Intercomparison of headspace sampling methods coupled to TD-GC-MS/O to characterise key odorants from broiler chicken litter

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INTERCOMPARISON OF HEADSPACE SAMPLING METHODS COUPLED TO TD-GC-MS/O TO CHARACTERISE KEY ODORANTS FROM BROILER CHICKEN LITTER

by

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Abstract

Since limited studies exist on the emissions of odours from tunnel ventilated broiler sheds under the Australian climate, this research study aims to determine the key odorants in the headspace of litter at ambient temperature across the poultry production cycle in two seasons (winter and summer) using headspace sampling coupled to TD-GC-MS/O analysis. Dynamic dilution olfactometry analysis was performed on litter odour samples producing odour concentrations ranging from 1421 to 115372 OU/m^3 and from 604 to 104379 OU/m^3 for winter and summer litters with greatest emission encountered from winter caked wet litter that sustained high amount of water and low pH. Analysis of litter odorant composition employing headspace sampling coupled to TD-GC-MS/O provided a greater understanding of the fate of odorants in the litter during bird growth cycle. The study also showed that characterise odorous volatiles can be correlated with dynamic dilution olfactometry responses. The results revealed that the odorous contributions were ketones, volatile fatty acids, sulfur and nitrogen compounds that were highly offensive substances, which impose significant effect on the odour annoyance from the emissions compared to other chemical functionalities. The assessment of activated carbon, silica gel and zeolite as a potential odour reducing strategy was directly applied to litters. The studies exhibited mixed trends in chemical and sensory responses and selectivity in reducing the volatilisation of odorants attributed to the efficacy of the additive itself, heterogeneous condition of litter particles in contact with the reduction materials and the exposed surface area. Based on the chemical and sensory responses, activated carbon and silica gel exhibited noticeable interactions on excessively wet litter with trial litters appeared remarkably drier and friable than the control and zeolite sets. However, complete elimination of odour or decrease in odour hedonic tone was unachievable mainly due to emission of ammonia from trial sets. Therefore, it is evident that no one product is capable of reducing or removing all volatiles presents in the emission of odours from poultry shed litter. Appropriate litter management within the shed conditions would still be the best method to avoid or reduce the generation of odours at source point before considering application of odour control products.

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ABSTRACT

While investing substantial efforts to satisfy the demand for food intake among expanding population, intensive livestock industries in many countries are burdened with increasing environmental issues, mainly odour nuisance. This is further worsened with escalating urban encroachment into rural landscapes, concurrently contributing to odour emission complaints. Since limited studies exist on the emission of odours from tunnel ventilated broiler sheds under the Australian climate, this research study aims to determine the key odorants in the headspace of litter at ambient temperature across poultry production cycle in two seasons (winter and summer) using headspace sampling coupled to TD-GC-MS/O analysis.

Dynamic dilution olfactometry analysis was performed on litter odour samples producing odour concentrations ranging from 1421 to 115372 OU/m^3 and from 604 to 104379 OU/m^3 for winter and summer litters, respectively. However the greatest emission was encountered from winter caked wet litter that sustained high amount of water and low pH value influence on odour emissions. During the study, bird's body mass was observed to correspond strongly with odour concentration for both sampling seasons in comparison to other variables investigated. Moisture content and pH values from winter litters exhibited reasonably adequate correlations with odour concentration, suggesting that odour concentration/emission rate can be minimised with proper maintenance of the litter moisture content and pH.

Analysis of litter odorant composition employing headspace sampling coupled to TD-GC-MS/O provided a greater understanding of the fate of odorants in the litter during the bird growth cycle. Tenax TA sorbent tube and direct headspace sampling techniques were used to collect volatiles from litters that were further analysed using TD-GC-MS/O in facilitating speciation of the key odorants. The litter headspace study showed that the concentration of volatiles determined directly from the litters was generally higher than for sorbent tube method, suggesting that poultry odours are predominately generated from the litter

bedding materials before being released into the broiler production environment and transported to local receptors. The study also showed that characterised odorous volatiles can be correlated with dynamic dilution olfactometry responses. The results revealed that the odorous contributions were of ketones, volatile fatty acids, sulfur and nitrogen compounds that were highly offensive substances, which impose significant effect on the odour annoyance from the emissions compared to other chemical functionalities.

The assessments of activated carbon, silica gel and zeolite as potential odour reducing strategy were directly applied to litters. The studies exhibited mixed trend in chemical and sensory responses and selectivity in reducing volatilisation of odorants attributed to the efficacy of the additive itself, heterogeneous condition of litter particles in contact with the reduction materials and the exposed surface area. In general, all tested adsorbents decreased litter moisture content, increased litter pH and reduced volatilisation of organic compounds at diverse rates. Based on chemical and sensory responses, activated carbon and silica gel exhibited noticeable interactions on excessively wet litter with trial litters appeared remarkably drier and friable than the control and zeolite sets. However, complete elimination of odour or decrease in odour hedonic tone was unachievable mainly due to emission of ammonia from trial sets. Therefore, it is evident that no one product is capable of reducing or removing all volatiles present in the emission of odours from poultry shed litter. Appropriate litter management within the shed conditions would still be the best method to avoid or reduce the generation of odours at source point before considering application of odour control products.

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ACRONYMS & ABBREVIATIONS

VOC	Volatile organic compound
VOSC	Volatile organic sulfide compounds
HS	Headspace
TD	Thermal desoprtion
GC	Gas chromatogaphy
MSD	Mass spectrometry detector
ODP	Olfactory detection port
GC/O	Gas chromatography/olfactory
TD-GC-MS/O	Thermal desorption –gas chromatography-mass spectrometry/olfactory
OU/m^3	Odour unit per cubic metre
DHS	Dynamic headspace
SHS	Static headspace
SPME	Solid phase micro-extraction
FID	Flame ionisation dtector
PID	Photo ionisation detector
TOF	Time of flight
E-nose	Electronic nose
AEDA	Aroma extract dilution analysis
MDGC	Multi dimension gas chromatography

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S. M. Pillai, G. Parcsi, X. Wang, E. Gallagher, M. Dunlop and R. M. Stuetz (2010) 'Assessment of direct headspace analysis of broiler chicken litter odorants' Chemical Engineering Transactions **23**,pg: 207-212.

S. M. Pillai 'Headspace analysis of chemical odorants from tunnel ventilated broiler litter' Poster presented at Department of Environment, Climate Change and Water NSW Clean Air Forum 2010, Australia.

Pillai, S. M., Wang X., Parcsi G., Gallagher E., Dunlop M. and Stuetz, R.M. 'Spatial and seasonal odour emission characteristics of litter from tunnel ventilated broiler sheds' Proceeding of 20th International conference of the clean air society of Australia and New Zealand, Auckland, NZ, August 2011.

CHAPTER ONE
Introduction

1.1 Introduction

Agricultural livestock practices in many countries are under pressure to satisfy the demand for food intake by their expanding population [1]. Substantial efforts have been conceded to raise the number of livestock production that subsequently increased numerous environmental issues; odour, noise and dust nuisance. Furthermore, escalating living cost in many large cities around the world has forced urban residents to move into rural suburbia, infringing into landscape areas allotted primarily for intensified livestock activities [2-6].

These rural urban changes have resulted in increasing number of odour annoyance complaints on the livestock facilities [4]. Odour complaints vary from minor displeasure to terminations of operations, as obnoxious odour constantly become a nuisance affecting community's life quality, property and social enjoyment [7-8]. Offensive odour released from intensified animal operations can contain large amount of dust, microorganisms and odorants that are primarily produced from animal manure, bedding materials, animal body parts and the animal feed within the facilities [9-11]. As a result, these emissions may exhibit significant impacts on the environment, human health and animal and also on their products [12]. Studies have revealed that some volatiles in the emission plumes cause impacts through dispersion from the point of source to sensitive receptor (i.e. local populations) [13].

Since limited research have been conducted in the poultry emissions compared to bovine and porcine productions, issues related to gases emission and waste management from broiler productions are becoming critical with the industry experiencing tremendous growth world widely [3]. However, the lack of scientific data and reliable method to measure emissions from broiler buildings remain as significant limitations to assess broiler odour impact and to implement regulations to minimise odour impact [14]. Like other livestock odours, broiler odour is also made of complex mixture of volatiles produced from microbial

degradation of organic matter that may have significant impacts on environment and human health. It is therefore necessary to investigate the emission of odour from broiler facilities to provide improved air quality conditions for residents living near these facilities as well as sustaining the broiler production industry.

1.2 Australian broiler industry

Meat chicken (i.e. broiler) production has been an important component in the Australian livestock sector for the past 40 years. It was first initiated in the 1950s with chickens produced based on backyard concept in the outskirts of Sydney city. Subsequently, meat chicken production and consumption increased by many folds with the improvement in the chicken meat strain and efficacy in meat processing. Integrated meat chicken systems instigated in Australia in the 1960s significantly facilitated in the establishment of Kentucky Fried Chicken (KFC) restaurants. Moreover, genetically enhanced nutrition and improved processing technologies and husbandries in the 1970s furthered the development with new breeding strains introduced in the local market.

Broilers are mainly grown in tunnel ventilated sheds using seven to nine weeks growth cycle. Greater number of broiler sheds can be found in the highly populated states as New South Wales, Victoria and Queensland than the other states in Australia. Currently, Baiada and Inghams are two main integrated companies with more than 800 contracted broiler growers nationwide supplying at least seventy percent of Australian chicken meat demands.

According to the Australian Bureau of Agricultural and Resources Economic (ABARE), production of chicken meat has increased from 564,271 tonnes in 1998/1999 to 832,456 tonnes in 2008/09 (Figure 1.1). Although there was a significant increase in the chicken meat retail price in 2006, the demand among the consumers remained notably high as the cost was comparatively cheaper than the other types of meats available in the market (Figure 1.2). A further increase in the growth is anticipated in the production of broilers from 2010 with reduction in feed prices as well as expected increases in the availability of feed variety and quality. With increasing production, expanding populations and

emerging urban encroachment, broiler production is facing extreme challenge to balance increased chicken meat productions for consumers as well as to sustain the industry from environmental threats such as odour annoyance complaints. In order to secure the wellbeing of the broiler productions and the community living near the broiler production, appropriate odour impact regulation and odour abatement strategies must be implemented.

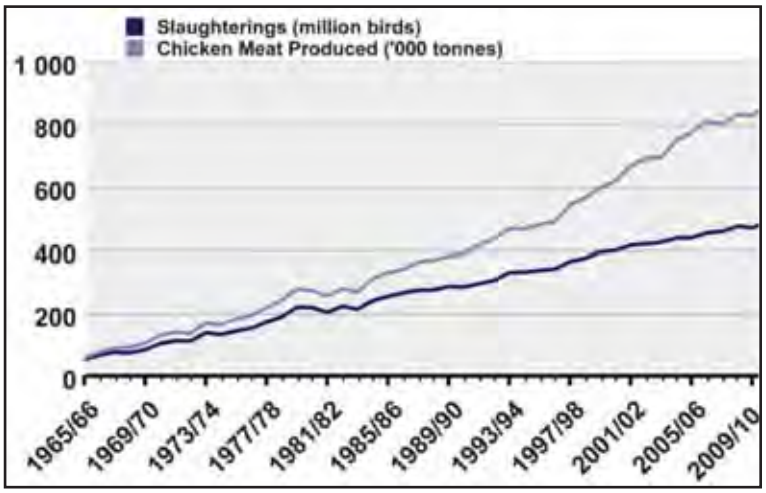


Figure 1.1 Meat chicken production between 1965/66 to 2009/10 [15].

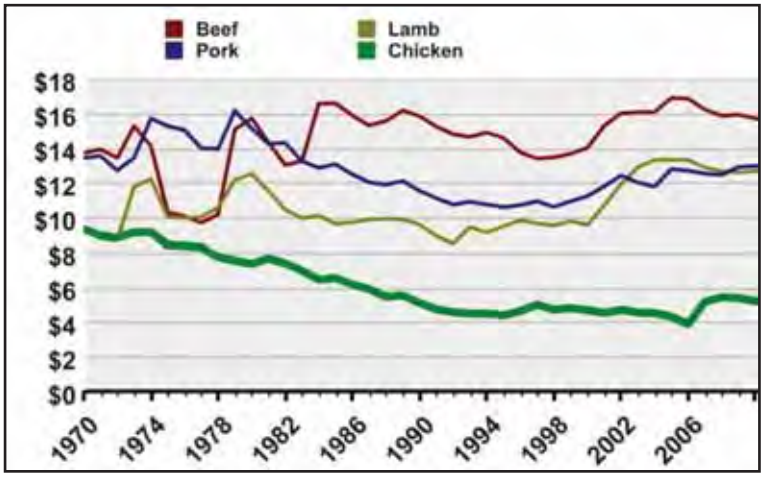


Figure 1.2 Comparison of per kilo chicken meat price with the other type of meats from 1970 to 2006 [15].

