Identification and Prioritisation of Odorants within the Volatile Organic Compounds (VOC) Emissions from Tunnel Ventilated Broiler Houses in Australia

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Gavin Parcsi
School of Civil & Environmental Engineering, The University of New South Wales, Sydney, Australia

Xinguang Wang
Centre for Water & Waste Technology, The University of New South Wales, Sydney, Australia

Erin Gallagher, Neale Hudson and Mark Dunlop
Queensland Department of Primary Industries, Animal Research Division, Toowoomba, Queensland, Australia

Gautam Chattopadhyay
School of Civil & Environmental Engineering, The University of New South Wales, Sydney, Australia

Richard M. Stuetz
Centre for Water & Waste Technology, The University of New South Wales, Sydney, Australia

ABSTRACT

The continued expansion in population of established cities leads to rural encroachment, this rural encroachment results in a decline in the chief barrier against malodours, that of distance. Associated to the population growth is an increased demand upon primary industries to produce greater quantities of food stuffs to satisfy the consumers. Intensive livestock practices are one of the most effective ways to produce the quantity and consistent quality of livestock produce that is in increasing demand from the general population. However the operation of most intensive livestock operations results in an environmental impact that is often difficult to monitor and assess; that of their odour output.

The production of broilers (meat chickens) is one example of intensive livestock practice that is under increasing pressure to minimise the impact that it has upon the surrounding environment with respect to odour production.

Understanding the emissions from intensive livestock practices is the only way to develop guidelines for operators in order to minimise or at least understand the emissions of their facilities at different production cycle times.

The Australian Poultry Cooperative Research Centre (P-CRC) is funding a significant project that is investigating the odour and dust emissions from typical mechanically (tunnel) ventilated poultry houses; one of the aspects of this project is the analysis of non-methane volatile organic compounds.

The NMVOC analysis will be performed by collecting pumped sorbent tubes and subsequent assay using thermal desorption – gas chromatography – mass spectrometry (TD-GC-MS) and also thermal desorption – gas chromatography – mass spectrometry and olfactometry (TD-GC-MS/O.) The simultaneous detection using mass spectrometry and olfactometry allows for the odorants within the matrix to be identified and subsequently prioritised.

INTRODUCTION

Intensive livestock practices throughout the world are under pressure from local authorities, industry and residents to reduce the impact that they have on the local environment; part of their impact comes from their odour emissions. Frequently overlooked when drafting regulations; the odour emissions from agricultural practices are often more noticed by local receptors than other factors that are easier to quantify, however without legislation or guidelines in place operators are often forced to achieve unrealistic targets for odour emissions.

Local receptors regularly have fears from the health effects from the odour emissions from different intensive livestock practices, and the subjective nature of the sense of smell yields different psychological effects on different people. The odour detection value of most compounds is far below the level required to cause harm, it is primarily the nuisance of the disagreeable odour that causes most complaints. Schiffman[1] concluded that more research was required to ascertain if there is a need for guidelines to be established for the odour emissions from livestock facilities based upon health implications.

The analysis of odorants within a matrix is performed using gas chromatography – olfactory (GC-O), a technique that was first reported by Fuller et al in 1964 when the human olfactory sense was used as a detector for the detection of odorous compounds in the gas chromatograph effluent. This work involved the analysis of perfumes, however as the technique has developed it has been adopted for the analysis of odorants in food and beverages and also odours from various agricultural and waste management operations.
There have been several studies undertaken at different geographical locations around the world focusing on different intensive livestock practices, the majority of these have focused upon swine finishing sheds or dairy facilities, comparatively little of the research has focused upon poultry facilities.

