



Addressing odour abatement and assessment knowledge gaps using PTR-ToFMS

by Grant Brown, Michael Atzeni, Simin Maleknia and David Mayer
December 2018



AgriFutures™
Chicken Meat

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Foreword

Effective odour management underpins the sustainable growth and expansion of the Australian chicken meat industry, yet, odour abatement strategies are largely ‘black boxes’ in terms of their action and efficacy. This is because our knowledge of the complex biochemical and physical processes driving odour emissions is rudimentary. While an improved understanding of these processes is necessary to develop better odour abatement strategies in the future, the critical requirement is the ability able to assess abatement strategies objectively.

To that end, AgriFutures Australia is heavily invested in odour research to better understand and objectively assess poultry odour emissions, including the evaluation of alternative odour measurement techniques that do not rely on the human nose. This latest research builds on previous mass spectrometry findings, and demonstrates that state-of-the-art, high-resolution, mass spectrometry using a proton transfer reaction time-of-flight mass spectrometer (PTR–ToFMS), complemented by other odour assessment methods, provides significant benefits to industry-funded odour research projects.

PTR–ToFMS analysis enabled the detection of a wide range of poultry production-related odorants at the sheds (source) and downwind. Several key compounds that likely implicated in odour nuisance (low detection thresholds; unpleasant odour characteristics) were detected in the samples. PTR–ToFMS also enabled detection of odorant differences in a variety of litter conditions.

Additionally, the project demonstrated that PTR–ToFMS data can be used to develop a useful odour prediction model that may reduce reliance on human-based evaluations (e.g. olfactometry) in the future. Odour abatement strategies can be critically evaluated in terms of odour and odorant reductions at-shed and downwind, using odour prediction modelling and PTR–ToFMS data, and cross-checked by olfactometry.

Effectively reducing odour nuisance will likely require management of the key odorants that can be detected by receptors. Future research should focus on identifying and suppressing these key odorants.

This project was funded from industry revenue, which was matched by funds provided by the Australian Government. This report is an addition to AgriFutures Australia’s diverse range of over 2000 research publications and it forms part of our Chicken Meat R&D program, which aims to stimulate and promote RD&E that will deliver a productive and sustainable Australian chicken meat industry that provides quality wholesome food to the nation.

Most of AgriFutures Australia’s publications are available for viewing, free downloading or purchasing online at: www.agrifutures.com.au.

John Harvey
Managing Director
AgriFutures Australia

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- Chris Cameron of Platinum Composts, who supplied the liquid composting ‘accelerator’ and provided advice and co-operation during the odour abatement trials.

Abbreviations

DAF	Department of Agriculture and Fisheries, Queensland
GC–MS	gas chromatography – mass spectrometry
MS	mass spectrometry
N ₂	Nitrogen gas (Grade 5.0 unless otherwise stated)
OTV	odour threshold value
OAV	odour activity value
ou, OU	odour unit (1 ou = dilution threshold at which 50% of panel can detect an odour)
ppb	parts per billion (v/v, unless otherwise specified)
PTR–MS	proton transfer reaction with mass spectrometry (usually with a quadrupole mass spectrometer)
PTR–ToFMS	describes the technique – ‘proton transfer reaction ‘time-of-flight’ mass spectrometry’ and the instrument – ‘proton transfer reaction ‘time-of-flight’ mass spectrometer’
SIFT–MS	selected ion flow tube – mass spectrometry
VOC	volatile organic compound
v/v	volume per volume – is the ratio of the volume of substance contained in the total volume of a solution
m/z	mass to charge ratio (see Glossary)
UPS	uninterrupted power supply

Glossary

Molecular mass: the mass of the whole molecule, without protonation

Protonation: the addition of a proton (H⁺) to an atom or ion

Protonated mass: the mass of the ion plus the mass of an additional proton

Mass to charge ratio (m/z): is the molecular mass (m) of an ion divided by its charge number (z). In mass analysis, typically one or more electrons are taken from molecules to create charged ions. The charge number is the number of electrons removed (for positive ions). The x-axis in a mass spectrum is expressed in units of m/z. Since z is usually 1, the m/z value and mass are usually the same value.

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Executive Summary

What the report is about

Odour emissions from meat chicken sheds sometimes impact the surrounding community. These odour impacts and associated concerns present an ongoing challenge to the chicken meat industry in Australia. At present, the effectiveness of various odour abatement strategies being used by the industry is poorly understood. Defensible odour measurement and abatement data is necessary to justify the cost, and support the uptake, of odour abatement techniques.

This report builds on previous odour research funded by *AgriFutures Australia* to find ways to assess and measure poultry odour more objectively, conveniently and cost-effectively. It describes the use of state-of-the-art, high-resolution mass spectrometry (PTR–ToFMS) to determine the chemical composition of odour emissions from meat chicken sheds, and evaluate odour abatement strategies in terms of reductions in the compounds that contribute to odour impacts. This research provides deeper insight into the key odorants that abatement methods should be targeting and demonstrates the use of high-resolution mass spectra data for predicting odour concentration.

Who is the report targeted at?

The report is targeted at researchers, producers, consultants and regulators concerned with the assessment of meat chicken odour nuisance, and the evaluation of odour abatement techniques. The report provides evidence-based recommendations that will potentially enable future research and odour assessment to be performed more objectively, based on a better understanding of the complex chemistry and key compounds associated with meat chicken odour impacts.

Where are the relevant industries located in Australia?

The Australian chicken meat industry involves the participation of around 700 growers and 40,000 employees. Chicken meat production occurs in all Australian states, and typically in close proximity to major metropolitan centres. According to Australian Bureau of Agricultural and Resource Economics, chicken meat currently makes up 25% of meat production in Australia, and that is expected to rise to 28% by 2018–19.

Background

The chicken meat industry requires defensible data on odour emission and the efficacy of odour abatement methods to facilitate growth and expansion into new areas. Due to the unpredictability of odour emission rates and influence of the surrounding environment to disperse odours, there is a need to characterise and measure downwind odours at the farm boundary or receptor locations. The current study used state-of-the-art mass spectrometry for both in-shed and downwind assessment of meat chicken farm odours, and evaluating odour abatement strategies.

Aims/objectives

The overarching objective of Australian poultry odour research over the past decade has been to develop ways of objectively quantifying poultry emissions to aid assessment and address knowledge gaps. The specific aims of this project were to evaluate and demonstrate the utility of PTR–ToFMS in field and laboratory situations; to characterise meat chicken odour; and to relate the efficacy of abatement methods to changes in concentrations of key odorants and reduced odour concentration.

Methods used

The project methodology was as follows:

- Establish methodology for field and laboratory analysis of odorants using PTR–ToFMS,

- Identify and resolve issues using PTR–ToFMS for poultry odour analysis,
- Identify the key masses reliably revealed by PTR–ToFMS,
- Collect and analyse a range of poultry odour samples (at-shed and downwind) from two farms that used different odour abatement methods,
- Analyse these samples using PTR–ToFMS and dynamic olfactometry data, and build a database of spectra and odour concentration measurements,
- Develop calibration models to directly relate the spectra measurements to odour concentrations and then estimate the odour concentration of future unknown samples.

Results/key findings

PTR–ToFMS has proven useful for characterising, assessing and quantifying meat chicken odours. A suite of compounds, including many known odorants, were reliably detected and measured in real-time.

Use of PTR–ToFMS in the field, while desirable, is currently limited because of practical and logistical issues. These could be partially overcome in the future with a suitable mobile research laboratory or more robust PTR–ToFMS.

Use of pooled PTR–ToFMS mass spectra data provided good prediction of odour concentration ($R^2 = 78.4\%$) across the farms sampled.

Odour abatement potential and efficacy was evaluated in terms of reductions of key odorants, and the odour concentration based on olfactometry. Evaluations using odour predictions based on the mass spectra of samples collected at the source may be more meaningful than olfactometry measurements.

Implications for relevant stakeholders

Ability to use PTR–ToFMS mass spectra data to predict odour concentration at meat chicken sheds will support the use of this technology to assess the efficacy of odour abatement methods in terms of odour and odorant concentrations. This capability will empower the industry to make decisions regarding the adoption of odour abatement strategies.

Routine measurement of poultry odours will remain laboratory-based in the foreseeable future. While highly desirable, use of PTR–ToFMS to analyse dynamic odour plumes in the field is logistically difficult and impractical.

Quality odour research depends on targeted, cost-effective collection of odour data. Mass spectrometry is data-rich and partly fulfils that need, however, olfactometry cannot be completely replaced.

Recommendations

To reinforce the outcomes of this research, it is recommended that:

- Additional odour samples from a range of farms, across different integrators, be collected and analysed by olfactometry and mass spectrometry,
- Additional odour prediction models be developed based on at-farm MS emissions data to account for differences between integrators and growing regions,
- This research be published in an open access journal for the benefit of industry and odour researchers.

Introduction

Odour impacts are a key environmental issue for Australian meat chicken producers. Growth and expansion of the industry is subject to the ability to minimise odour nuisance to neighbours and the community. Successful odour management requires the efficacy of odour abatement strategies to be assessed in an objective, meaningful and reliable way.

Odour abatement methods have traditionally included biofilters, vegetation buffers, stacks, windbreaks and absorbents (Gutarowska, 2014; Ullman, 2004), and optimising diets to minimise excretion of undigested components (Sharma et al., 2017). Formation of odour is multifactorial and, arguably, an effective odour abatement method is reducing the amount of malodour generated in-shed by maintaining dry, friable litter. This is largely achieved with effective ventilation, although litter conditioning may also be necessary to reduce ‘caking’, prevent anaerobic conditions and accelerate drying. One difficulty for industry and researchers has been how to objectively measure odour and, therefore, question the efficacy of odour abatement techniques and products.

Odour has traditionally been assessed using olfactometry, which determines odour detection thresholds using a combination of gas dilution equipment (an olfactometer) and trained human assessors. While still regarded as the only standardised method for odour measurement, olfactometry can’t be used to determine the origins and constituents of a particular odour, or to continuously measure odour in real time. Complementary instrument-based techniques that can measure odorous compounds are necessary for achieving these outcomes.

Researchers have attempted to predict poultry odour concentration using electronic nose (sensor array) odour ‘fingerprints’ as a proxy for olfactometry, and concluded the current chemical sensor technology was too insensitive and non-specific for poultry applications (Atzeni et al., 2016b). Subsequently, a trial using Selected Ion Flow Tube – Mass Spectrometry (SIFT–MS) demonstrated the benefits of real-time mass spectrometry to understand poultry odour emissions, but the mass resolution was considered insufficient (Atzeni et al., 2016a). This led to the current investigation of proton transfer reaction time-of-flight mass spectrometry (PTR–ToFMS). PTR–ToFMS allows for chemical speciation at greater resolution than is possible with SIFT–MS and may provide the additional information needed to accurately measure poultry odour emissions.

PTR–ToFMS is a specified method of chemical ionization for the analysis of trace concentrations of volatile organic compounds (VOCs) in air (Ionicon, 2008). The technique allows for real-time detection and quantification of VOCs with high sensitivity and low limits of detection.

This research project aimed to:

- Improve odour assessment by using PTR–ToFMS to characterise the volatile organic compounds (VOCs) present in meat chicken odour emissions, at source and downwind; and
- Evaluate odour abatement efficacy in terms of reductions in the concentration of odorous compounds generated during meat chicken production.

Objectives

This project had the following objectives:

- Develop laboratory methods for PTR–ToFMS to analyse and characterise poultry odour,
- Develop field methods for using PTR–ToFMS on-site at meat chicken farms,
- Measure odorants downwind from meat chicken farms to identify differences that can be attributed to litter conditions, for the purpose of demonstrating the efficacy of maintaining dry friable litter as an odour impact abatement strategy,
- Provide direction for future research based on acquired knowledge of the capabilities of PTR–ToFMS.

Methodology

Field monitoring programs were conducted across four meat chicken farms (hereby referred to as Farm A, Farm B, Farm C and Farm D) in south-east Queensland from November 2015 to May 2017. All four farms had tunnel ventilated sheds equipped with computer-controlled mechanical ventilation systems. Due to practical limitations of deploying the PTR–ToFMS in the field, all sampling sites were located within 1.5 hr drive of the laboratory to minimise time between sample collection and analysis. Samples of odorous air collected at the farms were subjected to VOC analysis using PTR–ToFMS and odour concentration assessment using olfactometry. Sampling was restricted to weeks four to eight of the grow-out cycle, for the following reasons:

- Odour complaints are less common prior to week four; and
- The chemical composition of odour early in the batch may be affected by the smell from fresh bedding emissions (e.g. pine smells) that may confound the interpretation of the mass spectra and subsequent prediction of odour concentration.

The methodology can be broken down into the following sequence: Odorous air sampling; VOC analysis using PTR–ToFMS; odour concentration assessment using dynamic olfactometry; and calculation of odour activity values (OAV) from VOC concentrations and published odour threshold values (OTVs) for individual VOCs.

Odorous air sample collection

Samples of odorous air were collected for PTR–ToFMS analysis and dynamic olfactometry. As the PTR–ToFMS analysis only requires a very small amount of sample, the same sample bag was also able to be used for olfactometry assessment, which eliminated the need for collecting duplicate samples. Odour samples were divided into two categories: direct-shed measurements and downwind-of-shed (hereafter called ‘downwind’) measurements. Direct-shed measurements are those samples that were collected directly from the exhaust fans on the shed with the aim of getting samples with minimal dilution. Downwind measurements are those that were collected some distance from the exhaust fans of the shed and are representative of the ‘plume’ of air as it may be experienced by neighbours. It was expected that downwind samples would be mixed (multiple sheds contributing), diluted, and contain VOCs from the surrounding environment.

A pilot study was conducted to develop methods for both direct-shed and downwind sample collection. Initially, field sampling was carried out using the ‘lung principle’ sampling technique commonly used for collecting olfactometry samples in accordance with AS4323.3:2001 (Standards Australia, 2009). This method involves the use of an air-tight container and vacuum pump (Figure 1) to draw the sample into a bag made of inert material (polyethylene terephthalate). Using this method, collection time was approximately 10 min per sample. This timeframe proved to be an issue, particularly for downwind samples, as the dynamic position and dilution of the odour plume can change within this time and may even move away or rise above the sampling position. On review of these techniques, and with the project objectives in mind, a simplified, rapid, grab-sampling method was adopted to maximise representative odour content and minimise delays between sample collection and analysis.



Figure 1: Initial sampling methods used to collect downwind (left) and direct shed (right) samples, with air being drawn into the sample bag using a vacuum pump using the lung principle.

A ‘grab’ sample collection method was used for collecting the majority of samples (Figure 2). This method allows for rapid sample collection, which was needed to capture unpredictable downwind plumes. For direct shed samples, the method involved using a 5 L sample bag with a collar supporting the opened end and holding the sample bag directly up to the fans. The sample bag was first allowed to ‘prime’ for roughly 1 min to line the inside of the bag with the exhaust air. The bag was then purged of this air to expel any contaminants that may have been on the inside surface of the sample bag. After purging, a full sample was taken by again holding the bag by the collar and allowing the exhaust air to fill the bag for approximately 1 min.



Figure 2: The ‘grab’ sampling technique adopted for rapid sample collection for shed exhaust odours (left) and downwind plumes (right).

Summary of sampling methods

- Two sampling techniques were required during this project; one was developed to take direct-shed samples at the exhaust fan face, and the other was developed to capture odour emissions downwind of the sheds.
- Samples were initially collected using a traditional technique that utilises the ‘lung principle’ to capture air emissions. This technique was abandoned because extended sampling duration was not suitable for collecting air from dynamically moving odour plumes.
- A simplified ‘grab sample’ technique was adopted for rapid sample acquisition, which was critical for downwind samples.

Odour assessment using dynamic olfactometry

Olfactometry is the traditional, and standardised, way to measure odour concentration. It is determined by measuring the odour detection threshold using a combination of gas dilution equipment (an olfactometer) and trained human assessors. In this project, odour concentration of air samples was determined by forced-choice, dynamic olfactometry using a Scentroid SC300 mobile automated dynamic dilution olfactometer (Scentroid, 2013)(Figure 3). This olfactometer complies with the Australian/New Zealand Standard for Dynamic Olfactometry AS/NZS 4323.3:2001 (Standards Australia/Standards New Zealand, 2001). The conduct of the odour assessment also complied with this Standard.

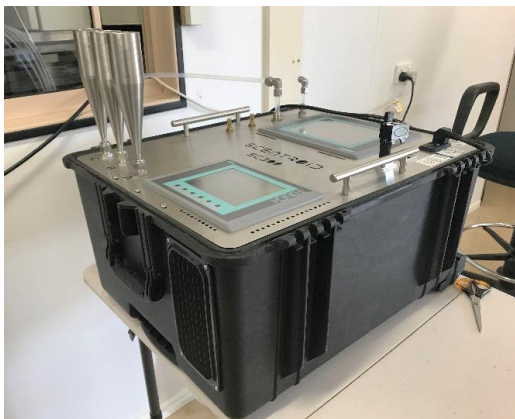


Figure 3: ‘Scentroid SC300’ mobile olfactometer used for odour assessment. Trained and qualified air quality assessors (right) were employed to analyse odorous samples.

During a typical odour sample assessment session, each panellist was firstly screened with the reference gas (n-butanol) to ensure their detection threshold was within the required concentration range of 20–80 ppb. Samples collected at the poultry farms were then analysed, usually in the order they were collected. Each sample was diluted and presented to the panellists in one of the three ports, while the other two ports emitted clean, odour-free air. The panellists were required to sniff each of the ports and determine whether they could detect a difference between them. Each panellist was allowed a maximum of 15 s for this assessment. The panellists indicated via a touchscreen whether they were certain, uncertain or guessing that they could detect the odour, as well as identifying which port the odour (if detectable) was emitted. This process was repeated, doubling the concentration of odorous air each time, until each panellist had entered a “certain and correct” response for two consecutive presentations, thus completing a ‘round’. Three rounds were completed for each sample provided

sufficient sample was available. The results of the first round were discarded and panellists' responses were screened in accordance with the Standard. Weak downwind samples and background samples were occasionally unable to be analysed strictly to Standard (because three rounds could not be completed). Nevertheless, these non-standard results were required for comparison with the mass spectra and used for odour prediction modelling.

For consistency, the pool of panellists was restricted to the same eight people. Five to seven of the panellists were used for each olfactometry session depending on availability.

Odour concentrations were expressed as odour units per cubic metre (ou/m³).

Summary of olfactometry methods

- Dynamic olfactometry was carried out during this project to measure the odour concentration of air samples.
- A panel of five to seven trained odour quality assessors was employed for odour concentration analysis.
- This allowed for an odour concentration assessment to be paired with the chemical concentration data collected by the PTR–ToFMS.

VOC sampling and analysis using PTR–ToFMS

Instrument and calibration

A PTR–ToFMS (*TOF1000*, Ionicon Analytik, Innsbruck, Austria) was used to analyse air emissions from meat chicken farms. PTR–ToFMS is a technique used to detect, identify and quantify very low concentrations of VOCs in an air sample. Using this technique, it is possible to determine the chemical constituents present, and their abundance. Principles and applications of PTR–ToFMS (and the similar technique of PTR–MS) have previously been described (Blake et al., 2009; Brillì et al., 2014; Capelli et al., 2013; Feilberg et al., 2010).

Briefly, the PTR–ToFMS is comprised of an ion source coupled with a drift tube and a time-of-flight mass spectrometer with a high mass resolution. VOCs were detected in real-time through proton transfer reactions occurring between H₃O⁺ ions produced from water vapour in the ion source, as the sample gas was introduced into the drift tube. In order for these reactions to occur, compounds must have a proton affinity greater than that of water (691 kJ mol⁻¹). Some compounds, including hydrogen sulfide (H₂S), have a proton affinity only slightly higher than water and this makes them difficult to measure accurately.

PTR–ToFMS uses mass selectivity to separate compounds. This means that any protonated compounds with the same mass to charge ratio (*m/z*) were unable to be individually quantified. Therefore, data from the PTR–ToFMS was analysed in terms of protonated molecular masses (referred to in this report as 'masses') for which 'possible' VOCs or odorants could be assigned based on the measured mass.

Additionally, a process called 'fragmentation' occurs for many compounds, meaning that compounds can be split into fragments that have a series of different molecular weights. Some of these fragments may have identical weights to other VOCs, giving the impression that more or less of a given compound is present in a sample than is actually there. The patterns of these fragmentations are dependent on the specific conditions in the PTR–ToFMS drift tube and, therefore, previously reported fragmentation patterns may not apply to different instruments. Experimentally determining fragmentation patterns for poultry related VOCs was not undertaken during this project.

The PTR–ToFMS was operated with ion drift tube conditions, with 600 V applied to the tube with a maintained pressure of 2.1–2.2 mbar. Drift tube temperature was set at 80 °C and the inlet flow was controlled to 100 mL/min. Raw data from the PTR–ToFMS was interpreted using *PTR–MS Viewer* software (version 3.2.8.0, Ionicon, Innsbruck, Austria). This software was used to correct for mass-shifting of the mass spectra before being used to calculate the concentration (ppb) of individual masses (which represent known or suspected poultry odorants).

To ensure accuracy and account for instrument drift, a suite of calibration gasses (*Air Liquide Specialty Gasses, USA*) were regularly used to calibrate the PTR–ToFMS throughout the experiments. For gases with concentration greater than 100 ppb, the standards were diluted with instrument grade nitrogen gas (Grade 5.0, Coregas, Yennora, NSW, Australia) to ensure the instrument’s detector was not saturated when the gas was introduced. A selection of custom gas mixtures containing a range of compounds known to be present in exhaust air from meat chicken sheds were also used to test the instrument’s response (listed in Appendix A).

Laboratory testing of odorant emissions from litter

Prior to field deployment of the PTR–ToFMS, laboratory-based tests were carried out to confirm that the PTR–ToFMS was capable of detecting common poultry VOCs, most of which originate from the litter. Dry and wet litter samples were used because it was expected that wet litter would produce different VOCs and have higher VOC emission rates. Litter was collected from a meat chicken shed and transported to DAF’s laboratory for PTR–ToFMS analysis.

For the litter analyses, an isolation flux hood was used to introduce the sample into the instrument (Figure 4). Instrument grade nitrogen was used as sweep-air. The sweep-air entered the hood with a regulated flow rate of 500 ml/min through the outer port, and sample gas was drawn from the central port directly into the inlet of the PTR–ToFMS. Very high concentrations of VOCs occasionally developed within the flux hood and therefore needed to be diluted (using instrument grade nitrogen) at the inlet to the PTR–ToFMS to keep the concentrations within the instrument’s detectable range. The hood was placed on a stainless steel surface and flushed with the sweep-air in between litter samples until VOC concentrations returned to very low levels.