1.3 Aim of research

Due to limited studies on odour emissions from broiler production sheds, data correlating analytical with olfactory responses as well as data under Australian climates is scanty. Further research is required to determine the key odorants produced directly from the meat chicken (broiler) litter material at ambient temperature. To achieve the aim of the research, a direct headspace sampling technique coupled to thermal desorption-gas chromatography-mass spectrometry/olfactory (TD-GC-MS/O) was developed and compared with sorbent tube sampling method to assess the composition of odorants from broiler litters used in tunnel ventilated sheds. The generated data anticipated to be informative in establishing link between variations of odorants in the emissions during broiler growth and to improve the air quality and waste management practices within broiler facilities.

1.4 Experimental objectives of research

In order to achieve the aim of the project, four research objectives are outlined as:

1. Development of direct headspace sampling technique using thermal desorption-gas chromatography-mass spectrometry/olfactory (TD-GC-MS/O) in order to assess the compositions of odorants from broiler chicken litters.
2. Apply the TD-GC-MS/O technique to characterise and quantify the odorants from the litter used in poultry production sheds.
3. Understand the relationship between the variations in the emission pattern of the odours in tunnel ventilated poultry sheds.
4. Evaluating abatement strategies in order to reduce emission of odorants at source within broiler chicken litter samples and improve the policy frameworks for defining buffer zone surrounding area.

1.5 Thesis Organisation

This thesis contains eight sections. **Chapter 1** introduces the Australian broiler industry and the challenge faced by the industry to sustain meat chicken production, concurrently confirming the main aim and objectives of the research project.

In **Chapter 2**, the basis to conduct this research is stated, discussing on the background of broiler management in the tunnel ventilated broiler sheds and the importance to perform odour study in reducing the existing scientific gaps within study area. A comparative review on odour sampling and analysis techniques assisting in selecting and developing the headspace TD-GC-MS/O method to study odour emitting from broiler litter material can be found in this chapter. Subsequently, **Chapter 2** ends with literature review on odour control strategies in poultry facilities.

The details of sampling site and techniques for litter collection and analysis procedures used to study broiler litter odours from both winter and summer climate are appropriately discussed in **Chapter 3**. This chapter is divided into three main sections as: a) dynamic dilution olfactometry analysis b) development and application of headspace TD-GC-MS/O analysis and c) abatement analysis.

Chapter 4, 5 and 6 contain results and discussion of olfactometry, headspace TD-GC-MS/O and abatement studies, accordingly. Findings of project experiments are concluded with future research recommendations in **Chapter 7**. Thesis subsequently ends with appendices containing tables, figures and calibration curves and list of references used in this project.

CHAPTER TWO

Literature Review

2.1 Odour science and assessment

2.1.1 Human odour perception

The human odour perception is a complex sense that is yet to be completely understood, especially to relate a smelt sensation with its chemical properties [16]. The human nose discriminates thousands of chemical at parts per billion level of concentration in the air at ambient temperature [8]. Stimulation of human olfactory is equally important as other human senses suggest acceptance or rejection. A perceived odour often alerts or provides a warning of dangers existing around human beings and the environment [12].

Odours are perceived through a group of odour receptor cells in the human olfactory epithelium located above the nasal cavities in the nose and are connected to the olfactory bulbs at the base of the human brain [17]. For odours to be detected by these receptors, volatiles must dissolve in the mucus layer in the olfactory system [18-19]. Only substances that do not present or exist on the human olfactory epithelium will be sensed and interpreted. The odour receptors bind odorants before generating and passing electrical signals to the olfactory bulb in the forebrain for interpretation.

Human odour perceptions vary from one individual to another due to physiological and psychological parameters. Women are often found to be more sensitive in detecting odour than man influenced by hormonal discrimination between the genders. Studies have previously revealed a decrease in olfactory sense observed in aged people and with poor health conditions [7].

2.1.2 Odour science

Odour is a perceived effect on human sense of smell due to the presences of odour containing one or more volatiles [7, 19-20]. Odour producing volatiles are defined as odorants. An odour is only detected by human nose when it is above the odour detection threshold. The impacts and alertness of odours differ from person to person depending on the type and concentration of perceived odorants. Frequent occurrence and detection of offensive odour trigger annoyance in exposed population encouraging formal odour nuisance complaints. There are four properties in association with odour incidence; concentration and intensity, threshold limit, characters and hedonic tone[17, 21]:

a) Odour concentration and intensity

Odour concentration is expressed as odour unit per cubic meter (OU/m^3) which means the number of dilution required to dilute a unit volume of odour to be detected. All odours are only detectable at a concentration of 1 OU/m^3. Odour concentration (OU) is measured using an olfactometer and a group of human odour detectors. Meanwhile the odour intensity refers to a dimension to quantify strength of an odour as some odours perceived are stronger than others. The intensity of an odour is measured based on intensity of a reference gas (e.g. n-butanol) and defined using scales as not perceptible, weak or strongly perceived. The intensity of an odorant usually corresponds directly with the concentration of that odorant, as a logarithmic or power function [22-23]. Generally, odorant intensity increases directly with concentration [7] and slows with large dynamic range [19]. At higher concentration, odorants exhibit distinct intensities but this is not applicable for all odorants as some odorants require greater variation in concentration to impose a shift in odour intensity [7]. The Weber-Fechner law is used to relate odour intensity and concentration (Equation 1),

$$I = k_w \log (C/C_o) + Const \qquad \text{(Equation 1)}$$

with I= intensity of odour, k_w= dimensionless Weber-Fechner constant, C= concentration of odorant, C_0= concentration of odorant at the detection threshold, Const= constant related to the use of mean intensity levels.

b) Odour threshold limit

The odour threshold refers to the minimum odour concentration required to produce an odour sensation in 50% of odour observatory panels with certainty. Two types of odour threshold often studied are detection threshold and recognition threshold. Detection threshold exhibits minimum concentration needed by a human nose to identify the existence of an odour. In contrast, the recognition threshold expresses the minimum concentration required for an assessor to correctly identify the character of an odorant. Estimation of odour threshold values varies depending on the nature of chemical and the age, gender and state of health of assessors.

c) Odour character

The odour character provides the entire descriptive quality of an odour. Expression of odour quality depends significantly on assessor's odour receptor and perceived experience that could assist in identifying the correct vocabulary to describe the odour sensation.

d) Odour hedonic tone

Odour hedonic tone expresses the pleasantness or unpleasantness of an odour that is related to odour nuisance and concentration [24]. On a hedonic tone scale ranging from -5 to +5, the lowest value represents the most unpleasant odour and the highest value shows the most pleasant odour. The odour offensiveness increases proportionally with the increase in odour concentration [7]. The degree of pleasantness or unpleasantness is subjective and influenced by psychological and emotional factors of assessors. Studies have shown hedonic tone may be the most influencing factor in increasing odour complaints than other odour properties [25-26].

Continuous exposure to obnoxious odour from a production facility may instigate affected sensitive receptors to report an odour nuisance. While assessing odour complaints, five factors should be considered carefully are [20]:

a) frequency of the occurrence of offensive odour
b) strength of odour perceived
c) duration, precisely when and length of time the odour perceived
d) offensiveness of odour
e) location of odour generated

Although the odour assessment regulations appear to be simple, application in real situation of the standard to solve odour annoyance is rather a difficult task attributed to subjectivities in odour properties and measurement methods.

2.1.3 Impact of odour

Atmospheric emissions from livestock productions often contain large amount of dust, microorganisms and volatile organic compounds, primarily produced from piling manure, bedding materials, ventilation fans, animal and animal feed within the facilities [1, 3, 10-11, 27-29]. This is often observed in shed used for poultry production [30]. As a result, the emissions produced may impact the environment, health of human and animal and their products including meat, milk and eggs [1, 12, 30-34] as well as create a nuisance to local receptors. In addition, the continuous exposure to such emissions can result in environmental stress and attribute to psychological and depressive impacts in residents living near production facilities causing adverse and chronic health impact on the health of neighbours [20, 25]. A recent study from swine manure revealed existence of six hazardous air pollutants in the headspace of swine manure odour [35].

The effect of odours on human health may not be instantly visible like physical injuries. According to the World Health Organisation (WHO), health is defined as a state of complete physical, mental and social well being. Health of an

individual cannot be predicted merely with the absence or non-appearance of diseases [7, 25]. Low or below odour threshold concentrations of odorants may affect the nervous system of human with or without conscious. Common physical odour impacts symptoms on human health include; irritation in nose, eye and throat, breathing difficulties, cough, chest tightness, skin irritation, headache, nausea, loss of appetite, fatigue and vomiting [12, 20, 25, 36-37]. Nimmermark matched some symptoms with chemical compounds responsible or capable to observe health impact [7]. Long term perception of odour may cause mental illness including confusion, depression, anxiety, anger, sleeping difficulties, annoyance and reduced quality of life [7].

Adaptation and change in odour perception in workers from livestock operations can be attributed to frequent exposure to high concentrations of odorants [36]. Adaptation is greater for unpleasant odours than to pleasant odours. An immediate discomfort reaction can be anticipated from an individual who has had a past experience even though the intensity of the unpleasant odour is at an acceptable level. The nature of unpleasant odorants influence ones decision to accept, tolerate or reject an odour instantly, however adaptation does not occur when an odour appears to be pungent [12, 36].

In contrast, in moderate conditions, no direct correlation has been observed for livestock odour exposure and symptoms [25]. In a study by Radon and co-workers on livestock odour, the impact on human quality of life and the level of odour annoyance was found to be inversely correlated [38]. Nadadur and co-workers also reported that concentrations of odour and adverse health effects were relatively linear [39]. Burne and Rogers analysed shift in olfactory responses of chickens after exposed to odorants [40]. This study revealed significant behaviour change in chickens exposed to faecal odorants as the chickens apparently shook their heads often and suppressed pecking in response to faecal odorant which is probably due to irritating properties of the tested odorants [40]. Low food pecking in chickens is known to affect the growth and performances of broilers as meat chicken. Schiffman suggested that further scientific understanding of livestock emissions is needed to correlate odour

exposure and health symptoms and that our inability to regulate emissions, in order to protect the public is also due to insufficient emission data [12, 39].

2.1.4 Odour and odorant collection

The collection of odours and odorants from sample matrix at ambient condition is often critical and challenging. Standards have been established for volatile organic chemical samplings in order to preserve the originality and the reliability of the odour content [41]. Techniques of volatiles collection include direct sampling of gas into gas bags and pre-concentration method comprising of solvent extraction, sorbent tubes and solid phase micro-extraction. The pre-concentration stage involves enrichment and collection of representative amount of volatiles, especially those with low concentration, on a suitable medium prior to analysis.

2.1.4 1 Gas bags

Whole air samples are usually collected using gas bags for olfactometry analysis at point source or area source. Bags made of Tedlar and Nalophan are commonly employed for gas sampling as these bags have high capability in terms to sustain the composition of odour samples with minimal degradation of odorants in a given time frame. Although bags sampling is quite straight forward, precaution must be practised while transporting sampled bags from site to laboratory to avoid leakage and decomposing of gas samples.

2.1.4.2 Liquid extraction

Solvent extraction and steam distillation (or distillation under vacuum) are common extraction methods used to obtain low concentrated volatiles, especially to study fat odour [42]. The existence of solvent within extracted matrix restricts the range of chemicals analysed that concurrently requires increased detection limits attributed to introduction of large amount of solvent onto GC column [43]. Moreover, solvent extraction techniques are time consuming due to tedious preparation processes and suffer from the formation of artefacts produced [44-47], plus are costly due to disposal of used solvent [48]. Solvent extraction and injection can be inappropriate for volatiles that

sustain a high affinity with the diluents. Continuous injection of liquid extracts onto a GC column, especially when obtained from concentrated samples, may contaminate the GC column that reduces the partitioning efficacy and shelf life of the column. An alternative approach is to consider thermodynamical equilibrium between the sample matrix and the gas phase, especially when the sample is a non fluidic or solid sample [42].

2.1.4.3 Cryogenic enrichment

Cryogenic pre-concentrating involves condensation of chemicals from gaseous samples at extremely low temperature such as -50°C and -75°C. The main advantage of this technique is the ability of the method to capture all volatiles present in a matrix with minimal formation of artefacts. However, due to focusing of volatiles at extreme temperature below dewpoint, icing effect of water often becomes a severe challenge that reduces the efficacy of this sampling and analysis techniques [43, 47, 49]. Another disadvantage of cryogenic sampling is possible decomposition of volatiles during rapid heating of the trap to transfer the sample onto a GC column [49-50].