The emissions from different intensive livestock operations comprise different chemicals and odorants, Wright et al[2], Hobbs et al[3] and Jacobson et al[4] studied and reported on the different compounds that were identified in the emissions for different intensive livestock facilities; the comparisons drawn by Hobbs et al[2] serve to highlight these differences. As different compounds have different odour detection thresholds, some species that gave an olfactometry response did not always correspond to a response from any other detector, conversely some compounds with large detector responses gave little or no olfactometry response. Speculation is often made as to the identity of the compound based upon it odour characteristic and associated compounds within the matrix. More specific studies have been undertaken that focus on one particular intensive livestock operation; studies carried out by Kai & Schäfer[5], Blunden et al[6] focussed upon the chemical analysis of emissions from swine facilities, Rabaud et al[7] analysed the emissions from dairy facilities. Work specifically relating to intensive broiler production has been primarily focused upon the general quantification of the odour emissions and not the identification of the odorants, Hayes et al[8] and Pescatore et al[9] both chose to report upon the ammonia emissions from intensive poultry facilities, whilst Williams[10] reported upon the relation between dust and odour from broiler houses.
The desired output of the P-CRC project is an emission model that can then be applied to existing facilities looking to expand or to new facilities to assess their potential odour impact on the local environment with the use of a dispersion modelling software such as CALPUFF or AUSPLUME, the work presented herein is that of the analysis of NMVOC's and selected organic odorants from selected poultry facilities.

EXPERIMENTAL METHODS

The results that are presented here focus on sampling that took place at two broiler facilities in Australia during the summer 2005 – 2006. Both facilities were mechanically ventilated to achieve tunnel ventilation within the poultry houses; one was located in Queensland, a dry sub tropical climatic region in North Eastern Australia, and the other in Victoria, a more temperate climate in South Eastern Australia. Samples were collected from the same shed on the site in each state and from the same exhaust fan to ensure consistency of the data acquired.

Samples were collected on sorbent tubes containing either a Tenax TA sorbent (for n-C_7 to n-C_{30} compounds) or a Carbotrap 300 sorbent (a blend of Carbopack C, Carbopack B and Carbosieve SIII for ethane to n-C_{20}) (Markes International, UK), using calibrated sampling pumps. The sample volumes were recorded for each tube to allow for relative quantification. The use of sorbent tubes allows for field sampling to be performed at various locations throughout Australia without the limitations and logistical challenges poses by the use of Tedlar™ odour bags or sampling canisters, in addition work presented by Koziel et al[11] indicated a greater sample recovery from sorbent tubes over sampling canisters and sampling bags. The use of different sorbents ensures that the compounds identified in

subsequent analysis accurately represent the suite of compounds that are being emitted from the poultry houses. Further work has involved the use of different mixed sorbent tubes to ensure that the compounds identified from the Tenax TA and Carbotrap 300 sorbents is an accurate representation of the composition of the emissions.

The analytes were thermally desorbed from the sorbents and refocused within the cold trap of the thermal desorber (Markes Unity, Markes International, UK), this allowed for the formation of an analyte 'slug' that would be injected into the gas chromatograph for subsequent separation and identification. The cold trap is a general purpose graphitised carbon type to allow a wide range of analytes to be assessed.
Initial sample analysis was performed using only GC-MS, where the compounds were identified using gas chromatographic separation and mass selective detection (Agilent 6890N GC, 5973NMSD, Agilent Technologies) with a HP-5MS capillary column (30m x 0.25mm x 0.25µm Film Thickness, Agilent Technologies). The use of a general purpose column allowed for the initial identification of species that may be present. The results yielded from the results presented here have lead to the use of a different column, these results will be presented in future papers. The flow rate of the gas chromatograph was maintained at a constant pressure using helium as the carrier gas. The oven was temperature programmed for a total run time of 44.00min, (50°C for 2 min, 5.00°C/min to 250°C hold for 2 min) this provided adequate separation of the eluting compounds. The mass selective detector was operating in continuous scan mode (50 – 550 m/z). The mass spectra were recorded using the Agilent ChemStation software and analysed offline using the Enhanced Data Analysis package (Agilent Technologies).
The identification of the volatile organic compounds relied upon the matching of the acquired mass spectra with the ChemStation data bases (initially only NIST02, later both NIST02 and Wiley275). Identification of the compounds present within the matrix yielded a large number of different classes of compounds including aromatics, sulphur containing organic species, nitrogen containing species, aldehydes, ketones, alcohols, terpines and other general hydrocarbons.

