					
	1.42	1.96					
	5.21	3.40					
	2.67	0.98					
	4.98						
	10.71					9.56	
	1.82	4.37					
	1.56	3.63					
	1.38	3.73					
	1.96						
	2.10					2.58	
	4.35						
	3.59	4.38			4.86		
	15.77						

1         Week 3 Dry Litter         19.27           2         Week 3 Wet Litter         41.81         1674.           3         Week 4 Dry Litter         1038.97         1246.           5         Week 4 Dry Litter         41.99         63.2           5         Week 4 Dry Litter         41.18         137.5           6         Week 4 Dry Litter         41.18         147.5           7         Week 4 Job Litter         100.68         38.21           7         Week 4 Job Litter         107.58         47.48         63.2           8         Week 4 Job Litter         107.58         47.48         1052.           10         Week 4 Mont Litter         107.58         47.58         29.21         34.38         145.4         156.77           11         Week 5 Dry Litter         107.58         47.58         29.21         28.11         220.1           13         Week 5 Dry Litter         107.58         29.21         28.76         47.61         136.72           14         Week 5 Dry Litter         28.41         47.281         22.01.         28.76           13         Week 5 Dry Litter         39.25         41.61         28.76           15 <t< th=""><th>₽</th><th>Sample group ID</th><th>Methyl Mercaptan</th><th>Dimethyl Sulfide</th><th>Dimethyl Disulfide</th><th>Dimethyl Trisulfide</th><th>H₂S</th><th>Ammonia</th></t<>	₽	Sample group ID	Methyl Mercaptan	Dimethyl Sulfide	Dimethyl Disulfide	Dimethyl Trisulfide	H₂S	Ammonia
2         Week.3_Wet litter         41.81         1674.           3         Week.3_Normal Excreta         103.897         103.897         1246.           4         Week.4_Dry litter         100.68         332.5         100.68         332.5           5         Week.4_wet Litter         90.79         35.21         34.38         147.18         1471.8           7         Week.4_wet Litter         214.49         67.40         35.21         34.38         314.54         1052.3           8         Week.4_wet Litter         214.49         67.40         34.38         314.54         1052.4           10         Week.4_wet Litter         107.58         47.58         29.21         34.38         1361.1           11         Week.5_Dry Litter         107.58         47.58         29.21         34.38         1361.1           12         Week.5_Dry Litter         107.58         47.58         23.20.1         31.6.51         31.6.5           13         Week.5_Dry Litter         107.58         47.58         23.11         22.01.           13         Week.5_Wet Litter         107.58         47.58         23.13         47.61           14         Week.5_Wet Litter         107.58         2	1	Week_3_Dry Litter					19.27	
3         Week_3_Normal Excreta         1038.97         1246.           4         Week_4_Dry Litter         41.99         6.32.1           5         Week_4_Dry Litter         332.5           6         Week_4_wet Litter         100.68         332.1           7         Week_4_Wet Litter         314.54         105.6           8         Week_4_Wet Litter         107.58         47.58         31.45.4         105.1           10         Week_4_Wet Litter         107.58         47.58         29.21         34.38         1361.1           11         Week_4_Wet Litter         107.58         47.58         29.21         34.38         1361.1           12         Week_5_Dry Litter         107.58         47.58         29.21         31.45.4         1052.4           13         Week_5_Dry Litter         107.58         47.58         29.21         31.45.4         1052.7           14         Week_5_Wet Litter         107.58         29.21         31.45.4         1052.7           14         Week_5_Wet Litter         107.58         29.21         28.83         47.81         2201.           15         Week_5_Wet Litter         107.58         29.23         28.47         28.76	2	Week_3_Wet Litter					41.81	1674.91
4         Week_4_Dry Litter         41.99         63.2           5         Week_4_Dry Litter         100.68         332.5           6         Week_4_Wet Litter         141.8         147.1           7         Week_4_Wet Litter         314.54         1052.           8         Week_4_Wet Litter         107.58         47.58         29.21         31.38         141.18           10         Week_4_Wet Litter         107.58         47.58         29.21         31.35         1361.1           11         Week_5_Dry Litter         107.58         47.58         29.21         31.35         1361.1           11         Week_5_Dry Litter         107.58         47.58         29.21         31.34         1361.1           12         Week_5_Dry Litter         107.58         29.21         31.35         1361.1           13         Week_5_Dry Litter         28.33         47.58         28.11         2201.1           14         Week_5_Wet Litter         39.25         41.61         1367.27           15         Week_5_Wet Litter         39.25         41.61         1667.27	e	Week_3_Normal Excreta					1038.97	1246.90
5         Week_4_Dry Litter         100.68         38.2.5           6         Week_4_intermediate litter         414.18         1477.3           7         Week_4_wet Litter         90.79         35.21         34.38         314.54         1052.           9         Week_4_wet Litter         107.58         90.79         35.21         34.38         314.54         1052.           9         Week_4_wet Litter         214.49         67.40         34.38         314.54         1052.           9         Week_4_wet Litter         107.58         47.58         29.21         34.38         314.54         1361.           10         Week_5_Dry Litter         107.58         47.58         29.21         34.38         1361.           11         Week_5_Dry Litter         217.74         1361.         28.11         2301.           12         Week_5_Wet Litter         107.58         47.58         28.14         28.14           13         Week_5_Wet Litter         28.04         1361.         28.76         47.281         201.           14         Week_5_Wet Litter         16         Week_5_Wet Litter         28.76         41.61         1367.27           16         Week_5_Wet Litter <td< td=""><td>4</td><td>Week_4_Dry Litter</td><td></td><td></td><td></td><td></td><td>41.99</td><td>63.20</td></td<>	4	Week_4_Dry Litter					41.99	63.20