2.1.4.4 Adsorption on sorbent material

Focusing of volatiles onto sorbent materials or cold trap offers adequate approach to obtain micrograms and nanograms per litre of concentrated volatiles, resulting in the least amount of amendments on the gas sample and sample matrix and interference of solvent. The desired volatiles are adsorbed on a sorbent material or cold trap at a preset flow rate prior to thermal desorption. Basic prerequisites are the choice of sorbents which are dependent on the affinity of desired chemical, appropriate breakthrough volume for all volatiles present in a gaseous sample, low water affinity, high recovery of volatiles during thermal desorption, low reactivity with volatiles adsorbed and the absence of the formation of artefacts [42-43, 51-52]. Since no one sorbent material is capable of adsorbing all kinds of volatiles and most sorbent material has affinity towards a particular volatile functionality [53-54], the development and usage of multi-bed sorbent tubes enabled advanced level of focussing of volatiles' [55]. Common sorbent materials available commercially include Tenax

TA, Chromosorb carbon molecular sieves, graphitized carbon and multi-bedded sorbent materials such as Carbograph, Carbotrap C and Carbotrap/ Carbosieve.

2.1.4.5 Solid phase micro-extraction (SPME)

SPME involves the partitioning of compounds between a vapour headspace and an organic phase silica fibre exposed to the headspace. The fibre is coated with thin layer of polydimethylsiloxane (PDMS) and carboxenepolydimethylsiloxane (Carboxen-PDMS) that adsorbs volatiles in the headspace of the sample. Two main categories of fibre coatings comprise of (i) pure liquid polymer: PDMS and polyacrylate (PA) and (ii) solid particles: Carboxen-PDMS, divinylbenzene-PDMS (DVB-PDMS), Carbowax-DVB and DVB-Carboxen-PDMS. Subsequently the fibre is thermally desorbed in a GC injection port held at a preset temperature to release the adsorbed volatiles onto a GC column for separation and characterisation.

The invention of SPME in the 1990 by Arthur and Pawliszyn was mainly to study water pollutant [52, 56]. Currently, numerous publications on SPME are available discussing the choice of fibre selectively based on targeted chemicals with wide spread application in environmental, medicinal, pharmaceutical, food and beverage and natural products research areas. SPME is a suitable technique to study volatiles with high volatility; however, agitation and long period of sampling may be required to release chemicals with low diffusion ability into the headspace of the sample matrix prior to adsorption. This technique is suitable to be applied to study low concentrated volatiles in the sample matrix. An advantage of SPME is its cost efficiency that involves one-step sampling stage as well as its portability to be used in the laboratory and for on-site sampling [52, 57]. The SPME extraction can be coupled to static headspace sampling for simultaneous analysis of gases that are less volatile [52], thereby reducing sampling preparation steps. Some limitations of SPME include formation of artefacts from fibre used for adsorption [58], difficulties in calibrating the SPME equipment [59] and in sustaining the extraction reproducibility to obtain valid results [54].

2.1.5 Principle of headspace odour sampling

Headspace (HS) analysis is a non destructive technique used to separate volatiles above a liquid or solid prior to instrumental analysis [46, 50-51]. It is a simple technique to collect and analyse volatiles quantitatively and qualitatively with the least amount of deterioration and amendment of the chemicals. The first headspace study separating a gas phase of a liquid was reported by Harger, Bridwell and Raney in 1939 [54]. The first static HS and dynamic HS coupled to gas chromatography (GC) system were attempted in 1958 and 1970, respectively. Currently, the HS samplings are preferred over other sampling methodologies due to its simplicity and robustness and its application to automation in various research areas including: perfumery analysis; waste, agricultural/livestock, water and environmental pollutant monitoring; food, beverages and flavour quality assurance assessment; medical and forensic analysis [54]. Table 2.1 shows some applications of HS related to waste, agricultural/livestock, water, food and beverages and other volatile study areas.

Major advantage of HS technique is the elimination of solvents and the reduction of extractant interferences that sustains the originality of volatiles studied [51, 57, 60-62]. Chen and co-workers successfully used an automated static HS sampler coupled to a gas chromatography system to monitor and quantify the concentrations of odorous compounds during aeration in swine wastewater [60]. The study revealed increased sampling of volatiles with less interference commonly found in the wastewater and enabled identification of degrading volatile organic compounds during aerobic processes. Kallio and co-workers reported on the changes of volatiles in roasted ground coffee as an indicator of storage time using static HS sampling [63]. Other interesting applications of HS include assessment of floral volatiles in relation to pollination, measurement of volatiles released from photosynthesis tissues responding to changes in light and temperature and analysis of emissions from plants induced by herbivore damage [51]. Minor drawback of the headspace sampling techniques is related to the cleanliness of sampling apparatus, but this can be overcome with good laboratory practices to enhance the repeatability and reproducibility of the sampling method [52].

2.1.5.1 Static headspace sampling (SHS)

SHS is the simplest solvent free direct sampling technique that can be applied above a sample matrix [64]. Sample is placed in a vial (or sample vessel) and heated at a specified temperature in order to reach equilibrium between the condensed and the gas phase. Heating of sample matrix increases volatilisation of chemicals prior to removal of aliquot of the gas phase onto sorbent material or directly on GC column for analysis. The efficacy of the extraction is mainly influenced by the volatilisation of chemicals from sample phase to the gas phase. The greater the volatilisation of chemicals, the higher the concentration of chemicals in the gas phase, that increases the sensitivity of SHS and detectability of gas chromatography system [65]. However, achieving an equilibrium state is not essential for all investigation, as heating of sample may degrade the sample and its volatiles, especially in fruits, vegetables and juices analysis [66]. The most amount of SHS application is reported in the natural products, pharmaceutical, clinical, food, aroma and forensic analysis attributed to reduced biasness and time consumption with the elimination of tedious sample preparation [57], resulting in significant increase in sensitivity, stability and reproducibility [54]. Some limitations of SHS include: difficulties in analysing large molecular weight compounds, requirement for regular calibration and inability to quantify these volatiles [57].

2.1.5.2 Dynamic headspace sampling (DHS)

DHS strips volatiles of a sample matrix in a sample vessel using a continuous flow of a gas stream under non equilibrium conditions [67]. Stripped volatiles are concentrated onto a sorbent material or cold trap prior to GC analysis. Two mode of DHS volatiles extraction are open stripping and closed stripping [51]. In open DHS system, problems relates to increases in temperature and humidity or an accumulation of damaging vapours in the headspace are eliminated by a constant air stream. Whereas, using closed-loop stripping, volatiles, especially analytes with low concentrations, are enriched onto sorbent materials during continuous circulation of the headspace air inside closed chambers with minimum air contaminants. Unlike SHS, low yield of compounds can be minimised using DHS [65, 68].

Table 2.1 Applications of HS sampling in waste, agricultural, water, food and beverages and other volatile study areas.

Ref	Sample matrix	Extraction method	Analysis method	Aim of analysis
[69]	Poultry house wall fan air sample	Multi-bedded tube Carbopack C and X	TD-GC-MS	Characterisation of poultry volatiles during and between production cycles
[70]	Concentrated animal feeding operation gas sample	Multi-bedded sorbent using charcoal, silica gel and XAD resin	GC-MS/MS	Assessment of a new sorbent material to capture volatile organic compounds and volatile fatty acids in shorter time period
[71]	Swine lagoon, building and pit fans and poultry house	Canister	GC-MS/PFPD	Measurement of sulfur containing volatiles
[72]	Dairy and cattle farm air	DHS with Tenax TA and Carbotrap	GC-MS	Comparison of volatiles obtained at cattle and dairy farms
[73]	Swine manure	HS-SPME (PDMS-Carboxen)	GC-MS	Characterisation of gas effluent from animal shed
[74]	Plastic waste recycling	DHS with Tenax TA	GC-MS	Characterisation of emission from plastic waste recycling plant
[75]	Wooden flooring	DHS with Tenax TA	GC-MS	Determination of environmental impact of emissions from wooden flooring
[76]	Soil and litter	SHS	GC-MS	Variation of emission between soil and ecosystem
[77]	Historical paper	SHS-SPME	GC-MS	Estimation of pH of historical paper

Table 2.1 Applications of HS sampling in waste, agricultural, water, food and beverages and other volatile study areas (cont).

Ref	Sample matrix	Extraction method	Analysis method	Aim of analysis
[78]	Ventilation filter	HS pre-concentrated onto cold trap	TD-GC-MS	Analysis of emission of ventilation filter based on sensory and chemical response
[79]	Industrial and urban facility gas	DHS with Tenax TA	TD-GC-MS	Identification of odorous volatiles correlated with olfactometry responses
[80]	Municipal solid waste	HS-SPME	GC-MS	Analysis of volatiles released during aerobic biological process
[81]	Urban waste disposal bins	DHS using sorbent tube	GC-MS	Determination of levels of volatiles from urban household waste disposal bin in real and controlled condition
[82]	Water	HS-SPME	GC-ITMS	Analysis of chemicals for taste and odour
[83]	Wastewater	HS-SPME	GC-FID	Determination of volatile fatty acids
[84]	Wastewater	DHS with Tenax TA	GC-MS	Identification of odorous volatiles
[85]	Honey	Purge and trap	GC-MS	Improvisation of HS method for honey volatiles sampling

Table 2.1 Applications of HS sampling in waste, agricultural, water, food and beverages and other volatile study areas (cont).

Ref	Sample matrix	Extraction method	Analysis method	Aim of analysis
[86]	Grape	HS-SPME	GC-MS	Identification of marker volatile of grape
[87]	Orange juices	DHS with Tenax TA, SHS using Tenax TA Purge and trap	GC-FID GC-MS	Aroma response with differences in aroma sampling technique
[88]	Fennel	Direct DHS on cold trap	GC-MS	To study biodiversity of aromatic plants
[89]	Olive oil	HS-SPME using PDMS and PDMS-DVB, DHS with Tenax	GC-TOF-MS TD-GC-MS	Identify the efficacy of HS technique to study volatiles of olive oil

2.1.6 Odour measurement

2.1.6.1 Dynamic dilution olfactometry

A dynamic dilution olfactometer is an instrument used to dilute an odorous gas sample continuously with odour free air prior to assessment [8]. Olfactometers are mainly constructed using stainless steel and high quality Teflon materials to minimise adsorption, permeation and contamination of tested odorous gas. The use of dynamic dilution olfactometer is prevalent, especially to estimate odour emission rates and odour impact assessment [20, 90]. Some countries have established their own odour concentration estimation standard for olfactometer in order to produce consistency in odour measurement and comparable results between laboratories. The most recent standard adopted in Australia and New Zealand is AS/NZS 4323.3:2001. This standard has been based on the European CEN 13725 [91].

Gas samples are collected in odour bags (typically using Tedlar or Nalophan) from odorous sources and are mixed with odourless air in a mixing chamber of the olfactometer before presenting to a group of trained odour panellists for detection at smelling ports (Figure 2.1). Odour panels used for olfactometry analysis are screened using standard odorous gas (n-butanol) according to selection criteria based on AS/NZS 4323.3:2001. The odour concentration is defined as determined by producing dilutions of the original odour sample at which 50 % of the odour panel are able to detect the perceived odour that are expressed as odour unit per cubic metre, OU/m^3 [92-93]. The dilutions of the gas sample are initiated from higher to lower levels of dilution to prevent condensation of concentrated odour along the inner pathway of the olfactometer.

Figure 2.1 Dynamic dilution olfactometer designed with two smelling ports.

There are two modes for odour detection using dynamic dilution olfactometry [8] as:

a) Yes or no method

The application of yes or no technique is simple, with panellist only indicating if they can detect an odour at the sniff ports. When an odour is perceived, the panellists respond by pushing a button. Currently, this technique is rarely applied for odour studies.

b) Forced choice method

The forced choice technique is a much more sensitive, accurate and reliable odour detection technique than the yes or no technique. With more than one sniff port used, only one port will contain the diluted odour sample while the other passes odour free air. Selection of sniff port containing the odour is arbitrary by the olfactometry system; therefore the panellists do not have any prior knowledge of odour containing sniff port. They are forced to predict the detection of an odour from either one port.

The dynamic dilution olfactometer has significant applications in the waste, livestock and wastewater treatment areas [9, 74, 93-95]. Numerous efforts to identify the relationship between the odour concentration, dust particles and intensity have been documented in the past [96] attributed to its simplicity and reliability as an odour measurement principle. Currently, no one equipment or system is comparable to olfactometer in providing objective data on odour threshold value determination [95], assisting to estimate odour emission rates, and dispersion modelling and impact assessment. In addition, due to the simplicity in the application and design of olfactometer, a trained operator can easily operate an olfactometer with minimal additional equipment.

However, the olfactometry analysis has its own limitations attributed to subjectivity in the measurement that is affected by human emotion [97] and the requirement for regular calibration for consistency and accuracy in measurement, which is often a difficult attempt. Olfactory sensitivity to environmental odour of an individual is known to decline with age and vary between gender [94]. Female panels were observed to possess better sensitivity to odour than male panels. The reliability of odour intensity and odour concentration produced can be disputed as the olfactometer depends on human olfactory sense and emotion. In addition, olfactometer lacks the ability to provide quantitative and qualitative information on the odorants present in a gas sample. Yang and Hobson expressed measurement of odour concentration using an olfactometer that lack information on offensive odorants is less useful when it comes to abate odour nuisance [90]. However, these disadvantages can be amended by incorporating the application of olfactometry technique with other advanced instrumentations, such as the gas chromatography and electronic nose that may provide much more reliable and useful data.

