Improving odour management and abatement performance using Olfactory GC-MS

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ABSTRACT

The measurement of odorous emissions is usually assessed either as odour concentrations (OC) by dilution olfactometry or by the chemical analysis of the odorous compounds such as hydrogen sulphide or the separation of complex gas mixture using analytical instrumentation such as gas chromatography. These techniques either provide information on the perceived effect of the emission (olfactory) or characterise the odours in terms of their chemical composition (analytical) but provide limited information on the relationship between odour impact and the chemical composition. The integration of chemical and olfactory techniques using olfactory-gas chromatography allows for the correlation of chemical and sensory measurements via the coupling of an olfactory port to a GC. The incorporation of mass spectrometry (GC-MS-O) enables individual odorants to be separated, identified and characterised according to their intensity and character. GC-MS-O analysis of emissions from poultry sheds has shown that samples vary in terms of their chemical compositions (i.e. different odorants profiles) as well as the different intensities measured and demonstrates the potential benefits that GC-MS-O analysis can offer in identifying key chemical markers for odour management in terms of odorant removal (i.e. receptor impact) and abatement loading due to chemical saturation.

1 INTRODUCTION

Complaints due to odour annoyance have become a major issue for intensive livestock, waste management and wastewater treatment operators as the repeated release of unpleasant odours from these facilities can constitute a nuisance to a local population (Gostelow *et al.,* 2003). This impact has become more significant with the expansion

of suburbia and the associated rural encroachment, resulting in residential and commercial properties becoming in closer proximity to these facilities than in the past. Traditionally, odour management has been maintained by the use of buffer distances between industry and receptors or by the installation of odour abatement systems that either collect and dispersion the emission or treat the emission to acceptable level to limit receptor impact. Conventional odour abatement systems include chemical scrubbers, biofilters, bioscrubbers and biotrickling filters. Often these systems do not deliver the expected reduction in odour emissions and / or meet their original design specifications in terms of removal efficiency, resulting in the emission of odorous compounds to local receptors leading to odour complaints. The cause of these process failures is often due to inadequate characterisation of the emission source in terms of odour composition and mass loading. A secondary effect of inadequate odour composition information is the ineffective evaluation of odour control systems performance during its operation.

The design and optimisation of odour management and abatement systems is based on an understanding of the emissions present in the facilities with background environmental conditions. Typical odours emitted from intensive livestock, waste management and wastewater treatment facilities usually consist of a wide range of odorants; the essential components being hydrogen sulphide (H_2S), methanethiol, dimethyl sulfide, aldehydes and some ketones. Most odour abatement designs are based on the use of one or two key odorants such as H_2S, reduced sulphur compounds and / or VOC to determine the loading capacity for the system. This approach often doesn't adequately account for the actual composition and individual concentrations that vary over time and rank the emission differences in terms of odorant removal (i.e. receptor impact) and abatement loading due to chemical saturation.

The measurement of odours can either be assessed as odour concentration units (OU) by dilution olfactometry (using the CEN or equivalent national standard for dilution olfactometry) or analytical techniques such as the use of surrogates chemical markers (like H_2S) or the chemical analysis of odorous mixtures by chromatographic techniques such as gas chromatography coupled with mass spectrometry (GC-MS) for quantification of individual compounds (Gostelow *et al.,* 2001). Sensory measurements employ human panels (Figure 1) to characterise the odours in terms of their perceived effect but give no information regarding composition, whereas analytical measurements characterise odours in terms of their chemical composition but give little information as to their sensory impact. Current chemical methods for odour monitoring can include field sampling and laboratory analysis (Figure 2) of gaseous emissions such as H_2S, volatile organic carbon (VOC), and ammonia measurements and the continuous in-situ monitoring of H_2S, volatile organic carbon (VOC), and ammonia.

Figure 1. Olfactory analysis of odour samples.