6         Week_4 intermediate litter         414.18         1477.3           7         Week_4 wet Litter         90.79         35.21         34.38         314.54         1052.3           8         Week_4 wet Litter         214.49         67.40         34.38         314.54         1052.3           9         Week_4 wet Litter         107.58         47.58         29.21         34.38         314.54         1052.3           10         Week_4 wet Litter         107.58         47.58         29.21         34.38         314.54         1052.3           11         Week_5 Dry Litter         107.58         47.58         28.33         472.81         2201.3           12         Week_5 Dry Litter         28.03         472.81         2201.3         28.14           13         Week_5 Dry Litter         28.64         472.81         2201.3         28.76           14         Week_5 Dry Litter         39.25         41.61         28.76         47.61         28.76           15         Week_5 Wet Litter         Week_5 Caecal_excreta         39.25         41.61         28.76           17         Week_5 Caecal_excreta         39.25         41.61         1667.27         1667.27	ഹ	Week_4_Dry Litter					100.68	382.50
7         Week-4_wet Litter         90.79         35.21         34.38         314.54         105.24           8         Week-4_wet Litter         214.49         67.40         35.11         31.35         1185           9         Week-4_wet Litter         107.58         47.58         29.21         517.74         1361.           10         Week-4_wet Litter         107.58         47.58         29.21         517.74         1361.           11         Week-5_Dry Litter         107.58         47.58         28.11         28.11         201.           12         Week-5_Dry Litter         Neek-5_Dry Litter         28.83         472.81         2201.           13         Week-5_Wet Litter         28.65         39.25         41.61         28.76           14         Week-5_Wet Litter         39.25         41.61         28.76         201.           16         Week-5_Wet Litter         39.25         41.61         28.76         41.61           17         Week-5_Wet Litter         39.25         41.61         1667.27         1667.27	9	Week_4_intermediate litter					414.18	1477.82
8         Week-4_Wet Litter         214.49         67.40         611.85           9         Week-4_Wet Litter         107.58         47.58         29.21         517.74         1361.3           10         Week-4_Wet Litter         107.58         47.58         29.21         517.74         1361.3           11         Week-5_Dry Litter         107.58         47.58         28.33         472.81         2201.3           12         Week-5_Dry Litter         Neek-5_Dry Litter         28.33         472.81         2201.3           13         Week-5_Wet Litter         28.65         39.25         41.61         28.76           14         Week-5_Wet Litter         39.25         41.61         28.76         201.3           15         Week-5_Wet Litter         39.25         41.61         28.76         28.76           17         Week-5_Wet Litter         Mixed         39.25         41.61         1667.27	2	Week_4_Wet Litter		90.79	35.21	34.38	314.54	1052.42
9         Week-4_Wet Litter         107.58         47.58         29.21         517.74         1361           10         Week-4_Normal Excreta         107.58         47.58         29.21         517.74         1361           11         Week-5_Dry Litter         28.83         472.81         23.11         23.11           12         Week-5_Dry Litter         28.83         472.81         2201           13         Week-5_Ory Litter         28.65         472.81         2201           14         Week-5_Wet Litter         39.25         41.61         28.76           15         Week-5_Wet Litter         39.25         41.61         28.76           17         Week-5_Wet Litter Mixed         39.25         41.61         28.76           18         Week-5_Cacal excreta         1667.27         1667.27	∞	Week_4_Wet Litter	214.49	67.40			611.85	
10         Week_4_Normal Excreta         28.11           11         Week_5_Dry Litter         28.13           12         Week_5_Dry Litter         28.83           13         Week_5_Dry Litter         472.81         2201.           14         Week_5_Wet Litter         8.83         472.81         2201.           15         Week_5_Wet Litter         8.76         8.76         8.76           16         Week_5_Wet Litter         39.25         41.61         1.61           17         Week_5_Wet Litter_Mixed         39.25         41.61         1.667.27	6	Week_4_Wet Litter	107.58	47.58	29.21		517.74	1361.36
11       Week_S_Dry Litter       28.11         12       Week_S_Dry Litter       28.33         13       Week_S_Dry Litter       472.81       2201.         14       Week_S_Wet Litter       28.76       28.76         15       Week_S_Wet Litter       39.25       41.61       21.61         17       Week_S_Wet Litter_Mixed       39.25       41.61       16.         18       Week_S_Caccal_excreta       1667.27       1667.27	10	Week_4_Normal Excreta						
12     Week_5_Dry Litter     28.83     472.81     2201       13     Week_5_Dry Litter     28.76     28.76       14     Week_5_Wet Litter     28.76     28.76       15     Week_5_Wet Litter     39.25     41.61       16     Week_5_Wet Litter     39.25     41.61       17     Week_5_Wet Litter Mixed     39.25     41.61       18     Week_5_Caecal excreta     1667.27	11	Week_5_Dry Litter					28.11	
13       Week_5_Dry Litter       28.76         14       Week_5_Wet Litter       28.76         15       Week_5_Wet Litter       39.25       41.61         16       Week_5_Wet Litter       39.25       41.61         17       Week_5_Wet Litter_Mixed       36.25       1667.27         18       Week_5_Caecal_excreta       1667.27       1667.27	12	Week_5_Dry Litter			28.83		472.81	2201.39
14     Week_5_Wet Litter     28.76       15     Week_5_Wet Litter     41.61       16     Week_5_Wet_Litter     41.61       17     Week_5_Wet_Litter_Mixed     1667.27	13	Week_5_Dry Litter						
15     Week_5_Wet Litter     39.25     41.61       16     Week_5_Wet Litter     17     Week_5_Wet_Litter_Mixed       18     Week_5_Caecal_excreta     1667.27	14	Week_5_Wet Litter					28.76	
16 Week_5_Wet Litter 17 Week_5_Wet_Litter_Mixed 18 Week_5_Caecal_excreta	15	Week_5_Wet Litter			39.25		41.61	
17 Week_5_Wet_Litter_Mixed 18 Week_5_Caecal_excreta 1667.27	16	Week_5_Wet Litter						
18 Week_5_Caecal_excreta 1667.27	17	Week_5_Wet_Litter_Mixed						
	18	Week_5_Caecal_excreta					1667.27	