2.1.6.2 Electronic nose (E-nose)

The first concept of an electronic nose or artificial nose was proposed at the University of Warwick, UK in 1982 [98-99]. The e-nose comprises of an array of electronic chemical sensors with partial specificity and an appropriate pattern-recognition system that are capable to determine odours [97, 99-101]. The sensors interact physically and chemically with the gases containing volatiles sending signals to a processor. A dynamic equilibrium develops with constantly absorbed and desorbed volatiles at the sensor's surface [99]. The requirement for e-nose analysis varies accordingly to gas sensors fitted within the system. The efficacy of an e-nose depends on the implementing concept and the number of sensors and their sensitivity and selectivity of the compounds detected [93, 102].

Schaller and co-workers have listed some basic prerequisites for gas sensors to be selected for e-nose analysis as: high in sensitivity towards chemicals; low in sensitivity towards humidity and temperature; medium selectivity; respond to varieties of compounds in the headspace of a sample; high in stability and reproducibility; short reaction and recovery time; robust and durable; easy to calibrate and integrate data analysis technique [99]. A variety of major gas sensors are available commercially for e-nose [99, 103] including: metal oxide sensors (MOS); conducting-polymer sensors (CP); quartz crystal microbalances (QCM); surface acoustic wave transducers (SAW); bulk acoustic wave sensors (BAW); piezoelectric devices based on quartz crystal oscillators; metal oxide semiconductor field effect transistors (MOSFET) and similar to the metal oxide semiconductor field effect but based on silicon carbide instead of silicon (SiC).

E-noses are reported to detect compounds at considerably lower levels than the human nose but it still has limited selectivity for chemical detection [97]. Other limitation is the sensitivity of chemical detection under field operating conditions attributed to environmental variable such as humidity [99]. E-nose has been applied to a range of different applications including: quality control of raw and manufactured products process; freshness and maturity monitoring; shelf life analysis; authenticity analysis of fine product; classification of scents and

perfumes and microbial pathogen detection [56, 99, 104-105]. Only fewer studies have been published on the usage of e-nose for environmental monitoring especially for odour assessment from livestock area and wastewater treatment plant [106-108]. The limited use could be the due to lack in quantitative output and negative effect of high humidity and temperature in agricultural air causing distraction on the sensitivity and detectability of e-noses [93]. However with improvement in overcoming limitation of e-nose, its potential for application in agricultural vicinities is increasing gradually [93, 97, 109-110]. Pan and co-workers studied the factors impacting human odour perception and strength of downwind odour from a variety of livestock areas using e-nose. The study produced consistent and accurate measurements employing an e-nose that showed the effect of distance of source and air temperature even though some disadvantages were observed during analysis [100]. In another study, Pan and Yang introduced a newly developed portable intelligent e-nose fitted with humidity and temperature sensor to analyse livestock and poultry odour [111]. The device is anticipated to assist farmers in odour management of their farms

2.1.6.3 Gas chromatography-mass spectrometry (GC-MS)

GC-MS is a powerful combination of a gas chromatograph and a mass spectrometer for rapid separation and characterisation of volatiles in complex mixtures. Due to its constant reliability and repeatability, GC-MS offers better choice of tool in analysing volatiles in various areas of study, especially in tracking organic pollutants in the environment. Consideration should be given in determining GC parameters such as carrier gas, column, detector types and GC run for successful chemical investigations. Carrier gas chosen for volatiles analysis must be inert in order to prevent oxidation of volatiles. Usually ultra high purity helium or nitrogen gases are recommended as suitable GC flow gases. Choice of column selected for gas sample elution in a GC system can be critical. During analysis, fundamental requirements of separation columns are the ability to detect and fragment compounds consistently while minimising oxidation and adsorption of volatiles onto stationary phase of the column. Mainly there are two types of separating column available commercially; packed

column and capillary column. The packed columns are large stainless steel coil with dimension of 1-5 m in total length and 5 mm in inner diameter whereas capillary columns are thin fused-silica capillary with dimension of 10-100 m in length and 250 µm in inner diameter. Currently, there are various capillary columns available, differing in polarity that can be purchased to improvise detection limit and partitioning of volatiles [19, 112]. With prominent expansion in the separation technology, capillary columns provide higher resolution with narrowed peak of chemicals than of packed columns [113].

Analytes eluting from a column is subsequently characterised using an appropriate detector coupled to the GC system. Current development in the GC instrumentation exhibits potential to incorporating more than one detector for chemical speciation and quantification. Mass spectrometer is a universal detector that is frequently associated with GC system attributed to its significant compatible with the separation system and capability of matching unknown volatiles tested with programmed chemical database like, National Institute of Science and Technology chemical database (NIST). Due to speciation limitations in detectors, selectivity of targeted compounds may aide in choosing the most suitable detector to be linked to a GC system. For example, flame ionisation detector (FID) functions rapidly in detecting hydrocarbons but is insensitive to sulfur species. The use of sulfur chemiluminescence (SCD) and nitrogen chemiluminescence (NCD) are recommended to improve detection of sulfur and nitrogen compounds, respectively in samples studied.

2.1.6.4 Gas chromatography-mass spectrometry/olfactory (GC-MS/O)

The greatest challenge in odour research remains in the difficulty to establish the inventory of instruments to isolate and characterise compounds that are odour potent and responsible for sensory properties [17, 61, 114-115]. A practical approach to solve odour episode is to utilise the human nose concurrently with the GC system, defined as GC/O or GC/Sniff [46-47, 61, 116]. The first GC/O principles were published by Fuller and co-workers in the 1964 on selected odour active compounds from a complex perfume mixture [16, 117-118]. At early stages, the GC/O system suffered of low reproducibility of data

generated and nuisance of hot effluent emitting directly from the GC column onto panel nose at the detector's port [117-118]. Subsequently, modified version of GC/O re-merged the application of taste and odour analysis in perfumery, food and beverage industries in the 1970s, especially to understand the impact of odorants on food flavours and to identify the cause of off-odours and taints [16, 61, 114]. The utilisation of a GC coupled to instrumental detector (MS, PID or FID) and human olfactory detector (O) allows substantial verification of odour active chemicals and their respective odour qualities and intensities using the human nose as the detection limit [119]. In order to conduct study of unknown odorants, the application of GC-MS/O is highly recommended.

Although the employment of a human nose to detect odour seems to be simple, some technical aspect of this tool need careful consideration in order to reduce experimental biasness. An olfactory interface system consists of volatile transfer line inserted with column similar to the GC system and nose cone for sample sniffing (Figure 2.2). During GC-MS/O analysis, the column in olfactory transfer line is simultaneously heat at an optimum temperature to present volatiles to human nose for characterisation at the olfactory detection port (ODP). The flow of volatiles emerging at the end of column in GC can be split into the MS and ODP at a preferred ratio using a split connector fixed in the GC system. Concurrently, GC carrier gas flows across the olfactory interface to force forward the flow of volatiles through the phase while preventing condensation of chemicals along the transfer line. A make up humidified gas flow carried from outside of the transfer tubing to the nose port mixing with the analytes and provide a comfortable environment for the panel to assess the sampled gas without distraction. Flow rate of humidified air in GC-MS/O system must be set at an optimum value [113-114]. Low flow rate causes low velocity of the compounds and discomfort to the sniffing panels due to release of hot effluent from GC system. In contrast, high flow rate dilutes concentration of odorants deceasing detection and identification of volatiles by panel.

Figure 2.2 Olfactory detection port showing nose cone and heated transfer lines.

The GC-MS/O laboratory must be odour free with controlled temperature and sufficient ventilation during analysis. Odour panel records perceived odorant's quality and intensity and measurement of duration of occurrence using odour input devices such as the microphone and hand button with varied strength [16]. The final output of the GC-MS/O analysis conducted on a sample consists of an aromagram from olfactory detection response and a total ion chromatogram from GC-MS. Careful association of the spectra assists in identification of odour potent volatiles merely by overlaying the data obtained from the instrumental and olfactory responses. The most challenging aspect of the GC-MS/O set up is to prevent the ingression of atmospheric air into the system through the human olfactory port, attributed to the variation in operating pressure of the MS employing high vacuum and ODP at atmospheric pressure [119-121] that can be overcome using make up gas devices to sustain higher pressure within the GC-MS/O system. Delahunty and co-workers and Van Ruth have written extensive reviews on the GC/O techniques that can be applied in various field of study [16, 117].

Primarily, the GC/O consists of four categories as CharmAnalysis, AEDA, posterior intensity analysis and OSME as [16, 45, 61, 113, 117, 122]:

a) CharmAnalysis and AEDA

CharmAnalysis and aroma extraction dilution analysis (AEDA) are dilution analysis determining odour detection threshold of compounds eluting from GC column, excluding psychophysical estimation of odorants individual odour intensity. The CharmAnalysis is based on the length of time (start and end) that an odour can be detected by a human nose sniffing at the GC odour port and the number of dilutions of the sample that produced an odour response at a particular retention time [114]. Peak areas obtained on Charm odorgram correspond to measurement of odour intensity of the volatiles emerging from the GC [114]. This technique consumes more time as at least 4 dilutions are needed and requires many sniffers. Aromagram of CharmAnalysis is plotted according to instant response against retention index based on Equation 2, with dv as the dilution value, F as the dilution factor and n as the number of odour response perceived [16].

$$dv = F^{n-1}\, di \qquad \text{(Equation 2)}$$

$$\text{Charm value} = \int_{peak} dv$$

The aroma extraction dilution analysis (AEDA) dilutes odour sample with solvent prior to GC analysis and determines the odour dilution factor that corresponds to the highest dilution in which odour compounds are detected by sniffers. This technique only reports on maximum dilution values of perceived odour. The AEDA aromagram represents the plot of factor of dilution against retention index. The main difference between CharmAnalysis and AEDA is that the CharmAnalysis estimates the dilution value over the entire time compounds elute whereas AEDA provides the maximum dilution value for each compounds. Limitations of CharmAnalysis and AEDA include deviation of rank orders of intensities of odorants and involve laborious and time consuming procedure [46] even though most odorants are identified using these methods [68].

b) Posterior intensity analysis

Posterior intensity analysis is not frequently used as it quite complex in task for the assessors. It records odour intensity as volatiles are eluted from GC system [117]. Scale used by the assessor differs and complicates the assessment process.

c) OSME

OSME (smell in Greek) developed by McDaniel and co-workers is an efficient and approachable technique to estimate odour intensity [16, 117]. OSME quantifies each chemical's odour intensity in the GC effluent. In comparison to AEDA and CharmAnalysis, OSME provides odorant peak, quality, intensity, duration and maximum perceived time of an odorant. Aromagram produced of OSME GC/O technique is called as osmegram. The osmegram exhibits plot of odour intensity values against retention time. Intensity estimations of odour can be conducted using a variety of intensity scale such as 0-2 or 0-4, ranging from odour perceived extremely weak to extremely strong. Volatiles eluting of GC require no dilution for olfactory assessment. In contrast to dilution analysis, intensity analysis is strongly based on psychophysical parameters since intensity of each volatile is presented for olfactory evaluation without dilution. In addition, elimination of dilution steps reduces analysis time besides direct comparison of osmegrams on GC-MS spectra. Some disadvantages of OSME are allocation of little time period for odour characterisation during rapid elution of peaks, decrease in assessor's efficacy due to fatigue in human olfactory and non linear trend in instrumental and sensory response.

Some limitations of GC-MS/O are:

a) Individually eluting odorants from GC column may not represent odour in absolute environment. Differences between single odorant against interactions of entire odorants in an odour impose considerably varying perceived effect.

b) Human breathing cycle may impact the detection and sensitive. During exhalation, there are chances for the olfactory panel members to miss match or identify an odorant with narrow occurrence.
c) Long GC/O runs cause fatigue in human olfactory and decreased sensitivity of odorants [16, 113]. Optimum GC/O run time reported is within 25 minutes of analysis. Occasionally, panels may feel unmotivated and lack in alertness because of the existence of small number of odorants with low odour intensity in samples tested [113, 117].
d) Variation in human olfactory sensitivity may produce irregular data sets that are difficult to conclude.

In general, the GC/O analysis techniques have extensive applications in numerous areas of study. Table 2.2 and Table 2.3 list some examples of recent applications and their outcomes using GC/O to study volatiles of varieties of foodstuff and beverages. Compared with foods and beverages, absolutely fewer applications of GC/O have been attempted and reported from livestock and environmental odour researches as shown in Table 2.4. The utilisation of GC/O in the wastewater management and agricultural topics anticipated to contribute significantly to odour assessment and remedy in order to provide a better understanding of odour profiles.

Table 2.2 Application of GC/O technique studying volatiles released of foodstuffs.