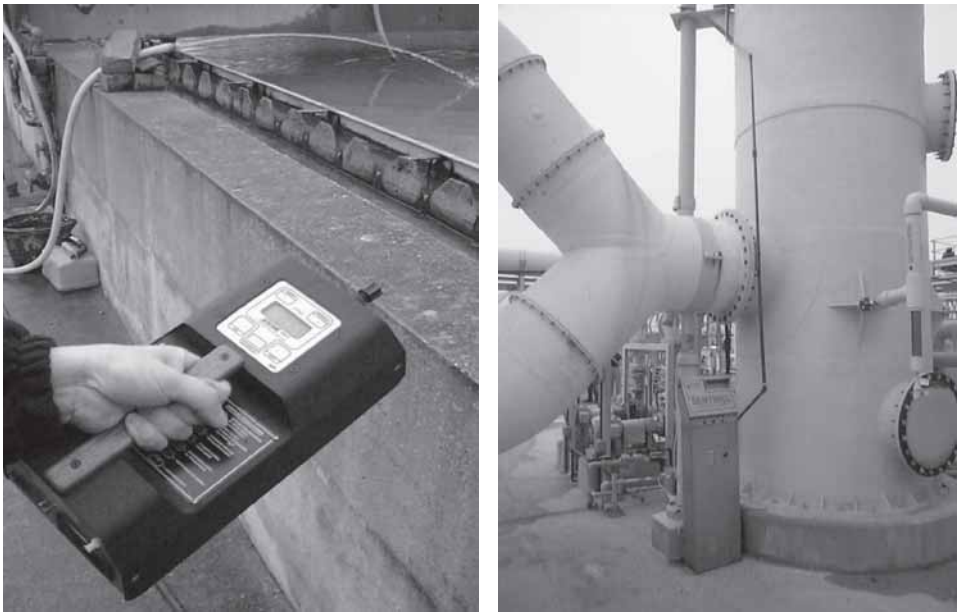

Figure 2. Field and continuous monitoring of H_2S.

More recently the integration of chemical and olfactory techniques has been applied to odour analysis to allow the correlation of chemical and sensory measurements via the coupling of an olfactory port to gas chromatograph-mass spectroscopy (GC-MS-O). GC-MS-O (Figure 3) allows individual odorants to be separated and identified individually as well as allowing the odour contribution for each compound to be characterised. The olfactory detection port (ODP) consists of a nose cone where panellists perceive the separated odorous compounds by continuously sniffing the GC column effluent and characterises it in terms of intensity and an odour description. The end of GC column is split into two streams via a column splitter (Figure 4) that directs column effluent to the MS and ODP via heated transfer lines.

Figure 3. Olfactory-GC-MS showing odour detection port (ODP) on right.

Olfactory-GC and Olfactory-GC-MS is well established in other science fields such as food aroma's and taste and odours in drinking water but has limited application to environmental odour analysis until recently. In drinking water taste and odours (or off-flavours) monitoring GC-MS-O analysis has been successfully applied to the characterisation of common off-flavours such as geosmin and MIB (Hochereau and Bruchet, 2004) and has been used to produce odour wheels (Figure 5), which relate the odour descriptors to the chemical composition of odorants (Suffet *et al*., 1999).

Figure 4. Column splitter directing column effluent to the MS and ODP.

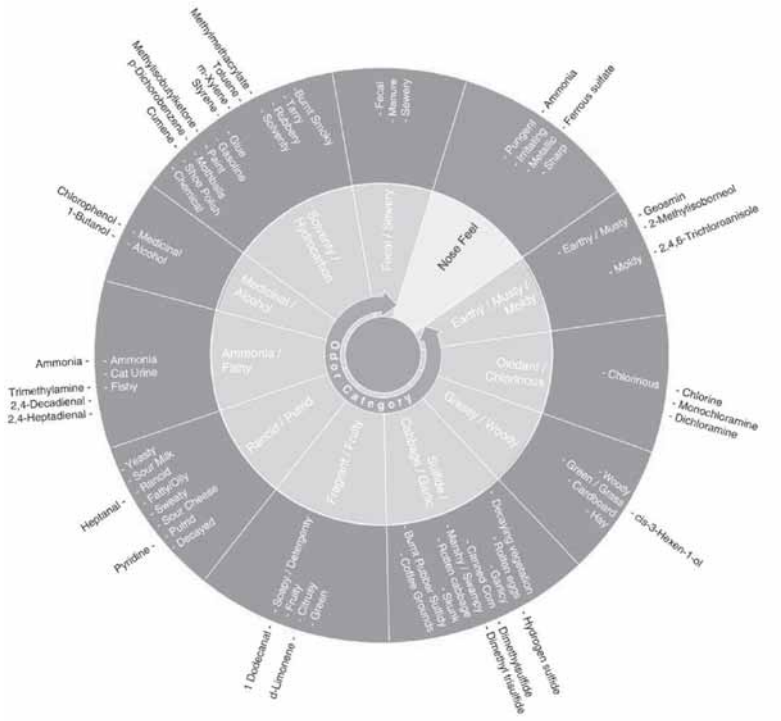

Figure 5. Example of odour wheels for off-flavours in drinking water (Suffet *et al*., 1999).