₽	Sample group ID	Nonana	Butanoic acid, I methylpropy
			ester
1	Week_3_Dry Litter	5.08	
2	Week_3_Wet Litter		
ŝ	Week_3_Normal Excreta		
4	Week_4_Dry Litter		
ъ	Week_4_Dry Litter		
9	Week_4_intermediate litter		
7	Week_4_Wet Litter		
∞	Week_4_Wet Litter		
6	Week_4_Wet Litter		
10	Week_4_Normal Excreta		
11	Week_5_Dry Litter	2.15	
12	Week_5_Dry Litter		
13	Week_5_Dry Litter	1.11	
14	Week_5_Wet Litter		
15	Week_5_Wet Litter		
16	Week_5_Wet Litter		6.37
17	Week_5_Wet_Litter_Mixed		26.36
18	Week 5 Caecal excreta		

## Table A. 15. continued

# Table A. 16. VSC and ammonia emission rates (ng/m²/s) from a laboratory pen trial: gas concentrations measured using TD-GC-SCD and TD-GC-NCD

## Appendix L. Dataset of emissions and litter conditions from a laboratory pen (PTR-TofMS)

## Including:

Table A. 17.	Laboratory pen trial litter conditions, PTR-TofMS
	sample descriptions and instrument temperatures
Table A. 18.	Emission rates (ng/m²/s) from a laboratory pen
	trial: gas concentrations measured using
	PTR-TofMS