Later work involved splitting the gas-chromatograph effluent between the mass selective detector and an Olfactory Detection Port (ODP2 Gerstel GmbH & Co., Germany) The scan range of the mass selective detector was increased at this stage to provide a more reliable match to the spectral databases (35 – 550 m/z). The mass spectra were recorded using the Agilent ChemStation software and the odour chromatograms were recorded using the Gerstel ODP Recorder software. Analysis was performed offline using the Agilent ChemStation Data Analysis software.

To optimise the use of the human nose as a detector the split between the MSD and ODP was initially set at 1:1, before being refined to 2:3 (MSD:ODP), these split ratios were calculated using the Gerstal Column Calculator (Gerstel GmbH & Co., Germany.) These calculations were based on a column flow of 1.6mL.min^{-1} for the

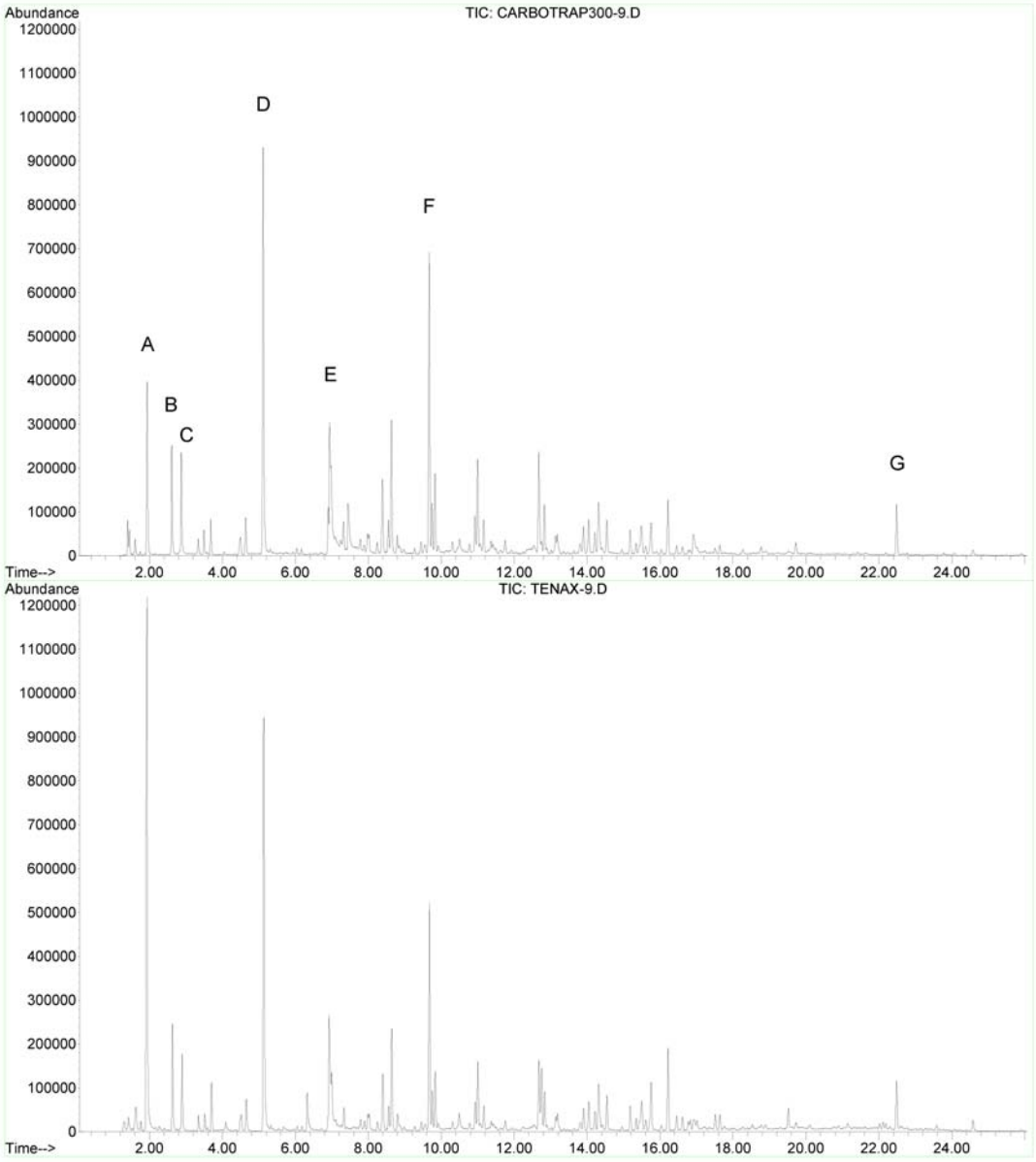
carrier gas Helium with an initial temperature of 50°C with the flow programmed to be constant flow as the temperature increases.