GC-MS-O applications for the assessment of environmental odours has mainly focused on characterising changes in composition of odorous emissions from various agricultural and waste management operations such as swine finishing and poultry sheds and dairy facilities. Studies (Kai and Schäfer, 2004; Wright *et al.*, 2005; Parcsi *et al.,* 2007) have shown that emissions from different intensive livestock operations comprise different chemicals and odorants and that 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. Additionally speculation is often made as to the identity of the compound based upon it odour characteristic and associated compounds within the matrix.

This paper will describe the application of using olfactory-GC-MS for the characterisation of non-methane volatile organic compounds (NMVOC) emissions from tunnel ventilated broiler sheds in Australia and discuss how this technique can be more broadly applied to improve the design and optimisation of odour abatement performance through improved understanding of variations in the composition of odorous emissions in terms of receptor impact (i.e. different odorant profiles) and chemical loading on odour abatement systems.

2 MATERIALS AND METHODS

The results that are presented here focus on odorous samples from two tunnel ventilated broiler sheds in Queensland and Victoria, Australia. 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 different sorbents ensures that the compounds identified in subsequent analysis accurately represent the suite of compounds that are being emitted from the poultry sheds. The analytes were thermally desorbed from the sorbents and refocused within the cold trap of the thermal desorber (Markes Unity, Markes International, UK).

Sample analysis was performed using a GC-MS (Agilent 6890N GC, 5973NMSD, Agilent Technologies) coupled to an Olfactory Detection Port (ODP2 Gerstel GmbH & Co., Germany) (Figure 3). The compounds were identified using gas chromatographic separation and mass selective detection with a HP-5MS capillary column (30m x 0.25mm x 0.25µm Film Thickness, Agilent Technologies). 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) for GC-MS only analysis. 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 (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.

GC-MS-O analysis involved splitting the gas-chromatograph effluent between the mass selective detector and an Olfactory Detection Port. 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 panellist as an odour 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.

In addition to the collection and analysis of NMVOCs, odour bags were collected onsite and analysed at local laboratories (as determined by dynamic dilution olfactometry as per CEN standards), this allows for the comparison to be drawn between the NMVOC emissions and the odour concentrations.

3 RESULTS

A range of odour samples were collected during four sampling programs from two tunnel ventilated broiler sheds in Queensland and Victoria, Australia in order to characterisation of NMVOC emissions over the chicken growing out cycle (typically 9 weeks).

3.1 GC-MS analysis

GC-MS analysis revealed 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 6 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). Table 1 shows a list of predominant NMVOC compounds that were isolated and identified within the matrix of the exhaust emissions from the poultry sheds.