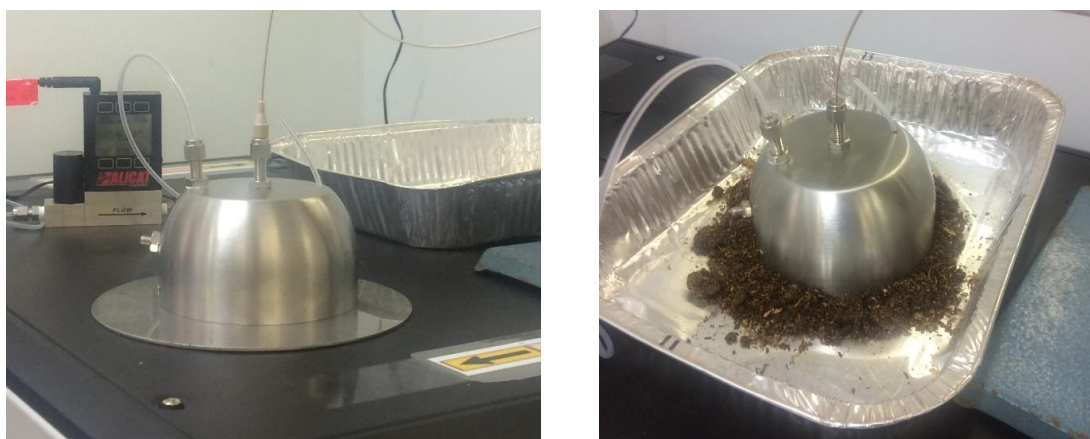


Figure 4: Flux hood used for collecting gas emissions directly from litter. The hood was placed on a stainless steel surface (left) and flushed with N₂ in between measurements of emissions from litter samples (right).

Field deployment of PTR–ToFMS

To minimise time between collection and analysis of odorous air samples, the PTR–ToFMS was deployed on-site at two meat chicken farms in South East Queensland (Figure 5). It was anticipated that deploying the PTR–ToFMS in the field would allow for timely analysis of samples and minimise

the chance of confounding effects from storing odorous samples in bags for prolonged periods, i.e. odour decay. Additionally, the PTR-ToFMS has a real-time analysis readout, which enables more targeted and discerning analysis, as the operator can quickly determine if the sample contains the expected compounds.



Figure 5: PTR-ToFMS field deployment set-up.

Despite the anticipated benefits, it was found that transporting and using the instrument in the field was extremely challenging. Some reasons for this include:

- The instrument must undergo a 25 min shutdown procedure before it can safely be packed and securely fastened for transport. A trailer was customised to safely transport the instrument, compressed gas cylinders and uninterrupted power supply (UPS).
- A lengthy start-up time of 3–24 h is required for internal pumps to reach the desired vacuum pressure, to reach the operating temperatures, and for the whole system to be stable.
- Once the instrument is turned on in the field, it could not be readily moved from its position to allow the instrument to be kept within an odour plume.
- Fluctuating ambient temperatures resulted in temperature variations within the drift-tube and mass spectrometer, which affects the accuracy and resolution of the instrument.
- There are insurance and security considerations when using the instrument for extended periods at a location.

Upon these realisations, field analysis of samples was discontinued, and all future samples were collected in sample bags and transported back to the laboratory for analysis.

Summary of PTR–ToFMS and field deployment of the instrument

- PTR–ToFMS is a technique used to detect, identify and quantify very low concentrations of organic gases (VOCs) in an air sample.
- Using this technique, it is possible to determine the chemical constituents of an air sample. Many compounds cannot be identified or quantified with absolute certainty due to the presence of other compounds with the same molecular mass, or by fragmentation of compounds during the ionisation process.
- Data from the PTR–ToFMS was analysed in terms of *protonated molecular masses* for which ‘**possible**’ VOCs or odorants could be assigned based on the measured mass.
- To ensure accuracy and account for instrument drift, a number of calibration gases were regularly used.
- Prior to deploying the instrument in the field, wet and dry litter samples were analysed with the PTR–ToFMS in the laboratory to confirm the ability of the instrument to detect a range of poultry odorants.
- The PTR–ToFMS instrument was deployed in the field to allow for samples to be analysed within minutes of collection. Several problems were encountered when doing this— including lengthy start-up times and the inability to move the instrument once it was set-up for sample analysis.
- Due to the challenges encountered with deploying the PTR–ToFMS in the field, the research team decided that future samples would be transported back to the laboratory to be analysed.

Odour threshold values and calculation of odour activity values

Odorous volatile organic compounds can be assessed by comparing individual odour threshold values (OTV). OTVs are the minimum concentration at which a single compound can be detected by a human assessor (Parker et al., 2012). This means that compounds with low OTVs can be detected at lower concentrations. Due to the inherent subjective nature of determining odour thresholds, published OTVs can vary considerably. In this report, OTVs for individual compounds were calculated using the geometric mean of the published values to give one single OTV for each compound (Appendix B).

Odour activity value (OAV) can be used to theoretically express how much a single compound adds to the overall perceived odour. Odour activity is defined as the ratio of the concentration of a single compound to the OTV for that compound. In theory, the larger the OAV, the more likely that compound will contribute to the total odour of a complex gas mixture (Parker et al., 2012), which can be useful in identifying the major components causing high odour concentrations and potentially contributing to odour impacts.

Odorant concentrations and OTVs expressed in ppb units were converted to units of $\mu\text{g}/\text{m}^3$ (Equation 1) before calculating single compound odour activity values (Equation 2). As PTR–ToFMS was unable to distinguish between individual odorants with the same mass, the OTV assigned to each protonated mass was determined by calculating the geometric mean of the OTV for the possible compounds at that mass.

$$C = \frac{C_{ppb} \times MW}{(R \times T \div P)}$$

Equation 1

Where:

C is the odorant concentration in $\mu\text{g}/\text{m}^3$

C_{ppb} is the odorant concentration in ppb

MW is the molecular weight of the odorant

R is the universal gas constant ($8.3144 \text{ L.kPa.mol}^{-1}.\text{K}^{-1}$)

T is the air temperature (K)

P is the air pressure (kPa)

Note– the term (**R×T÷P**) is approximately 24.05 at 20 °C

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

Equation 2

Where:

OAV is the odour activity value

C is the odorant concentration in $\mu\text{g}/\text{m}^3$

OTV is the single compound odour threshold value

Summary of odour activity value (OAV) calculations

- OAVs were calculated based on the concentrations of odorous chemicals detected using PTR–ToFMS.
- An OAV provides an estimate of how much a compound may contribute to overall odour concentration.
- Published odour threshold values were used to calculate OAVs for known compounds.

Results and discussion

Laboratory-based analysis of litter odorants

Prior to using the PTR–ToFMS to measure odorant concentrations at meat chicken farms, laboratory-based tests were conducted using litter collected from a meat chicken farm. The main aim of this activity was to confirm that the PTR–ToFMS was capable of detecting the various volatile organic compounds (VOCs) associated with poultry odour, and to evaluate the instrument’s ability to detect differences in chemical composition in litter type; i.e. wet litter and dry litter.

Several litter samples were collected on day 38 of the grow-out cycle from Farm A. Two samples were designated as wet litter and two samples were from dry litter conditions. The wet litter samples were collected from under the drinker lines, as this location contained consistently wetter litter, and the dry samples were taken from an area of the shed that was consistently dry, as reported by the grower.

Mean odorant concentrations were calculated for each molecular mass (selected masses in Figure 6, full range of masses in Figure C1 of Appendix C). There were 91 distinct masses detected, with 55 masses corresponding with odorants previously reported from poultry emissions (Appendix B). In addition to the masses shown in Figure 6, a high response from the PTR–ToFMS analysis was on mass 43, but it is believed that this peak was due to fragmentation of other compounds. Many VOCs, when ionized, have fragments that occur at mass 43, consequently, it is not considered to be one of the masses of interest in this project, in terms of potential odour nuisance.

The litter results confirmed that PTR–ToFMS can detect compounds of interest previously reported in poultry odour. The PTR–ToFMS also measured relative differences in the concentration of the masses from each litter type. Some of these included compounds with unpleasant odour character and were in concentrations much higher than their OTV (Table 1). OAV was calculated for the masses and we found that some masses had much greater OAV than others, indicating that they are likely to make a greater contribution to the perceived odour.

The masses with the highest OAV in the dry litter (49.01, 63.02, 87.04, 89.05, 103.07 and 132.08) and the wet litter (49.01, 87.04, 89.05, 91.05 and 126.97) are of significant interest. Differences in the dominant odorants are likely to explain differences in odour character between wet and dry litter. For the dry litter, the masses with the largest OAV (based on the possible compounds) have character described as sharp, sour, rancid, mushroom, cheese, stench and faecal, whereas the character of wet litter is dominated by descriptions of rotten cabbage, sour, rancid, buttery, garlic, foul, pungent and onion.

Results from this experiment showed that the PTR–ToFMS has the capability to measure VOCs emitted from poultry litter, as well as providing the means to observe differences in the VOCs emitted from different litter conditions—a crucial step prior to the ability to detect meat chicken odorants downwind.

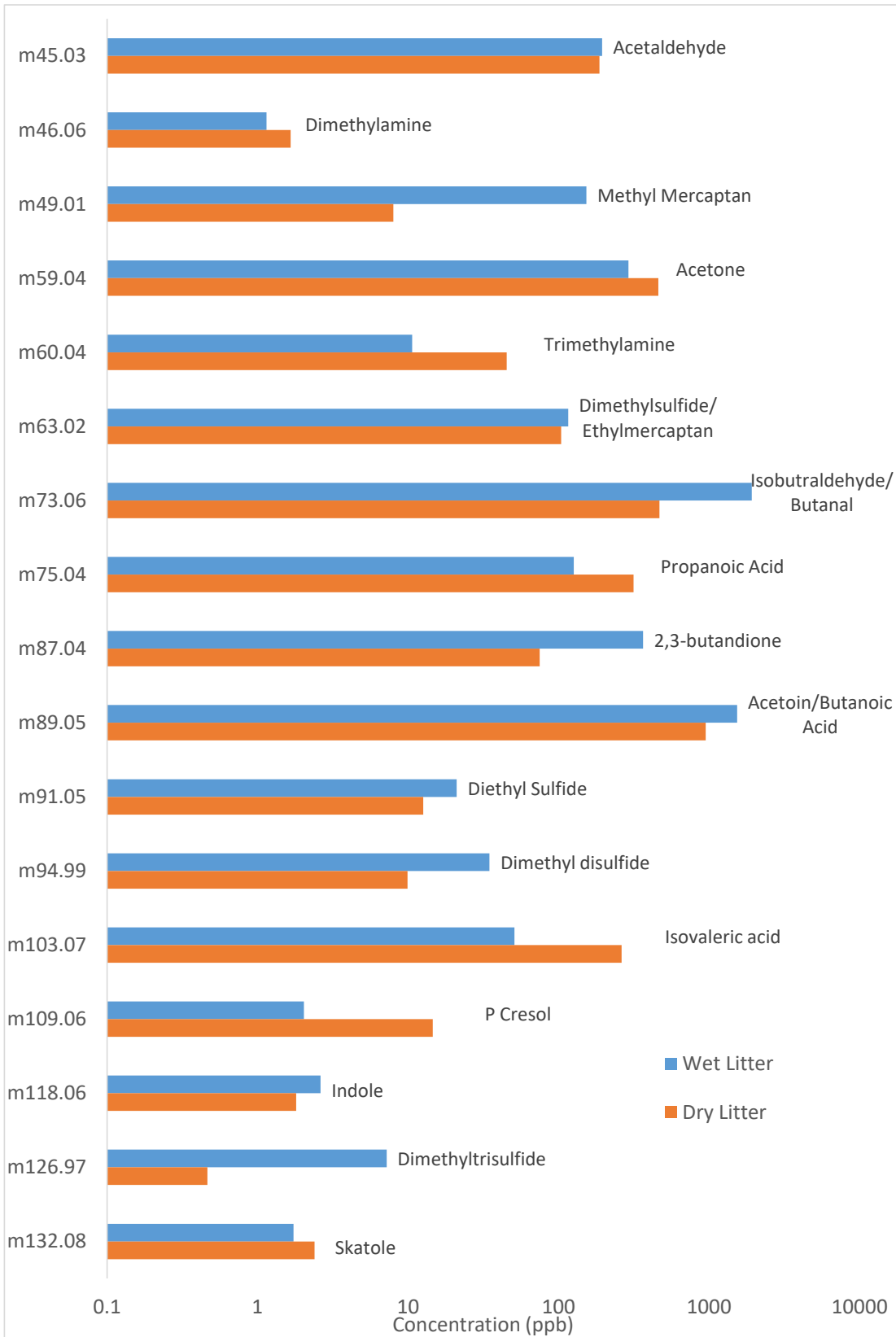


Figure 6: Concentration (ppb; logarithmic) of detected masses (labelled with possible compounds) from wet (blue bars) and dry (orange bars) litter samples (n=3). The possible compounds have been previously identified in poultry and are above their detection threshold. The full range of masses detected can be found in Appendix C.

Table 1: Selected masses and corresponding possible odorants detected in wet and dry litter.

Protonated mass (H+)	Possible compounds	Odour character	OTV# (ppb)	OAV in dry litter	OAV in wet litter
49.01	Methyl mercaptan	Rotten cabbage	0.02	400	7676
60.08	Trimethylamine	Fishy, ammonia	0.44	103	24
63.02	Dimethyl sulfide; Ethyl mercaptan	Natural gas, rotten vegetables	0.3 [0.1; 0.4]	346	386
87.04	2,3-Butanedione	Sour, rancid butter	0.05	1498	7299
89.05	Butanoic Acid; Ethylacetate; Isobutyric acid	Butter, mushroom, rancid, sharp	2.0 [0.2; 30; 1.5]	475	769
91.05	Diethyl sulfide	Garlic, foul	0.03	420	702
94.99	Dimethyl disulfide	Pungent, garlic	0.3	33	115
103.07	Isovaleric acid; 2-methylbutyric acid; pentanoic acid	Rancid, cheese, stench	0.3 [0.1; 2.0; 0.2]	875	169
109.06	P-cresol	Faecal, tarry	0.05	292	40
118.06	Indole	Faecal	0.03	60	87
126.97	Dimethyl trisulfide	Pungent, garlic, onion	0.01	46	720
132.08	Skatole	Faecal	0.006	398	289

#Geomean of OTV from individual compounds, listed in square brackets

Summary of litter compound analysis with PTR–ToFMS

- Prior to taking measurements directly from meat chicken sheds or downwind, laboratory trials were conducted on wet and dry litter.
- 91 masses, representing various VOCs, were observed in detectable quantities from the litter samples. 55 of these masses correspond with previously reported poultry odorants. This demonstrated that PTR–ToFMS is capable of detecting poultry odorants from litter under laboratory conditions.
- PTR–ToFMS analysis showed a substantial difference in the mass spectra from dry litter compared to wet litter. Higher concentrations of masses seen in wet litter compared to the dry litter samples, included:
 - 49.01 (possibly methyl mercaptan, i.e. ‘rotten cabbage’)
 - 73.06 (possibly isobutyraldehyde, i.e. ‘pungent’)
 - 87.04 (possibly 2,3-butanedione, i.e. ‘sour’ and ‘buttery’)
 - 89.05 (possibly acetoin and butanoic acid, i.e. ‘mushroom’ and ‘rancid’)
 - 91.05 (possibly diethyl sulfide, i.e. ‘garlic’ and ‘foul’)
 - 94.99 (possibly dimethyl disulfide, i.e. ‘garlic’ and ‘pungent’)
 - 126.97 (possibly dimethyl trisulfide, i.e. ‘pungent’, ‘garlic’ and ‘onion’)
- Using OAV calculations, the PTR–ToFMS improved our understanding of the odorants likely to be dominating the odour from wet and dry litter. Differences in the character of these odorants may be useful for explaining why wet and dry litter smell differently. **The existence of multiple ‘possible’ odorants for some masses creates uncertainty during OAV calculations.**
- This provided sufficient evidence to move on to collecting samples in the field.

Analysis of at-shed odorants

A total of 59 samples were taken directly from sheds at Farms A, B and C. These samples were analysed with a PTR–ToFMS to determine the concentration of VOCs present. Average concentrations

for masses were calculated (selected masses in Figure 7; full range of masses in Figure C2 of Appendix C; and full list of previously detected poultry odorants and the concentration ranges of their corresponding protonated mass in Appendix D).

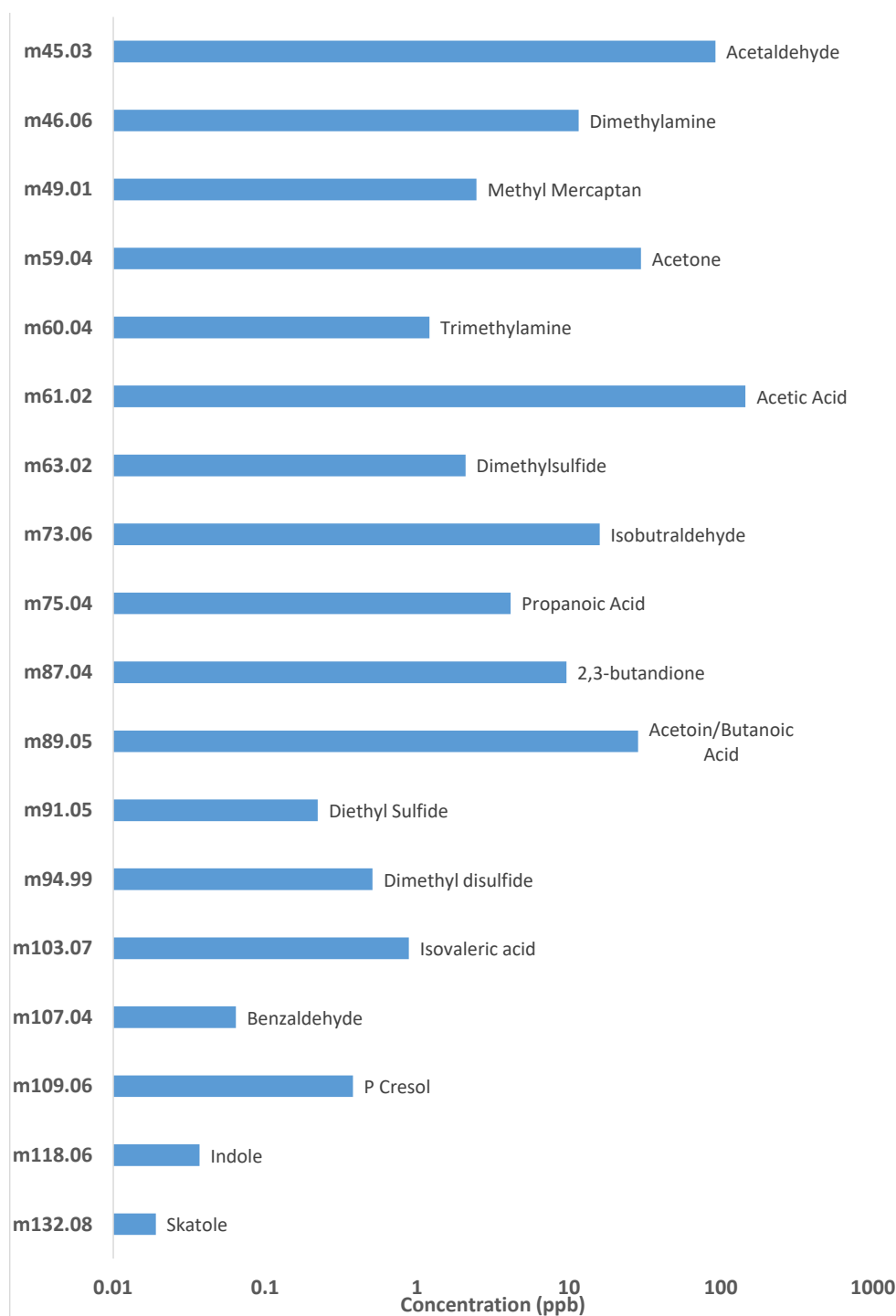


Figure 7: Average concentration for selected masses from all 59 samples taken directly from the exhaust fans at all sheds. Masses are labelled with previously reported poultry ‘possible’ odorants on a logarithmic scale. Compounds up to mass 157 were detected (Figure C2 in Appendix C)

A large number of the compounds were detected in very low abundance (<1 ppb). In contrast, mass 61.02 (possibly acetic acid) at 145ppb had the highest average concentration for any single mass.

Acetic acid is a common compound and has been previously detected in odour emission from intensive livestock operations (Feilberg et al., 2010; Lin et al., 2012; Rosenfeld & Suffet, 2004; Trabue et al., 2010). It has a relatively high odour detection threshold (360 ppb) and a ‘vinegary’ odour character (Ruth, 1986), which suggests it is not a strong malodorant that would cause odour nuisance.

In terms of potential odour nuisance, of more interest are those compounds with unpleasant odour characteristics that were present in concentrations above their odour threshold value. These are the compounds that are considered most likely to be causing odour nuisance. One such example is mass 87.04 (possibly 2,3-butanedione), which has a reported odour character of ‘rancid’ with an odour detection threshold of 0.05 ppb (Nagata, 2003), and was present with an average concentration of 13.2 ppb. This means that it was present at approximately 260 times greater than the OTV, which makes it a candidate for contributing to odour nuisance. Also of note is mass 49.01 (possibly methylmercaptan) with a ‘rotten cabbage’ odour character, which was detected at an average of 2.9 ppb, but has a very low odour detection threshold of 0.02 ppb. Despite only being detected at average of 2.9 ppb, this is still 145 times higher than its odour detection threshold. Additional discussion about the contribution of other measured masses to the odour is described in more detail in the *Odour activity value* section.

Summary of in-shed compound analysis and bird age effects

- 59 direct shed air samples were taken from three meat chicken farms in South East Queensland.
- The majority of the masses detected were in sub parts per billion quantities.
- Mass 61.0284 (likely acetic acid) was the most abundant single compound on average being emitted directly from the sheds. While measured in high concentrations, acetic acid has a relatively high odour threshold and a ‘vinegary’ odour character and is therefore not likely to be a primary contributor to odour impacts.
- Some compounds likely to contribute to odour impacts, because they have low odour threshold and unpleasant odour character, included:
 - Mass 87.0411 (likely 2,3-butanedione) with a ‘rancid’ odour character was detected at 260 times higher than its odour detection threshold
 - Mass 49.0106 (likely methylmercaptan) with a ‘rotten’ odour character and occurring 145 times above its odour detection threshold.
- This is an indication that odour may be related to the increases in concentration of only a few key compounds (addressed further in the *Odour unit prediction modelling* section).

Downwind compound analysis

Mean concentrations of odorants downwind from sheds

Odour impacts occur downwind from farms (i.e. the source of the odour) after the odour has been subjected to dispersion, dilution and also potential changes in odour chemistry. Odour chemistry may change due to chemical reactions, interaction with moisture, UV exposure and addition of odour from the surrounding environment. In order to understand the odorants that contribute to odour impacts, we need to know what compounds are present, and in what concentration, downwind of the source.

A total of 31 samples were taken at varying distances downwind from the sheds at Farms A, B and C. Distances varied from 10 m to 600 m from the sheds. Downwind samples were analysed with a PTR–ToFMS to determine VOC concentrations. As with the direct shed samples, the downwind samples were collected on-site in sample bags and transported back to the laboratory for analysis, generally

within two hours of collection. Average concentrations for selected masses were calculated (Figure 8, full list of masses presented in Figure C3 in Appendix C), but only show those samples that were taken a minimum of 50 m away from the sheds. At this distance, samples were considered to be beyond the direct influence of the shed exhaust fans and therefore more representative of ‘downwind’ odours.