	Type	Moisture content (%)	Aw	Hd	Litter temperature (°C)	PTR-TofMS inlet Temperature	PTR-TofMS drift Temperature	Equivalent Litter Sample from TD- GC-MS and TD-GC-SCD analysis (Table A. 15Table A. 16)
	Dry Litter	7.05	0.491	5.92	25.0	130	80	
	Dry Litter	7.60	0.492	6.16	25.0	130	80	
	Dry Litter	22.4	0.837	6.03	25.0	130	80	
	Wet Litter	18.3	0.878	6.08	25.0	130	80	
	Wet Litter	43.5	0.988	6.35	25.0	130	80	
	Wet Litter	31.3	0.963	5.92	23.0	130	80	
	Normal Excreta	63.7	0.987	5.91	25.0	130	80	
	Dry Litter	18.1	0.809	6.09	23.2	130	80	1
	Dry Litter	18.6	0.802	6.24	27.0	130	80	
	Dry Litter	19.6	0.845	6.15	25.0	130	80	
	Wet Litter	61.4	0.996	7.21	27.5	130	80	2
	Wet Litter	64.9	0.975	6.70	28.5	130	80	
	Wet Litter	54.2	0.989	7.68	27.9	130	80	
	Normal Excreta	71.6	0.983	6.44	25.0	130	80	£
	Normal Excreta	77.5	0.992	6.84	25.0	130	80	
	Wet Excreta	76.4	0.989	5.00	25.0	130	80	
	Dry Litter	13.1	0.733	6.15	24.2	130	80	4
	Dry Litter	25.9	0.840	6.85	24.3	130	80	5
	Dry Litter	19.3	0.820	6.27	25.5	120	06	
Ľ	itermediate Litter	38.8	0.958	6.72	26.2	120	06	6
	Wet Litter	65.4	0.981	6.89	23.8	130	80	7
	Wet Litter	69.7	0.988	5.41	23.7	130	80	8
	Wet Litter	51.4	0.943	7.31	27.5	120	06	6
	Normal Excreta	72.7	0.997	5.27	25.0	120	06	10
	Dry Litter	21.7	0.822	6.70	24.3	120	90	11
	Dry Litter	28.1	0.915	7.75	26.2	120	06	12
	Dry Litter	16.7	0.755	6.58	25.3	120	90	13
	Wet Litter	64.6	0.971	5.06	24.2	120	06	14
	Wet Litter	67.5	0.982	5.08	24.2	120	90	15
	Wet Litter	59.3	0.966	5.53	25.6	120	06	16
	Normal Excreta	76.8	0.987	5.26	25.0	120	90	
	Normal Excreta	76.2	066.0	5.4	25.0	120	90	
Š	ection Wet Litter	58.2	0.974	7.61	25.6	120	06	
Ň	ection Wet Litter	62.1	0.975	7.82	25.6	120	90	
ć	<b>Mixed Wet Litter</b>	59.4	0.980	6.13	25.6	120	06	
~	<b>Mixed Wet Litter</b>	69.2	0.988	6.29	25.6	120	06	17
	Caeral Evereta	86 G	200 0	с 11	75.0	120	OD	18

Table A. 17. Laboratory pen trial litter conditions, PTR-TofMS sample descriptions and instrument temperatures

Je	Sample Description	Replicate	Bird age	Week
	Week_2_Dry Litter	1	13	2
	Week_2_Dry Litter	2	14	2
	Week_2_Dry Litter	ŝ	14	2
	Week_2_Wet Litter	1	13	2
	Week_2_Wet Litter	2	14	2
	Week_2_Wet Litter	ŝ	14	2
-	Neek_2_Normal Excreta	1	13	2
	Week_3_Dry Litter	1	19	ŝ
	Week_3_Dry Litter	2	20	ŝ
	Week_3_Dry Litter	æ	20	ŝ
	Week_3_Wet Litter	1	19	ŝ
	Week_3_Wet Litter	2	20	ŝ
	Week_3_Wet Litter	ŝ	20	ŝ
-	Neek_3_Normal Excreta	1	19	£
-	Neek_3_Normal Excreta	2	20	ŝ
	Week_3_Wet Excreta	Ч	20	æ
	Week_4_Dry Litter	1	26	4
	Week_4_Dry Litter	2	26	4
	Week_4_Dry Litter	ŝ	27	4
3	eek_4_intermediate litter	1	27	4
	Week_4_Wet Litter	1	26	4
	Week_4_Wet Litter	2	26	4
	Week_4_Wet Litter	ŝ	27	4
-	Neek_4_Normal Excreta	1	27	4
	Week_5_Dry Litter	1	33	ß
	Week_5_Dry Litter	2	33	S
	Week_5_Dry Litter	£	34	ß
	Week_5_Wet Litter	1	33	ß
	Week_5_Wet Litter	2	33	ß
	Week_5_Wet Litter	ŝ	34	ß
-	Neek_5_Normal Excreta	1	33	ß
-	Neek_5_Normal Excreta	2	34	ß
Š	eek_5_Wet_Litter_section	1	33	ß
Š	eek_5_Wet_Litter_section	2	34	ß
3	eek_5_Wet_Litter_Mixed	1	34	ъ
3	eek_5_Wet_Litter_Mixed	2	34	5
-	Week_5_Caecal_excreta	1	33	2