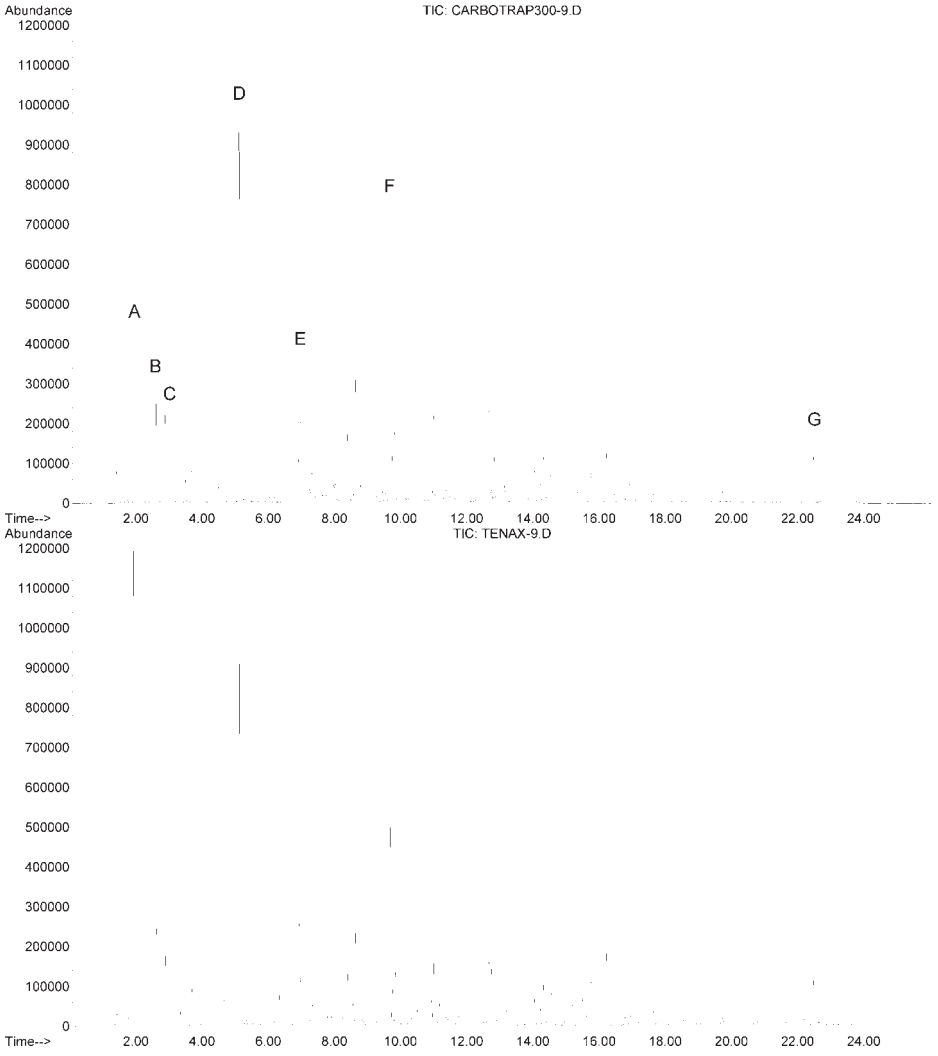

Figure 6. GC-MS analysis of sorbent tubes: Carbotrap300 (top spectra) and Tenax TA (lower spectra). (A – 1-butanol, B – dimethyl disulphide, C – toluene, D – styrene, E – N-butyl-1-butanamine, F – 4-ethyl-decane, G – butylated hydroxytoluene).

3.2 GC-MS-O analysis

GC-MS-O analysis allows the simultaneous collection of olfactory and mass spectral data from GC analysis. Figure 7 shows a typical total ion chromatogram with the odour chromatogram overlayed to identify the odorants within the matrix. The results shows that only a small number of the compounds present are identified by the operator as odorous, and therefore could be potentially responsible for the odorous emissions from the poultry shed samples. Figure 7 also shows that the intensity of odorous compounds can be scaled from 0-3 thereby identifying the most odorous compounds and the one's that are more likely to cause offensive to local receptors. Table 2 lists the NMVOCs that were isolated and identified by the ODP operator as being odorous. The most predominant odorants in the poultry emission matrix was determined to be dimethyl disulphide and 2, 3-butanedione (diacetyl). The ODP operator can also include voice activated odour descriptors to describe the character of odorants (Figure 8).

3.3 Variations in odorant profiles

The correlation of dominant odorants from the poultry shed emissions (Table 2) with the results of dilution olfactometry has shown that odour emission trends can be strongly linked to the abundance of these specific compounds. Figure 9 illustrates the relationship over the grow-out cycle between the abundance of dimethyl disulphide as acquired by mass spectral data and odour concentrations (determined by dilution olfactometry). The results have been normalised to the volume of air that was being exhausted from the shed at the time of sampling and shows that the variations in odour and NMVOC emissions can be linked to the either the bird age or bird mass. Figure 10 supports these observations and shows that the emissions of two key odorants (dimethyl disulphide and 2, 3-butanedione) are also subject to diurnal variations which is most likely the result of bird activities within the shed over the 24 hours due to feeding and lighting cycles.

Table 1
Non-methane 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

Table 2
Odorants identified using olfactory detection port (from Figure 7).

Compound family	Compound	Odour Threshold Value (ppb)[1]
Sulphur	Dimethyl Disulphide	0.16 – 12 0.005 – 0.10
	Dimethyl Trisulphide	
Ketones	2,3-butanedione (diacetyl)	2.3 – 6.5
	2-butanone	50,000
	Acetophenone	65
	3-hydroxy-2-butanone	800