The compounds detected with the highest concentration in the downwind samples were, in descending order, mass 45.0335 (likely acetaldehyde), mass 59.0491 (likely acetone) and mass 61.0284 (likely acetic acid). Acetaldehyde is classed as an ‘aldehyde’ compound with a low odour detection threshold of 1.5 ppb and an odour character described as ‘yoghurty’ and ‘fruity’. Acetone (solvent odour character) and acetic acid (vinegar odour character) were present in concentrations below their odour threshold values. Therefore, while present in high concentration, Acetone and Acetic acid would likely make no contribution to the perceived odour.

As with the direct shed samples, the downwind samples contained concentrations of mass 87.0441 (likely 2, 3-butanedione) and mass 49.0106 (likely methylmercaptan) that were above their odour detection threshold values. 2,3-butanedione was detected at an average of 1.22 ppb, which is above the odour threshold value, and methylmercaptan was detected at 1.1 ppb, which is also higher than its odour threshold value. While these are very small concentrations, the combination of low threshold values and unpleasant odour character make these compounds likely candidates for contributing to odour impacts from poultry facilities at receptor distances.

Also of note in the downwind samples is the presence of other sulfur-containing compounds, including mass 63.026 (likely dimethyl sulfide or ethyl-mercaptan) and mass 91.0567 (likely diethyl sulfide). Downwind of the source, these were present in readily detectable concentrations using PTR–ToFMS. These compounds are reported to have a ‘foul’, ‘garlicky’, ‘pungent’ odour character and low odour detection thresholds (Appendix B). Based on the concentrations that these compounds were measured downwind from the sheds (concentrations were approximately 10 times greater than their OTV), they are candidates for contributing to odour nuisance.

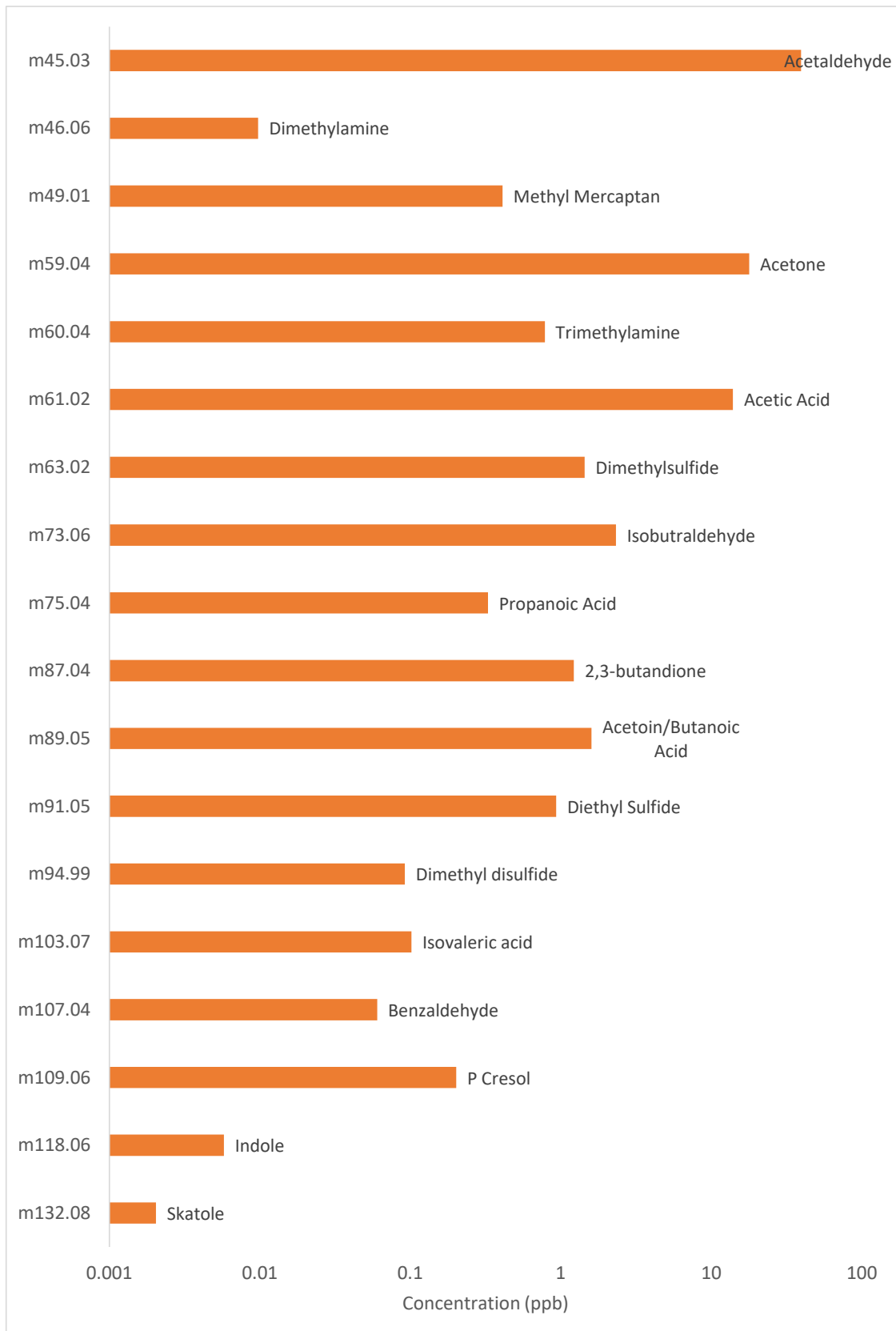


Figure 8: Average concentration (ppb) for selected masses in downwind samples (n=19) on logarithmic scale. Compounds up to mass 157 were detected (Figure C3 in Appendix C).

Summary of compound analysis and detectability downwind

- A total of 31 samples were taken downwind of the fans at three meat chicken farms.
- 19 of those samples were taken between 50 and 600 m downwind.
- Mass 45.0335 (likely acetaldehyde), mass 59.0491 (likely acetone) and mass 61.0284 (likely acetic acid) had the highest concentrations from the average of the 19 samples.
- Mass 63.026 (likely dimethyl sulfide) and mass 91.0567 (likely diethyl sulfide) were detected in the majority of downwind samples, even at 600 m from the source. These sulfur containing compounds have low odour detection threshold and unpleasant odour character.

Distance effects on odorant concentrations

Throughout this project, samples were taken at various distances downwind from meat chicken sheds to determine the potential effects of distance on the detectable odour, as well as the corresponding differences in the chemical composition. A total of 31 downwind samples were taken, with the majority collected between 50 and 100 m from the source, as this was generally the limit of the detectable plume on the sampling days. Some samples were collected as close as 10 m away from the shed, that is, within the influence of the exhaust fans, and up to a maximum distance of 600 m downwind. Figure 9 shows a comparison between a sample taken 10 m away from the exhaust fans of a meat chicken shed located at Farm A and one taken 600 m downwind at the same farm. The concentration of masses for the sample taken 10 m downwind are similar to the average downwind sample seen above (Figure 8). In this sample, mass 45.0335 (likely acetaldehyde) was present in the highest concentration, with mass 61.0257 (likely acetic acid) and 46.0651 (likely dimethylamine) also being present in high quantities.

When comparing the 10 m sample with the 600 m sample, some mass concentrations from the latter are particularly interesting. For example, the concentration of mass 91.0576 (likely diethyl sulfide) is only slightly lower at 600 m than in the sample collected at 10 m. As previously discussed, this compound has a low odour detection threshold and an unpleasant odour character. Therefore, we suggest this compound may contribute towards odour nuisance downwind of these meat chicken farms. Mass 87.0441 (likely 2,3-butanedione), another key odorant, reduced in concentration as it moved downwind from the source but was still present in detectable quantities by PTR-ToFMS at 600 m downwind. Levels of 'decay' seen in other key odorants are discussed in the following section.



Figure 9: Concentration (logarithmic) of selected masses detected in a single sample 600 m downwind of the source (red) and a single sample 10 m (green) from the source. Compounds up to mass 157 were detected (Figure C4 in Appendix C)

Odour concentration reduction over distance

Odour concentration, measured in odour units (ou), decreased exponentially with distance from the source due to plume dispersion (Figure 10). The curve includes a lower asymptote (indicating the 'background level'), reaching a minimum value of 11.7 ou. Shed emissions were around half-strength by 10 m downwind, and quarter-strength by 50 m downwind. By 120 m, the odour was effectively below detection threshold (Table 2). While the R^2 value of 0.68 for odour decay curve appears reasonable, it must be noted the data are predominantly from morning samples collected after sunrise and they may not reflect what happens under the more stable atmospheric conditions, or during a thermal inversion, when the plume is channelled along the lower parts of the landscape (katabatic flow). Unfortunately, such conditions are difficult to capture in practice.

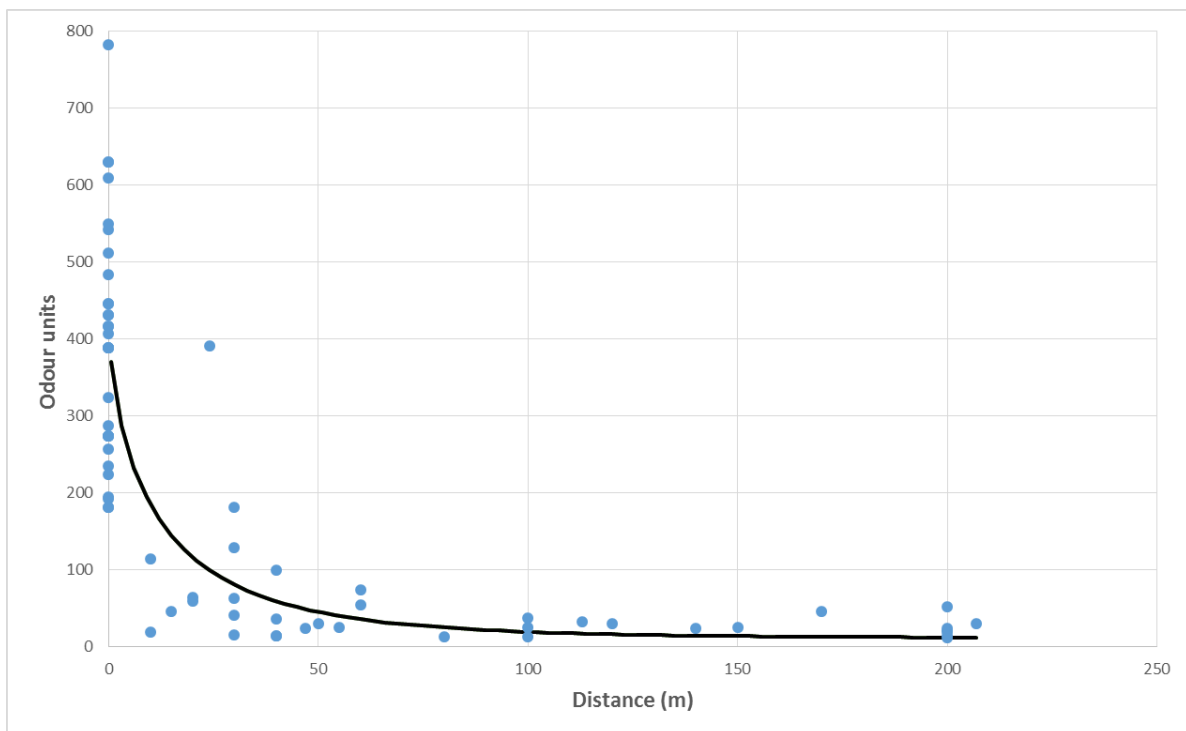


Figure 10: Reduction in odour concentration (ou) over distance based on all downwind samples.

Exponential-decay curves were also fitted to a range of masses of interest from an odour prediction modelling perspective (Table 2, $0.01 < R^2 < 0.51$). Some odorants were observed to rapidly dissipate once they leave the source. The overall trend for most masses indicates that by 100 m downwind of the source, the average concentration of most odorants had dropped below 99%.

Of specific interest are the compounds with lower odour thresholds, i.e. those compounds that are detectable by human receptors even at very low concentrations. For example, mass 109.06 (likely p-cresol) has a very low odour threshold value of 0.054 ppb, with an odour character described as 'faecal, tarry' and was still detectable at over 300 m downwind of the source. It is these types of compounds that are more likely responsible for odour impacts downwind.

It should be noted that the measured downwind concentrations are a result of the surrounding environment and weather at the time of sampling. These residual concentrations are not transferable to other farms or environmental conditions.

Table 2. Fitted exponential decay curves for masses corresponding to compounds of interest

Odour (ou)	Possible compound	R ²	Value	Distance (m) to reduction by-				
			at shed	50%	75%	90%	95%	99%
		0.68	370	10	24	48	69	123
m43.05	Propene	0.31	3.79	9	17	29	38	58
m45.03	Acetaldehyde	0.24	90.3	32	64	107	139	213
m46.06	Dimethyl amine	0.24	0.12	8	16	26	34	53
m49.01	Methyl mercaptan	0.38	2.45	8	16	26	34	52
m59.04	Acetone	0.04	32.0	48	96	160	208	320
m60.08	Trimethyl amine	0.10	1.21	15	30	50	65	100
m61.02	Acetic acid	0.34	145.2	6	12	20	26	40
m63.02	Dimethyl sulfide	0.43	2.09	13	27	45	58	89
m69.06	Isoprene	0.01	1.68	85	171	283	369	567
m71.04	Numerous compounds	0.51	24.0	8	15	25	32	50
m73.06	Numerous compounds	0.38	15.9	8	16	27	35	53
m75.04	Propanoic acid	0.26	4.13	5	9	15	20	30
m75.08	Butanol	0.36	0.38	7	13	22	29	45
m79.05	Benzene	0.19	0.21	21	42	70	91	140
m87.04	2,3-butanedione	0.52	9.62	9	18	30	39	60
m87.08	Isovaleral-dehyde	0.15	0.34	15	31	51	66	102
m89.05	Butanoic acid	0.41	28.5	5	10	16	21	32
m89.09	Pentanol	0.19	0.68	10	21	35	45	70
m91.05	Diethyl sulfide	0.36	0.22	9	18	29	38	58
m94.99	Dimethyl disulfide	0.40	0.51	8	16	26	34	52
m95.04	Phenol	0.30	0.25	12	25	41	53	82
m103.07	Isovaleric	0.25	0.88	5	9	15	20	30
m109.06	P-cresol	0.40	0.36	52	103	172	224	344
m117.09	Hexanoic acid	0.15	0.08	13	26	43	56	86
m118.06	Indole	0.05	0.04	14	27	45	59	91
m123.08	4-ethyl phenol	0.32	0.09	8	16	27	35	53
m129.09	Ethylmethyl butenate	0.18	0.04	14	28	47	62	95
m129.12	Octanal	0.32	0.04	19	38	63	82	126
m131.10	Propyl butyrate	0.33	0.12	8	15	25	33	50
m132.08	Skatole	0.32	0.02	11	22	36	47	72
m137.13	Terpines	0.30	0.13	44	87	145	188	289
m143.14	Nonanal	0.32	0.01	13	26	43	56	85

Summary of reduction in odour concentration with distance downwind

- At 10 m from the source, most key masses were present at readily detectable quantities.
- At 100 m downwind, some odorous compounds still are present in detectable quantities using PTR–ToFMS. Most compounds have reduced to less than 1% of their original concentration by 100 m.
- Some compounds are still above the odour threshold value at 567 m.
- Measured downwind concentrations are a result of the surrounding environment and weather at the time of sampling. These residual concentrations are not transferable to other farms or environmental conditions.

Odour activity value

High concentration of an odorous compound does not necessarily translate to an intense or strong smell. It depends on the odour detection threshold (odour threshold value, OTV) for the compound and how many times greater concentration the odorant is in the air compared to the OTV. For example, if the OTV of a compound is 1 ppb and the actual concentration of the odorant in the air is 10 ppb, then it is at 10 times the concentration at which an average person may be able to detect it as a weak smell. The odorant would need to be diluted by more than 10 times in order for the odorant to no longer be perceived as a smell.

Some compounds measured in high concentrations during this project may not be recognised as odorants, or may have high detection thresholds. There are also some compounds that are known to be odorous, but their odour threshold value has not been reported and is therefore not available (Refer to Appendix B for odour threshold values). For compounds which have a reported OTV, OAV may be useful in determining which individual compounds are contributing the most to an odour. Simply put, OAV can be used to gauge how much a single compound contributes to the overall odour of a gas. As Parker et.al. (2012) explained, odours are not always additive. Antagonistic and synergistic reactions occur between compounds and this is not accounted for in OAV calculations. Single compound odour activity values were calculated for selected individual odorants using the mean, minimum and maximum measured concentrations from in-shed samples (Figure 11) and for downwind samples (Figure 12).

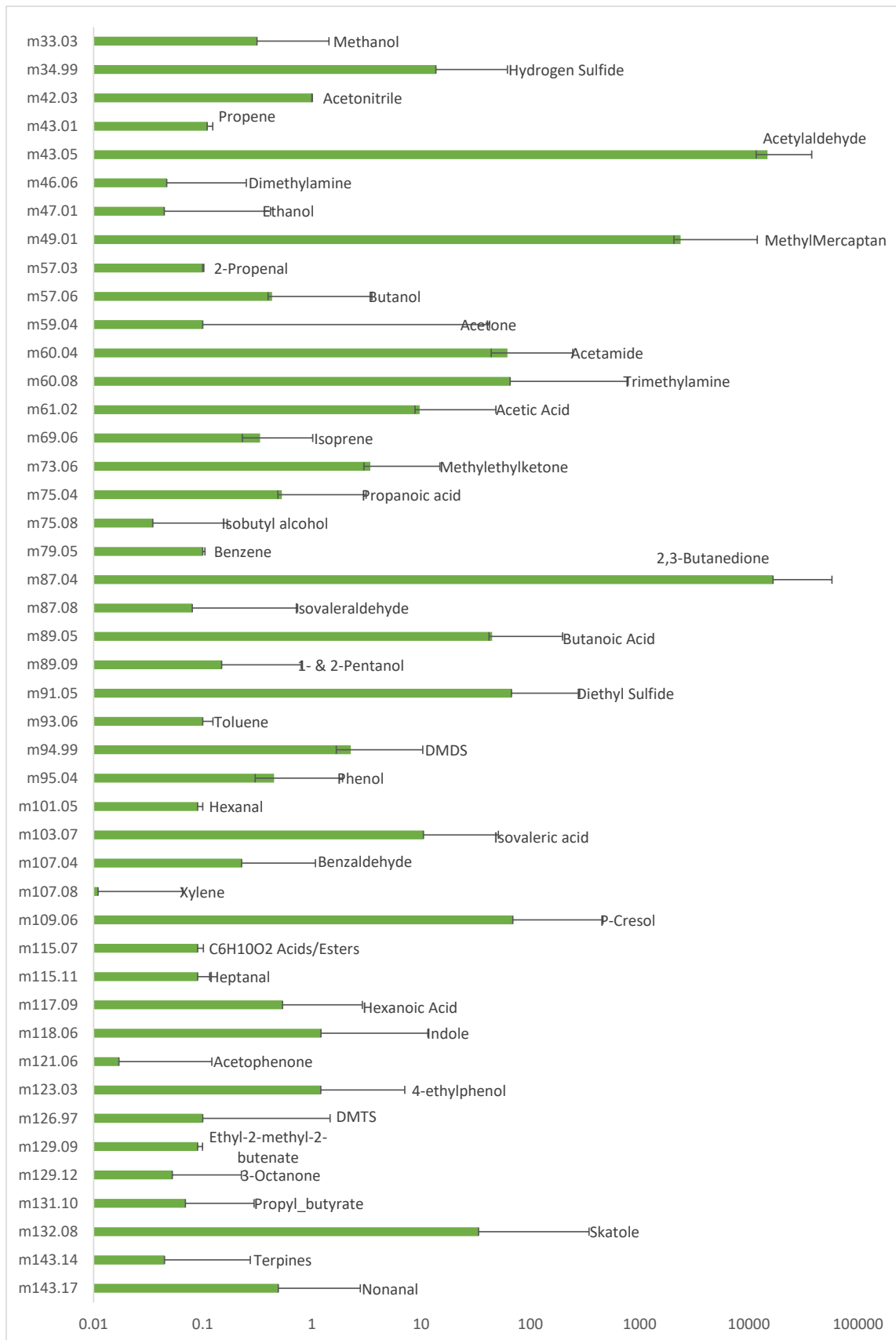


Figure 11: Average odour activity value (OAV) (horizontal axis; unitless ratio values) for selected individual odorants coming directly from the shed exhaust fans. Bars show data range on logarithmic scale.

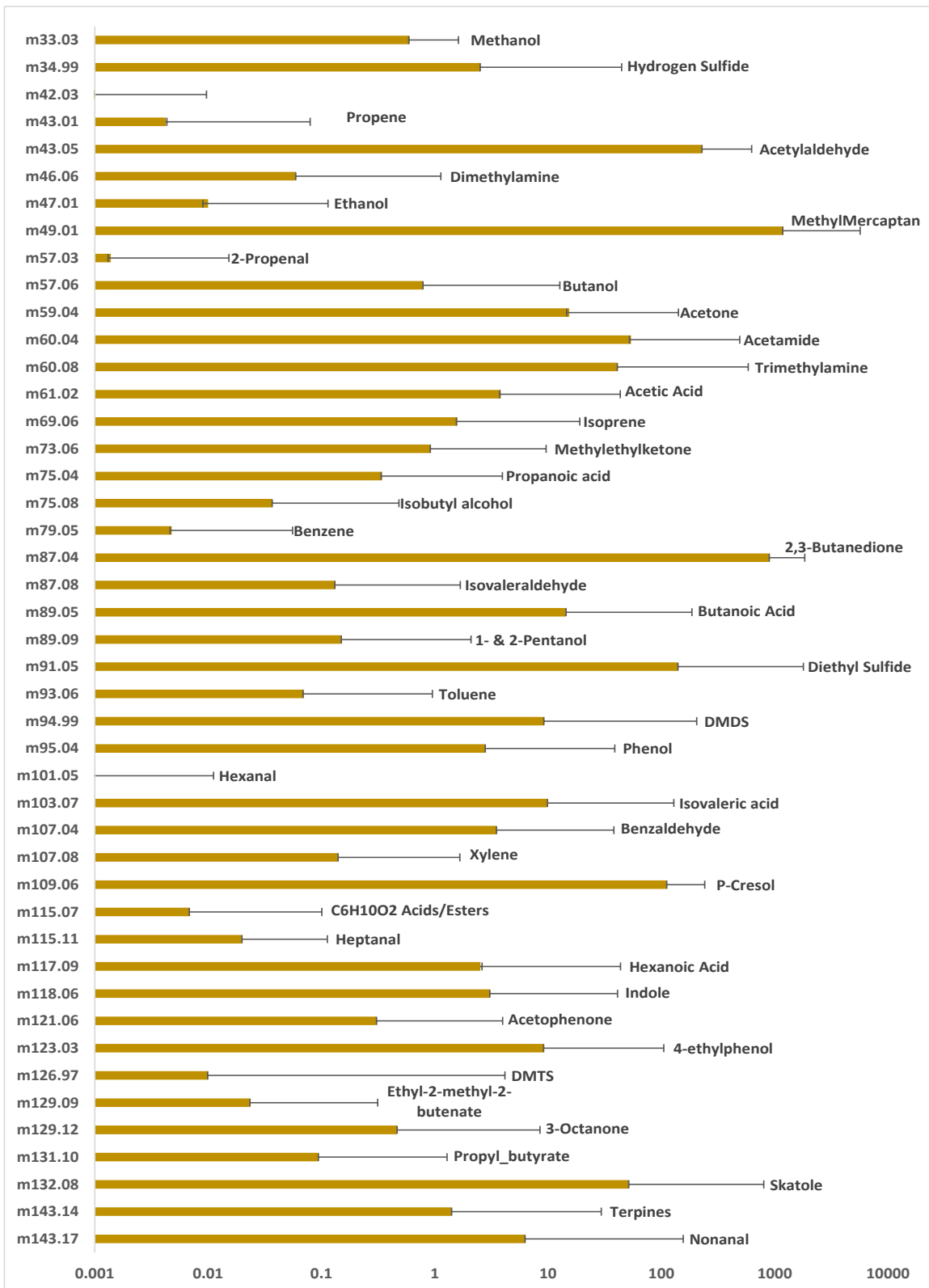


Figure 12: Average odour activity value (OAV) (horizontal axis; unitless ratio values) for selected individual odorants detected downwind of the exhaust fans. Bars show data range on logarithmic scale.