ated with c	ompound	d masses															
34.988	41.039	42.034	43.018	43.054	43.000	45.034	46.065	47.013	47.049	49.011	55.054	57.032	57.070	59.049	60.044	60.081	61.028
33.988	40.031	41.027	42.011	42.047	42.000	44.026	45.058	46.006	46.042	48.003	54.047	56.025	56.063	58.042	59.037	59.074	60.021
0.03	17.66	1.06	175.48	42.41	217.80	73.09	0.12	5.85	29.66	5.99	16.88	3.86	12.01	72.14	2.98	3.95	505.13
0.02	10.30		216.74	15.52	232.18	20.53	0.02	6.47	12.95	0.35	11.99	2.97	10.54	31.89	1.35	1.70	484.41
0.06	26.24	0.05	797.94	36.45	834.14	110.11	0.10	10.04	25.27	1.00	35.98	11.43	30.29	86.54	3.76	7.36	1487.75
0.10	36.99	2.00	325.64	86.35	411.80	123.66	0.61	1.64	30.96	15.76	53.16	2.45	55.95	138.52	0.86	34.17	197.20
	36.09	1.75	748.19	118.52	866.39	243.47	0.12		130.56	6.15	122.42	6.91	58.00	340.53	13.66	1.54	705.79
0.10	28.68		699.25	56.50	755.51	137.74		7.65	16.28	1.89	45.14	9.72	28.08	92.59	4.13	3.01	999.44
0.66	39.98	1.99	435.16	102.60	537.54	308.05	0.57		379.21	7.10	70.55		82.71	113.75	-0.38	98.26	958.02
0.05	40.88	1.86	1086.45	61.73	1147.83	124.17	0.24	7.79	15.72	1.24	41.99	10.62	28.99	121.17	3.60	25.75	1440.37
0.08	60.92	5.06	1400.11	88.72	1488.38	69.63	1.49	9.41	2.45	10.54	52.94	8.49	36.18	595.07	8.39	116.30	1155.37
0.13	51.90	2.77	1238.87	69.08	1307.56	82.93	0.98	12.62	22.55	4.25	35.45	9.41	34.05	271.70	8.76	38.34	1462.93
0.31	7.32	7.48	75.50	9.96	85.43	29.35	4.79	21.51	1.92	10.68	18.63	1.34	4.94	122.67		479.16	87.30
11.50	48.00	18.89	82.25	57.13	139.30	175.02	21.62	32.82	195.12	90.80	22.08	1.43	53.90	181.54		2330.61	161.94
2.30	14.81	10.03	99.57	22.32	121.84	40.33	13.41	13.16	12.43	69.38	30.25	1.16	14.27	278.08		1327.82	66.58
2.81	152.94	10.43	905.65	158.94	1064.19	1220.57	1.29		651.79	15.86	55.07		436.26	352.58		493.73	1787.41
	14.47		187.62	34.79	222.33	273.00	6.75	3.72	154.70	1.52	124.86	2.09	4.88	126.35		69.37	244.02
0.29	33.01		786.85	74.33	860.91	954.64	1.01	28.05	367.00	3.69	148.07	6.01	11.71	501.02	19.18	14.04	1568.92
0.04	38.39	10.24	948.82	72.02	1020.52	38.29	2.66	5.43	7.01	16.41	38.11	13.05	26.78	559.54	4.22	214.70	1022.73
0.28	15.08	10.14	289.89	25.25	315.04	19.07	13.22	15.61	1.67	13.98	13.55	0.62	10.70	419.29		582.49	118.85
	27.57	8.31	465.14	49.14	514.11	40.49	3.81	3.12	1.30	16.92	27.20	1.95	13.56	779.37	13.64	228.25	164.23
0.30	20.75	18.64	206.26	22.67	228.85	23.23	27.41	12.92	2.56	34.37	19.38	0.28	25.15	407.51		764.23	55.92
2.89	125.78	8.85	314.14	114.97	428.91	210.44	8.85	4.70	162.75	39.63	57.59		444.42	312.31		810.08	250.59
36.67	179.33	6.76	188.20	470.20	657.83	526.66	2.82		1225.31	468.35	100.27		469.38	164.72		221.88	233.48
0.72	122.08	19.82	185.74	59.62	245.25	90.33	19.41	34.89	44.53	25.27	193.86		412.95	531.20		1371.39	53.96
0.54	93.95	0.81	438.33	204.63	642.62	255.02	5.70		802.62	17.99	159.37	5.79	48.49	646.82	27.04	36.49	972.53
0.19	68.41	6.62	968.19	108.50	1076.32	50.11	1.34	4.80	28.49	14.63	22.96	3.28	47.77	511.01	9.31	109.70	756.34
0.14	49.52	34.89	575.79	61.28	636.86	42.70	13.97	12.49	1.46	25.58	26.45		73.24	691.34		1314.57	98.03
0.12	66.76	14.23	1188.82	128.20	1316.58	46.45	1.57	5.22	10.07	36.50	63.21	2.06	66.58	836.71	13.06	183.25	643.24
0.20	749.55	31.19	1600.33	299.02	1898.61	120.59	1.28		425.28	3.63	241.42		3824.64	285.77	14.96	5.21	3211.67
0.62	1080.80	46.85	4501.02	401.74	4901.17	234.32	8.07		509.95	27.67	374.56		5231.02	571.90	17.29	134.24	6432.36
6.16	714.07	32.23	2997.57	339.15	3335.59	263.33	2.46		1289.17	236.67	330.81		3902.43	525.87	18.86	37.90	3613.76
2.12	331.53	8.77	1084.93	435.92	1520.09	400.87	2.43		2238.18	33.40	192.72		1143.43	607.55	23.72	11.70	2344.35
2.17	233.55	8.18	2057.25	575.03	2631.11	353.63	1.98		2095.49	24.16	247.94	43.46	108.32	927.49	36.94	17.88	4088.66
1.05	371.68	51.49	120.98	77.08	197.95	123.00	23.76	52.87	23.73	65.94	439.80		2003.82	825.89		2047.47	213.54
2.05	24.64	59.33	108.34	31.25	139.53	105.82	17.44	61.26	13.54	4.73	56.49	4.84	39.67	106.56	6.58	201.18	433.02
14.08	2437.37	104.66	115.31	664.08	778.62	315.05	7.48		458.81	422.08	869.97	18.11	7327.02	414.40		66.606	295.36
136.15	3448.04	159.29	1064.06	1152.55	2215.06	302.92	4.36		846.36	1597.50	651.40		10483.63	412.90	15.87	160.29	3647.36
201.47	1464.11	44.14	772.27	2125.65	2895.34	947.79	16.74		2354.25	565.77	201.12		1896.27	589.12		2573.61	2273.52

laboratory pen trial: gas concentrations measured using PTR-TofMS

irom a lá	
ng/m²/s) t	_
n rates (ı	
Emissio	
18.	
Table A.	

Refer t	o Appendix I for comp	ounds possibl	ly associa	ted with a
		TOF protonated mass	33.033	34.988
Sample ID	Sample Description	Molecular mass	32.026	33.988
1	Week_2_Dry Litter		114.08	0.03
2	Week_2_Dry Litter		60.64	0.02
ŝ	Week_2_Dry Litter		217.53	0.06
4	Week_2_Wet Litter		1200.04	0.10
5	Week_2_Wet Litter		1949.62	
9	Week_2_Wet Litter		331.61	0.10
7	Week_2_Normal Excreta		522.73	0.66
00	Week_3_Dry Litter		340.27	0.05
6	Week_3_Dry Litter		1101.07	0.08
10	Week_3_Dry Litter		375.06	0.13
11	Week_3_Wet Litter		1250.58	0.31
12	Week_3_Wet Litter		2327.36	11.50
13	Week_3_Wet Litter		2975.20	2.30
14	Week_3_Normal Excreta		1831.51	2.81
15	Week_3_Normal Excreta		581.73	
16	Week_3_Wet Excreta		450.12	0.29
17	Week_4_Dry Litter		639.64	0.04
18	Week_4_Dry Litter		785.57	0.28
19	Week_4_Dry Litter		817.03	
20	Week_4_intermediate litter		1653.46	0.30
21	Week_4_Wet Litter		1909.70	2.89
22	Week_4_Wet Litter		1138.45	36.67
23	Week_4_Wet Litter		3244.99	0.72
24	Week_4_Normal Excreta		919.30	0.54
25	Week_5_Dry Litter		321.10	0.19
26	Week_5_Dry Litter		1698.58	0.14
27	Week_5_Dry Litter		561.18	0.12
28	Week_5_Wet Litter		1122.96	0.20
29	Week_5_Wet Litter		1808.98	0.62
30	Week_5_Wet Litter		1582.05	6.16
31	Week_5_Normal Excreta		807.97	2.12
32	Week_5_Normal Excreta		1099.21	2.17
33	Week_5_Wet_Litter_section		336.79	1.05
34	Week_5_Wet_Litter_section		45.74	2.05
35	Week_5_Wet_Litter_Mixed		1861.16	14.08
36	Week_5_Wet_Litter_Mixed		2519.65	136.15
37	Week_5_Caecal_excreta		3893.05	201.47