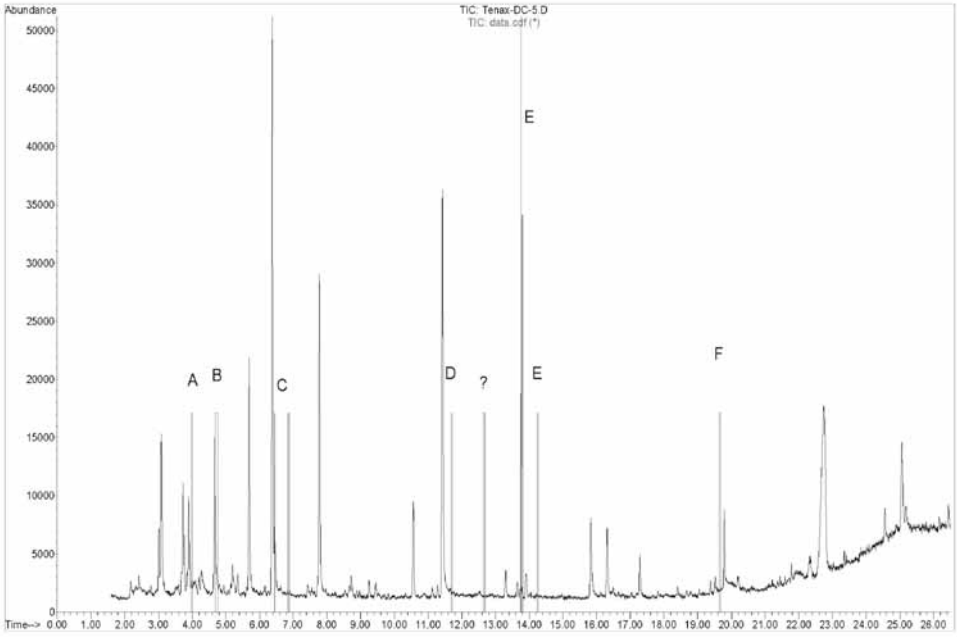

Figure 7. GC-MS-O analysis showing total ion chromatogram and odour chromatogram (A – 2-butanone, B – 2, 3-butanedione, C – dimethyl disulphide D – 3-hydroxy-2-butanone E – dimethyl trisulphide and F – acetophenone).

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

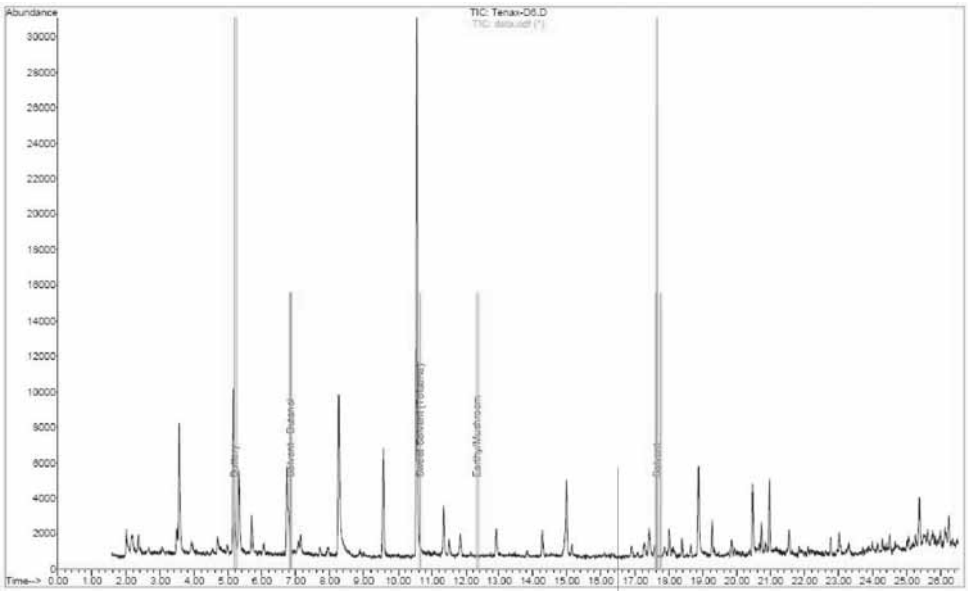

Figure 8. GC-MS-O analysis showing the additions of odour descriptors on the odour chromatogram.