The odorous compounds with the highest calculated odour activity values and their ‘odour characteristics’ are listed in Table 3. Most have unpleasant characteristics, for example, ‘rancid’, ‘rotten’ or ‘faecal’, and may be negatively perceived by receptors. A dominant presence of these compounds in poultry emissions may contribute to odour impacts.

Table 3: The compounds with the highest mean odour activity value (OAV) for at-shed and downwind.

References in square brackets [] (refer to footnotes). A full list of identified compounds and their odour threshold values is provided in Appendix B.

Protonated mass (H+)	Molecular mass	Likely compounds	Odour character	Odour threshold (min) (ppb)	Odour activity value (avg)	
					In-shed	Downwind
87.0441	86.036	2,3-Butanedione	Buttery, rancid, fat [4]	0.05 [8]	1856	899
45.0335	44.026	Acetaldehyde	Fruity [2]	1.5 [9]	805	229
49.0106	48.003	Methyl Mercaptan	Rotten cabbage [5]	0.02 [5]	339	132
109.0648	108.056	P-Cresol	Faecal, tarry [1]	0.054 [8]	269	98
91.0576	90.050	Diethyl Sulfide	Rotten [3]	0.033 [8]	67	46
60.0444	59.037	Acetamide	Mousey	2.83 [8]	61	15
89.0597	88.0524	Butanoic Acid/ethylacetate/isobutyric acid	Mushroom, rancid, cheesy	1.5 [10]; 0.19 [8]	44	12
132.0808	131.075	Skatole	Faecal [1]	0.006 [8]	33	718
61.0443	60.021	Acetic Acid	Vinegary [2]	363 [10]	15	ND
60.0808	59.0735	Trimethylamine	Fishy	0.44 [5]	10	6
94.9984	93.9911	Dimethyldisulfide	Pungent, garlic [8]	0.3 [8]	ND	4

References: [1] NCBI (2017); [2] Snyder (2013); [3] Lebrero et al. (2011); [4] Parcsi (2010); [5] Rosenfeld and Suffet (2004); [6] Liang et al. (2005); [7] Zahn et al. (2001); [8] Nagata (2003); [9] Ruth (1986); [10] Schiffman et al. (2001).
ND; not detected in the highest 10.

The majority of compounds producing the higher odour activity values in the shed and downwind samples were the same. This means that the compounds contributing most to odour (i.e. the highest odour activity) directly at the sheds are, in general, the same compounds contributing to odour downwind.

In terms of in-shed compounds, mass 87.0441 (likely 2, 3-butanedione) was calculated to have the highest OAV (1856), indicating this compound has the highest individual contribution to odour concentration out of all measured compounds. This compound has a very low OTV of 0.05 ppb, meaning it can be detected by human receptors at extremely low concentrations. Mass 45.0335 (likely acetaldehyde) with an OAV of 805, and mass 49.0106 (likely methyl-mercaptan) with an OAV of 339, also have high OAV for the in-shed samples.

For downwind measurements, mass 87.0441 (likely 2,3-butanedione) had the highest OAV of 899. It is therefore likely that this compound is a strong contributor to the perceived odour of meat chickens at the sheds and downwind. Mass 132.0808 (likely skatole) had the second highest calculated OAV at 718. This is substantially higher than the OAV calculation for the shed measurements for this compound. It is possible that the persistently high OAV for this compound is an indication that it may

contribute more to odour downwind than at the sheds, and may explain some of the perceived differences in odour character between odour around the sheds and odour detected downwind. However, it remains unclear as to whether the increase in this mass is a real effect, or caused by an additional source of skatole in the environment.

Summary of odour activity value (OAV)

- OAV is useful for determining how much a single compound may contribute to perceived odour concentration.
- This project identified 11 compounds that contributed most to odour at-shed and downwind.
- Most of these compounds are the same at the sheds and downwind.
- These compounds have low OTVs and have a most unpleasant odour character associated with them.
- While many of these compounds are present in very low concentration, the associated OTV translates to high odour activity.
- These 11 compounds are likely candidates for causing odour nuisance from meat chicken farms.

Odour abatement trials: in-shed composting

PTR–ToFMS is potentially useful for evaluating the efficacy of odour abatement products or practices because it enables odorant concentrations to be measured. A primary driver for odour emissions is the fresh excreta being deposited on the litter by the birds (Hobbs et al., 2004). Malodour is released directly from the excreta due to the ongoing microbial break-down of feed that started in the gastrointestinal tract. Malodour continues to be released as the excreta breaks down within the litter. Improving the composition and levels of microflora in the litter with microbes that produce fewer odorous by-products is a viable proposition as an odour reduction strategy. Composting spent litter for reuse as bedding, and potentially seeding it with beneficial microbes, may provide potential odour abatement benefits, as the microflora are already present and well established in the composted litter.

The efficacy of using composted litter in poultry sheds to reduce odour emissions was evaluated with PTR–ToFMS at Farm B and Farm C during three discrete trials:

- **Trial 1 (Farm B)** – A commercially available compost ‘starter’ product was applied to the litter along the drinker lines before bird placement. Four of the eight sheds were treated with this method, and the other four were left untreated. PTR–ToFMS samples were taken from all eight sheds at weeks 3, 4 and 6 of the batch. Results over the three sampling dates were combined with the treated sheds compared to the untreated sheds for compound abundance using ANOVA.
- **Trial 2 (Farm C)** – The spent litter from Trial 1 was removed, windrowed, and fully composted for 9 weeks. The fully composted litter was then used to cover half the floor of two adjacent sheds, and wood shavings were used to cover the other half in both sheds. The four remaining sheds used fresh bedding (wood shavings) only.
- **Trial 3 (Farm B)** – A 50:50 blend of the composted litter from Trial 1 and fresh wood shavings was used to cover the entire floor of two adjacent sheds. The six remaining sheds used fresh bedding (wood shavings).

Changes in the odour concentration (olfactometry) and changes in concentrations of selected masses (PTR–ToFMS) were measured during the three trials (Table 4). The three trials generated mixed

results, with only *Trial 2* yielding a significant reduction in odour concentration. By contrast, odour concentration increased for *Trial 3*, and *Trial 1* showed no significant difference in the treated sheds compared to the untreated. More trials would be necessary to establish any trends.

Trial 1, which had no significant reduction in odour concentration, was conducted in a particularly dry, hot period, so the litter tended to be dry and friable. The research team, following discussions with the supplier of the compost 'starter', concluded that 'seeding' fresh, dry bedding in-shed to kick-start composting is not a reliable technique because the shed environment during prolonged dry weather was thought to hinder the desired microbial growth.

In *Trial 2*, a significant reduction in odour concentration was measured in the treatment sheds compared with the control sheds. Measurement of odorants with PTR-ToFMS showed that 34 of the 39 monitored masses decreased, but only mass 109.06 (possibly p-cresol) decreased significantly.

In *Trial 3*, odour concentration increased (but not significantly) despite four masses decreasing significantly (59.04, 75.04, 101.09 and 117.09; possibly acetone, propanoic acid, hexanal and hexanoic acid, respectively). We suggest that this may be due to an increase in the vast majority of the masses corresponding to odorants. The processes that were acting to reduce odorants in *Trial 2* were apparently not present in *Trial 3*.

In general, maintaining dry, friable litter resulted in similar odour concentrations, regardless of whether wood shavings or composted litter was used as the bedding. Based on our trial results, use of fully composted litter provided no consistent difference in odour compared to using fresh bedding.

While the efficacy of maintaining dry friable litter for odour abatement purposes could not be conclusively shown in these trials, they demonstrate the utility of PTR-ToFMS for detecting chemical differences in the odour emissions arising from different litter treatments.

Table 4. Effects of litter treatments on odour units (OU) and the masses for the key odorants, by trials. *P* = probability level (of a true difference); and mean levels for the listed treatments. Bolded/shaded entries are significant (*P* < 0.05).

	Trial 1			Trial 2			Trial 3		
	<i>P</i>	Normal	Compost starter on fresh bedding	<i>P</i>	Normal	Half-shed compost, half-shed fresh bedding	<i>P</i>	Normal	Blended compost & bedding
OU	0.73	146	134	0.036	274	108	0.23	449	621
Protonated Mass									
m43.05	0.76	3.76	3.61	0.28	0.68	2.04	0.21	1.23	2.23
m45.03	0.60	101	107	0.86	82	77	0.10	53.4	72.6
m46.06	0.69	0.21	0.23	0.32	0.105	0.035	0.09	0.035	0.097
m47.04	0.83	0.65	0.76	0.47	0.85	0.41	0.14	-0.12	0.23
m49.01	0.20	2.55	2.15	0.21	1.65	0.99	0.66	2.24	1.90
m59.04	0.54	23.1	22.3	0.06	29.6	17.2	0.009	22.7	32.7
m60.08	0.68	1.53	1.66	0.48	0.36	0.47	0.06	0.77	2.24
m61.02	0.80	91	97	0.16	280	121	0.12	47	94
m63.02	0.88	2.04	2.01	0.22	2.24	1.29	0.09	0.74	1.19
m69.06	0.69	1.51	1.58	0.16	1.74	1.16	0.37	1.07	1.23
m71.04	0.82	21.7	22.4	0.29	27.5	16.3	0.28	11.8	21.3
m75.04	0.76	1.93	1.80	0.09	8.7	3.1	0.049	0.82	2.59
m75.08	0.67	0.27	0.24	0.26	0.60	0.34	0.07	0.09	0.29
m79.05	0.40	0.25	0.21	0.24	0.22	0.12	0.11	0.10	0.15
m87.04	0.83	9.51	9.14	0.18	8.8	5.0	0.64	5.8	6.9
m87.08	0.47	0.28	0.36	0.86	0.25	0.19	0.06	0.28	0.46
m89.05	0.87	21.7	22.3	0.33	31.5	17.6	0.25	10.0	21.9
m89.09	0.81	1.05	1.14	0.73	0.22	0.53	0.29	0.31	0.84
m91.05	0.33	0.21	0.17	0.34	0.24	0.14	0.23	0.076	0.159
m93.06	0.021	0.235	0.098	0.25	0.125	0.073	0.54	0.080	0.117
m94.99	0.18	0.55	0.43	0.17	0.34	0.21	0.80	0.49	0.45
m95.04	0.13	0.29	0.22	0.06	0.225	0.136	0.21	0.202	0.261
m101.09	0.26	0.033	0.011	0.50	0.088	0.063	0.006	0.025	0.070
m103.07	0.89	0.42	0.43	0.43	1.20	0.65	0.14	0.18	0.89
m107.08	0.10	0.040	0.012	0.34	0.045	0.011	0.34	0.012	0.042
m109.06	0.72	0.38	0.45	0.034	0.300	0.086	0.98	0.32	0.33
m117.09	0.12	0.112	0.041	0.42	0.090	0.061	0.037	0.019	0.031
m118.06	0.09	0.108	0.003	0.35	0.091	0.043	0.24	0.011	0.016
m121.06	0.025	0.051	0.019	0.84	0.022	0.023	0.56	0.016	0.024
m123.08	0.49	0.085	0.063	0.08	0.079	0.016	0.19	0.029	0.062
m126.97	0.09	0.047	-0.012	0.37	0.045	0.020	0.09	-0.005	0.006
m129.09	0.048	0.059	0.033	0.45	0.043	0.026	0.25	0.025	0.032
m131.10	0.33	0.179	0.117	0.28	0.180	0.096	0.43	0.053	0.086
m132.08	0.09	0.057	0.002	0.41	0.048	0.024	0.63	0.005	0.007
m137.13	0.013	0.345	0.071	0.51	0.122	0.183	0.66	0.055	0.067

Summary of using PTR–ToFMS to measure odour abatement

- Three trials were conducted using several combinations of fresh bedding and fully composted litter at the start of a grow-out. Significant ($P < 0.05$) odour reduction was only observed during one trial with the use of composted litter.
- With small differences in perceived odour concentration, it is suggested that using the PTR–ToFMS to measure associated small reductions in odorants would be very challenging.
- Significant changes in odorant concentrations were measured with the PTR–ToFMS, but these did not correlate well with changes in perceived odour concentration.
- The application of composted litter (seeded with a composting accelerator) did not provide consistent or meaningful reduction of odour during our trials. It is recommended that re-evaluation of the PTR–ToFMS in odour abatement trials be conducted only when an odour mitigation strategy has been proven to be reliable and effective.

Odour unit prediction modelling

This section describes statistical analysis of the odour concentration data (from dynamic olfactometry) and the odorant concentrations (measured with the PTR–ToFMS). The aim was to use a range of statistical modelling approaches that would allow the odour concentration to be predicted from the PTR–ToFMS data. The olfactometry data is summarised in Appendix E.

All analyses were conducted using *GenStat* (VSN, 2016). The multidimensional nature of the data-set was investigated with discriminant analysis, looking to separate the groups of odour concentrations (from olfactometry) categorised as low (< 100 ou), medium (100 to 300 ou) and high (> 300 ou).

Regarding the development of a prediction equation for odour concentration, the relatively high degrees of correlations amongst the masses can cause problems with regression models. No transformations were used, as these tend to lower the relative contribution of the high odour concentration values (which are obviously the most important in terms of complaints). A range of established and developmental regression models were investigated, including general linear models, partial least squares methods, ridge regression, regression trees, random forests, ensemble methods, and hybrids of regressions and binary trees.

The discriminant analysis (Figure 13) showed good separation of the odour-unit groups. Stepwise cross-validation determined 17 variables as optimal (using more tended towards over-fitting), where the fit (R^2) to the existing data is improved but at the expense of the expected fit for any new data. At 17 variables, the misclassification rate was an acceptably low 4.4% (4 out of 90 samples were misclassified).

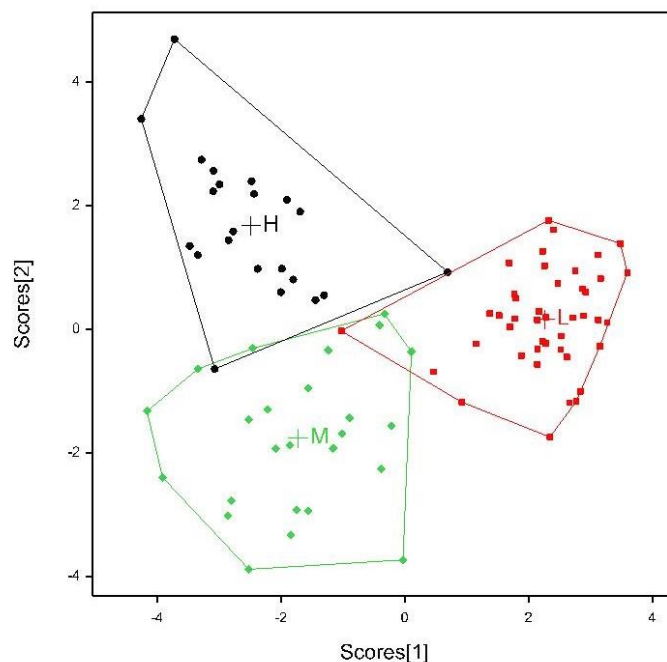


Figure 13. Discriminant analysis showing separation between odour concentrations; low (L; <100 ou), medium (M; 100 to 300 ou) and high (H; >300 ou). The group centroids are marked with the crosses.

In developing a prediction equation for odour concentration, all regression methods tended to give about the same degree of fit when based on the same dataset. General linear models were preferred, as the fitted linear coefficients directly represent the contributions of each mass. The identified ‘probable odorants’ were limited to positive effects only. However, any of the other masses which fitted as a negative coefficient were retained, as in this complex system there remains the possibility that they may be masking or suppressing the effects of other odorants. Figure 14 shows the relationship for the best ‘probable odorant’, mass 95.04 (possibly phenol). The amount of the total variation explained by this relationship (R^2) was 43.4%.

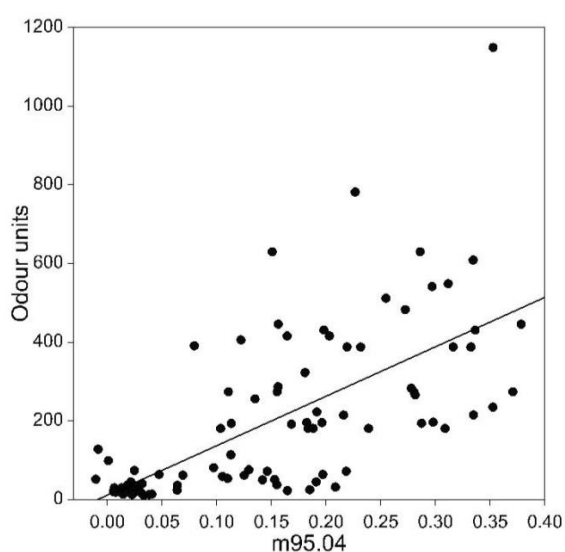


Figure 14. Relationship between odour units and mass 95.04 (possibly phenol).

Odour is a complex concept, and obviously caused by more than any single odorant. In developing multiple models, correlations amongst the predictor variables (the masses) do cause problems. However, these methods are valid if the correlations remain similar over time (Dormann, 2013), as may be expected. The main drawback is that no ‘unique best’ model exists, and alternate models utilising different predictors will often give the same degree of fit. This feature can actually be used to an advantage, as recent developments adopting ensemble models (namely, the average prediction of many alternate models) have repeatedly shown their superior predictive ability over any single candidate model (Baker, 2008; Krishnamurti, 2000; McIntyre, 2005; Mevik, 2004; Song, 2013).

Alternate step-forward multiple regression models were developed, taking three to six predictor variables. Above six variables the improvement in fit for each additional variable was generally less than 1%, so not warranted. The degree of fit (R^2) improved with more variables, with averages of 67.5% for the models with three variables to 74.0% for six variables. As expected, the averages of these candidate models (i.e. the ensemble prediction) gave the best fit ($R^2 = 78.4\%$), as this utilises the combined predictive power of these different combinations of the predictors. This relationship is shown in Figure 15. There is still some scatter, but it is evident that predictions of ‘low odour’ (say < 200 ou) result in most observed values being in that range. Similarly, predictions of 200 to 400 ou and the ‘higher values’ are also generally in that range. For interest, the dominant predictors from the ensemble models are listed in Table 5.

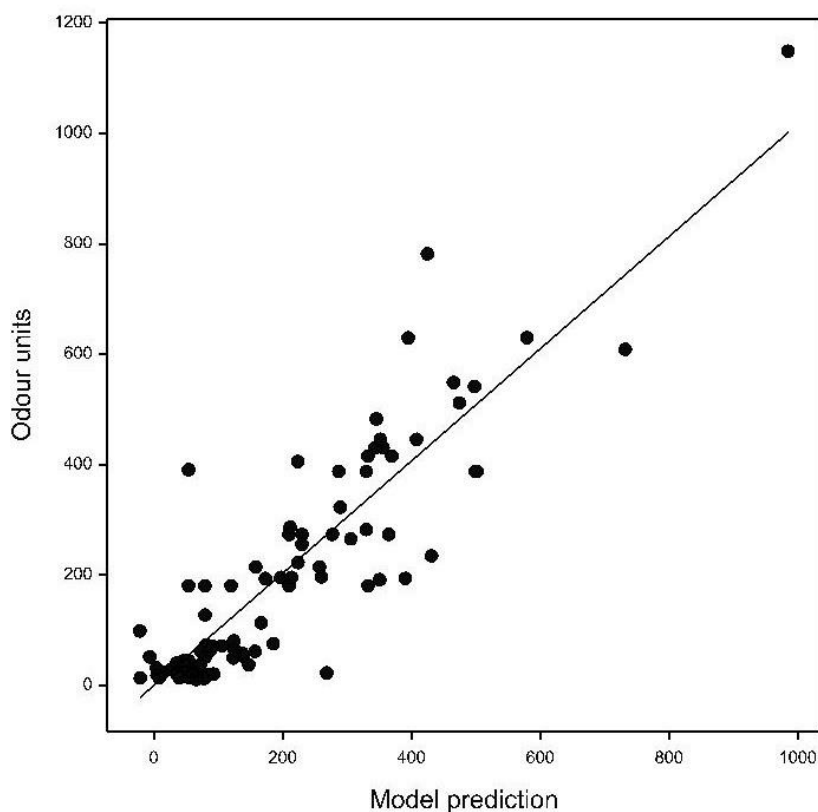


Figure 15. Relationship between odour units and the ensemble model predictions.

Table 5. Key variables in the ensemble multiple regression models (recognised 'poultry odorants' are shaded).

Protonated mass (H ⁺)	Compound	Effect
43.01		negative
49.01	Methylmercaptan	positive
55.05		negative
59.04	Acetone	positive
71.04	numerous compounds	positive
80.04		positive
83.08		positive
87.04	2,3-Butanedione	positive
93.06	Toluene	positive
103.07	Isovaleric, pentanoic, 2-Methyl-butanoic acids	positive
114.03		negative
115.11	Heptanal	positive
125.12		negative
126.97	Dimethyl trisulfide	positive
143.14	Nonanal	positive
165.07		positive

The parameters for the four 6-parameter linear models that were used for the ensemble prediction model are summarised in Table 6. The x terms are listed in descending importance. The models have the general form shown in Equation 3.

$$OU = \text{intercept} + (b_1 \times x_1) + (b_2 \times x_2) + \dots + (b_6 \times x_6) \quad \text{Equation 3}$$

Where:

OU is the odour concentration

b_n are model parameters (Table 6)

x_n terms are the concentration of associated (odorant) masses (ppb)

Table 6. Coefficients (b_n) and terms (x_n) for the four 6-parameter models used for the ensemble predictions for odour concentration (ou).

	Model 1	Model 2	Model 3	Model 4
R ² (%)	72.7	72.2	74.7	76.3
<i>Intercept</i>	57	69	30.5	53.2
b_1	10.06	-0.709	-1.927	-2.152
x_1	m71.04	m43.01	m43.01	m43.01
b_2	427.1	14.7	-4.64	349
x_2	m80.04	m71.04	m55.05	m80.04
b_3	390	477.7	429.4	191.5
x_3	m93.06	m80.04	m80.04	m83.08
b_4	-1006	-2256	26.5	29.89
x_4	m114.03	m114.03	m87.04	m87.04
b_5	304	-1610	211.8	209.2
x_5	m126.97	m125.12	m103.07	m103.07
b_6	-1384	4596	-2768	-1439
x_6	m143.10	m165.07	m143.17	m143.10

Statistically, mass 43.01 is the primary predictor variable in three of the models, which was unexpected and warrants further explanation. This mass does not directly correspond with any recognised poultry odorant, however, numerous other compounds fragment to this mass, including some important odorants like acetic acid and 2,3-butanedione. As the fragmentation patterns are consistent, the masses involved tend to be highly correlated. Therefore, unimportant masses in terms of odour can become excellent proxies for the important masses in the odour prediction modelling, for example, mass 43.01. From the correlation matrix in Appendix F, it can be seen that this mass is highly correlated with numerous masses including mass 89.05 (possibly acetoin or butanoic acid), mass 91.05 (possibly diethyl sulfide) and mass 61.02 (possibly acetic acid).