Table <i>∔</i>	A. 18. continued																							
		TOF protonated mass	61.065	63.026	68.050	69.070	71.049	73.065	75.044	75.080	79.054	78.967	80.049	81.070	82.065	83.060 8	83.086	34.081	85.065	87.044	87.080	37.117 8	9.060 8	960.6
Sample ID	Sample Description	Molecular mass	60.058	62.019	67.042	68.063	70.042	72.058	74.037	74.073	78.047	77.960	79.042	80.063	81.058	82.053 8	82.078	33.074	84.058	86.037	86.073	36.110 8	8.052 8	8.089
1	Week_2_Dry Litter		6.81	3.95	0.37	3.73	28.57	8.56	19.06	0.85	1.33	0.02	4.09	2.52	1.09	0.91	5.22	0.47	41.13	16.18	0.85	0.42 1	74.86	9.26
2	Week_2_Dry Litter		5.95	3.02	0.34	4.31	67.18	37.56	20.40		1.12		4.61	3.07	0.57	1.04	6.74	0.59	33.79	54.74	4.95	Ч	66.45	9.51
ŝ	Week_2_Dry Litter			10.51	1.22	14.16	219.15	73.33	72.17		7.23		23.30	7.42	2.69	2.51	14.61	1.33	119.40	96.95	13.83	2	49.56	29.64
4	Week_2_Wet Litter		5.49	19.83	1.47	16.79	341.34	70.08	23.51		2.40	3.49	21.83	24.20	5.40	2.50	13.07	1.30	146.99	92.60	23.08	0.92 5	47.90	33.98
5	Week_2_Wet Litter		8.00	36.62	2.36	29.22	735.54	240.42	68.92		8.05	3.24	60.83	15.31	8.18	2.67	8.81	1.31	163.22	249.31	49.06	11	579.99	
9	Week_2_Wet Litter		2.60	7.51	1.09	15.32	384.62	84.99	53.20		5.49		11.89	6.14	2.38	3.24	15.61	1.49	146.80	141.52	23.53	8	39.89	
7	Week_2_Normal Excreta		12.75	21.89	0.84	7.78	107.92	567.36	27.44		4.72		35.79	0.02	10.69	1.40	1.99	0.56	10.40	43.41	11.53	4	10.08	23.04
8	Week_3_Dry Litter			12.38	1.41	19.31	669.62	106.24	67.32		7.91	0.11	15.25	10.53	4.49	0.04	18.77	1.47	137.82	190.50	23.60	1	356.21	
6	Week_3_Dry Litter		7.02	21.54	2.62	15.97	1321.38	314.23	68.11	0.03	7.31	0.57	71.60	8.85	8.32	1.74	3.71	0.91	111.21	205.19	43.72	23	367.45	
10	Week_3_Dry Litter			99.10	1.62	16.30	886.13	136.33	71.31		6.70	0.17	19.92	6.18	4.92	1.33	3.41	0.67	109.68	153.66	29.98	1(	582.36	
11	Week_3_Wet Litter		18.45	49.27	2.07	8.36	54.53	53.35	7.30	0.32	2.30	4.41	98.53	5.83	4.38	1.61	1.26	1.70	10.24	82.78	7.13	0.12 8	35.40	0.05
12	Week_3_Wet Litter		87.40	88.97	3.35	12.53	53.89	472.98	15.48	0.93	3.38	23.52	108.90	2.20	13.63	3.91	2.01	3.97	9.76	74.30	6.94	0.94 8	30.91	1.07
13	Week_3_Wet Litter		47.51	76.62	3.23	14.88	88.60	209.25	10.73	0.57	3.37	7.36	191.62	5.09	12.16	2.48	0.96	1.99	17.39	97.18	13.46	0.06 1	36.99	
14	Week_3_Normal Excreta		38.32	46.77	3.41	73.20	526.86	1095.82	66.06	1.33	4.68	5.65	152.42	1.13	42.09	5.16	2.05	2.25	15.75	106.28	30.14	1	287.48	36.61
15	Week_3_Normal Excreta		14.04	11.15	0.81	7.60	131.27	16.13	8.86	0.19	2.01		19.27		20.06	0.50	5.75	0.80	15.77	250.15	26.82	2	38.65	L5.48
16	Week_3_Wet Excreta		50.59	14.56	1.39	15.44	302.37	35.12	31.51	0.95	4.89	0.86	1.93		9.76	0.42	6.32	1.06	50.37	.082.25	101.60	S	67.71	32.40
17	Week_4_Dry Litter		6.00	18.18	3.16	8.01	681.72	99.28	95.64		6.44	0.66	216.63	2.59	5.29	1.36	1.40	0.54	88.22	97.15	13.65	11	252.38	17.78
18	Week_4_Dry Litter		23.06	10.96	3.04	6.50	277.24	85.81	9.10	0.19	2.59	2.89	198.76	3.81	4.45	1.24	0.86	1.27	9.53	171.20	19.92	4	37.87	20.42
19	Week_4_Dry Litter		11.41	14.53	2.52	7.81	441.48	120.87	12.68	-0.07	3.47	0.29	181.01	0.48	4.88	1.52	0.40	0.52	34.81	166.00	17.74	9	67.46	l6.23
20	Week_4_intermediate litter		27.42	17.89	3.79	9.39	178.16	346.58	15.88	0.12	2.54	3.83	241.53	0.07	5.65	1.64	1.82	1.78	12.30	198.30	15.86	2	45.45	l2.48
21	Week_4_Wet Litter		32.02	167.60	2.88	15.93	260.17	2152.26	36.39	3.01	1.49	12.42	43.27	2.12	9.64	3.79	0.53	1.38	17.05	121.40	16.16	-0.06 4	08.56	l6.18
22	Week_4_Wet Litter		13.17	213.36	2.84	11.28	204.45	1451.84	33.99	2.77	1.95	52.98	12.38	2.10	31.90	6.10		0.79	10.05	101.46	11.19	£	54.04	19.03
23	Week_4_Wet Litter		48.41	102.57	4.68	16.15	145.68	6805.77	21.67	17.85	3.17	29.36	111.16	4.80	9.58	5.10	1.82	3.49	8.46	348.48	29.97	0.06 1	93.69	6.05
24	Week_4_Normal Excreta		28.46	51.83	1.93	11.14	45.60	176.45	60.59		3.98	0.36	11.61	0.39	30.03	3.04	4.92	0.95	8.09	102.04	11.65	-0.36	98.77	5.70
25	Week_5_Dry Litter		10.38	13.89	2.24	7.57	799.25	314.61	36.89	0.03	2.82	0.08	75.81	2.05	3.45	0.75	0.94	0.42	33.75	121.70	8.32	0.16 12	260.48	51.97
26	Week_5_Dry Litter		45.67	43.58	5.82	13.47	532.66	496.80	9.48	1.28	4.80	16.18	227.13	33.41	8.55	2.74	2.11	2.52	10.70	500.09	27.48	2.02 7	50.08	50.87
27	Week_5_Dry Litter		11.14	26.46	3.61	9.94	1179.06	562.54	31.48	0.31	4.65	2.15	117.41	5.36	4.81	1.33	0.82	0.68	52.01	130.92	11.99	0.15 2(	033.61	31.31
28	Week_5_Wet Litter		1.03	60.68	4.67	20.92	775.75	7603.16	204.21	19.68	4.03	14.20	8.62	1.71	18.67	2.88	1.90	1.76	8.38	574.39	12.35	2.55 18	388.34	97.61
29	Week_5_Wet Litter			83.27	5.58	32.14	3278.13	9958.50	381.28	31.77	8.92	19.16	20.61	5.13	21.01	4.07	1.58	2.46	22.50	752.24	21.44	2.99 59	914.38 3	39.90
30	Week_5_Wet Litter			229.55	4.27	34.41	2154.44	4317.69	363.68	31.74	54.51	43.53	21.59	7.29	19.04	6.30	1.91	1.62	31.96	895.62	25.47	0.08 39	994.70	74.48
31	Week_5_Normal Excreta		46.64	59.47	2.94	12.36	106.71	1977.09	63.07	3.60	7.36	3.45	5.75	0.52	58.44	5.54	6.43	0.99	5.92	280.23	14.74	0.05 3	14.61	l6.33
32	Week_5_Normal Excreta		19.21	90.84	3.96	22.86	448.29	364.02	289.47	6.19	21.13	0.23	5.04	3.19	77.04	6.78	5.75	1.39	15.96 1	.382.60	25.14	2.41 19	954.94	52.35
33	Week_5_Wet_Litter_section		73.03	45.10	3.37	12.40	55.53	16375.21	35.40	47.77	5.17	26.87	26.72	34.32	8.59	3.13	3.38	4.87	9.60	212.40	34.12	1.42 (	58.66	7.81
34	Week_5_Wet_Litter_section		37.90	157.08	4.37	16.06	49.53	1737.22	43.15	4.34	14.32	117.71	18.19	16.72	8.15	5.80	6.37	9.99	17.98	73.09	9.98	3.31 3	39.42	t2.03
35	Week_5_Wet_Litter_Mixed		37.95	378.35	5.20	15.24	51.20	13026.07	95.13	71.94	7.96	129.70	48.79	16.11	19.69	6.26	2.51	3.27	9.05	61.55	40.30	Ч	90.27	7.77
36	Week_5_Wet_Litter_Mixed			533.31	6.60	20.49	166.93	11716.48	604.51	41.24	12.86	50.59	40.12	23.77	33.83	11.50	1.93	3.44	15.70	82.15	30.31	0.02 23	363.30	17.61
37	Week_5_Caecal_excreta		116.41	298.50	13.87	44.50	85.53	333.70	80.17		7.27	1.38	5.83		37.86	3.57	4.38	1.49	9.82	44.84	5.64	0.13 1	62.66	3.62