Ref	Sample matrix	Extraction method	Analysis method	Odorants functionality
[123]	Chicken and beef meat	DHS with Tenax TA	GC-FID/MS/O (OSME)	Ketones, alcohol, aldehydes, ester
[124]	Green tea	Vacuum hydro distillation	GC-MS/O (OSME)	Alcohols, ketones, aldehydes, furan, phenolic, indole
[125]	Ham	DHS with Tenax TA	GC-MS/O (AEDA)	Sulfur compound, aldehydes, ketones, ester, volatile fatty acid, phenolic, furan
[125]	Ham	Solvent extraction	GC-FID/O (AEDA)	Aldehydes, ketones, esters, sulfur compound, volatile fatty acid, alcohol, unknowns
[126]	Fish sauce	HS-SPME	GC-MS/O (OSME)	Trimethylamine, sulfur, volatile fatty acids, pyrazines, phenolics, alcohol, furanone
[127]	Sea fig	Solvent extraction	GC-FID/O (CharmAnalyis and OSME)	Sulfur compound, nitrogen compounds, ketones, alcohols, aldehydes
[128]	Apple	DHS with Tenax TA	GC-FID/O (CharmAnalysis)	Esters, aldehydes, alcohol, and unknown odorants
[129]	Vanilla bean	Solvent extraction	GC-FID/MS/O (OSME)	Phenolics, aliphatic acids, alcohols, aldehydes, esters, ketone, unknown
[130]	Strawberry puree	HS-SPME	GC-FID/O (OSME)	Ketones, esters
[131]	Dried bell pepper	DHS with Tenax TA	TD-GC-FID/MS/O (OSME)	Aldehydes, ketones, sulfur compound, pyrazine, unknown

Table 2.2 Application of GC/O technique studying volatiles released of foodstuffs (cont).

Ref	Sample matrix	Extraction method	Analysis method	Odorants functionality
[132]	Parmigiano cheese	DHS using multi-bedded sorbent materials (Tenax, silica gel and molecular sieve trap	GC-MS/O (OSME and AEDA)	Acetals, aldehydes, volatile fatty acids, sulfur compounds, esters, ketones
[133]	Blue cheese	DHS with Tenax TA	GC-MS/O (AEDA and OSME)	Acetals, aldehydes, volatile fatty acids, sulfur compounds, esters, ketones, alcohols
[134]	Cheddar cheese	Bucal HS analysis and vacuum distillation using Tenax TA	GC-MS/O (OSME)	Sulfur compounds, ketones, aldehydes, esters, terpenes, unknowns
[135]	Buttermilk	Direct SHS	GC/O (AEDA)	Aldehyde, sulfur compounds, ketones, aliphatic acid
[136]	Dairy products	DHS	GC/O (dilution analysis)	Esters, aldehydes, aliphatic acids, ketones, sulfur compounds, indole,
[137]	Synthetic linseed oil in building	Dynamic HS using Tenax TA	TD-GC-MS/O (OSME)	Priority: hexanal, propanoic acid, hexanoic acid, trans 2 octenal, nonanal, butanoic acid,

Table 2.3 Application of GC/O technique studying volatiles released of beverages.

Ref	Sample matrix	Extraction method	Analysis method	Odorants functionality
[138]	Wine	HS-SPME	GC-FID/O (OSME)	Aldehydes, ketones, skatole, phenolics, indole
[139]	Cashew apple alcoholic beverage	Vacuum extraction on Porapak Q trap	GC-MS/O (OSME)	Ethyl esters, alcohols, volatile fatty acids, aldehydes
[140]	Chinese Yanghe Daqu liquor	Solvent extraction	GC-FID/MS/O (OSME)	Aliphatic acids, esters, higher alcohols, phenolics, acetals, sulfur compounds, ketones, aldehydes
[141]	Wines	Solvent extraction	GC-FID/MS/O (OSME)	Esters, aldehydes, alcohols, aliphatic acids
[121]	Drinking water	Solvent extraction	GC-MS/O (OSME)	Methylnaphthalene, geosmin, ethernanathrene, diisopropylnapthalene
[142]	Espresso coffee	HS-SPME (DVB/CAR/PDMS)	GC/O (CharmAnalyis)	-
[143]	Elderberry juice	DHS	GC-FID/MS/O	Aldehydes, alcohols, furan, ketones, phenolic
[144]	Wine cork	Solvent extraction	GC-FID/O (OSME)	Ethylic esters, non-ethylic esters, terpenes, phenolics, carbonyl compounds, aldehydes, ketones
[145]	Coffee industry waste gas	DHS with Tenax TA	TD-GC-MS/O	Aldehydes, ketones, sulfur compounds, pyrazines, pyridine,aliphatic acids, phenolics

Table 2.4 Application of GC/O technique studying volatiles released of livestock facilities and other field of researches.

Ref	Sample matrix	Extraction method	Analysis method	Odorants functionality
[35]	Swine manure	HS-SPME Carboxen/PDMS and Carbowax/DVB	MDGC-FID/MS/O (OSME)	Alcohols, aldehydes, aromatics, esters, ethers, fixed gases, hydrocarbons, ketones, volatile fatty acids, sulfur and nitrogen compounds, phenolic
[146]	Standard mixture	HS using Tenax TA	TD–MDGC–MS/O (OSME)	Priority: volatile fatty acids, phenol, skatole, indole, ketone
[147]	Swine barn particulates	HS-SPME (PDMS, Carboxen/PDMS and Carbowax/DVB)	TD-MDGC-FID/MS/O (OSME)	Alkanes, alcohols, aldehydes, ketones, volatile fatty acids, sulfur and nitrogen compounds, aromatics, furans
[59]	Swine barn air near source	HS-SPME (Carboxen-PDMS)	TD-MDGC-FID/PID/MS/O (OSME)	Priority: ketone, phenolic, volatile fatty acid
[59]	Swine barn air at distance source	HS-SPME (Carboxen-PDMS)	TD-MDGC-FID/PID/MS/O (OSME)	Priority: ketone, phenolics
[59]	Beef cattle air at near source	HS-SPME (Carboxen-PDMS)	TD-MDGC-FID/PID/MS/O (OSME)	Priority: nitrogen contain compound, volatile fatty acid, phenolic
[59]	Beef cattle air at distance source	HS-SPME (Carboxen-PDMS)	TD-MDGC-FID/PID/MS/O (OSME)	Priority: volatile fatty acid, phenolics

Table 2.4 Application of GC/O technique studying volatiles released of livestock facilities and other field of researches (cont).

Ref	Sample matrix	Extraction method	Analysis method	Odorants functionality
[36]	Dairy farm air	HS using Tenax TA	TD-GC-MS/O (OSME)	Volatile fatty acid, methyl esters, ethyl esters, acetate, alcohols, aldehydes, ketone, halogenates, amines, hydrocarbons
[36]	Dairy farm air	HS using Carboxen	TD-GC-MS/O (OSME)	Volatile fatty acid, methyl ester, acetates, alcohols, aldehydes, halogenates, amine, sulfoxide, hydrocarbons
[148]	Synthetic swine air	HS using Tenax TA and Carboxen	GC-FID/O (OSME)	Priority: volatile fatty acis, sulfur compounds, phenolics, alcohols, indoles, skatoles
[149]	Swine manure	Liquid extraction	GC-MS/O (OSME)	Indole, skatole, phenolics, volatile fatty acids
[150]	Burnt fire samples	HS-SPME (PDMS/DVB) and (DVB/CAR/PDMS)	GC-MS/O (OSME)	Benzene, furan, aldehydes, phenolics, ketones
[151]	Wastewater	DHS using Tenax TA	GC-FID/MS/O (OSME)	Sulfur compound, ketones, aromatic, volatile fatty acid, alcohol, terpenes
[152]	Commercial male fragrant	Solvent extraction	GC-FID/O (OSME)	Terpenes, esters, aldehyde, ketone
[153]	Treated water	Closed loop stripping	TD-GC-MS/O (OSME)	Phenolics, phtalates, diacid esters, aliphatic alkenes, benzothiazole, aliphatic hydrocarbons
[153]	Treated water	Liquid extraction	GC-MS/O (OSME)	Tert butylphenol and 8 unknown chemicals

2.1.7 Summary of odour assessment

There is no one universal odour analysis technique applicable for all types of odour assessment. Table 2.5 depicts the advantages and disadvantages in selecting potential evaluation applications to achieve the objective of a study. Objective(s) of an odour study to be conducted and the conditions persist in an odour collection environment must be carefully reviewed prior to analysis, technique selection, since inappropriately chosen assessment method will cause substantial bias. For best outcome, it will be beneficial to implement combination of more than one assessment technique to study odour in order to establish relationships between odour emissions and its odorant compositions.

Table 2.5 Comparisons of odour analysis techniques.

Analysis technique	Advantage	Disadvantage	Aim of application
Olfactometry	Measurements link to human odours perceptions	a) Lack of odorant speciation b) Complex in liquid phase odorants concentrations or emissions c) Lacking of sensitivity and accuracy d) Difficult for onsite sampling stages	a) Odour emission rate estimation b) Odour reduction modelling c) Odour impact assessment
GC-MS/O	a) Quantitative and qualitative analysis of odour b) Usage of appropriate detectors in determination of unknown odorant c) Estimation of physical or chemical models of odorants transformations or mass transfer e) High in accuracy and precision	a) Expensive and complex b) Difficult for onsite sampling c) Require sample pre-concentrating apparatus	a) Development of analytical and sensory related study b) Fate of odorants c) Odour control estimation

2.2 Broiler production and management

2.2.1 Broiler production in Australia

Broiler or meat chickens are grown in tunnel ventilated shed with a dimension of 150 m by 15 m, housing up to 40,000 chicks at a time (Figure 2.3). The sheds are built with ventilation fans at one end to draw air through the shed over the chickens from one end to other (creating a tunnel effect). Prior to bird placement, the floor of the shed will be sanitised and covered with thick layer of bedding material for the brooding broilers. The shed integrators decide on choice of bedding depending on availability and cost of the materials (Table 2.6). Feed and water lines run the length of the shed to enhance the growth chicken as broilers (Figure 2.4). A complete growth cycle of broiler consists of 7 to 9 weeks with the first harvest of birds occurring in week 5 and the last in week 7. Sheds will be cleaned after removing all birds preparing for next batch of broilers to reduce risk of diseases being passed between batches.

Figure 2.3 Tunnel ventilated shed used for poultry production showing extraction fans.

Figure 2.4 Tunnel ventilated poultry shed facilitated with feeder and water lines.

Table 2.6 Bedding materials in Australian poultry shed [154].

State	New Bedding material (%)				
	Sawdust	Wood shaving	Rice hull	Straw	Paper
New South Wales	40.2	34.7	23.7	1.0	0.4
Queensland	26.4	71.2	-	0.9	1.5
South Australia	-	65.9	-	34.1	-
Tasmania	100.0	-	-	-	-
Victoria	-	50.0	50.0	-	-
Western Australia	100.0	-	-	-	-

2.2.2 Odour generation and transport mechanisms

Production of odour from a sample surface can be explained with concept similar to water or a liquid volatilisation. The mass transfer processes or volatilisation of substances from solid to gas or liquid to gas varies under the influences of a number of environmental factors [5, 7, 155-156]. Changes in temperature and humidity in the environment may lead to a change in emissions. In terms of liquid to atmospheric evaporation, such as in the liquid manure pond to air involves numerous interrelated processes. The amount of volatile mass transferred between phases depends on energy flow to the molecules. Volatilisation cannot be anticipated at all times due to variations in emission's generating locations of a liquid to the surface. The thickness of the boundary layer is dependent on the air velocity, where a higher velocity will increase evaporation and decrease the layer thickness. Usually in a liquid, kinetic energy of a molecule is higher at the boundary level between phase attributed to closer exposure of the air movement and temperature which subsequently assist the molecule in breaking the inter relationship of the substance with the liquid prior to diffusion into gases phase.

Hudson and Ayoko reported on greater influence on the Henry coefficient of a substance to volatilise than turbulent due to high impact of temperature [155]. Another factor that can influence the diffusion of volatiles is the chemical reaction occurring within the emission source. Emission of volatiles would develop with increase in concentration in the liquid boundary. Considering the mechanism of odour emission and factor affecting the emission rates, it is highly important to estimate the odour emission rates under conditions presenting the original production in the environment before selecting the odour sampling technique.

2.2.3 Factors affecting odour release in animal production facilities

Odours produced of animal sheds vary significantly with classification of animal, temperature, humidity, and other weather conditions, such as ventilation rates or wind forces, housing type, manure properties or characteristics and animal species and their production operations. In poultry production, large amount of

the odorous compounds originate from the litter material in comparison to decaying feed, dead chicken and bird feathers [9, 27, 157-159]. As the poultry litter soils with birds' excreta, urine, spilled feed and water and feathers across the broiler growth period, the generation of emission is expected to be elevated. Production of odour in animal facilities is primarily attributed to the degradation of organic matters and undigested feed material under aerobic and/or anaerobic conditions [21]. At aerobic conditions, uric acids, proteins and animal fats degrade into ammonia, amines, indole, skatole and volatile fatty acids. Sulfide containing chemicals break down into dimethyl disulfide and dimethyl trisulfide. In contrast, in litter areas with excess moisture content and lowered pH value, anaerobic bacteria degrade sulfur compounds into hydrogen sulphide, thiols, mercaptans and volatile organic sulfide compounds (VOSC).