Two previously recognised poultry odorants with high OAVs included in the models were methyl mercaptan (mass 49.01) and 2,3-butanedione (mass 87.04). In an earlier investigation, both of these odorants also showed promise in combination (2-parameter model) for predicting odour concentration using SIFT-MS data (Atzeni et al., 2016a).

Summary of odour prediction models using PTR–ToFMS data

- An ensemble of linear regression models enabled a good prediction ($R^2 = 78.4\%$) of odour concentration based on PTR–ToFMS measurements of VOCs.
- One of the primary predictor variables used in the models was mass 43.01, which is not known to relate specifically to any known poultry odorant. Other poultry odorants are known to fragment to this mass within the PTR–ToFMS. We suggest that one issue with basing a model on an ‘unimportant’ odorant is that if the mixture of fragmenting odorants changes, perhaps due to changes in odour formation processes within the litter, the reliability and strength of the odour prediction model may reduce.
- Additional data is required to strengthen the prediction model and to demonstrate that it can be applied to other farms (in other regions, with different feed rations or using other bedding materials).

Conclusions

PTR–ToFMS provided the ability to analyse the chemical constituents of odour emissions from meat chicken farms, including the litter, direct shed emissions and downwind odours. This analysis provided insight into a number of compounds that may be most responsible for odour nuisance, and the abundance of these downwind of the sheds.

Many compounds were consistently detected in the in-shed samples and in the downwind air samples. The most interesting of these compounds in terms of potential odour impacts downwind are the compounds with the highest calculated OAV (Table 3). These compounds included 2,3-butanedione, acetaldehyde, methylmercaptan, P-cresol, diethylsulfide, dimethyldisulfide, acetamide, butanoic/isobutyric/acetic acids and skatole. All of these are known odorants and have been previously reported in research on poultry odour emissions (Chang & Chen, 2003; Lin et al., 2012; Parcsi, 2010; Parker et al., 2010; Trabue et al., 2010; Yuan et al., 2017). They have low odour threshold values, unpleasant odour character and were present in readily detectable quantities, even downwind, using PTR–ToFMS. While the overall trend of the concentration of odorants is to decrease with distance, the rate of ‘decay’ is odorant dependent, with several of these odorants still persisting beyond 100 m downwind (Table 2). These compounds are likely candidates for causing odour impacts downwind of the source. Efforts to reduce the concentrations of these compounds is likely to result in reductions in odour experienced at receptor distances.

Limitations of using PTR–ToFMS for odour analysis

Utilising PTR–ToFMS for odour analysis is not without its challenges. A limitation of using this instrument to evaluate odour emissions is the difficulty in accurately determining concentrations of certain known odorants that have ‘proton affinities’ very close to that of water (H_2O). This issue is highlighted with the instrument’s capability to detect hydrogen sulfide (H_2S)—a known odorant with an unpleasant odour character and low odour detection threshold. While it is possible to use PTR–ToFMS to accurately measure H_2S (Feilberg et al., 2010), it requires extensive expertise to correctly calculate the back-reactions that inhibit the ability of the instrument to accurately quantify compounds like H_2S . Calculating fragmentation patterns and back-reactions was considered to be outside the scope of this study.

The PTR–ToFMS instrument has multiple reagent ion modes; H_3O^+ (predominately used for samples during this project), O_2^+ , and N_2^+ . Alternate reagent ions have different ionization energies that provide greater ability to separate and detect compounds with the same mass. However, using multiple reagent ions increases the time needed to analyse each sample, as the instrument needs to be reconfigured and stabilised after switching ions. This can cause significant delays between sample collection and analysis. For this reason, multiple reagent ions were not used during this study.

The ability to rapidly analyse samples with PTR–ToFMS within a matter of minutes of collection was anticipated during the planning stages of this project, based on the understanding the PTR–ToFMS instrument could be set up and used on location. However, deploying the instrument on location proved more challenging than expected, as the instrument requires anywhere between three to 24 hours to stabilise, depending on the length of time it was turned off, before it can be used confidently.

Furthermore, the instrument must be shutdown prior to moving to protect several sensitive components within the instrument. This prevented the instrument from being able to be moved around on-site once it was transported into the field. These problems subsequently impacted the coordinated olfactometry sessions that had been arranged. Considering these challenges, the project team decided after the first field trial that the instrument would remain in the Toowoomba laboratory and all subsequent samples would be transported back for analysis.

Odour sample collection downwind of source

Odour sample collection downwind of meat chicken farms proved to be very challenging. Once an odour plume is exhausted from a shed, its fate is affected by wind, terrain and atmospheric stability, which makes it very difficult to track the path of an odour plume in order to get a meaningful air sample. Confidence in the plume's path decreases the further away from the source the sample is taken, and it is more difficult to determine if the sample being taken is still representative of the initial odour plume that is being exhausted from a meat chicken shed, as other sources may influence what is being captured by the sampling technique. In downwind sample collection, the research team often experienced difficulty in locating a plume that was stable for long enough to take a representative sample before the plume dissipated or changed direction.

Furthermore, as was experienced in this project, it can be difficult to collect meaningful samples because areas surrounding meat chicken farms have vegetation (e.g., long grass, wooded areas) or access may be restricted by fences or property boundaries. Moreover, these areas also contain their own suite of VOCs that can be detected by PTR–ToFMS and can increase the odour in a sample being analysed with olfactometry.

Odour prediction modelling

PTR–ToFMS mass spectra data was used to develop an ensemble regression model to predict odour concentrations. Linear regression modelling using different numbers and combinations of parameters was required to determine the optimal number and choice of parameters. An ensemble of four 6-parameter models suited our data, as they captured the best of all the single models and gave a better fit than any single model. There was little gain using more parameters.

The ensemble model ($R^2 = 78.4\%$) is considered to be at an acceptable level of accuracy to use in a research capacity for predicting odour concentrations from PTR–ToFMS mass data. Under its current parameterisation, the model is not suitable for use with mass spectra data from other types of instruments. However, with additional data sets and expert guidance in parameter selection to suit a wider range of instruments, the model can evolve into a more generic one that others can also use.

Implications

Odour abatement assessment

Rapid advances in mass spectrometry over the last decade have changed the way poultry emissions assessment will be conducted in the future. Historically, GC–MS has been the standard for VOC identification. GC–MS will remain useful for positively identifying and quantifying odorants, but has its own limitations, such as requirement for sample pre-concentration that can selectively include and exclude specific odorants. In our experience, GC–MS analysis has been unreliable for poultry odour characterisation resulting in inconsistencies and anomalies that have often raised more questions than they have answered.

Time-of-flight mass spectrometry characterises poultry odour in real-time at a resolution suitable for insightful odour assessments. Numerous poultry-related VOCs, including many key odorants, can now be identified and quantified with reasonable confidence, without ‘confirmatory’ GC–MS analyses.

GC–MS is becoming more portable and practical, but until it proves more reliable and convenient for poultry odour speciation, it is unlikely to provide significant benefits to poultry odour research in the near future.

The processes generating the key odorants that cause odour nuisance are likely to become a focus for odour abatement research, and will require MS instruments such as PTR–ToFMS. The chicken meat industry should continue to evaluate new analytical technologies as they become available.

Odour concentration prediction

The chicken meat industry has been seeking the ability to measure odour concentration without relying on the human nose. The ensemble regression model developed in this project predicts odour concentration from the mass spectra data. This represents a giant leap forward and will reduce future needs for dynamic olfactometry once the model has been tested and validated on other farms.

This will be particularly so for downwind samples. It is rarely possible to perform dynamic olfactometry completely ‘to standard’ on the weaker samples, and therefore a chemistry-based prediction is justifiable. For this reason alone, instrumental techniques that enable odour concentration to be predicted from specific chemical data are particularly desirable for research at receptor distances.

The potential to use PTR–ToFMS, instead of dynamic olfactometry, to calculate odour concentrations provides opportunities to conduct odour research more cost-effectively in future.

Recommendations

Based on the findings, we recommend:

- Current odour abatement methods be critically assessed using PTR–ToFMS to determine their likely efficacy in suppressing key odorants and to provide industry with defensible scientific data.
- Future odour abatement research focuses on developing methods that will reduce emission of the key odorants identified in this project as the likely cause of odour nuisance from meat chicken farms.
- Paired olfactometry and mass spectrometry analyses be conducted across a wider range of farms, within and across integrators, to test the veracity of the odour prediction model, and to improve its utility. It may emerge that a separate model is required for each integrator or different geographical regions due to differences in the breed, rations, climate, shed design and management practices.
- Investigate the potential synergistic or antagonistic effects of odorants on receptors. This project was able to identify single compounds that are likely responsible for contributing to odour nuisance on an individual basis. However, the effects these compounds have on each other was not considered in this research, but is critical for accurately assessing odour abatement strategies using mass spectrometry instruments (Nagata, 2003).

Appendix A

Calibration gases used for analysis with PTR-ToFMS

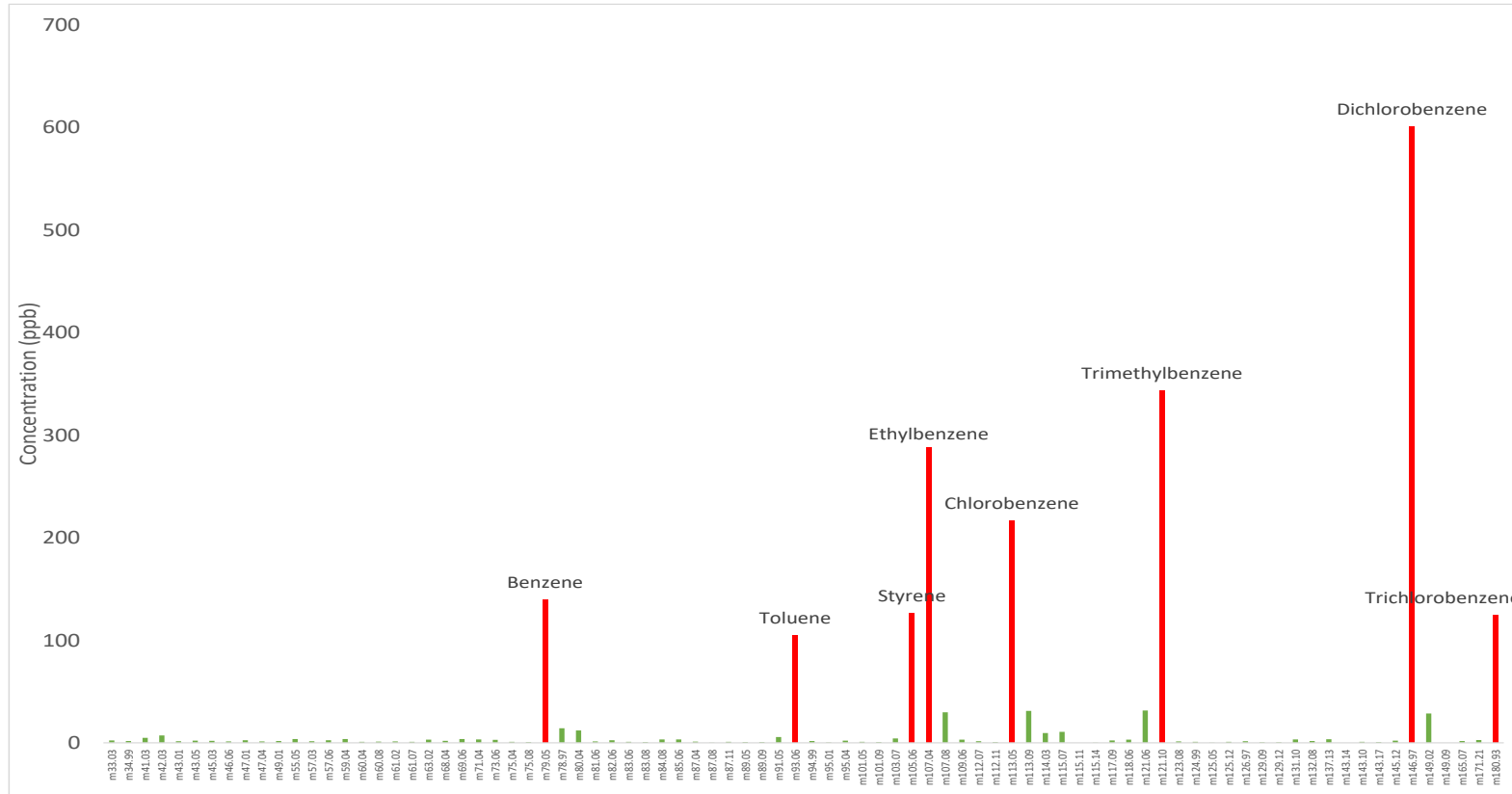


Figure A1: PTR-ToFMS output for the TO14a calibration gas mix. Red bars indicate gases present in the mixture. Green bars are background noise or fragmented masses.

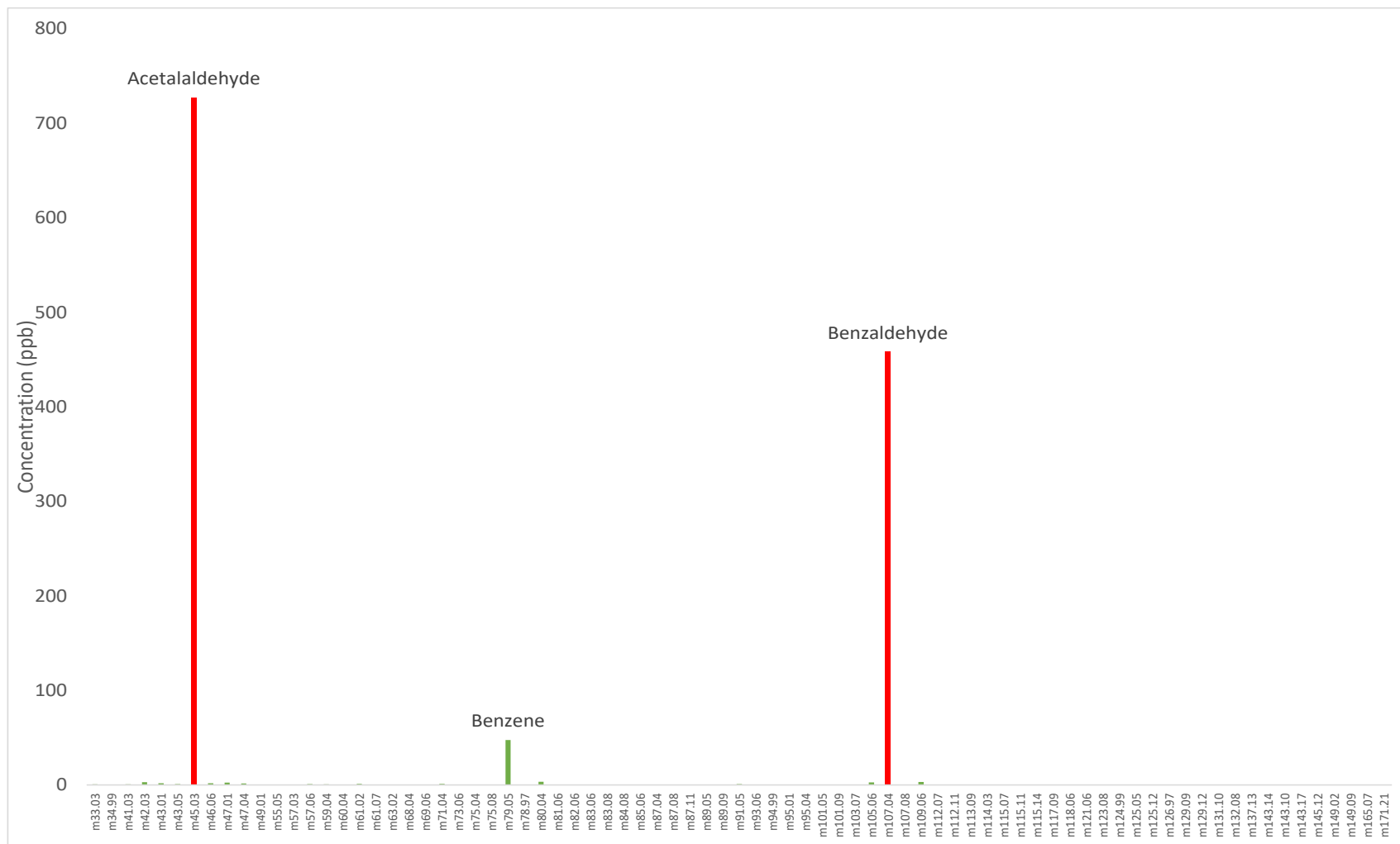


Figure A2: PTR-ToFMS output for a calibration gas mix. Red bars indicate the two gases present in the mixture. Green bars are background noise or fragmented masses.

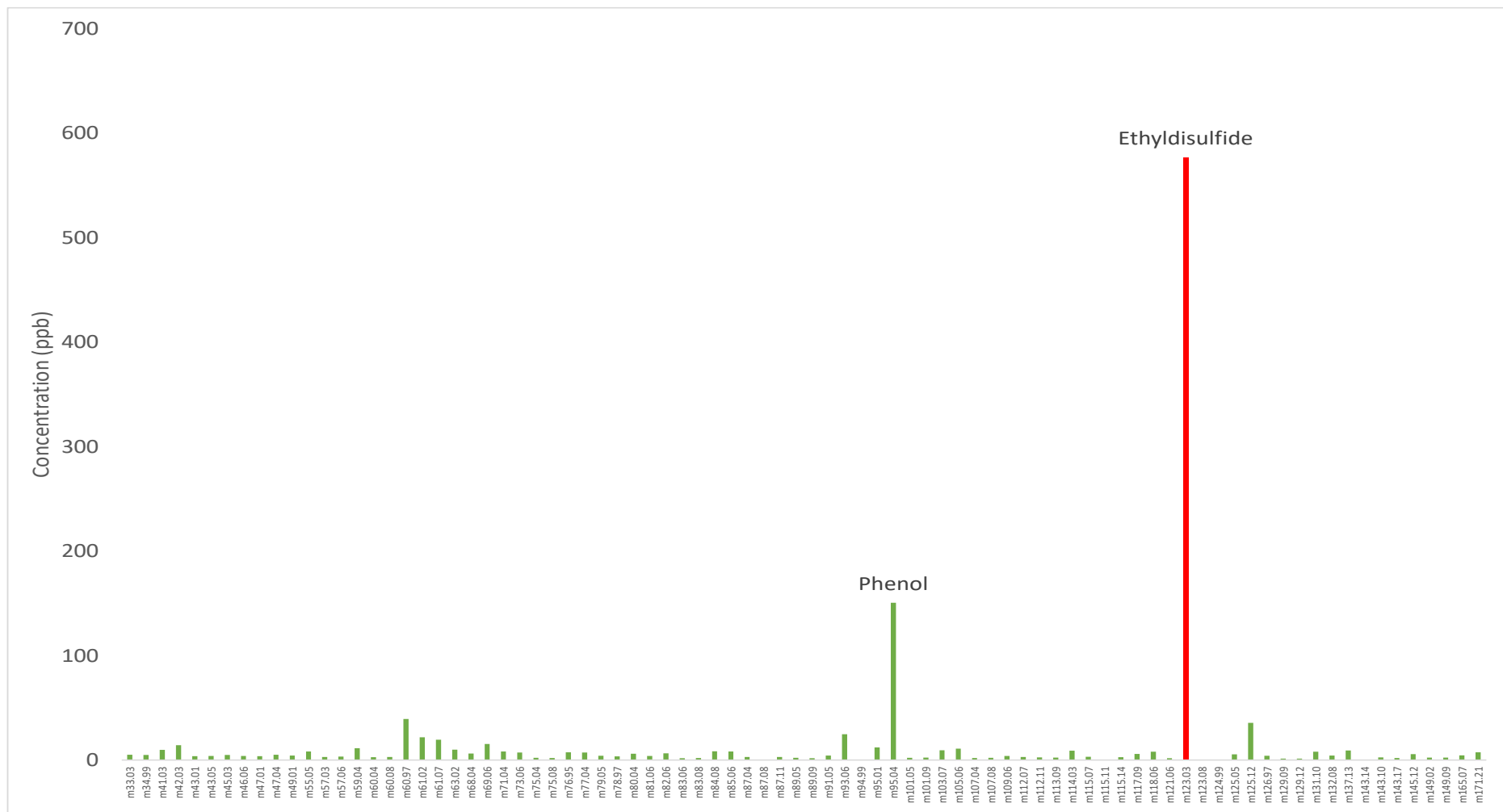


Figure A3: PTR-ToFMS output for a calibration gas mix. The red bar indicates gas present in the mixture. Green bars are background noise or fragmented masses.

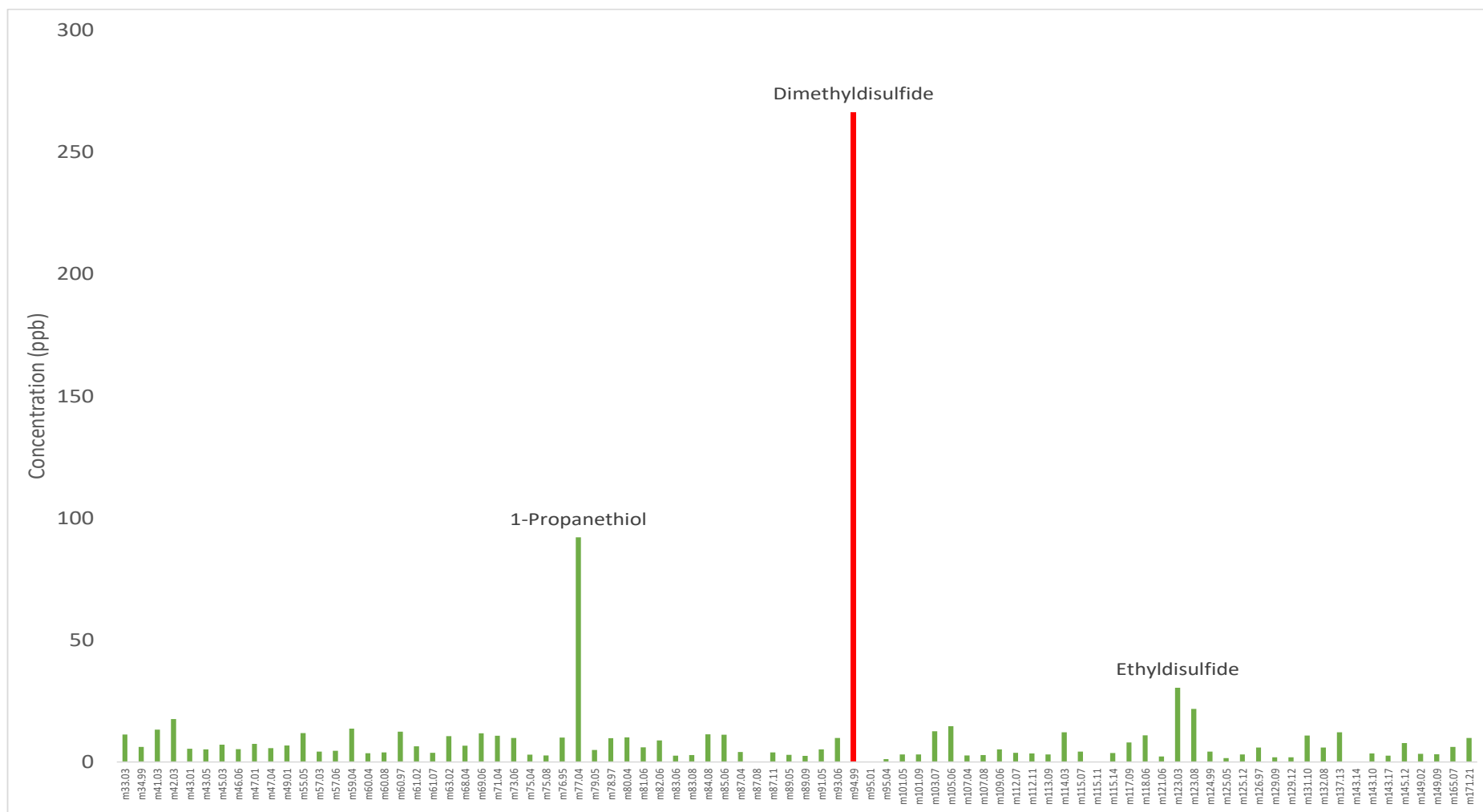


Figure A4: PTR-ToFMS output for a calibration gas mix. The red bar indicates the gas present in this mixture. Green bars are background noise or fragmented masses.