The use of the Gerstel ODP2 allowed for the odorous compounds within the matrix to be identified from the large number of compounds that were present. It was noted that only a few of the compounds that were identified with the mass selective detector were responsible for the odour of the emissions. Figure 2 illustrates a typical total ion chromatogram with the odour chromatogram overlayed to identify the odorants within the matrix, it clearly shows that only a small number of the compounds present are odorants, and are potentially responsible for the odour from the poultry facilities.
In addition to the collection and analysis of sorbent tubes, odour bags were collected onsite and analysed at local laboratories, this allows for the comparison to be drawn between the VOC emissions and the odour level as determined by dynamic dilution olfactometry as per CEN standards.

RESULTS

The collection and subsequent analysis of the samples revealed some interesting trends. Primarily it became very clear that there was a marked variation in not only the abundance of species that were present during the grow-out cycle, but also the species that were present varied throughout the cycle.

Figure 1 Typical Total Ion Chromatogram (TIC) produced from the TD-GC-MS analysis of sorbent tubes. The top spectra is that of a Carbotrap300 sorbent tube and the lower is from a Tenax TA sorbent tube.



The above figure shows two typical total ion chromatograms (TIC's) from one of the sampling locations. Both samples were collected under identical conditions, on the same day, from the same duty fan on the same shed at the same ventilation rate. The only difference was the sample volume, the Carbotrap300 was 2.91L and the Tenax TA was 3L. The compounds labelled are A – 1-butanol, B – dimethyl disulphide, C – toluene, D – styrene, E – N-butyl-1-butanamine, F – 4-ethyl-decane, G – butylated hydroxytoluene (BHT).