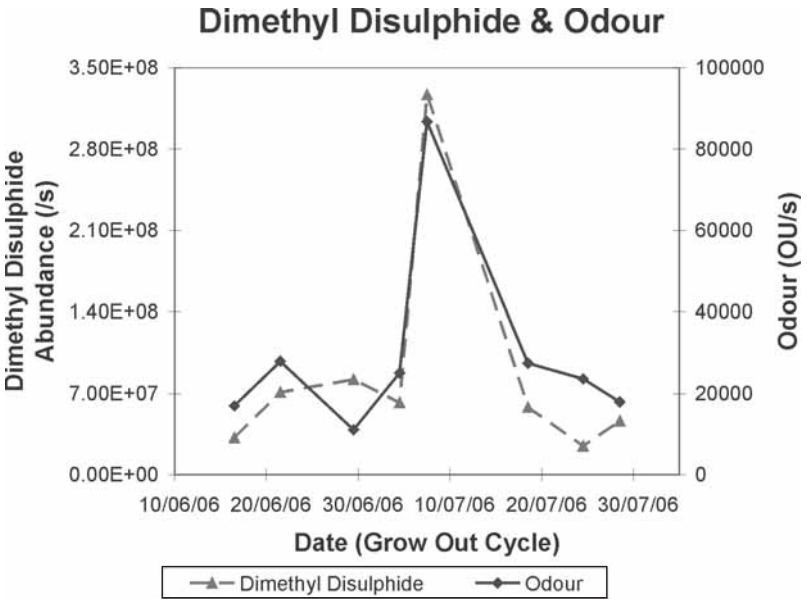

Figure 9. Variations of odour and dimethyl disulphide at different stages of a typical chicken grow-out cycle.

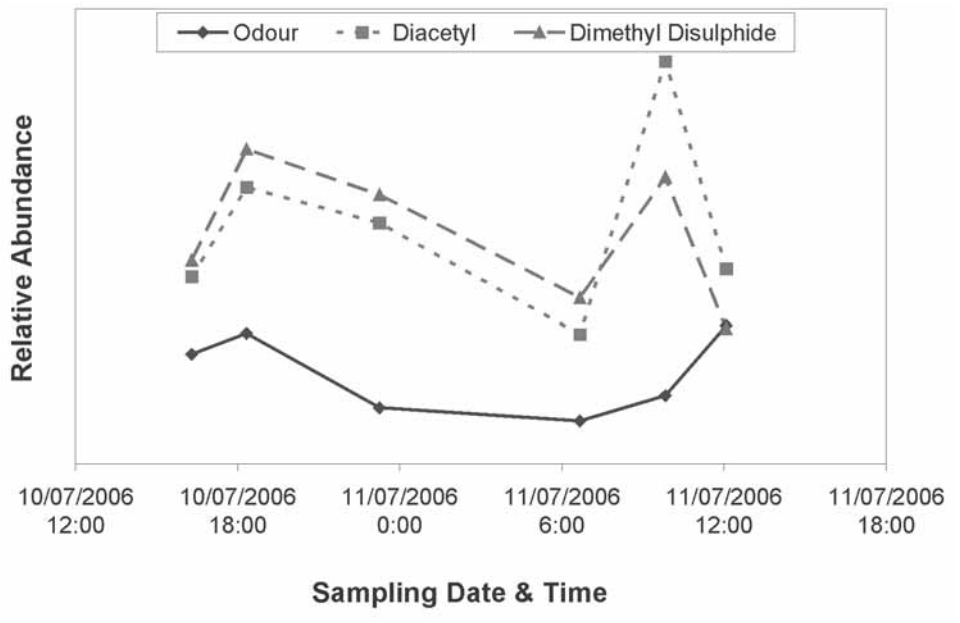

Figure 10. Diurnal variations of odour and two key odorants.

4 CONCLUSIONS

The GC-MS analysis of samples from different poultry sheds revealed that that there is a complex matrix of non-methane volatile organic compounds that form the emissions from these facilities. The simultaneous collection of olfactory and mass spectral data via GC-MS-O analysis demonstrated that only a small number of the NMVOC's present in the matrix are responsible for the resulting odorous emissions. Olfactory-GC-MS analysis was able to identify the key odorants in the poultry emissions samples as dimethyl disulphide and 2, 3-butanedione. These compounds were determined to be the most odorous over the chicken grow-out cycle and showed that distinct odorant profiles occur due the different growth stage during poultry shed production (i.e. the age of the bird or the total mass of birds within the shed). The GC-MS-O analysis also showed that diurnal variations in odorants compositions where also influenced by chicken activity within the poultry sheds.

As odour abatement process failure is often due to inadequate characterisation of the emission source in terms of odour composition. The application of olfactory-GC-MS analysis offer a potential approach to identify key odorous markers from different emission sources as demonstrated with the analysis of poultry shed emissions.

The ability to identify compounds that have greater receptor impact will enable improved design of odour abatement systems to remove specific odorous compounds. Improved characterisation of odorous emissions will also enable more effective evaluation of odour control systems performance during its operation.

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