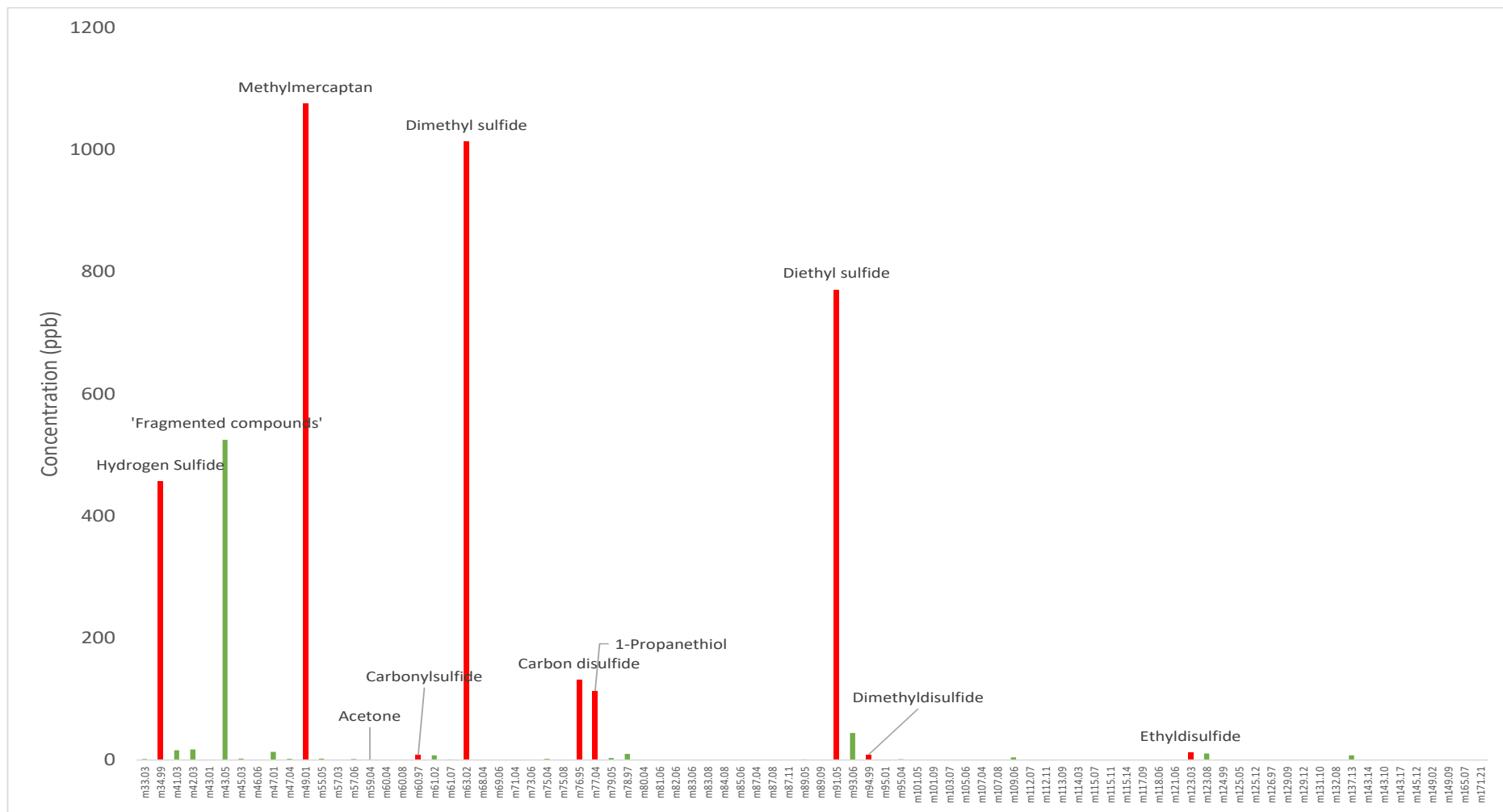


Figure A5: PTR-ToFMS output for a calibration gas mix. Red bars indicate gases present in the mixture. Green bars are background noise or fragmented masses.

Appendix B

Table B1. Full list of identifiable compounds, protonated masses, odour character descriptions and odour threshold values.

TOF protonated mass (H+)	Molecular mass	Possible compounds	Possible odour character	OTV (ppb) [geometric mean]	References (reported previously for meat chickens)
33.0335	32.0262	Methanol	alcoholic	3000	(Trabue et al., 2010)
34.9877	33.9877	Hydrogen Sulfide	rotten eggs	0.15	(Trabue et al., 2008)
42.0338	41.0266	Acetonitrile	aromatic, sweet	22000	(Trabue et al., 2010)
43.0542	42.0470	Propene; Pentanol	aromatic	22000; 21500	(Trabue et al., 2010) (Nagata, 2003)
45.0335	44.0262	Acetaldehyde	fruity, yoghurt	1.5	(O'Neill & Phillips, 1992)
46.0651	45.0578	Dimethylamine	ammonia, fish-like	46	(Ruth, 1986)
47.0491	46.0419	Ethanol	pleasant, alcoholic	340	(Trabue et al., 2010)
49.0107	48.0034	MethylMercaptan	Rotten cabbage	0.02	(Ruth, 1986)
57.0320	56.0247	2-Propenal	coal-like	28000	(Trabue et al., 2008)
57.0699	56.0628	Butanol; 2-Methyl-1-Propene	sweet, musty; banana	320, 351	(Trabue et al., 2008)
59.0491	58.0419	Acetone	solvent, nail polish	58.1	(Trabue et al., 2010)
60.0808	59.0735	Trimethylamine	fishy, ammonia	0.44	(Rosenfeld & Suffet, 2004)
61.0284	60.0211	Acetic Acid	vinegar	363	(Jiang & Sands, 2000) (Murphy et al., 2012)
61.0648	60.0575	n-Propanol; Ethylenediamine	pleasant, alcoholic	231, 340	(Chang & Chen, 2003) (O'Neill & Phillips, 1992)
63.0263	62.0190	Dimethyl sulfide; Ethylmercaptan	natural gas; rotten vegetables	0.12, 0.4	(Murphy et al., 2012) (Nagata, 2003)
69.0699	68.0626	Isoprene	petrol-like	134	(Trabue et al., 2010)
73.0648	72.0575	1- & 2-Butanal; Isobutyraldehyde	solvent; pungent; rancid	135, 27.5	(Chang & Chen, 2003) (O'Neill & Phillips, 1992)
75.0441	74.0368	Propanoic acid	rancid, cheesy	27.7	(Trabue et al., 2008)
75.0804	74.0732	Isobutyl alcohol; n- and 2 Butanol	sweet, musty; banana	320, 490	(Trabue et al., 2008) (O'Neill & Phillips, 1992)
79.0542	78.0470	Benzene	petrol-like	4500	(Chang & Chen, 2003)
85.0648	84.0575	3-Methyl-2-butanal	chloroform	84000	(Jiang & Sands, 2000)
87.0441	86.0368	2,3-Butanedione	sour, butter, rancid	0.05	(Nagata, 2003)
87.0804	86.0732	2-Pentanone; Isovaleraldehyde	rancid; sour; butter; malt	147, 2.3	(Trabue et al., 2010)
87.1168	86.1096	Hexane	petrol-like	16009	(Murphy et al., 2012)
89.0597	88.0524	Acetoin; Butanoic acid; Ethylacetate; isobutyric acid	butter; mushroom; alcohol; rancid	n/a; 0.19; 30; 1.5	(Chang & Chen, 2003) (Nagata, 2003) (Schiffman et al., 2001)

Table B1 cont'd

TOF protonated mass (H+)	Molecular mass	Possible compounds	Possible odour character	OTV (ppb) [geometric mean]	References (reported previously for meat chickens)
89.0961	88.0888	1- & 2-Pentanol; 2- & 3-methyl-1-Butanol	disagreeable	0.033	(Parcsi, 2010)
91.0576	90.0503	Diethyl Sulfide	garlic, foul	0.033	(Nagata, 2003)
93.0699	92.0626	Toluene	solventy	159	(Chang & Chen, 2003)
94.9984	93.9911	DMDS	pungent, garlic, metallic	0.3	(Jiang & Sands, 2000)
95.0491	94.0419	Phenol	medicinal, tarry	5.6	(Nagata, 2003)
101.0961	100.0888	Hexanal	camphor	696	(Trabue et al., 2010)
103.0754	102.0681	Isovaleric acid, pentanoic acid, 2-methylbutyl acid	rancid, cheesy, stench	0.08, 2, 0.2	(Nagata, 2003; O'Neill & Phillips, 1992; Schiffman et al., 2001)
105.0699	104.0626	Styrene	aromatic	149	(Murphy et al., 2012)
107.0492	106.0419	Benzaldehyde	almonds	12.1	(Murphy et al., 2012) (Trabue et al., 2010)
107.0856	106.0783	Xylene	aromatic	70	n/a
109.0648	108.0575	P-Cresol; Benzyl alcohol	faecal, tarry	0.054; 200	(Trabue et al., 2010) 50
115.1118	114.1045	Heptanal	rancid, citrus	14	(Chang & Chen, 2003)
115.1482	114.1409	Octane	petrol-like	7940	(Chang & Chen, 2003)
117.0910	116.0837	Hexanoic Acid; Ethyl butyrate	goat-like, fruity	7.1; 27	n/a
118.0651	117.0578	Indole	faecal	0.03	(Schiffman et al., 2001)
121.0648	120.0575	Acetophenone	pungent, orange, jasmine	1283	(Trabue et al., 2010)
123.0805	122.0732	4-ethylphenol	woody, medicinal	0.7	(Trabue et al., 2010)
126.9705	125.9632	DMTS	pungent, garlic, metallic, onion	0.012	(Murphy et al., 2012; Trabue et al., 2010)
129.0910	128.0084	Ethyl 2-methyl-2-butenolate	n/a	812	(Murphy et al., 2012)
129.1274	128.1201	3-Octanone	pungent	35.7	(Murphy et al., 2012)
131.1067	130.0994	Ethyl-2-methylbutyrate; Propyl butyrate	mild, floral, rose	94; 108	(Trabue et al., 2010)
132.0808	131.0735	Skatole	Faecal	0.006	(Nagata, 2003)
137.1325	136.1252	Terpines (alpha- & beta-pinene, limonene)	pine, woody, camphor	377; 177	n/a
143.1431	142.1358	Nonanal	orange-rose, dusty	2.5	(Murphy et al., 2012)
143.1795	142.1722	Decane	N/A	620	n/a

Appendix C

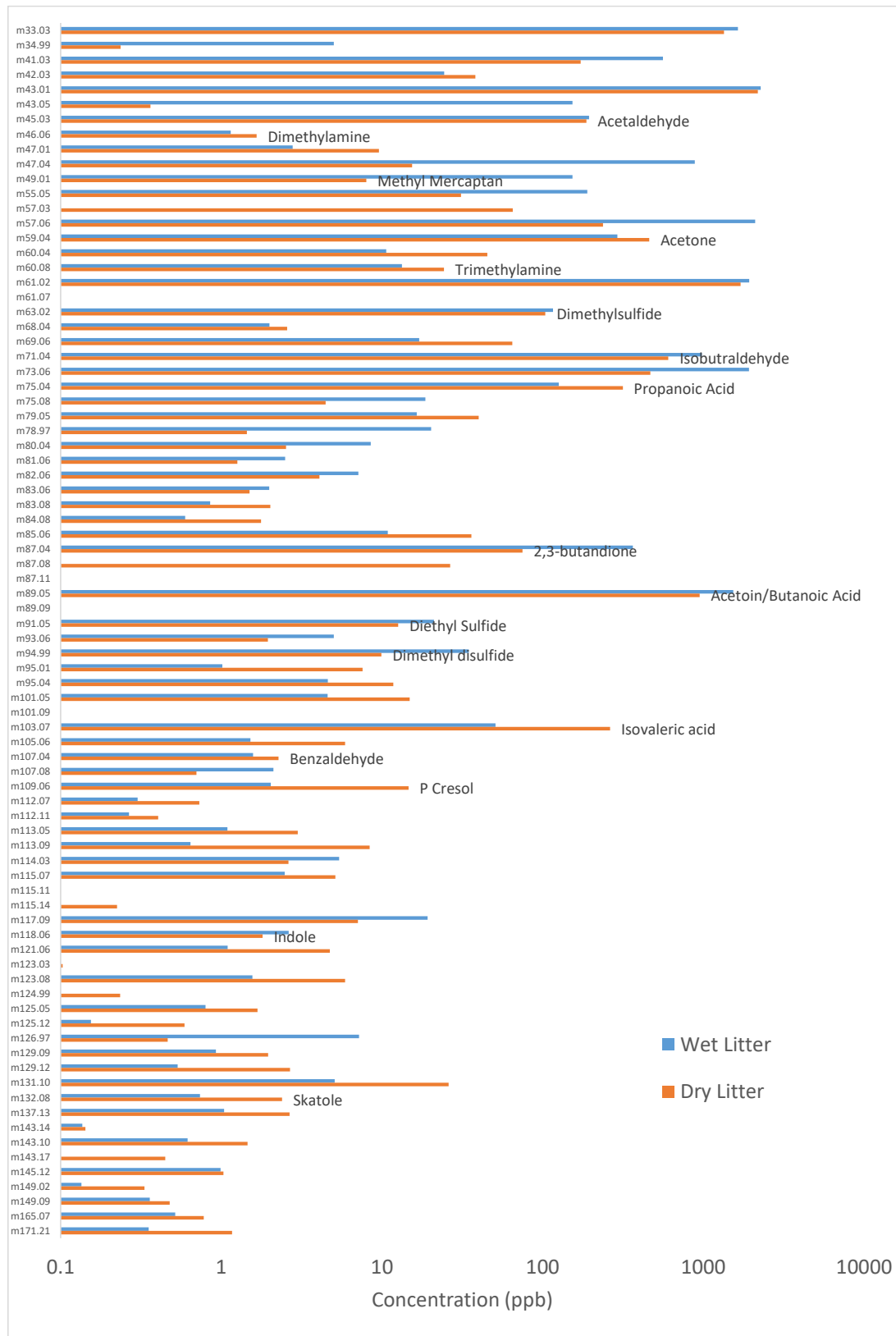


Figure C1: Full range of masses detected in wet litter (blue) and dry litter (orange).

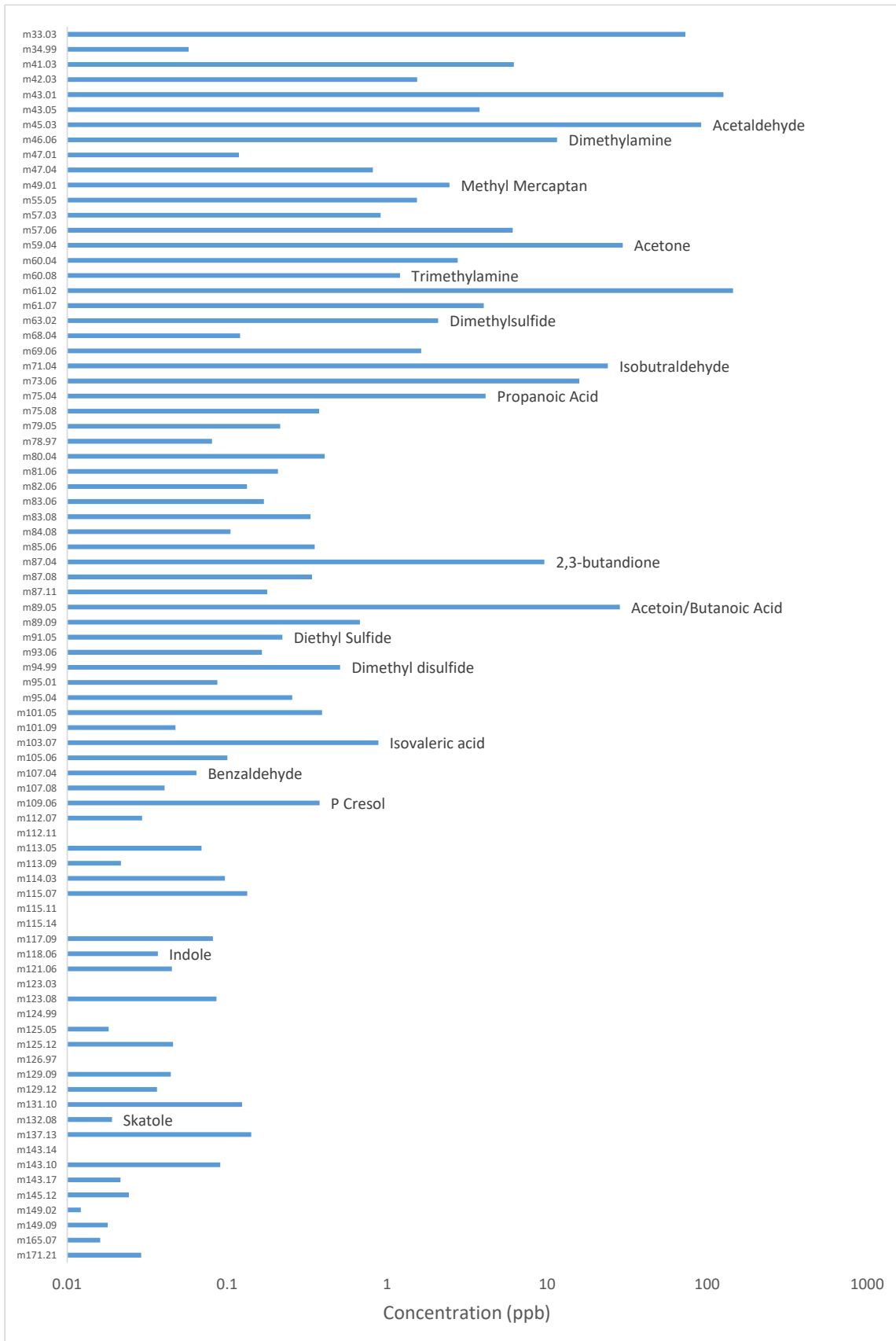


Figure C2: Full range of masses detected from all in-shed samples. Average concentrations shown in parts per billion.

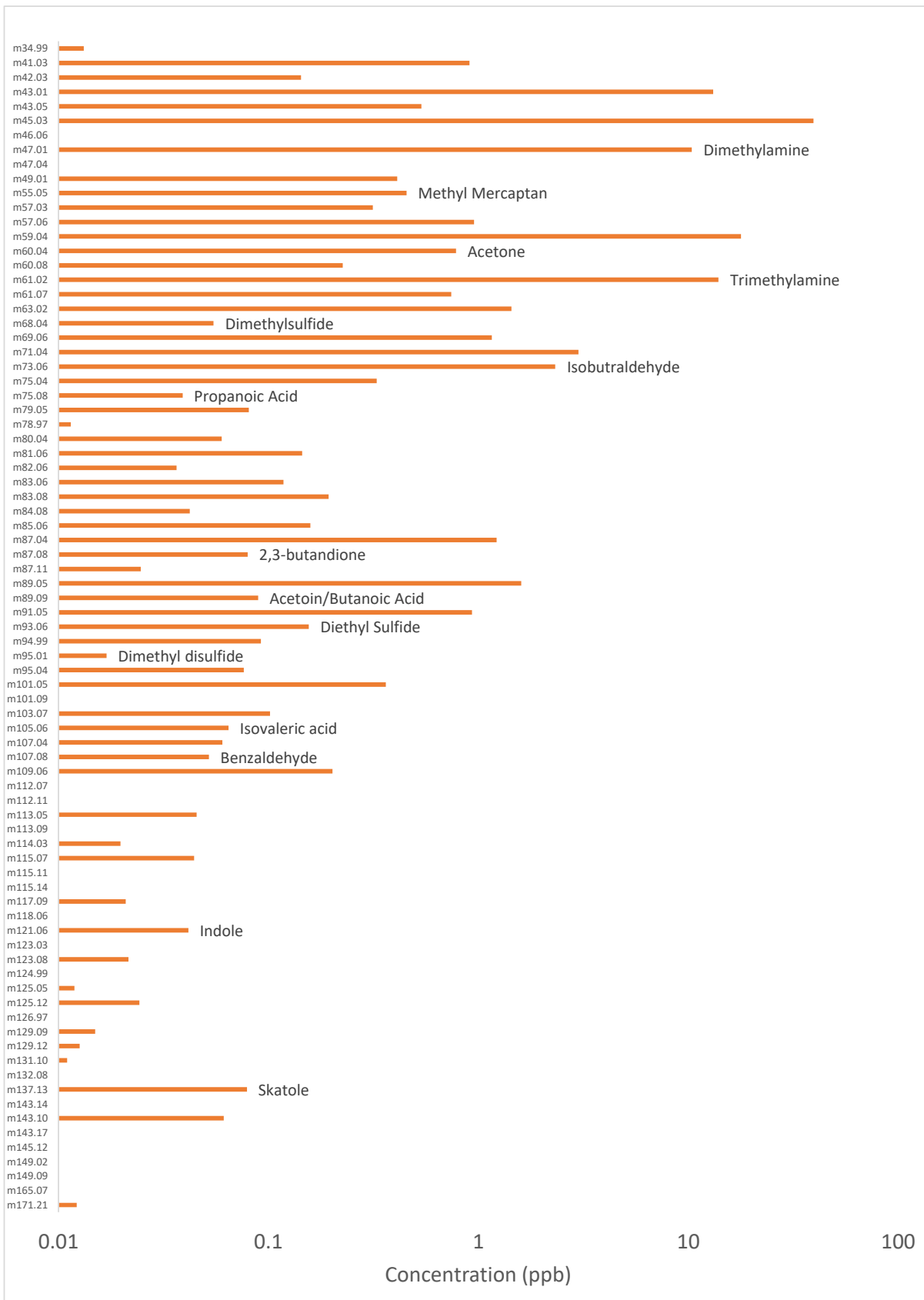


Figure C3: Full mass range detected in all downwind samples greater than 50 m from the shed.