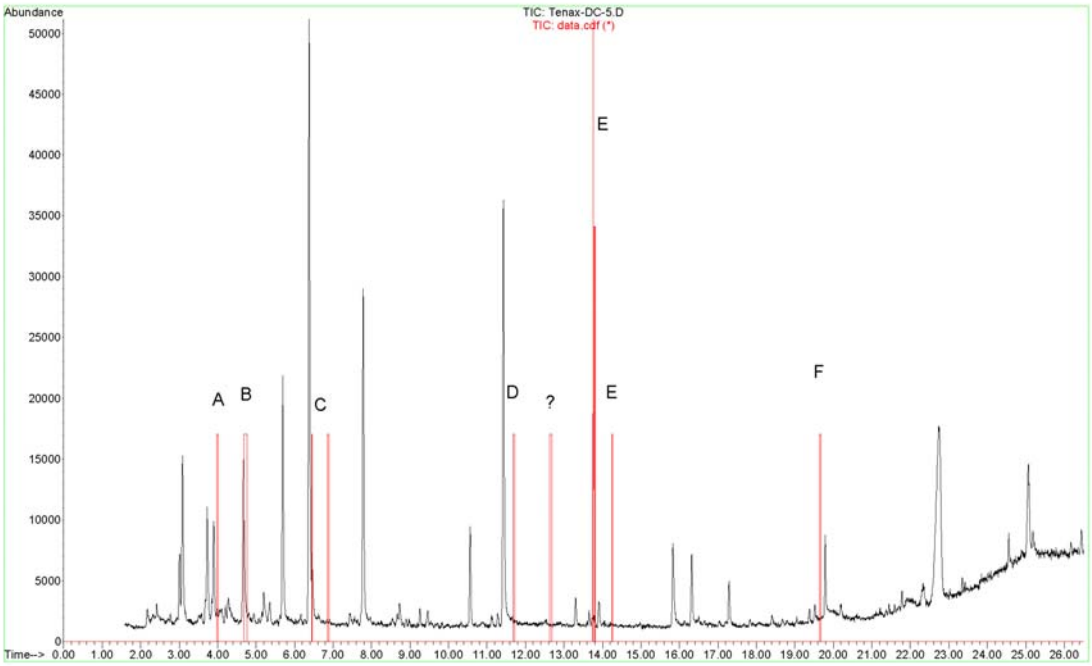
There is an extensive suite of compounds that have been identified within the matrix of the exhaust emissions of the poultry sheds. Below is a table of some of the predominant compounds that have been identified.

Table 1. Volatile Organic Compounds Identified using GC-MS

Compound Family	Compounds Isolated
Aromatics	Toluene o-Xylene p-Xylene Benzene 1-ethyl-4-methyl-benzene 1-ethyl-2-methyl-benzene Acetophenone Benzaladehyde Phenol Styrene
Sulphur	Dimethyl Sulphide Dimethyl Disulphide Dimethyl Trisulphide
Aldehydes	Butanal 3-methyl-butanal Cyclohexanal Hexanal 2-ethyl-1-hexanal
Ketones	2-butanone Diacetyl 3-methyl-2-butanone 3-hydroxy-2-butanone
Nitrogen	Trimethylamine
Alcohols	1-butanol Cyclohexanol
Carboxylic Acids	Acetic Acid
Terpines	α-pinene β-pinene Limonene Camphene Camphor Carene Eucolyptol
Other Hydrocarbons	Tetradecane Hexadecane Tetrahydrofuran

With the connection of the ODP it was possible to collect simultaneous olfactometry data and mass spectral data. With training the operator can discern the compounds and assess their relative intensities and record this data with the Gerstel ODP Recorder Software (Gerstel, GmbH & Co., Germany.) The resulting spectra pairs can be overlayed to determine the identity of the odorants identified. However sometimes there would be an olfactometry response that did not have a mass spectral response, these compounds remain to be identified.

Figure 2 Typical TIC and ODP Chromatogram



The figures labelled in the chromatogram are A – 2-butanone, B – 2,3-butanedione, C – dimethyl disulphide D – 3-hydroxy-2-butanone E – dimethyl trisulphide and F – acetophenone. All of these compounds are known odorants and from the table below it can be seen that their relative abundances often have little relation to their individual impact.

Table 2 Odorants Identified using Olfactory detection port

Compound family	Compound	Odour Threshold Value (ppb)♦
Sulphur	Dimethyl Disulphide	0.16 – 12
	Dimethyl Trisulphide	0.005 – 0.10
Ketones	2,3-butanedione (diacetyl)	2.3 – 6.5
	2-butanone	50,000
	Acetophenone	65
	3-hydroxy-2-butanone	800