Major factors that affect odour generation in animal facilities include: facility temperature; dry matter content within shed; pH of the litter; C/N-ratio; ventilation rate of the shed; manure storage time within animal building; ratio between exposed area and volume; area of manure surface and feeding [7]. Additionally in poultry facilities, the emission rates from poultry operations depend on the time of a year and day, weather condition, bird size, wind condition, housing type, manure properties or characteristics and animal species [160]. The odorant compositions and concentrations are highly influenced by the density of the shed and the type and rate of decomposition attributed to microbial activities within the bedding litter [160]. Large number of birds results in increased excretion and accumulation of large amount of faecal materials on and in the bedding materials that promotes generation of obnoxious odours. Subsequently, as the birds mature through the production cycle, gain in bird body mass contributes significant increase in manure excretion and emission of odours. In addition, excessively wet litter due to water spillage and deposition of wet manure attributed to dietary upset of birds, heightens remarkably anaerobic odour generation within production cycle [161]. Poorly maintained or imprecisely set drinker lines increases localised wet area in the bedding favouring greater emission generations.

2.2.4 Odour emissions from poultry production facilities

As an attempt to regulate odour emission and implement odour abating strategies, livestock odours are subjected to a variety of emission measurement for impact assessment. Among the published livestock odour studies, research has mainly focused on piggery and dairy emissions [6, 27] with only a handful of studies been carried on poultry farm odours even though these facilities are becoming vulnerable to odour complaints by their neighbours [3, 162]. It is also evident that poultry odour emission studies lack of synergism between the researches performed, as most poultry studies to date have chosen to have odours at the ventilation exhaust instead of the litter material. Emission estimation measured at ventilation to the atmosphere would provide an estimation that is smaller than at the source point, resulting in inefficiency of abatement design and management. Point source measurements also provide significant knowledge of the pathway of the emission during its generation that can be related to the detection of odours at a receptor point, incorporating ventilation rate. Schaefer identified more compounds in swine manure than in the air samples from an animal building [149].

Lack in standardised sample collection and analysis techniques are evident from published literature, especially for the integration of sensory and analytical responses for emission studies (Table 2.7). Studies have been performed to characterise the key odorants responsible of odour offensiveness within swine manure, wastewater, cattle and dairy facilities [35-36, 59, 148, 163-164]. In contrast, most poultry odour studies have focussed on ammonia and dust as the odour marker compound to estimate the magnitude of the entire emission [165-172]. As odour comprises of complex mixture of odorants, the application of performing assessment using selected volatile(s) as an odour marker to resemble the total odour is most likely an inappropriate technique due to lack of consideration on the variations in chemical/physical characteristics of odorants.

Table 2.7 Published study on poultry odour.

Ref	Source	Analysis technique	Volatile type
[173]	Dry manure	Dynamic dilution olfactometer	Odour
[174]	Poultry manure	Liquid extraction GC-MS	Volatile organic compounds
[96]	Exhaust fan air	Dynamic dilution olfactometer	Odour
[175]	Litter bed	Passive diffusion sampler	Ammonia
[176]	Poultry air sample	Olfactometer and multi gas monitor	Odour and ammonia
[172]	Exhaust fan air	Portable monitoring unit	Ammonia
[177]	Poultry wastes	Ambient air analyser based on FTIR	VOC
[170]	Exhaust air	Passive sampler	Ammonia
[158]	Broiler litter gas	Photo acoustic multi-gas analyser	Nitrogen compounds
[178]	Poultry feather	HS-SPME-GC-MS	VOC
[106]	Exhaust fan air	Dynamic dilution olfactometer Electronic nose	Odour
[179]	Exhaust fan	Dynamic dilution olfactometer	Odour
[169]	Air within broiler production	Open path line averaged laser spectrometry	Ammonia
[167]	Litter		Dust emission

2.2.5 Knowledge gaps in poultry emission data

Numerous odorous assessment studies have been performed at cattle and piggery farms with only a handful at the poultry facilities. Data obtained from other livestock facilities are incomparable with poultry due to large variation in their biological classification, behaviour and the environment of their productions. The lack of poultry odour emission rates and their compositions across a production cycle in different climates using different litter sources makes the management and regulation of emission very challenging. Physical condition and emission variations at litter sources will provide an improved understanding of the release of odours from the bedding surface and enable improved management through odour control such as dilution before reaching the sensitive receptors [149]. Ultimately, the collection and analysis method used for volatiles from the litter should be conduct at ambient temperature with least alteration made to the sample matrix and its emission composition [3]. The aim of this research study is to determine the key odorants produced directly from tunnel ventilated broiler litters at ambient temperature using headspace sampling methods coupled to TD-GC-MS/O and to produce correlation between analytical and olfactory responses that is anticipated to be informative evidence to reduce odour emissions and its annoyance complaints, concurrently improving the air quality and waste management practices within the broiler facilities.

2.2.6 Management of poultry odours

Offensive odours from animal facilities affect life quality and properties, subsequently encourage nearby residents to launch formal odour nuisance complaints to local government agencies [8, 25, 93]. Odour annoyance complaints on poultry productions in Australia have made the industry vulnerable to legal actions restricting and preventing the establishment and expansion of new and existing farms [179-180]. The application of odour abatement is required in the poultry facilities to sustain the existing productions and to further develop and design future farms to comply with the consumers' demand for chicken meat.

There is a variety of odour emitting sources existing within poultry facility. Large amount of soiled bedding material from broiler production sheds is a prominent source of odour emission attributing to high level volatilisation of chemicals during aerobic and/or anaerobic waste degradations. Constant accumulation of faeces, urine, dead chicken, feather and spillage of water and feed on bedding materials during broiler growth provide favourable environment for microbial growth and their activities in amending the fresh bedding and generating offensive odours [173, 181-182]. Secondary odour sources within poultry facilities are the shed walls, curtains and ventilation fans. Dust sticking to these features release odour molecules absorbed and transported within the shed area.

Odour plume generated from poultry waste material contains reactive chemicals from a variety of homologue. Ammonia, hydrogen sulfide, volatiles fatty acids and sulfur and nitrogen containing compounds are commonly detected in livestock odours that exhibit significantly intolerable characteristics at low concentrations. This is mainly attributed to their low olfactory detection threshold of the odorants [157] that trigger human olfactory responses causing discomfort and annoyance complaints. Studies on livestock odour samples revealed detection of chemicals capable of altering the environment, human quality of life and their properties and animal performance during production stages [7, 12, 25, 160, 162, 180, 183]. A recent study from a broiler farm in New

South Wales, Australia indicated a higher level of health impact than anticipated on population exposed to emissions from the tested facility [183]. Nevertheless, the absolute concentrations of volatiles and their direct health effects on human and birds are still unclear due to the limited research into poultry facilities world widely.

2.2.7 Odour control techniques

Since absolute prevention and elimination of livestock odours is unachievable, efforts to minimise the effect of the volatiles released onto sensitive receptors can be applied using various odour management practises. Odour control techniques can be categorised as:

a) biological treatment using odour destructive microorganisms and bio-filters.
b) chemical treatment with adsorption, oxidation and a variety of neutralising, masking and counteracting reactions.
c) dispersion using windbreak wall, ventilation fan, and buffer zone requirements.

The following section focuses on potential emission mitigation techniques developed and tested in the Australian climate that could be implemented in the tunnel ventilated broiler facilities to control odorous emissions.

2.2.7.1 Appropriate farm planning and development

As a primary strategy to abate emissions from poultry production facilities, incorporating development plans of intensified animal production with residential areas and their amenities may help to reduce emission annoyance complaints. At the initial stage, producers must recognise and estimate the magnitude of odour generation, site specification, weather condition, reduction strategies with ongoing costs and the implication of odour and other types of production of nuisance on nearby residents. Proper planning and operation of production facilities with sufficient knowledge/skill to operate the farm effectively with minimised annoyance imposed onto the neighbours is an essential

management requirement. On the other hand, environmental protection regulations applied to agricultural development strategies require modification in line with the developments in livestock farming [184-185]. This approach is important in order to balance the agricultural economy, welfare of livestock producers and the rapidly elevating urban encroachment [182]. In Australia, current animal facilities have significantly developed and increased in terms of their size and number of animals allotted into each farm. Therefore, existing buffer zone estimate established to prevent odour, dust and noise nuisance from animal facilities from reaching nearby neighbours are outdated and needs revision [186].

2.2.7.2 Best management practices

Effective shed management and manure handling are important factors into the control of odours and other environmental nuisance from production sheds [180]. Within production vicinities, manure and materials soiled with biological excretion from chickens are the most prominent sources to obnoxious emissions compared to ventilation fan, stack, feedlot and animal body. Therefore, odour control efforts initiated directly at the primary source would be beneficial in reducing the generation to the secondary sources. Before opting to install often costly odour mitigation technology, producers need to understand and correctly identify odour causing sources to improvise the efficacy, cost and time required for abatement. No one product or system has the ability to function efficiently to control odour at all types of environment application. Practising good housekeeping slows down odorant volatilisation even though it is difficult to be performed in an area congested with animals as shown in Figure 2.4. Implementing best management practices effectively manages and minimises odour formation and dispersion from the entire system rather than targeting selective species before released into the atmosphere.

2.2.7.3 Litter management

An essential aspect of best management practices is to maintain moisture content within production areas, especially in waste material. Reduction in litter moisture simultaneously reduces odour emissions through the inhibition of

anaerobic microorganism [160]. In broiler sheds, manure, urine and water spillage along drinker line are major factors attributing to increase in litter moisture content. Moreover, interruption in bird feed formula can cause poor bird health while increasing excretion of wet manure that further damp the bedding materials. Additionally, excessively wet litter lowers litter pH encouraging anaerobic degradation that increases offensive emanation within a shed [187].

Aeration of litter material allows sufficient oxygen supply to the litter and evaporates excess moisture from litter as well as promoting aerobic degradation. Removing extremely wet litter patches and replacing with new dry beddings during litter aeration alleviates emissions. However, aerating litter is a difficult task in animal dense sheds and limited information is available on the efficacy as an odour control technique. Appropriately installed drinker lines running along shed may reduce litter moisture content by preventing water spillage onto the bedding material. Producers must ensure water feed lines are established at a proper height and depth to avoid or minimise water leaks onto the litter.

In contrast, litter that is extremely low in moisture generates dust nuisance resulting in particles transporting odorous molecules into the shed air causing poor bird performances during production and the dispersion of odours from the facilities. Shed operational temperature should be maintained for litter to remain dry and friable with moisture held within 15 to 30 percent [160, 188]. Additional shed maintenance should include frequently cleaning exhaust fan, curtains and shed walls between new batches that will aid in elimination of condensed dust particle within the facility.

2.2.7.4 Feedstock management

The diet and composition of animal feeds are known to impact the emission of odours. Improved efficiency to convert feed to bird body mass will affect the composition of odours from broiler sheds. Undigested feed component in manure and fermenting feed stocks within a poultry shed can cause fluctuations

in the magnitude of odours being emitted. Gates and co-workers studied the impact of reduced crude protein in feed stocks and observed that the chicken excreta had a low moisture content and pH values [189]. Another similar diet study revealed that an increase in feed protein increased the concentration of ammonia in the shed emissions [175]. The authors also reported that the odour magnitude did not correspond with the decrease in ammonia.

Amon and co-workers studied the use of adding 2 % of clinoptilolite zeolite and 0.0165% of de-odorase, respectively to broiler feed at weeks 4, 5 and 6, attempting to increase the feed conversion rates in broiler chickens and found no observable difference in the emissions from the shed [190]. Graham and co-workers found that the use of feed enzyme, xylanese as a feed supplement, increased the growth of broilers and attributed to the improvement in the efficacy of the feed conversion to body mass and digestion of nutrient that simultaneously reduced excretion of manure and water [191]. However, the production of such enzymes at sustainable cost for application in poultry shed environments is often challenging. Therefore, the selection of nutrients in feed stocks may serve as a pathway for increasing or reducing the generation of odorants, especially nitrogen and sulfur containing chemicals. Odour generation may be effectively managed with further research into feed manipulation and the composition of odorants in the emissions.

2.2.8 Odour control technologies

The application of best management practices often produces varying emission results due to shed-to-shed operating conditions. In some cases the use of good housekeeping within poultry sheds may not be effective due to the nature and composition of the odorous emission and the formation pathways involved in its generation. In some circumstances, producers have considered applying odour and dust control technologies to reduce the impact of emissions on local receptors. These technologies include direct and indirect abatement and treatment systems that are used to manage the litter environment or to prevent the release of odours from poultry sheds. For many of the direct litter management approaches such as the addition of odour control products to litter, further assessment is required due to the lack of a mechanistic understanding of the abatement process. Technologies tested and recommended for use in the Australian poultry sheds are discussed in the following section [160, 179, 187].