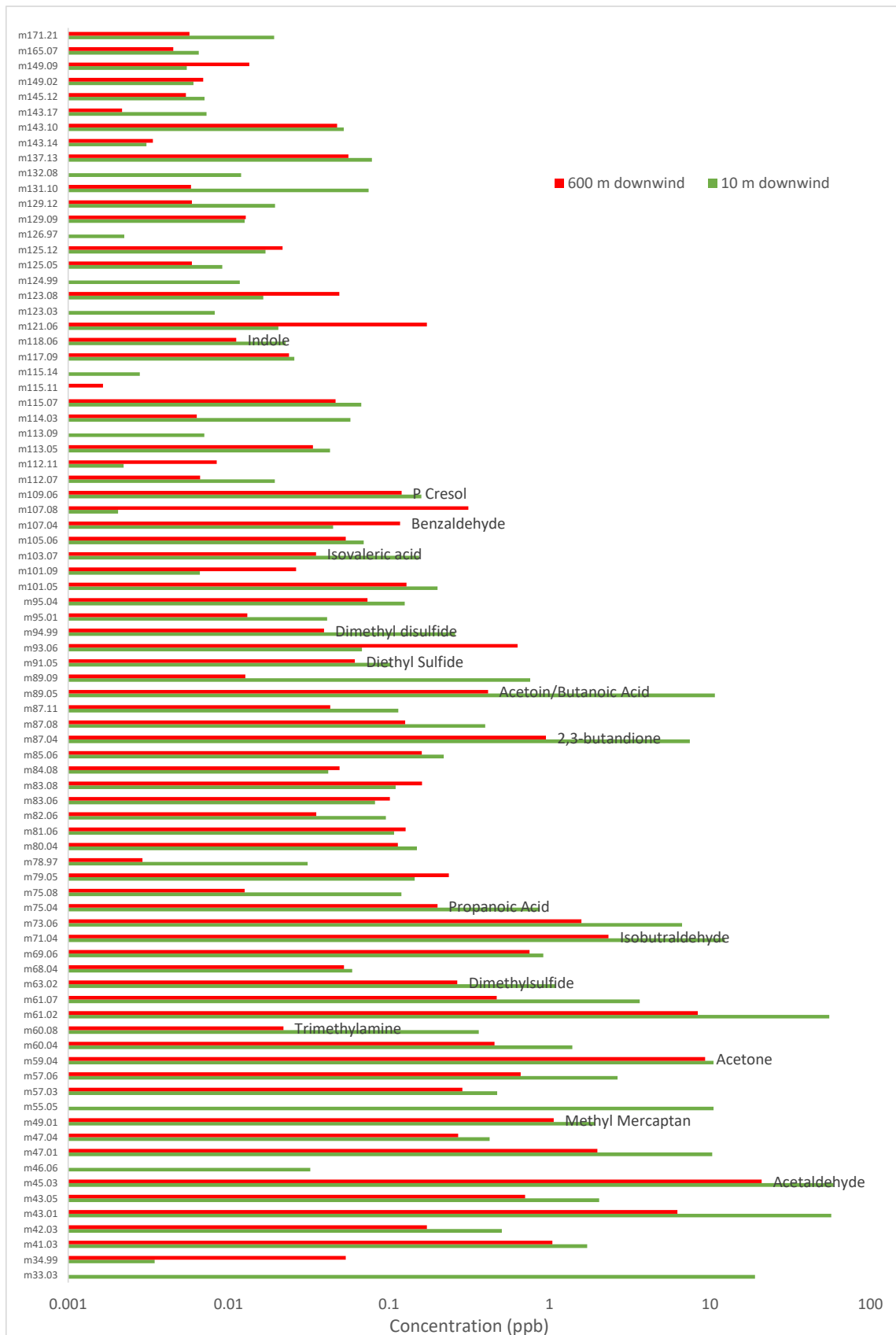


Figure C4: Full mass range detected in single samples taken 600 m and 10 m away from the shed.

Appendix D

Table D1. Concentrations in air for previously identified compounds present in poultry production.

Name	Monoisotopic Mass (g/mol)	Chemical Formula	Concentration in air (direct from fans)		
			Min (ppb)	Max (ppb)	Mean (ppb)
Alcohols					
methanol	32.026	CH4O	49.02	368.92	142.054
ethanol	46.042	C2H6O	3.81	36.11	14.26
propanol	60.058	C3H8O	4.45	45.65	22.23
butanol	74.073	C4H10O	0.51	24.33	4.88
Ketones					
acetone	58.04187	C3H6O	16.81	130.33	37.02
2-butanone	72.05752	C4H8O	0.29	1.98	1.01
2,3-butanedione	86.03678	C4H6O2	1.74	29.63	13.16
Aldehydes					
Formaldehyde	30.011	CH2O	5.66	23.33	10.7
Acetaldehyde	44.026	C2H4O	28.39	187.5	125.39
Isovaleraldehyde	86.073	C5H10O	1.78	27.25	10.26
Hexanal	100.089	C6H12O	0.33	1.89	0.82
Nonanal	142.136	C9H18O	0.11	1.28	0.41
benzaldehyde	106.042	C7H6O	0.11	1.25	0.43
Carboxylic Acids					
acetic acid	60.02113	C2H4O2	22.05	681.22	186.36
propanoic acid	74.037	C3H6O2	0.84	26.41	6.41
Isobutyric acid (2-methylpropanoic acid)	88.052	C4H8O2	0.38	3.26	1.56
butanoic acid	88.052	C4H8O2	0.26	4.34	1.38
pentanoic acid	102.068	C5H10O2	0.26	4.34	1.38
hexanoic acid	116.084	C6H12O2	0.19	1.22	0.39
benzoic acid	122.03678	C7H6O2	0.12	1.21	0.38
Sorbic acid	112.052	C6H8O2	0.15	1.24	0.49
Phenols					
phenol	94.04187	C6H6O	0.46	3.14	1.23
4-methylphenol	108.05752	C7H8O	0.22	2.11	0.79
4-ethylphenol	122.073	C8H10O	0.12	1.2	0.37
3-isopropylphenol	136.089	C9H12O	0.12	1.23	0.23

Name	Monoisotopic Mass (g/mol)	Chemical Formula	Concentration in air (direct from fans)		
			Min (ppb)	Max (ppb)	Mean (ppb)
N-Containing Compounds					
acetonitrile	41.027	C2H3N	1.21	7.09	3.12
acetamide	59.037	C2H5NO	0.12	1.2	0.37
indole	117.058	C8H7N	0.09	1.23	0.33
3-methylindole (skatole)	131.073	C9H9N	0.8	1.88	0.31
Pyrrrole	67.042	C4H5N	0.22	1.52	0.54
Pyridine	79.042	C5H5N	0.25	4.08	0.88
Methylamine	31.042	CH5N	0.02	118.07	11.29
Dimethylamine	45.058	(CH3)2NH	1.15	9.73	4.74
Trimethylamine	59.1112	C3H9N	1.31	24.02	5.35
heptanenitrile	111.18	C7H13N	0.09	1.23	0.33
S-Containing Compounds					
dimethyl disulfide	93.991	C2H6S2	0.79	8.13	3.14
dimethyl sulfone	94.009	C2H6O2S	0.63	3.56	1.38
tetrahydrothiophene 1,1,-dioxide (sulfolane)	120.025	C4H8O2S	0.01	0.89	0.21
Methylmercaptan (methanethiol)	48.003	CH4S	0.92	10.46	2.95
Diethylsulfide	90.05	C4H10S	0.21	1.47	0.72
Diethyldisulfide	122.022	C4H10S2	0.11	1.22	0.38
Dimethyl trisulfide	125.963	C2H6S3	0.09	1.23	0.38
Alkanes/Alkenes					
propene	42.047	C3H6	10.09	426.79	94.97
Cyclopropene	40.031	C3H4	1.83	33.01	8.63
2-methyl-1-propene (isobutylene)	56.063	C4H8	0.91	46.22	8.41
2-methyl-1,3-butadiene (isoprene)	68.063	C5H8	0.81	4.25	2.34
pentane	72.094	C5H12	0.12	2.23	1.65
cyclopentane	70.078	C5H10	0.22	1.89	1.23
cyclohexane	84.094	C6H12	0.49	2.28	1.01
pinene	136.125	C10H16	0.63	3.56	1.38
Ketene	42.0378	C2H2O	20.94	564.56	166.02
Cyclohexadiene	80.13745	C6H8	0.24	2.51	0.75
Acetophenone	120.152	C8H8O	0.12	1.21	0.39
Aromatic Compounds					
benzene	78.04695	C6H6	0.23	1.57	0.64
toluene	92.0626	C7H8	0.18	1.43	0.55
Halogenated Compounds					
dichloromethane	83.953	CH2Cl2	1.01	2.29	1.65
Indene	116.063	C9H8	0.11	1.22	0.49
chloroethane	64.008	C2H5Cl	0.23	1.22	0.88
pentanenitrile	83.073	C5H9N	0.183	1.43	0.48

a ND, not detected

References—(Jiang & Sands, 2000; Murphy et al., 2012; Parsci, 2010; Sharma et al., 2017; Trabue et al., 2010; Van Huffel et al., 2012)

Appendix E

Table E1. Olfactometry results from shed measurements.

Date	Farm	Shed ID	Litter type	Odour concentration (OU)	Trial ID	Bird age (days)
16/03/2016	B	1	Normal	266	T1	32
16/03/2016	B	2	Normal	196	T1	32
16/03/2016	B	4	Normal	181	T1	32
16/03/2016	B	5	Starter	181	T1	32
16/03/2016	B	6	Starter	196	T1	32
16/03/2016	B	7	Starter	197	T1	32
16/03/2016	B	8	Starter	215	T1	32
30/03/2016	B	3	Normal	51	T1	46
30/03/2016	B	4	Normal	38	T1	46
30/03/2016	B	5	Starter	64	T1	46
30/03/2016	B	6	Starter	72	T1	46
30/03/2016	B	7	Starter	72	T1	46
30/03/2016	B	8	Starter	76	T1	46
2/11/2016	C	1	Normal	215	T2	29
2/11/2016	C	2	Normal	283	T2	29
2/11/2016	C	5	Half Compost	81	T2	29
2/11/2016	C	6	Half Compost	50	T2	29
11/11/2016	C	1	Normal	323	T2	38
11/11/2016	C	6	Half Compost	192	T2	38
15/11/2016	B	1	Normal	782	T3	28
15/11/2016	B	2	Normal	416	T3	28
15/11/2016	B	7	Blended Compost	630	T3	24
15/11/2016	B	8	Blended Compost	1149	T3	21
22/11/2016	B	1	Normal	274	T3	35
22/11/2016	B	2	Normal	446	T3	35
22/11/2016	B	7	Blended Compost	630	T3	31
22/11/2016	B	8	Blended Compost	512	T3	28
29/11/2016	B	1	Normal	388	T3	42
29/11/2016	B	2	Normal	388	T3	42
29/11/2016	B	7	Blended Compost	416	T3	38
29/11/2016	B	8	Blended Compost	388	T3	35
28/03/2017	C	1	Normal	181		46
28/03/2017	C	2	Normal	256		46
28/03/2017	C	3	Normal	287		46
28/03/2017	C	4	Normal	483		46
28/03/2017	C	5	Normal	406		46
23/05/2017	C	1	Normal	431		31
23/05/2017	C	2	Normal	431		31
23/05/2017	C	3	Normal	274		31
23/05/2017	C	4	Normal	235		31
23/05/2017	C	5	Normal	181		31
23/05/2017	C	6	Normal	194		31
30/05/2017	C	1	Normal	446		38
30/05/2017	C	2	Normal	549		38
30/05/2017	C	3	Normal	223		38
30/05/2017	C	4	Normal	274		38
30/05/2017	C	5	Normal	388		38
30/05/2017	C	6	Normal	274		38
6/06/2017	C	5	Normal	609		45
6/06/2017	C	6	Normal	542		45

Table E2. Olfactometry results from downwind measurements.

Date	Sample ID	Sample	Odour concentration (OU)	Olfactometry to standard**	Distance (m)	Age (days)
16/03/2016	t10	Odour	62	no	10	41
16/03/2016	t20	Odour	36	no	20	41
17/03/2016	t30	Odour	62	no	30	42
17/03/2016	t15	Odour	45	no	15	42
17/03/2016	tb40	Background [#]	14	no	40	42
17/03/2016	t40	Odour	14	no	40	42
17/03/2016	t30b	Odour	128	no	30	42
17/03/2016	t10b	Odour	114	no	10	42
17/03/2016	tb10	Background	19	no	10	42
17/03/2016	t60	Odour	54	no	60	42
11/11/2016	b30	Odour	41	yes	30	42
11/11/2016	b50	Odour	30	yes	50	42
15/11/2016	t20b	Odour	64	yes	20	28
15/11/2016	t140	Odour	23	yes	140	28
15/11/2016	tb30	Background	14	no	30	28
22/11/2016	t60b	Odour	74	yes	60	35
22/11/2016	t170	Odour	45	yes	170	35
22/11/2016	t100	Odour	37	yes	100	35
22/11/2016	tb30b	Background	20	no	30	35
29/11/2016	t100	Odour	194	yes	100	42
29/11/2016	t55	Odour	25	no	55	42
29/11/2016	t47	Odour	23	no	47	42
29/11/2016	t24	Odour	391	yes	24	42
29/11/2016	tb30c	Background	24	no	30	42
28/03/2017	b30c	Odour	181	yes	30	46
28/03/2017	b40	Odour	99	yes	40	46
28/03/2017	bb30	Background	52	yes	30	46
23/05/2017	b40b	Odour	36	no	40	31
23/05/2017	b113	Odour	32	no	113	31
23/05/2017	b200	Background	11	no	200	31
30/05/2017	bb200	Background	20	no	200	38
30/05/2017	b30d	Odour	15	no	30	38
30/05/2017	b120	Odour	30	no	120	38
6/06/2017	b150	Odour	25	no	150	45
6/06/2017	b80	Odour	13	no	80	45
6/06/2017	b100	Odour	19	no	100	45
6/06/2017	b100b	Odour	13	no	100	45
6/06/2017	bb207	Background	30	no	207	45
6/06/2017	b40c	Odour	59	no	40	45
6/06/2017	b150b	Odour	21	no	150	45

Notes:

[#]'Background' was away from the perceived odour plume

**AS/NZS 4323.3-2001

Appendix F

Table F1. Correlation coefficients (r) for PTR–ToFMS masses in meat chicken emissions.

Protonated Masses	33.03	34.99	41.03	42.03	43.01	43.05	45.03	46.06	47.01	47.04	49.01	55.05	57.03	57.06	59.04	60.04	60.08	61.02	61.07	63.02	68.04	
33.03	1.00																					
34.99	0.52	1.00																				
41.03	0.67	0.62	1.00																			
42.03	0.79	0.63	0.92	1.00																		
43.01	0.69	0.58	0.89	0.93	1.00																	
43.05	0.56	0.40	0.83	0.70	0.70	1.00																
45.03	0.50	0.36	0.63	0.64	0.67	0.66	1.00															
46.06	0.52	0.23	0.41	0.52	0.52	0.43	0.74	1.00														
47.01	0.05	0.12	0.37	0.28	0.35	0.39	0.55	0.26	1.00													
47.04	0.73	0.43	0.74	0.73	0.70	0.55	0.34	0.38	-0.05	1.00												
49.01	0.84	0.56	0.69	0.71	0.67	0.66	0.58	0.51	0.28	0.56	1.00											
55.05	0.23	-0.21	0.01	0.06	0.09	0.13	0.16	0.31	0.08	0.21	0.12	1.00										
57.03	0.53	0.50	0.69	0.80	0.88	0.52	0.64	0.50	0.40	0.42	0.56	0.07	1.00									
57.06	0.51	0.44	0.88	0.71	0.69	0.88	0.53	0.23	0.38	0.65	0.59	0.04	0.42	1.00								
59.04	0.28	0.24	0.33	0.30	0.21	0.30	0.39	0.43	0.19	0.20	0.23	0.26	0.18	0.15	1.00							
60.04	0.58	0.52	0.78	0.74	0.71	0.65	0.65	0.55	0.34	0.54	0.57	0.19	0.61	0.55	0.81	1.00						
60.08	0.40	0.08	0.10	0.25	0.12	0.24	0.38	0.68	-0.05	0.14	0.27	0.33	0.13	-0.05	0.61	0.45	1.00					
61.02	0.66	0.62	0.89	0.93	0.99	0.66	0.65	0.49	0.36	0.67	0.65	0.04	0.89	0.69	0.18	0.68	0.06	1.00				
61.07	0.45	0.12	0.34	0.40	0.54	0.61	0.61	0.56	0.25	0.28	0.47	0.32	0.51	0.34	0.11	0.36	0.39	0.47	1.00			
63.02	0.69	0.54	0.91	0.90	0.93	0.78	0.79	0.65	0.43	0.69	0.72	0.16	0.81	0.73	0.46	0.86	0.28	0.91	0.52	1.00		
68.04	0.56	0.44	0.56	0.58	0.49	0.48	0.54	0.60	0.24	0.44	0.52	0.30	0.43	0.35	0.89	0.89	0.61	0.47	0.28	0.69	1.00	
69.06	0.27	0.23	0.36	0.32	0.27	0.33	0.45	0.49	0.24	0.22	0.25	0.29	0.25	0.17	0.98	0.83	0.59	0.24	0.19	0.52	0.92	
71.04	0.73	0.52	0.86	0.91	0.95	0.72	0.72	0.60	0.28	0.70	0.67	0.14	0.78	0.68	0.20	0.68	0.26	0.92	0.60	0.89	0.48	
73.06	0.62	0.54	0.88	0.77	0.80	0.84	0.67	0.37	0.41	0.61	0.71	0.05	0.58	0.91	0.18	0.63	0.03	0.78	0.44	0.81	0.41	
75.04	0.61	0.66	0.91	0.93	0.95	0.65	0.60	0.41	0.38	0.64	0.64	-0.05	0.87	0.70	0.20	0.69	0.01	0.97	0.33	0.89	0.47	
75.08	0.60	0.58	0.86	0.89	0.94	0.75	0.71	0.49	0.46	0.53	0.65	0.00	0.91	0.68	0.19	0.68	0.13	0.94	0.57	0.89	0.45	
79.05	0.63	0.37	0.70	0.75	0.84	0.66	0.57	0.53	0.28	0.65	0.61	0.31	0.79	0.59	0.17	0.57	0.21	0.80	0.67	0.78	0.46	
78.97	0.89	0.62	0.74	0.80	0.72	0.58	0.48	0.44	0.14	0.70	0.88	0.11	0.53	0.59	0.20	0.57	0.19	0.71	0.33	0.72	0.52	
80.04	0.73	0.23	0.14	0.40	0.23	0.15	0.23	0.42	-0.09	0.29	0.56	0.22	0.23	0.01	0.11	0.16	0.57	0.21	0.32	0.22	0.31	
81.06	0.33	0.26	0.31	0.36	0.34	0.27	0.35	0.33	0.22	0.26	0.29	0.20	0.35	0.19	0.25	0.34	0.26	0.34	0.33	0.37	0.42	
82.06	0.81	0.50	0.58	0.74	0.73	0.48	0.53	0.61	0.07	0.67	0.64	0.33	0.62	0.42	0.20	0.51	0.40	0.71	0.61	0.68	0.53	
83.06	0.63	0.30	0.42	0.58	0.56	0.35	0.45	0.51	0.14	0.46	0.50	0.31	0.56	0.26	0.19	0.40	0.36	0.55	0.51	0.54	0.49	
83.08	0.47	0.39	0.27	0.45	0.42	0.17	0.34	0.38	0.03	0.25	0.34	0.09	0.47	0.10	0.11	0.25	0.31	0.44	0.35	0.36	0.41	
84.08	0.63	0.54	0.49	0.68	0.62	0.33	0.44	0.51	0.10	0.46	0.48	0.15	0.60	0.31	0.14	0.39	0.31	0.65	0.37	0.55	0.48	
85.06	0.70	0.57	0.85	0.88	0.90	0.76	0.84	0.66	0.40	0.62	0.74	0.16	0.80	0.69	0.31	0.74	0.30	0.88	0.60	0.92	0.59	
87.04	0.75	0.47	0.84	0.86	0.92	0.69	0.58	0.45	0.20	0.76	0.66	0.18	0.72	0.69	0.17	0.66	0.16	0.88	0.58	0.85	0.44	
87.08	0.57	0.08	0.28	0.40	0.39	0.54	0.59	0.64	0.19	0.25	0.60	0.34	0.39	0.26	0.13	0.28	0.55	0.32	0.80	0.44	0.30	
87.11	0.70	0.48	0.69	0.75	0.83	0.53	0.49	0.51	0.14	0.72	0.62	0.22	0.69	0.53	0.17	0.58	0.18	0.81	0.53	0.77	0.47	
89.05	0.67	0.55	0.92	0.93	0.97	0.76	0.68	0.51	0.34	0.68	0.67	0.06	0.83	0.74	0.18	0.70	0.15	0.96	0.51	0.91	0.45	
89.09	0.26	-0.14	0.14	0.22	0.35	0.48	0.47	0.51	0.16	0.10	0.23	0.35	0.36	0.17	0.03	0.18	0.45	0.26	0.88	0.33	0.12	
91.05	0.68	0.54	0.91	0.92	0.97	0.75	0.67	0.53	0.36	0.69	0.67	0.10	0.83	0.73	0.21	0.71	0.17	0.95	0.51	0.92	0.51	
93.06	0.14	0.17	0.30	0.30	0.24	0.27	0.14	0.12	0.22	0.19	0.16	0.11	0.17	0.28	0.14	0.23	0.10	0.23	0.09	0.22	0.33	
94.99	0.90	0.49	0.71	0.77	0.72	0.65	0.52	0.49	0.18	0.66	0.93	0.20	0.55	0.61	0.19	0.56	0.27	0.69	0.47	0.72	0.51	
95.01	0.63	0.26	0.55	0.55	0.59	0.60	0.42	0.28	0.19	0.45	0.63	0.22	0.41	0.57	0.16	0.48	0.20	0.53	0.57	0.58	0.34	
95.04	0.90	0.52	0.73	0.85	0.78	0.64	0.57	0.56	0.15	0.68	0.82	0.26	0.66	0.55	0.31	0.66	0.43	0.75	0.55	0.77	0.64	
101.05	0.41	-0.14	0.22	0.31	0.32	0.25	0.19	0.36	0.15	0.31	0.31	0.44	0.31	0.17	0.12	0.24	0.26	0.28	0.35	0.33	0.26	
101.09	0.76	0.74	0.70	0.77	0.65	0.49	0.44	0.38	0.03	0.62	0.68	-0.05	0.49	0.54	0.20	0.52	0.24	0.67	0.24	0.62	0.46	
103.07	0.57	0.61	0.88	0.90	0.88	0.71	0.62	0.46	0.36	0.54	0.61	-0.05	0.78	0.69	0.18	0.65	0.14	0.89	0.37	0.82	0.44	
105.06	0.36	0.43	0.50	0.53	0.52	0.40	0.30	0.31	0.22	0.36	0.39	0.13	0.48	0.40	0.15	0.39	0.08	0.54	0.23	0.49	0.47	
107.04	0.10	0.16	0.25	0.24	0.21	0.19	0.05	-0.02	0.12	0.15	0.14	0.01	0.18	0.20	0.07	0.19	-0.03	0.21	0.08	0.19	0.26	
107.08	-0.03	0.10	0.16	0.17	0.09	0.10	0.00	-0.01	0.08	0.05	-0.05	-0.01	0.03	0.15	0.04	0.06	0.04	0.09	-0.09	0.04	0.16	
109.06	0.41	-0.16	0.14	0.23	0.28	0.25	0.26	0.48	-0.04	0.36	0.29	0.47	0.20	0.14	0.10	0.19	0.37	0.21	0.49	0.30	0.29	
112.07	0.38	0.34	0.34	0.44	0.47	0.28	0.32	0.43	0.07	0.34	0.27	0.17	0.40	0.28	0.03	0.23	0.11	0.49	0.31	0.40	0.26	
112.11	0.11	0.12	0.05	0.08	0.03	-0.01	-0.04	-0.01	-0.02	0.05	0.09	0.06	0.06	0.01	0.11	0.09	0.12	0.05	-0.05	0.05	0.20	
113.05	0.67	0.32	0.51	0.63	0.57	0.48	0.50	0.56	0.19	0.52	0.63	0.24	0.51	0.39	0.16	0.43	0.41	0.54	0.54	0.58	0.39	
113.09	0.51	0.62	0.58	0.65	0.66	0.32	0.36	0.36	0.09	0.48	0.43	0.00	0.57	0.38	0.15	0.45	0.05	0.69	0.15	0.57	0.44	
114.03	0.67	0.43	0.51	0.61	0.67	0.47	0.47	0.62	0.09	0.60	0.60	0.32	0.57	0.41	0.16	0.45	0.33	0.65	0.57	0.64	0.48	
115.07	0.83	0.61	0.80	0.90	0.85	0.71	0.64	0.56	0.27	0.65	0.80	0.16	0.75	0.66	0.21	0.63	0.29	0.84	0.54	0.82	0.57	
115.11	0.17	-0.04	0.24	0.26	0.12	0.19	0.06	0.09	0.01	0.20	0.06	-0.05	0.01	0.25	0.06	0.11	0.17	0.11	-0.03	0.13	0.12	
115.14	0.02	0.26	-0.07	0.01	-0.05	-0.15	-0.14	0.09	-0.11	0.00	-0.07	0.01	-0.06	-0.11	0.06	-0.05	0.12	0.00	-0.15	-0.07	0.18	
117.09	0.51	0.55	0.88	0.77	0.76	0.85	0.57	0.37	0.41	0.58	0.62	0.01	0.60	0.87	0.20	0.60	0.01	0.77	0.34	0.78	0.45	
118.06	0.41	0.53	0.43	0.51	0.51	0.28	0.30	0.40	0.10	0.39	0.33	0.15	0.45	0.32	0.15	0.35	0.14	0.55	0.19	0.46	0.42	
121.06	0.18	0.24	0.41	0.36	0.35	0.30	0.15	0.06	0.17	0.33	0.20	0.06	0.22	0.37	0.08	0.29	-0.03	0.33	0.09	0.31	0.30	
123.03	0.05	0.02	-0.16	-0.09	-0.04	-0.17	-0.09	-0.02	0													