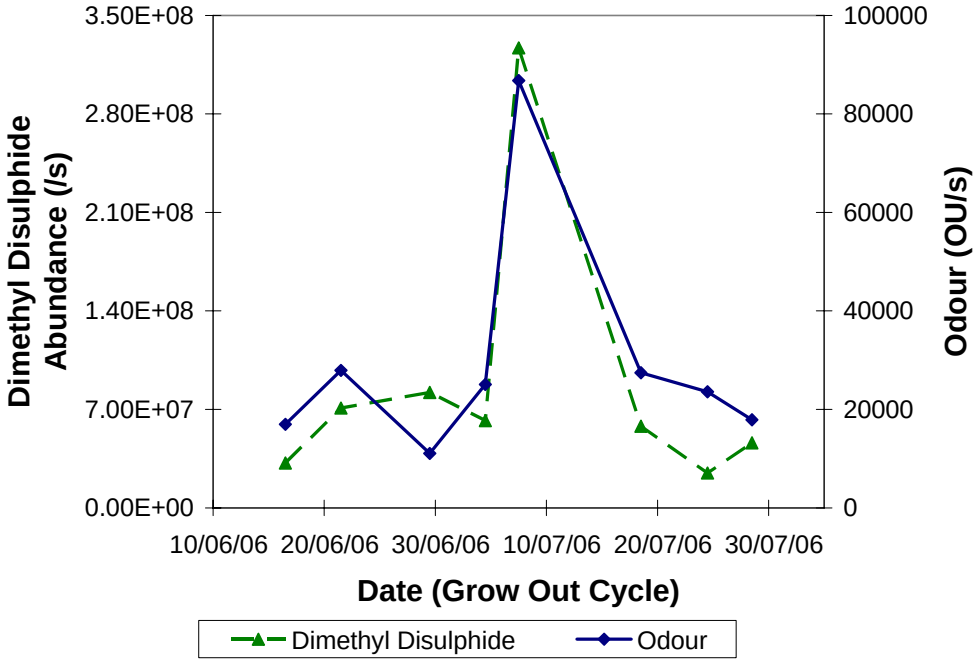
♦ Odour Detection Values reported by Leffingwell & Associates http://www.leffingwell.com/odorthre.htm

ANALYSIS OF RESULTS

With the collection of the vast data set, several trends have been identified, mostly associated with specific odorants. The results from the conventional dilution olfactometry have been compared to the abundance of some of the odorants and VOC's identified and it can be seen that there is a strong correlation between the odour levels detected and the abundance of specific odorants.

The figure below illustrates the odour level identified by the dilution olfactometry and the corresponding abundance of dimethyl disulphide recorded from the gas chromatograph – mass spectral data acquired. The results have been normalised to the volume of air that was being exhausted from the shed at the time of sampling.

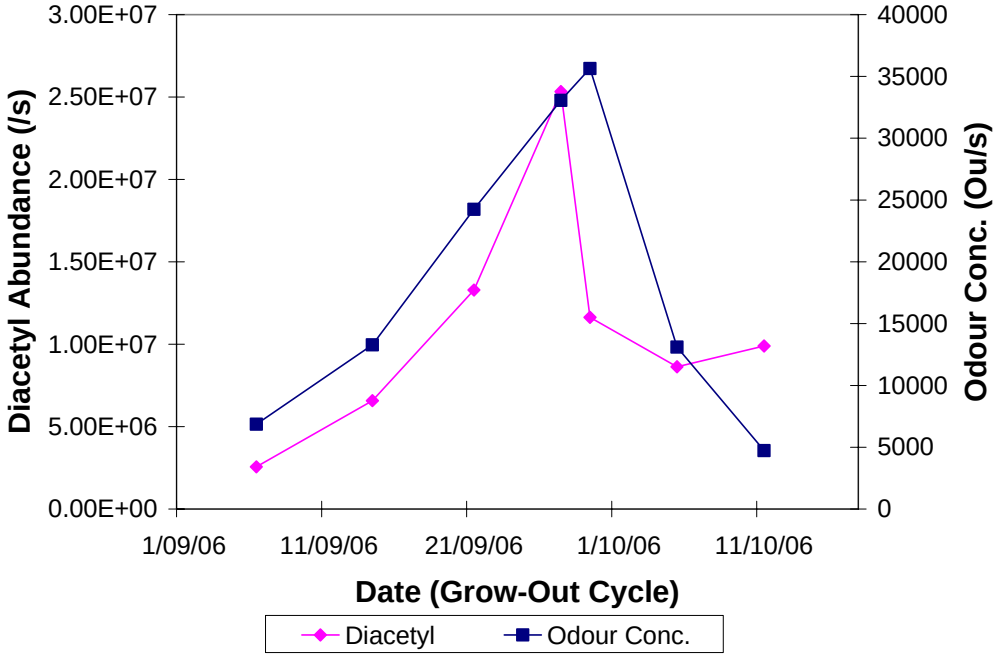
Figure 3 Variations of odour and dimethyl disulphide at different stages of a typical broiler grow-out cycle.