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Table A	. 18. continued																						
		TOF protonated mass	91.058	93.070	94.998	95.016	95.049	101.060	101.096 10	33.075 105	.070 107	049 107.	086 109.	965 112.	076 112.	112 113.0	060 113	.096 114	4.030 11	5.075 115	112 11	.148 11	7.091
Sample ID	Sample Description	Molecular mass	90.050	92.063	93.991	94.013	94.042	100.052	100.089 10	02.068 104	.063 106	042 106.	078 108.	111.	068 111.	05 112.0	112	.089 113	3.030 11/	4.068 114	.105 11′	1.141 11	6.084
1	Week_2_Dry Litter		0.66	1.21	0.16	3.12	0.01	1.48	0.57	69.6		0.0	60	0	10 0.0	9.0 0.6	6 0.	31 1.	.69	L.04 0	.16		1.19
2	Week_2_Dry Litter		1.33	0.14	0.82	1.46	0.85	2.15	0.48	7.11 0.	36 1.	92 0.0	1.4	0	10 0.0	2 0.5	6 0.	22 0.	.60 C	.59 0	52		1.18
£	Week_2_Dry Litter		4.38	0.80	2.06	6.47	0.98	6.70	1.50	27.10 1.	18 7.	27 0.3	28 3.3	6 0.3	28 0.1	7 1.6	4	83 1.	.83 1	L.63 2	29		3.59
4	Week_2_Wet Litter		4.96	3.09	36.80	4.02	2.31	5.96	5.68	17.89 3.	38 5.	21 1.7	78 5.1	3 0.	<u>.0</u>	1 2.8	3 1.	18 5.	.61 3	3.86 6	41 0	.08	2.27
5	Week_2_Wet Litter		13.06	3.57	55.98	2.53	2.11	12.32	6.51	36.73 4.	63 6.	38 2.9	9.7 9.6	2 0.3	31 1.0	2 3.8	2 1.	17 11	1.87 3	3.83 8	.63		4.66
9	Week_2_Wet Litter		6.21	1.62	3.03	5.49	2.34	7.88	2.58	26.84 1.	68 5.	31 0.(	5.4 5.4	1 0.	30 0.2	7 1.8	9 1.	13 2.	.74 1	.85 3	51		4.16
7	Week_2_Normal Excreta		4.07	0.51	1.08	5.71	2.90	2.01	1.13	9.89 1.	44 2.	72 0.3	26 0.8	9.0	32 0.3	9 2.4	8	Ŀ.	.02 1	l.16 0	66		4.41
8	Week_3_Dry Litter		15.04	2.21	5.88	4.80	4.25	5.19	3.81	31.87 2.	15 4.	59 2.4	47 4.2	8	88 0.3	3 1.2	7 1.	73 3.	.51 2	2.03 3	21		3.81
6	Week_3_Dry Litter		20.29	1.90	11.04	8.08	4.66	6.67	9.15	39.94 12	.65 1.	81 4.:	14 4.6	7 0.0	51 0.2	9 1.4	4 1.	67 6.	.08 2	2.12 8	.06		2.93
10	Week_3_Dry Litter		12.85	1.38	6.65	5.80	2.74	6.21	3.02	30.10 3.	32 1.	11 1.9	3.0	2 0.	24 0.3	2 0.8	9 1.	02 4.	.01 10	L.63 3	12		1.76
11	Week_3_Wet Litter		1.54	8.97	17.68	0.09	9.35	8.74	2.23	3.28 4.	72 2.	50 6.(	07 5.4	7 1.	72 0.0	8 2.0	4 2.	14 7.	.71 3	3.94 0	05 0	.48	1.71
12	Week_3_Wet Litter		2.29	20.44	77.91	4.86	7.47	11.26	2.20	6.94 4.	50 4.	16 5.8	30 6.7	7 3.3	34 0.5	7 3.5	7 1.	93 9.	.77 6	5.63 0	05 1	.57	4.24
13	Week_3_Wet Litter		1.98	7.94	37.17	13.36	5.54	8.57	4.22	3.94 3.	18 1.	58 2.8	32 4.5	1 1.	56 0.3	9 1.9	4 1.	39 17	7.32 4	0 00.1	12 0	.55	2.03
14	Week_3_Normal Excreta		19.24	7.03	17.27	5.50	18.48	8.52	1.68	31.41 4.	91 2.	16 1.5	53 6.3	7 1.:	1.3 1.3	4 4.2	4	85 4.	.50 3	3.26 4	72		.0.15
15	Week_3_Normal Excreta		2.25	0.76	0.79	7.33	0.30	0.09	1.83	2.43 0.	46 6.	33	0.7	0.0	52 0.7	2 1.1	5	74 3.	.30 0	.93 0	11		0.34
16	Week_3_Wet Excreta		4.99	3.48	6.24	33.39		6.06	0.49	9.58 1.	15 1.	37 0.3	36 2.6	3 0.9	33 0.5	1 1.0	5 0.	92 2.	.42 2	2.16 0	17		1.38
17	Week_4_Dry Litter		9.10	1.39	7.28	12.66	1.09	7.90	1.38	31.40 3.	98 2.	46 8.3	19 3.8	3 0.	18 0.C	8 1.6	1 0.	27 3.	.00	2.01 2	31		1.67
18	Week_4_Dry Litter		3.60	6.32	11.76	12.19	5.63	4.27	2.69	4.22 3.	04 1.	11 3.:	17 5.0	8 0.0	5 <b>0</b> 0.3	0 1.7	7 0.	57 3.	.83 2	2.13 2	50		1.42
19	Week_4_Dry Litter		4.79	1.21	3.51	8.81	1.89	7.34	1.88	6.70 2.	44 1.	3.5	53 3.6	8 0.1	51 0.0	7 1.2	3	24 5.	.15 1	L.70 1	91		0.71
20	Week_4_intermediate litter		2.91	9.38	10.30	7.01	7.73	4.97	2.26	4.78 3.	01 2.	20 5.(	9 6.4	6 1.	57 0.2	3 2.5	5 0.	83 6.	.23 3	3.01 0	82 0	.28	2.10
21	Week_4_Wet Litter		4.33	7.63	28.65	11.05	1.22	7.26	0.89	27.97 2.	28 1.	57 3.3	32 4.0	7 0.3	33 0.4	7 2.9	3.0.	10 11	1.13 6	5.13 2	85		9.25
22	Week_4_Wet Litter		4.14	14.34	116.65	19.17		3.64	0.61	1.73 1.	45 0.	39 0.4	42 3.4	.0 6	1.1 1.1	1 2.6	4 0.	01 15	5.24 3	3.41 0	.82 -0	.21	6.44
23	Week_4_Wet Litter		3.49	19.92	49.74	0.85	11.64	6.35	3.12	L5.46 4.	48 2.	24 4.4	40 6.8	2 1.9	9.0 0.6	5 4.3	5 0.	32 12	2.71 6	6.39 2	07 0	.10	0.85
24	Week_4_Normal Excreta		2.56	0.94	3.06	13.00	0.90	3.98	1.75	4.95 1.	15 2.	32 0.:	19 3.1	4 0.1	52 1.3	7 1.3	4	25 13	3.99 3	3.02 0	10		0.98
25	Week_5_Dry Litter		9.41	0.77	2.31	7.89	2.55	4.31	0.97	22.18 1.	65 0.	58 1.7	77 3.8	2 0.3	39 0.1	1 0.9	8	31 3.	.17 1	l.49 1	58		1.38
26	Week_5_Dry Litter		6.49	9.29	46.76		17.35	6.23	9.02	8.39 4.	65 2.	94 9.2	24 12.	56 2.:	1 0.2	9.3.9	4	87 7.	.91 4	l.09 2	52		2.62
27	Week_5_Dry Litter		15.11	2.12	8.82	12.40	3.97	6.02	2.04	22.68 3.	62 1.	24 3.8	30 6.2	9 0.	57 0.2	3 1.4	4	57 2.	.61 1	1.92 2	11 0	.18	1.79
28	Week_5_Wet Litter		15.80	7.03	28.03		7.67	7.35	0.29	39.72 3.	57 1.	21 1.:	11 4.3	0.0	95 0.7	9 1.8	3.0.	67 14	1.56 4	1.29 0	32 0	.26 1	3.17
29	Week_5_Wet Litter		55.55	8.50	54.68	11.73	11.36	13.54	0.46 1	66.83 5.	29 1.	77 1.9	96 5.5	2 1.	34 0.8	4 3.3	9	62 10	0.03 7	7.07 2	11		5.68
30	Week_5_Wet Litter		67.89	14.97	110.77	19.24	6.67	14.68	0.85 1	83.23 5.	21 5.	70 8.:	16 6.9	7 1.(	1.0 1.0	3 3.9	0 2.	41 19	9.48 7	7.59 2	.78		6.83
31	Week_5_Normal Excreta		3.23	2.31	16.10	15.38	2.78	5.68	2.87	l3.37 0.	94 1.	17 0.:	12 1.8	6 0.3	31 2.5	7 0.7	5	63 8.	.22 2	2.39 0	52		1.81
32	Week_5_Normal Excreta		14.68	3.77	4.24	13.49	8.10	9.61	0.25	92.60 2.	92 2.	19 2.3	39 7.9	9.0	32 2.6	5 1.2	6 0.	68 36	5.51 5	5.41 0	17		4.48
33	Week_5_Wet_Litter_section		3.69	16.09	142.03	1.47	22.53	11.21	7.32	8.93 6.	80 11	69 34.	95 8.4	6 2.	t5 0.5	0 3.9	6 2.	40 6.	.12 4	1.79 5	86 0	.06	4.97
34	Week_5_Wet_Litter_section		8.30	34.09	669.88	4.01	14.37	13.50	3.32	39.48 12	.97 13.	32 40.	43 13.	52 4.0	38 2.5	2 7.4	4 2.	60 12	2.00 10	0.95 -C	.01 5	.10	.2.58
35	Week_5_Wet_Litter_Mixed		3.39	8.12	610.37		50.15	7.13	7.16	38.38 6.	30 9.	19 31.	86 7.7	9 1.	39 0.7	5 3.3	5 3.	17 5.	.73 6	5.17 18	.28	(1)	1.29
36	Week_5_Wet_Litter_Mixed		13.54	10.22	159.58	34.21	90.44	12.87	5.79 1	81.58 9.	98 7.	38 18.	73 10.	58 2.:	1.2	3 3.5	8	70 6.	.53 9	9.80	.16	Ð	7.73
37	Week_5_Caecal_excreta		15.69	0.46	0.29	20.67	19.12	10.89	0.64	t2.77 9.	46 2.	15	63.	78 0.9	91 1.3	1 2.4	.0	29 36	5.10 6	5.93 0	21 0	.28	6.86