Table F1 *cont'd.*

Protonated																						
Masses	69.06	71.04	73.06	75.04	75.08	79.05	78.97	80.04	81.06	82.06	83.06	83.08	84.08	85.06	87.04	87.08	87.11	89.05	89.09	91.05	93.06	
33.03																						
34.99																						
41.03																						
42.03																						
43.01																						
43.05																						
45.03																						
46.06																						
47.01																						
47.04																						
49.01																						
55.05																						
57.03																						
57.06																						
59.04																						
60.04																						
60.08																						
61.02																						
61.07																						
63.02																						
68.04																						
69.06	1.00																					
71.04	0.26	1.00																				
73.06	0.20	0.80	1.00																			
75.04	0.24	0.86	0.78	1.00																		
75.08	0.25	0.87	0.78	0.94	1.00																	
79.05	0.25	0.81	0.66	0.72	0.78	1.00																
78.97	0.21	0.73	0.67	0.69	0.63	0.60	1.00															
80.04	0.09	0.31	0.10	0.15	0.21	0.31	0.59	1.00														
81.06	0.32	0.33	0.25	0.31	0.36	0.40	0.27	0.28	1.00													
82.06	0.25	0.75	0.53	0.61	0.64	0.76	0.74	0.61	0.56	1.00												
83.06	0.29	0.56	0.32	0.48	0.51	0.58	0.54	0.53	0.49	0.73	1.00											
83.08	0.20	0.40	0.16	0.39	0.40	0.41	0.41	0.49	0.49	0.64	0.81	1.00										
84.08	0.19	0.62	0.41	0.60	0.58	0.56	0.62	0.51	0.42	0.82	0.72	0.80	1.00									
85.06	0.37	0.90	0.81	0.84	0.87	0.79	0.73	0.32	0.46	0.75	0.59	0.49	0.66	1.00								
87.04	0.21	0.94	0.78	0.80	0.79	0.81	0.74	0.28	0.26	0.73	0.52	0.34	0.53	0.83	1.00							
87.08	0.18	0.50	0.35	0.23	0.45	0.54	0.44	0.61	0.31	0.59	0.48	0.28	0.33	0.53	0.40	1.00						
87.11	0.23	0.79	0.59	0.74	0.69	0.76	0.70	0.33	0.29	0.78	0.63	0.52	0.66	0.75	0.84	0.33	1.00					
89.05	0.23	0.97	0.83	0.93	0.92	0.80	0.72	0.22	0.30	0.67	0.50	0.34	0.57	0.89	0.92	0.41	0.76	1.00				
89.09	0.10	0.46	0.24	0.13	0.40	0.54	0.10	0.30	0.24	0.43	0.36	0.19	0.21	0.40	0.39	0.80	0.30	0.37	1.00			
91.05	0.28	0.96	0.82	0.92	0.91	0.84	0.72	0.23	0.39	0.71	0.55	0.40	0.62	0.91	0.91	0.41	0.77	0.99	0.37	1.00		
93.06	0.21	0.27	0.28	0.24	0.23	0.39	0.18	0.00	0.51	0.26	0.27	0.31	0.32	0.32	0.21	0.10	0.12	0.27	0.09	0.38	1.00	
94.99	0.21	0.74	0.69	0.65	0.64	0.69	0.94	0.63	0.29	0.73	0.55	0.38	0.53	0.74	0.76	0.57	0.70	0.72	0.27	0.72	0.18	
95.01	0.17	0.60	0.63	0.45	0.52	0.61	0.60	0.34	0.23	0.52	0.36	0.15	0.24	0.58	0.70	0.44	0.54	0.58	0.39	0.57	0.13	
95.04	0.35	0.80	0.65	0.69	0.71	0.78	0.86	0.65	0.47	0.84	0.70	0.56	0.67	0.82	0.80	0.59	0.76	0.76	0.37	0.80	0.36	
101.05	0.18	0.32	0.17	0.22	0.26	0.38	0.31	0.37	0.19	0.38	0.68	0.26	0.27	0.27	0.33	0.39	0.37	0.30	0.37	0.33	0.03	
101.09	0.18	0.69	0.62	0.68	0.59	0.47	0.77	0.44	0.28	0.69	0.45	0.48	0.67	0.68	0.64	0.31	0.61	0.66	-0.01	0.65	0.19	
103.07	0.23	0.87	0.78	0.91	0.89	0.68	0.65	0.18	0.33	0.57	0.43	0.35	0.58	0.84	0.76	0.34	0.60	0.93	0.24	0.93	0.39	
105.06	0.25	0.46	0.43	0.54	0.51	0.58	0.45	0.12	0.52	0.56	0.49	0.57	0.67	0.57	0.40	0.19	0.47	0.49	0.12	0.60	0.75	
107.04	0.17	0.18	0.18	0.21	0.20	0.33	0.13	-0.05	0.46	0.19	0.33	0.40	0.23	0.27	0.19	0.03	0.15	0.21	0.02	0.32	0.76	
107.08	0.09	0.13	0.14	0.12	0.08	0.19	0.01	-0.08	0.30	0.08	0.07	0.19	0.20	0.15	0.05	-0.07	-0.05	0.13	-0.03	0.22	0.91	
109.06	0.18	0.36	0.19	0.10	0.16	0.48	0.28	0.38	0.30	0.49	0.55	0.32	0.28	0.36	0.38	0.53	0.42	0.26	0.53	0.33	0.26	
112.07	0.06	0.47	0.32	0.43	0.41	0.44	0.42	0.23	0.15	0.60	0.40	0.42	0.71	0.47	0.39	0.26	0.50	0.42	0.24	0.44	0.16	
112.11	0.13	0.02	0.01	0.07	0.03	0.05	0.13	0.14	0.29	0.19	0.24	0.29	0.27	0.06	0.02	-0.05	0.19	0.01	-0.12	0.06	0.18	
113.05	0.18	0.60	0.45	0.48	0.53	0.60	0.62	0.60	0.56	0.73	0.58	0.39	0.51	0.66	0.58	0.60	0.57	0.56	0.38	0.57	0.14	
113.09	0.19	0.63	0.49	0.69	0.58	0.48	0.58	0.16	0.23	0.62	0.43	0.53	0.76	0.60	0.55	0.09	0.60	0.62	-0.01	0.65	0.32	
114.03	0.22	0.67	0.51	0.56	0.58	0.71	0.66	0.44	0.38	0.88	0.62	0.52	0.79	0.67	0.65	0.51	0.78	0.61	0.42	0.65	0.19	
115.07	0.26	0.85	0.76	0.81	0.83	0.79	0.83	0.52	0.49	0.84	0.68	0.59	0.78	0.89	0.80	0.55	0.74	0.84	0.34	0.87	0.40	
115.11	0.06	0.18	0.16	0.15	0.12	0.09	0.16	0.16	0.15	0.09	0.12	0.11	0.14	0.14	0.14	0.05	0.06	0.18	0.00	0.20	0.29	
115.14	0.06	-0.09	-0.14	0.00	-0.06	-0.04	0.10	0.10	0.05	0.25	0.15	0.33	0.51	-0.05	-0.16	-0.13	0.08	-0.11	-0.17	-0.05	0.19	
117.09	0.24	0.71	0.83	0.81	0.80	0.63	0.64	0.08	0.28	0.51	0.35	0.27	0.54	0.77	0.66	0.28	0.59	0.79	0.17	0.80	0.31	
118.06	0.18	0.47	0.38	0.53	0.47	0.44	0.50	0.21	0.29	0.67	0.42	0.50	0.83	0.51	0.40	0.10	0.59	0.46	0.05	0.50	0.24	
121.06	0.18	0.36	0.39	0.34	0.29	0.45	0.25	-0.08	0.49	0.28	0.28	0.30	0.27	0.41	0.36	0.02	0.25	0.37	0.02	0.48	0.87	
123.03	-0.05	-0.11	-0.10	-0.04	-0.03	-0.03	-0.05	0.08	0.01	0.18	0.00	0.08	0.22	-0.13	-0.11	-0.05	0.06	-0.11	0.02	-0.10	-0.18	
123.08	0.25	0.76	0.63	0.73	0.70	0.61	0.68	0.27	0.38	0.62	0.56	0.51	0.66	0.79	0.67	0.36	0.65	0.75	0.18	0.77	0.44	
124.99	0.16	0.17	0.09	0.18	0.17	0.25	0.22	0.25	0.26	0.53	0.30	0.42	0.66	0.21	0.12	0.09	0.34	0.14	0.07	0.19	0.09	
125.05	0.22	0.55	0.45	0.48	0.51	0.56	0.46	0.22	0.27	0.45	0.50	0.24	0.29	0.57	0.55	0.49	0.57	0.54	0.41	0.57	0.25	
125.12	0.27	0.45	0.28	0.37	0.41	0.51	0.37	0.23	0.46	0.61	0.72	0.77	0.73	0.53	0.38	0.31	0.57	0.39	0.30	0.48	0.42	
126.97	0.01	-0.08	-0.31	-0.02	0.04	-0.04	-0.10	0.16	-0.07	0.01	0.15	0.20	0.17	-0.09	-0.10	0.09	0.11	-0.07	0.16	-0.08	-0.26	
129.09	0.30	0.79	0.70	0.70	0.66	0.72	0.80	0.40	0.39	0.78	0.61	0.48	0.69	0.82	0.76	0.45	0.75	0.76	0.26	0.79	0.38	
129.12	0.24	0.71	0.68	0.69	0.60	0.56	0.73	0.24	0.32	0.57	0.51	0.38	0.49	0.69	0.74	0.24	0.67	0.71	0.06	0.74	0.35	
131.10	0.21	0.91	0.68	0.75	0.74	0.80	0.71	0.34	0.33	0.85	0.59	0.45	0.74	0.81	0.87	0.49	0.82	0.86	0.46	0.87	0.29	
132.08	0.14	0.49	0.37	0.52	0.48	0.47	0.48	0.21	0.29	0.68	0.43	0.48	0.78	0.49	0.44	0.17	0.61	0.48	0.12	0.51	0.19	
137.13	0.37	0.55	0.49	0.54	0.53	0.57	0.51															

Table F1 *cont'd.*

Protonated																					
Masses	94.99	95.01	95.04	101.05	101.09	103.07	105.06	107.04	107.08	109.06	112.07	112.11	113.05	113.09	114.03	115.07	115.11	115.14	117.09	118.06	121.06
33.03																					
34.99																					
41.03																					
42.03																					
43.01																					
43.05																					
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83.08																					
84.08																					
85.06																					
87.04																					
87.08																					
87.11																					
89.05																					
89.09																					
91.05																					
93.06																					
94.99	1.00																				
95.01	0.75	1.00																			
95.04	0.91	0.72	1.00																		
101.05	0.38	0.36	0.41	1.00																	
101.09	0.69	0.37	0.70	0.01	1.00																
103.07	0.63	0.42	0.69	0.20	0.67	1.00															
105.06	0.41	0.23	0.57	0.11	0.43	0.56	1.00														
107.04	0.13	0.11	0.34	0.06	0.15	0.26	0.70	1.00													
107.08	-0.01	-0.04	0.16	-0.11	0.12	0.32	0.57	0.58	1.00												
109.06	0.38	0.40	0.48	0.65	0.06	0.12	0.26	0.23	0.12	1.00											
112.07	0.34	0.18	0.41	0.18	0.37	0.41	0.52	0.05	0.12	0.25	1.00										
112.11	0.09	-0.06	0.13	0.05	0.27	0.04	0.27	0.16	0.11	0.02	-0.27	1.00									
113.05	0.67	0.57	0.72	0.42	0.53	0.48	0.29	0.10	-0.05	0.42	0.26	0.17	1.00								
113.09	0.45	0.16	0.52	0.04	0.68	0.66	0.66	0.25	0.27	0.08	0.66	0.13	0.13	1.00							
114.03	0.65	0.43	0.71	0.34	0.56	0.50	0.59	0.10	0.00	0.47	0.67	0.23	0.59	0.63	1.00						
115.07	0.83	0.60	0.91	0.35	0.78	0.82	0.66	0.34	0.20	0.38	0.51	0.17	0.73	0.64	0.75	1.00					
115.11	0.17	0.13	0.22	0.10	0.22	0.26	0.19	0.10	0.33	0.04	0.02	0.06	0.14	0.11	-0.01	0.20	1.00				
115.14	-0.05	-0.25	0.02	-0.10	0.17	0.01	0.45	0.03	0.21	-0.12	0.48	0.24	-0.07	0.41	0.36	0.07	-0.01	1.00			
117.09	0.61	0.42	0.59	0.15	0.61	0.81	0.58	0.21	0.17	0.08	0.44	0.11	0.43	0.58	0.56	0.77	0.22	0.09	1.00		
118.06	0.36	0.12	0.44	0.08	0.56	0.47	0.67	0.10	0.15	0.12	0.74	0.32	0.32	0.78	0.79	0.60	0.04	0.65	0.57	1.00	
121.06	0.24	0.21	0.42	0.02	0.26	0.43	0.71	0.81	0.75	0.30	0.10	0.17	0.16	0.33	0.21	0.43	0.25	0.00	0.34	0.19	1.00
123.03	-0.09	-0.14	-0.08	0.05	0.03	-0.13	0.07	-0.23	-0.16	0.00	0.22	0.20	-0.14	0.22	0.26	-0.01	-0.09	0.37	-0.06	0.35	-0.27
123.08	0.64	0.40	0.71	0.16	0.70	0.78	0.63	0.39	0.28	0.19	0.44	0.16	0.56	0.62	0.61	0.80	0.21	0.15	0.71	0.55	0.49
124.99	0.15	0.00	0.26	0.11	0.30	0.16	0.46	0.01	0.02	0.12	0.57	0.23	0.17	0.53	0.62	0.35	-0.03	0.64	0.23	0.73	0.02
125.05	0.52	0.43	0.54	0.53	0.24	0.44	0.35	0.25	0.06	0.62	0.22	0.14	0.50	0.19	0.49	0.53	0.08	-0.17	0.43	0.22	0.31
125.12	0.36	0.18	0.51	0.27	0.39	0.38	0.68	0.43	0.24	0.38	0.49	0.32	0.38	0.53	0.69	0.58	0.07	0.40	0.41	0.62	0.41
126.97	-0.10	-0.18	-0.08	0.16	-0.10	-0.06	-0.03	-0.24	-0.22	-0.03	0.15	0.07	0.02	-0.01	0.08	-0.04	0.05	0.25	0.03	0.13	-0.41
129.09	0.78	0.54	0.82	0.32	0.69	0.69	0.62	0.31	0.17	0.42	0.57	0.03	0.60	0.64	0.76	0.85	0.20	0.11	0.70	0.58	0.43
129.12	0.70	0.56	0.73	0.32	0.72	0.67	0.52	0.39	0.20	0.32	0.30	0.23	0.53	0.54	0.52	0.77	0.30	-0.02	0.67	0.42	0.48
131.10	0.69	0.52	0.77	0.34	0.68	0.76	0.56	0.15	0.16	0.44	0.62	0.11	0.59	0.71	0.84	0.83	0.13	0.16	0.67	0.68	0.34
132.08	0.37	0.16	0.45	0.11	0.57	0.48	0.62	0.09	0.10	0.14	0.66	0.40	0.35	0.73	0.81	0.60	0.01	0.58	0.54	0.92	0.17
137.13	0.47	0.23	0.60	0.13	0.53	0.59	0.78	0.49	0.42	0.22	0.40	0.35	0.34	0.65	0.64	0.66	0.12	0.31	0.56	0.62	0.60
143.14	0.38	0.34	0.56	0.22	0.33	0.43	0.50	0.61	0.33	0.30	0.08	0.11	0.34	0.30	0.26	0.50	0.14	-0.06	0.31	0.13	0.54
143.10	0.34	0.25	0.47	0.41	0.21	0.32	0.62	0.49	0.24	0.58	0.37	0.24	0.37	0.36	0.61	0.51	0.08	0.18	0.35	0.43	0.47
143.17	0.38	0.16	0.47	0.11	0.48	0.47	0.62	0.25	0.09	0.17	0.51	0.32	0.41	0.56	0.70	0.60	0.01	0.40	0.52	0.70	0.28
145.12	0.32	0.09	0.39	0.04	0.53	0.45	0.68	0.15	0.16	0.06	0.69	0.36	0.28	0.74	0.75	0.57	0.02	0.65	0.56	0.93	0.21
149.02	0.16	-0.02	0.26	0.05	0.31	0.32	0.58	0.08	0.14	0.05	0.74	0.10	0.13	0.66	0.62	0.41	0.00	0.65	0.43	0.83	0.12
149.09	0.14	0.00	0.25	-0.04	0.35	0.23	0.70	0.40	0.42	0.08	0.36	0.51	0.06	0.57	0.44	0.34	0.16	0.59	0.31	0.65	0.43
165.07	0.30	0.09	0.40	-0.04	0.51	0.45	0.69	0.20	0.22	0.10	0.68	0.30	0.27	0.77	0.74	0.56	0.05	0.63	0.53	0.93	0.27
171.21	0.25	0.06	0.35	0.02	0.46	0.41	0.70	0.17	0.22	0.07	0.68	0.29	0.21	0.74	0.73	0.51	0.03	0.67	0.52	0.93	0.26

note: Stronger correlations are highlighted in green ($r \geq 0.95$), orange ($0.95 > r \geq 0.9$) and yellow ($0.9 > r \geq 0.8$).

Table F1 *cont'd.*

Protonated																			
Masses	123.03	123.08	124.99	125.05	125.12	126.97	129.09	129.12	131.10	132.08	137.13	143.14	143.10	143.17	145.12	149.02	149.09	165.07	171.21
33.03																			
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114.03																			
115.07																			
115.11																			
115.14																			
117.09																			
118.06																			
121.06																			
123.03	1.00																		
123.08	0.40	1.00																	
124.99	0.57	0.17	1.00																
125.05	0.25	0.51	0.17	1.00															
125.12	0.00	0.68	0.45	0.36	1.00														
126.97	0.23	0.06	0.14	0.00	0.13	1.00													
129.09	0.12	0.81	0.30	0.54	0.60	0.08	1.00												
129.12	0.12	0.71	0.13	0.48	0.44	0.05	0.69	1.00											
131.10	0.08	0.72	0.42	0.53	0.57	0.04	0.81	0.66	1.00										
132.08	0.38	0.53	0.72	0.25	0.61	0.14	0.54	0.45	0.71	1.00									
137.13	0.19	0.59	0.50	0.30	0.58	0.12	0.64	0.50	0.62	0.61	1.00								
143.14	0.34	0.62	0.05	0.34	0.53	0.03	0.47	0.53	0.34	0.15	0.43	1.00							
143.10	0.07	0.56	0.28	0.56	0.90	0.07	0.55	0.42	0.52	0.44	0.48	0.47	1.00						
143.17	0.02	0.73	0.45	0.34	0.88	0.15	0.61	0.44	0.57	0.68	0.53	0.38	0.71	1.00					
145.12	0.35	0.55	0.69	0.17	0.68	0.19	0.57	0.39	0.62	0.88	0.63	0.15	0.48	0.75	1.00				
149.02	0.29	0.43	0.68	0.07	0.60	0.16	0.47	0.16	0.48	0.71	0.50	0.11	0.39	0.66	0.83	1.00			
149.09	0.28	0.31	0.52	0.13	0.43	0.06	0.28	0.35	0.34	0.64	0.54	0.15	0.33	0.43	0.64	0.43	1.00		
165.07	0.36	0.50	0.71	0.14	0.57	0.12	0.52	0.40	0.63	0.88	0.63	0.16	0.37	0.62	0.89	0.80	0.69	1.00	
171.21	0.32	0.52	0.73	0.14	0.61	0.16	0.54	0.36	0.59	0.87	0.62	0.16	0.41	0.69	0.91	0.85	0.68	0.95	1.00

note: Stronger correlations are highlighted in green ($r \geq 0.95$), orange ($0.95 > r \geq 0.9$) and yellow ($0.9 > r \geq 0.8$).

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