The above results were collected through one complete grow-out cycle, thus the trends of bird age and the bird mass can also be related to the level of odour that is being emitted from the shed.

The following figure shows the trend of diacetyl (2,3-butanedione) and odour across a similar grow-out cycle.

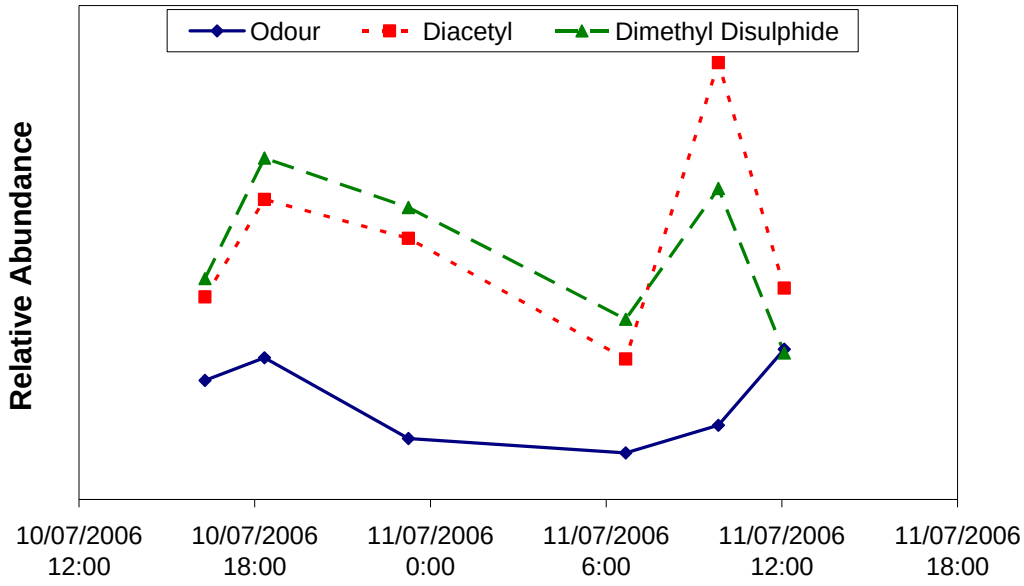
Figure 4 Variations of odour and diacetyl at different stages of a typical broiler grow-out cycle.



The impact of the odour from the sheds has been assessed primarily from data obtained from the samples that were collected earlier in the day, this allowed for the olfactometric analysis to happen on the same day as the samples were collected. However it was acknowledged that the variations in the odour and VOC/odorant across the grow-out cycle could also be subject to a diurnal variation as a result of the birds' activities within the shed. Thus the collection of a number of samples at different times of the day was undertaken and the resulting trends were clear when the data was analysed.

Overleaf is a plot that shows the level of odour detected and the abundances of diacetyl and dimethyl disulphide. It can be seen that the trends in abundances of the two chosen odorants are very similar, whilst the odour level recorded does not appear to follow the same trend. This could be due to the time between the collection of the odour samples in the Tedlar™ odour bags and the subsequent olfactometry analysis

Figure 5 Diurnal variations of Odour and two key odorants.