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TOF protonated 118.065 121.065 123.044 123.081 125.060 126.971 129.091 129.127 131.107 132.081 137.133 14 mass
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Sample Description Molecular mass 117.058 120.058 122.037 122.073 124.052 125.963 128.008 128.120 130.099 131.074 136.125
Week_2_Dry Litter 0.61 0.31 0.32 1.05 0.47 0.04 0.43 0.11 3.33
Week_2_Dry Litter 0.32 0.66 0.22 0.98 0.47 0.35 0.06 0.36 0.11 3.81
Week_2_UTy Litter U.90 I.38 I.90 I.05 U.28 IU   Week_2_UTy Litter 1 20 2.55 2.79 3.40 4.31 7.75 3.79 0.62 3.1
Week_2_Wet Litter 2.45 3.17 0.03 3.63 3.43 9.36 13.15 7.14 1.01
Week_2_Wet Litter 1.12 1.86 2.45 1.97 2.04 1.61 2.10 0.45
Week_2_Normal Excreta 1.72 0.33 0.28 0.59 1.02 0.19 0.81 0.43 1.13 1.08
Week_3_Dry Litter 1.42 3.83 0.03 2.68 2.13 0.17 1.66 1.12 3.34 0.59
Week_3_Dry Litter 2.18 2.14 3.92 1.43 0.29 4.27 6.30 7.67 0.97
Week_3_Dry Litter 1.24 2.05 0.29 2.05 1.17 0.19 1.74 1.96 3.41 0.52
Week_3_Wet Litter 2.01 1.66 0.45 2.38 1.09 2.06 5.80 6.22 1.88 1.31
Week_3_Wet Litter 4.32 1.97 1.58 3.13 2.10 6.19 5.14 3.66 4.05 2.90
Week_3_Wet Litter 2.44 1.58 0.52 2.67 1.52 2.22 3.94 3.52 2.18 1.59
Week_3_Normal Excreta 5.02 6.35 2.19 1.81 4.64 2.19 6.10 8.28 4.11 2.67
Week_3_Normal Excreta 0.80 7.73 2.79 0.25 0.86 0.13 1.00 0.03 0.08 1.20
Week_3_Wet Excreta 3.60 16.44 8.66 0.39 1.18 1.21 1.23 0.48 1.15 1.20
Week_4_Dry Litter 1.03 1.07 2.45 1.19 0.32 1.51 1.52 2.22 0.50
Week_4_Dry Litter 1.42 2.07 0.79 2.37 0.97 1.54 2.76 1.92 0.79
Week_4_Dry Litter 0.48 1.21 0.09 1.71 0.28 2.58 3.39 1.18 0.44
Veek_4_intermediate litter 1.98 2.84 0.91 2.81 1.39 1.91 2.77 2.45 2.42 1.5
Week_4_Wet Litter 3.14 1.87 0.91 2.13 1.74 4.50 7.08 1.88 8.77 3.14
Week_4_Wet Litter 1.33 0.98 0.56 2.54 1.84 34.02 4.34 2.64 4.65
Week_4_Wet Litter 4.28 2.18 1.57 2.81 1.67 8.55 3.89 2.99 4.23
Week_4_Normal Excreta 1.27 5.23 3.85 2.04 1.30 1.24 1.46 0.97 0.73
Week_5_Dry Litter 0.96 2.81 0.51 2.52 0.61 0.01 1.94 2.21 1.73
Week_5_Dry Litter 2.92 5.08 0.31 7.24 1.90 4.51 3.65 3.23 5.64
Week_5_Dry Litter 1.70 5.15 4.88 1.13 2.03 3.83 6.60 3.34 0
Week_5_Wet Litter 3.94 1.78 0.42 4.23 1.91 5.34 1.27 4.80 1
Week_5_Wet Litter 6.33 3.05 0.81 4.51 2.60 7.10 3.00 2.17 12.32 2.1
Week_5_Wet Litter 10.22 4.39 0.17 6.33 3.22 25.83 3.68 2.30 22.86 3.4
Week_5_Normal Excreta 0.51 3.17 2.27 1.49 1.06 2.54 1.40 0.43 0.68 2.26
Week_5_Normal Excreta 2.72 3.58 2.43 4.67 2.24 1.47 2.11 0.83 2.39 2.39
'eek_5_Wet_Litter_section 4.76 3.51 2.40 3.42 1.34 3.37 7.61 8.96 5.00 2.97
'eek_5_Wet_Litter_section 11.69 4.07 3.94 5.66 2.51 9.88 3.01 2.52 11.49 7.2'
Veek_5_Wet_Litter_Mixed 8.79 3.35 2.59 3.40 1.56 7.20 13.36 14.31 10.18 2.74
Veek_5_Wet_Litter_Mixed 19.47 2.49 1.33 4.64 1.96 9.48 14.46 11.73 14.65 3.89
Week 5 Caeral extreta 31 67 19 50 26 35 14 38 1 55 1 16 4 74 4 88 2 75 1 4

## Table A. 18. continued