2.2.8.1 Dry dust filtration

Dust from poultry sheds contains particles that are capable to absorb and transport volatile organic compounds into the air [167, 171]. Extremely dry litter and the application of high ventilation rates may result in the dust transportation. Dry dust filtration is a simple, cost effective technique that enables dust to be trapped in shed filters without major renovation to the poultry shed infrastructure. This device is found to be compatible with existing exhaust fans used in the tunnel ventilated sheds. However, clogging of the filters may require frequent cleaning to sustain efficacy in straining dust particles from the ventilated air stream. A study at an Australian broiler shed showed a dust reduction between 40 to 70 percent in the ventilated air, however olfactometry analysis exhibited limited and insignificant reduction in the odorous emission suggesting that the dust filtration technique was not highly recommended for odour abatement [179].

Another technology similar to dust filtration is electrostatic dust precipitation [166, 179]. Results suggest reductions in dust and ammonia between 40 to 60

percent for the ventilated air as well as improvement of the internal air quality of the shed [179]. The system could be a better option for shed operators than dust filtration system due to lower maintenance costs and the lack of interference within the shed ventilation system. Other dry dust control structures tested in poultry sheds include bio-curtains, fan hoods and windbreak walls (Figure 2.5). All these techniques have low installation cost with minimal operational costs. However, these approaches are not widely applied by producers as they rely on meteorological and shed condition to perform effectively. Additionally odour analysis of bio-curtains, fan hood and windbreak walls performance has been inconsistent.

Figure 2.5 Windbreak wall constructed at a broiler shed.

2.2.8.2 Adsorption

Activated carbon has been used in a number of industries to adsorb contaminants from water and air [192-194]. Contaminants are exchanged from the gas phase onto activated carbon that has high porosity and large surface areas as well as modified surface characteristics. In gas phase, adsorption methods often become inefficient due to large mass of dust particles in the odour clogging in the filter. Activate carbon can also be applied as direct control technique by adding granular activated carbon (GAC) to the litter bedding material.

Other material options available as adsorbing media are alumina or zeolite. Zeolite is a moderate cost natural adsorbent with excellent affinity for ammonia [187]. Amon and co-workers applied clinoplitolite zeolite on broiler litter and broiler feed as an attempt to control odour emission [190]. However the studies

revealed that the application of zeolite increased the emission of ammonia from the litter instead of reducing as expected. In addition, the use of generation of ammonia as an indicator is insufficient to control odour generation and/or management due to variations in formation between odours and ammonia emission over a production cycle [160]. Additionally, the application of zeolite was found to be unsuitable for application in poultry shed litter attributed to its high ability in retaining moisture within its particle, thereby saturating the shed litter. The application of equipping activated carbon filters to tunnel ventilated fans could benefit in controlling poultry shed odour, since the usage of carbon filters in similar industries has been proven to be efficient.

2.2.8.3 Bio-filtration

Bio-filtration reduces odour impact by absorbing and biodegrading odorous volatile organic compounds [160, 187, 195-196]. The technique could be applied to reduce odour impact by installing systems at the exits of ventilation fans, similar to activated carbon filters. In contrast to activated carbon filters, bio-filters contain micro-organisms responsible to destruct odorous volatiles and oxidise inorganic gases and vapours into non-odorous volatiles, water and carbon dioxide. Odorous gases can be treated by simple bio-filter systems or complex and automated bio-trickling filters. Bio-filter treats the odorous air by passing it through a packed material made of compost, wooden chip and soil or mixture of these materials with mineral nutrients to absorb volatiles. Subsequently, active micro-organism present in the packed material in the filter degrades pollutants in the gas stream before releasing non-odorous or decrease odorants to the outlet air.

The bio-filters require frequent maintenance between 2 to 5 years for medium replacement [197] depending on the type of media in order to maintain odour reduction efficiency. The effectiveness of a bio-filter depends on moisture content and pH values of the packed material and air passing through the bio-filter. Odorous air with high humidity and concentrated volatiles may overload the microorganisms resulting in reduced abating efficacy to degrade odorous volatiles or produce insignificant differences in the odour hedonic tone

compared to untreated emission. This factor hinders the application of bio-filter as a suitable remedy in broiler sheds due to the emissions containing concentrated volatiles and moisture content with large variations. Additionally, due to large volumes of air been emitted from tunnel ventilated sheds, the surface area is required to established effective filtration which is a major limiting factor in the poultry sheds.

2.2.8.4 Wet scrubbing

Wet scrubber abatement systems remove odorous volatiles by the absorption of odorants using suitable solvent or chemical and catalytic reagents [198-200]. Gas streams are passed through wet scrubbing agents to eliminate the odorous compounds which is then circulated through the catalytic and re-circulated back though the chemical scrubber. Due to treatment set up requirement and the high operating cost of such systems, wet scrubbing is not an odour control method that is not recommended for use in poultry productions [179]. Additionally, the technology requires constant ventilation rates to perform effectively and involves chemical solvents that may be harmful to broiler and workers if spillage occurs.

2.2.8.5 Odour neutralising/masking agents

Poultry producers may opt to use commercially available odour masking agents, neutralising agents, counteractants or surfactants to control odour at sources even though there has been limited scientific assessment of these techniques for poultry odour abatement [201]. Chemical odour abating products vary in ingredients and odour controlling mechanism and application. Odour neutralising chemical agents contain chemically active compounds with neutralising effects that are capable to alter the intensity or odour quality of an odorous air. The generation of tolerable odour or new non-odorous compounds is the proposed mechanism of abatement for the application of neutraliser. Moreover, application of neutralising chemicals is simple and quick and can be applied either by spraying as a liquid (Figure 2.6) or smeared on solids directly to control odours releasing from the source. Due to its simplicity and flexibility of implementation and suggested low capital costs, some poultry producers have

applied odour neutralising chemicals rather than wet scrubbers that require high capital investment [179].

Figure 2.6 Application of liquid spray at the exterior of a ventilation fan.

The effectiveness of odour neutralisers, however needs further scientific assessment as limited independent studies have been undertake to evaluate the performance of these chemicals against water for odour reduction. Furthermore, the mechanistic pathways for the chemical reactions with odours are unclear. Additionally, a range of different fogging systems have been applied to distribute the chemicals at housing with limited optimisation of their effectiveness. A laboratory study conducted by Bruchet and co-workers to evaluate the efficacy of selected neutralisers using three different composition and application methods on fresh municipal solid waste, compost pile and stored sludge showed the tested neutralisers were observed to increase the concentrations of odour compounds [202]. Another study using neutralisers diluted with small quantity of water was found to reduced odour concentration measurements better than those using large amount of water and without water [202].

Odour masking agents typically consist of aromatic oils that aim to add a pleasant odour on top of an unpleasant odour. No chemical reaction is involved and the total odour of the resultant mixture is greater than the original source even though it may be perceived as less objectionable. Bruchet and co-workers characterised a number of odour masking agents often used in the solid waste industry for abatement and found no or insignificant reduction of odours using masking agents with no modification made to the perceived olfactory hedonic tone [203]. Instead, some of the tested products increased the odour concentration in the perceived odour samples. During the study, a sweet smelling odour was perceived with the application of masking agents. Nevertheless, the olfactory panels rated the odour as unpleasant due to pungent and irritating olfactory sensation caused by ammonia release. An attempt to reduce ammonia and hydrogen sulfide emissions from piggery manure using a yeast based product revealed insignificant variations in the reduction of the emissions following the addition of the additives to field samples that showed only minor emissions reduction in comparison to laboratory scale tests of the same additives [204].

Counteractants and surfactants like odour neutraliser and masking agents also have limited application to alleviate odours from poultry sheds. Counteractants contains chemical groups that aim to change the character of offensive odours to one that is less objectionable, for most chemicals the mechanistic pathway is unclear but most likely involves chemical interactions between the agents and the odorants resulting in the formation of an odour that is expected to be less offensive rather than simply imposing a pleasant odour over an unpleasant odour. Whereas, surfactants are airborne scrubbing liquids that contain substances dissolved in solvent such as water. A proposed advantage of using surfactants compared to other chemical agents is that the chemical has biodegradable characteristics after reacting with the odour.

2.2.9 Summary

Effective design and management strategies allow for efficient odour control in poultry shed conditions. Best management procedures that are practiced in intensive animal facilities, can provide cost effective solutions to alleviate odour emission at both point and area sources. However, these practices must aim to inhibit anaerobic degradation of waste materials within a facility to prevent or reduce the generation of odours. In some situations, poultry producers can consider the use of odour reducing products or systems as a temporary odour control technology. The choice of approach is complicated since many products are available commercially and many of the products have limited scientific support to prove their application, especially in poultry sheds. The limitations, particular for chemical control products is due to poor characterisation of products in terms of chemical constituents and the lack of a mechanistic understanding of the reduction processes. In order for a odour control product and/or technique to be effective in reducing odour impact and complaints, an approach needs to be able to achieve at least a 90 % of reduction in concentration of the odorous emission [96]. Currently no one commercial odour control product or odour control system can achieve this level of performance for odour reduction.

CHAPTER THREE
Materials and Methods

3.1 Introduction

The Australian broiler market is an agricultural sector with significant contributions to the Australian economy. However, literature has revealed limited number of studies performed on the emission of odours from broiler shed with particularly reference to the origin of its formation. Sensory and analytical data on the composition and variability of odour emissions from poultry litter is unavailable for the Australian climate. The generation of such data would be valuable to understand odour emissions and to evaluate the efficacy and implementation of odour abatement strategies. In this study, attempts were made to improve the knowledge of emissions at the odour point source in the broiler shed. Litter materials across the complete broiler growth cycles were collected from two tunnel ventilated broiler sheds in Queensland during winter and summer climates with the assistance of Department of Employment, Economic Development and Innovation (DEEDI). Collected litter materials were transported to the UNSW Odour and Atmospheric Emission Laboratory in Sydney for analysis in sealed containers packed with cooling pads on the same day of collections.

Laboratory tests for investigating the litter odour were designed into 3 parts as: a) olfactometry analysis; b) headspace analysis and c) odour reduction analysis. Firstly, odour samples from the litter were collected in Tedlar bags using flux hood sampling method. These odour samples were analysed using dynamic dilution olfactometer according to the Australian and New Zealand Standard (AS/NZS 4323.3:2001) to determine the odour concentration of the samples. Secondly, headspace investigation was carried out to determine and quantify odorous and non-odorous volatiles emitting from litter material. A direct dynamic headspace sampling technique was established and compared to sorbent tube samples collected via flux hood of the litter. Volatiles retrained using both techniques were evaluated using thermal desorption-gas chromatography-mass spectrometry/olfactory (TD-GC-MS/O), in order to study

the variations of volatile organic compounds produced from the litter over broiler growth cycles. Finally, a laboratory scale odour reduction study was performed using the addition of activated carbon, silica gel and zeolite to odorous litter samples collected during winter and summer. Determinations of odorants were carried out using direct dynamic headspace sampling coupled with TD-GC-MS/O analysis. Moisture content and pH value of the litter materials collected were recorded concurrently to investigate the impact of these parameters on odour emissions.

3.2 Site description and sample collection

Two tunnel ventilated broiler sheds in the north eastern region of Australia were chosen as litter sampling sites (Figure 3.1). These well maintained ventilated sheds measured 150m by 15m and have the capability to house up to 44 000 broilers at a time (Figure 3.2). Each sheds has six to ten large ventilation fans operating at high speed at preset times to draw in air across the broilers and to control the level of humidity in order to minimise odour emanation in the sheds (Figure 3.3).

Figure 3.1 Sample collection site map.

Figure 3.2 Exterior of tunnel ventilated broiler sheds.

Figure 3.3 Interior of tunnel ventilated broiler shed equipped with large ventilation fans.

To determine the effects of seasons and broiler growth cycle on odour emissions, litters were taken from ventilated sheds in winter and summer for the complete broiler growth periods. Winter litter sampling was initiated in Shed 1 in Esk in July 2009 and ended in September 2009 whereas summer litter sampling was initiated in Shed 1 in Coominya in February 2010 and ended in April 2010. Litter sampling was performed in the sheds from week 0 with no birds to week 8 with all birds removed. The two sheds operations used similar litter management practises in the application covering their sanitised shed floors with fresh litter as bedding material. However, the composition of the fresh litter material differed from each other as winter sampling shed used a mixture of pine and eucalyptus shaving compared to summer sampling shed used hard shaving as bedding material (Figure 3.4 and Figure 3.5).