SUMMARY

As the population continues to grow the increased pressure upon intensive livestock operators from local authorities and residents to reduce their impact on the local environment takes many forms, one of the most difficult impacts to assess is the odour output from the specific facilities. The assessment of the concentration of the odour being emitted from these facilities is time consuming and a difficult process resulting in a need to develop emission based models that can be used to determine the dispersion of odours and odorants from these facilities. The poultry industry is one particular intensive livestock practice that faces regular pressure about its impact upon local receptors with respect to odour emissions. The research funded by the Australian P-CRC has revealed that there is a complex matrix of non-methane volatile organic compounds that form the emissions from poultry facilities, and only a small number of the NMVOC's present are responsible for the resulting odour. Comparison with results from traditional olfactometry shows there is a strong correlation between the odour concentration and the abundance of dimethyl disulphide. It is anticipated that with the completion of analysis of the second season of samples that an even greater emission model for the mechanically ventilated broiler houses can be developed. The comparative use of mixed sorbent tubes, passive samples and different columns will all be undertaken to ensure that the data set that is being acquired accurately represents the emissions.

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REFERENCES

1. Schiffman, S.S., *Livestock Odors: Implications for Human Health and Well-Being.* Journal of Animal Science, 1998. **76**: p. 1343-1355.
2. Wright, D.W., et al., *Multidimensional Gas Chromatography-Olfactometry for the Indentification and Prioritization of Malodors from Confined Animal Feeding Operations.* Journal of Agriculture and Food Chemistry, 2005. **53**: p. 8663-8672.
3. Hobbs, P.J., et al., *Emissions of volatile organic compounds originating from UK livestock agriculture.* Journal of the Science of Food and Agriculture, 2004. **84**: p. 1414-1420.
4. Jacobson, L.D., et al. *Odor Emissions and Chemical Analysis of Odorous Compounds from Animal Buildings*. in *Workshop on Agricultural Air Quality: State of the Science*. 2006. Bolger Conference Centre Pontomac, Maryland, USA.
5. Kai, P. and A. Schäfer, *Identification of Key Odour Components in Pig House Air using Hyphenated Gas Chromatography Olfactometry.* Agricultural Engineering International : the CIGR Journal of Scientific Research and Development, 2004. **VI**(04 006).
6. Blunden, J., V.A. Aneja, and W.A. Lonneman, *Characterization of non-methane volatile organic compounds at swine facility in eastern North Carolina.* Atmospheric Environment, 2005. **39**: p. 6707-6718.
7. Rabaud, N.E., et al., *Characterisation and quantification of odorous and non-odorous volatile organic compounds near a commercial dairy in California.* Atmospheric Environment, 2003. **37**: p. 933-940.
8. Hayes, E.T., T.P. Curran, and V.A. Dodd, *Odour and ammonia emissions from intensive poultry units in Ireland.* Bioresource Technology, 2005. **97**: p. 933-939.
9. Pescatore, A.J., K.D. Casey, and R.S. Gates, *Ammonia Emissions from Broiler Houses.* Journal of Applied Poultry Research, 2005. **14**: p. 635 - 637.
10. Williams, A.G., *Dust and Odour Relationships in Broiler House Air.* Journal of Agricultural Engineering Research, 1989. **44**: p. 175-190.
11. Koziel, J.A., et al., *Evaluation of Sample Recovery of Malodorous Livestock Gases from Air Sampling Bags, Solid-Phase Microextraction Fibers, Tenax TA Sorbent Tubes, and Sampling Canisters.* Journal of the Air and Waste Management Association, 2005. **55**: p. 1147 - 1157.

KEY WORDS
Odorant, GC-MS/O, olfactometry, poultry, odour, livestock, odor, chemical analysis, intensive livestock, broiler, poultry housing, mechanical ventilation, volatile organic compound, VOC, non-methane volatile organic compound.