Prior to sampling, ten points were fixed as sampling spots in the broiler shed to monitor odour variation with controlled environmental factors; five points in the middle section of the shed were used as dry litter spots and five points near nipple drinker were used as wet litter spots (Figure 3.6). Weekly, litter samples at each of these ten fixed points were collected within a 2 metre radius in clean and odour free sample bags before being transported to the UNSW Atmospheric Emission and Odour Laboratory in Sydney on the same day of collection. A volume of 2 litre of litter sample was collected at each fixed point. Details of shed environment during winter and summer are outlined in Table 3.1 and 3.2, respectively. Dry and wet litter samples were subjected to complete olfactometry and headspace analysis as dry composite and wet composite samples within 24 to 48 hours of collection to prevent loss and degradation of volatiles.

Figure 3.4 Pine and eucalyptus shaving used as fresh litter during winter climate.

Figure 3.5 Hard wood shaving used as fresh litter during summer climate.

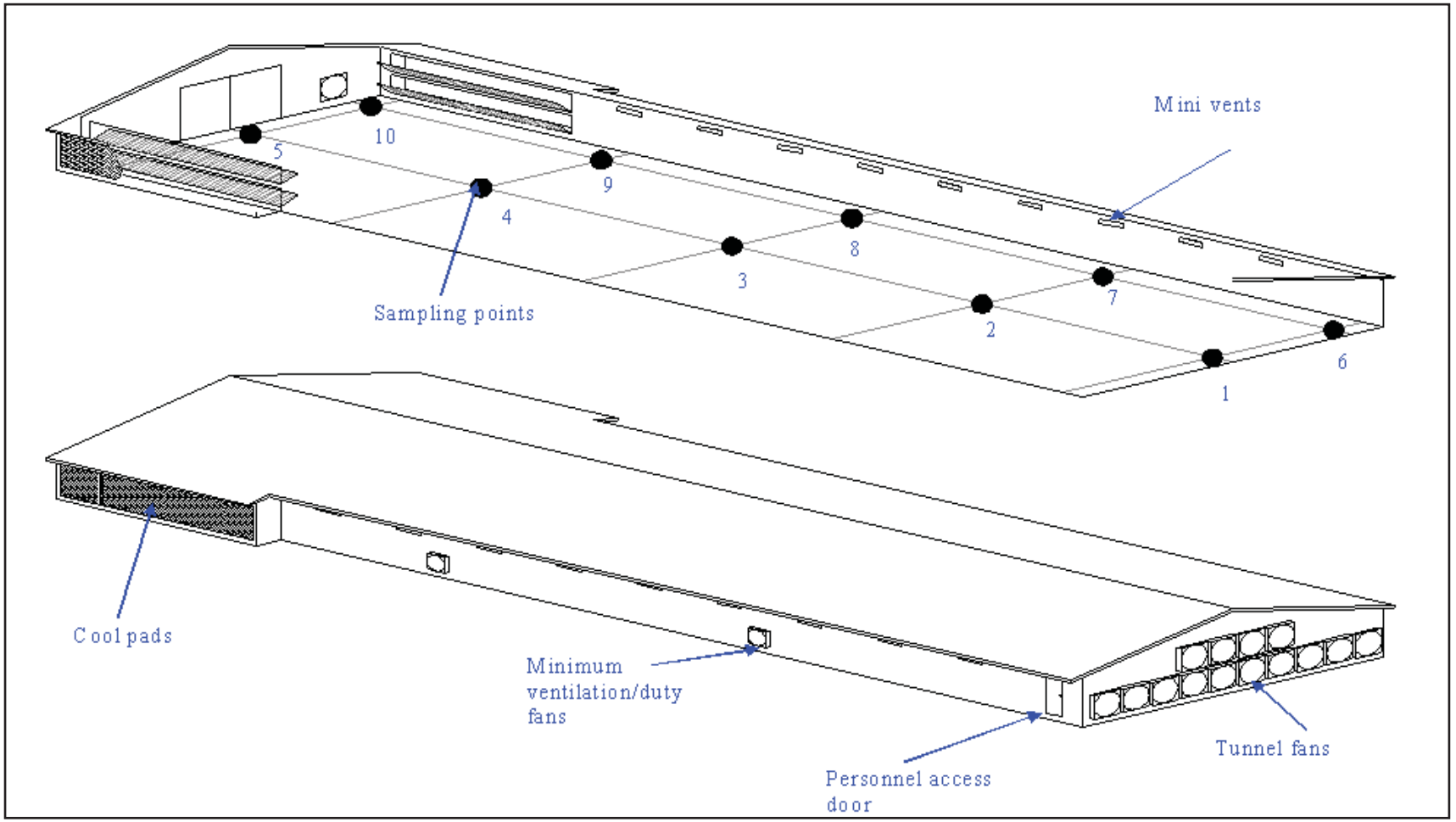


Figure 3.6 Litter sampling spots in the tunnel ventilated broiler shed.

Table 3.1 Winter sampling shed operational details.

Week number	Sample collection date	Bird number	Weight of live birds (kg)	Shed temperature °C	Average dry litter moisture (%)	Average wet litter moisture (%)
0	01/07/2009	0	0	29.2	44.30	41.74
1	14/07/2009	42960	0.1754	31.1	27.43	35.09
2	21/07/2009	42,600	0.282	29.5	25.64	41.97
3	28/07/2009	42,440	0.760	27.3	21.76	42.09
4	04/08/2009	42,320	1.269	25.4	26.14	53.54
5	11/08/2009	42,180	1.800	23.1	27.93	63.00
6	18/08/2009	19,410	2.510	22.8	27.74	45.07
7	25/08/2009	19,340	3.180	20.2	25.75	56.68
8	01/09/2009	0	0	23.4	22.22	58.23

Table 3.2 Summer sampling shed operational details.

Week number	Sample collection date	Bird number	Weight of live birds (kg)	Shed temperature °C	Average dry litter moisture (%)	Average wet litter moisture (%)
0	04/02/2010	0	0	29.1	28.80	30.14
1	09/02/2010	41000	0.084	31.5	29.04	29.73
2	16/02/2010	41120	0.167	29.2	21.74	23.02
3	23/02/2010	40283	0.667	27.9	21.24	23.57
4	02/03/2010	40159	1.170	25.2	30.81	28.74
5	09/03/2010	39978	1.712	23.4	33.97	29.20
6	16/03/2010	14034	2.359	22.3	30.32	35.98
7	23/03/2010	13902	3.256	21.4	28.72	31.58
8	30/03/2010	0	0	25.7	23.72	26.58

3.3 Olfactometry analysis

3.3.1 Indirect odour sampling

Flux hood sampling of the litter material was applied to obtain odour samples for odour concentration determination from each week during winter and summer seasons. The flux hood sampling method employed was according to the emission sampling procedure by Australian and New Zealand standard for 'area source emissions' sampling procedure (AS/NZS 4323.4:2009) [205]. Dry and wet litter odour samples were handled individually. The flux hood used for this study had an internal area of 0.1256 m^2.

Approximately, 8 L of homogenously mixed litter was spread in a shallow rectangular odour-free container (69 cm x 46.6 cm x 12.8 cm) which was covered with a flux hood and purged with high purity nitrogen gas (BOC Gases, Sydney, Australia) at ambient temperature for 25 min at a constant flow rate set at 5 L/min prior to sampling. After which a vacuum pump was used to create vacuum effect in the sampling drum to draw odour sample into a 30 L Tedlar bag attached at the sampling inlet for 10 min at a flow rate of 2 L/min (Figure 3.7). Litter odour samples were collected in duplicates for ensure repeatability and reproducibility of sampling activities. To prevent contamination and absorption of odour substance onto the sampling equipments, only Teflon tube lines and stainless steel fittings were used as connectors. Precaution was also taken to prevent entries of external atmospheric air into the flux hood by sealing the hood border with sufficient amount of litter material.

Figure 3.7 Olfactometry sampling using a flux hood and nitrogen purge.

3.3.2. Dynamic olfactometry analysis

To prevent losses and degradations of volatiles, odour samples were analysed on the same day of sample collection using a forced choice dynamic dilution olfactometer (Odormat, Singapore) (Figure 3.8). Six screened panellists were selected using n-butanol according to the AS/NZS 4323.3: 2001 standard [206]. Odour concentration measurements were performed in the UNSW Atmospheric Emissions and Odour Laboratory, according the AS/NZS 4323.3: 2001 standard (Figure 3.9). Broiler litter odour concentrations were reported in odour unit, OU. However, necessary precautions were practised during measurements in order to obtain reliable data sets. Ratios between individual threshold estimate and geometric mean of all individual threshold estimates were screened precisely to identify outliers from unfit panellist. Data produced by panellist with ratio greater than 5.0 or lower than -5.0 were not included for odour concentration calculations.

Figure 3.8 Forced choice dynamic dilution olfactometer set in the UNSW Atmospheric Emissions and Odour Laboratory.

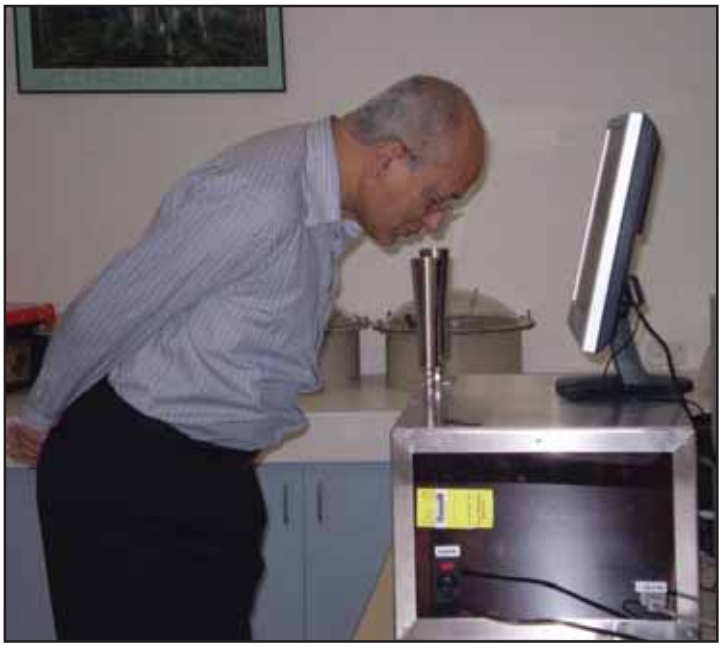


Figure 3.9 Panel sniffing at the UNSW Atmospheric Emissions and Odour Laboratory.

3.4 Development of headspace analysis techniques

Two headspace sampling methods coupled to TD-GC-MS/O have been applied in this study to determine volatiles/odorants qualitatively and quantitatively. Generally, both techniques involved thermal desorption, volatiles separation and characterisation of selected compounds.

3.4.1 Development of sorbent tube analysis

3.4.1.1 Sorbent tube sampling

A variety of sorbent materials are available to capture generic or targeted volatiles emitting from odour sources. In this study, sorbent tubes packed with 2,6-diphenylene-oxide polymer resin, namely Tenax TA were used to capture volatiles (Figure 3.10). Tenax TA is a hydrophobic and weak sorbent material, which has been widely used to retrain and analyse volatiles from water, environmental air, soil, human breath, plants and commercial products. The sorbent material is packed in a stainless steel tube with a dimension of 6.35 mm (outer diameter) and 89 mm (length) to allow a surface area of 35 m^2/g attracting volatiles, commonly compounds with C_7 to C_{10}. In addition, the use of stainless steel tube prevents the absorption of volatiles onto tube body material as well as being suitable for rough handling. All Tenax tubes are numbered on the outer body of the tubes. This feature assists operators in identifying between sampled and non-sampled tubes during sampling.

Figure 3.10 Example of sorbent tube, Tenax TA.

Each sorbent tube can be recycled as many as 100 times after careful conditioning and screening. This aspect makes sorbent tube sampling much more cost effective

compared to other available methods. However, Tenax TA tubes need to be handled cautiously to minimise contaminations before, during and after sampling. All tubes used in this study were carefully pre-conditioned at 335 °C for 35 min using a sorbent tube conditioner (TC 20, Markes International, UK) prior to use with selected tubes being screened (using TD-GC-MS analysis) to determine trace contamination and carryovers from previous sampling activities. During the sorbent tube pre-conditioning, clean nitrogen gas was flushed through the tube at a suitable flow rate to remove contaminants from sorbent material. Cleaned tubes were subsequently sealed with brass cap fitted with Teflon ferules and placed in a clean environment to prevent exposure to volatiles in the atmosphere. At all instance, operators used clean gloves to handle tubes, holding them in the middle of tubes to avoid contact of impurities on tube ends.

A fixed and sufficient flow rate is essential to collect volatiles onto sorbent tubes especially for quantification of chemical substances. Suitable flow rate of Tenax tubes varies from 50 to 200 ml/min. For this study, a flow rate of 100ml/min was chosen to prevent breakthrough of volatiles during sampling. Broiler litter volatiles collection onto sorbent material was performed as shown in Figure 3.11. Approximately, 8 L of litter material was spread into shallow rectangular odour-free container and sampled using a flux hood by purging with high purity nitrogen gas at a flow rate of 5 L/min for 25 min prior to sampling. A calibrated pump (SKC Air Chek 2000) was used to sample volatiles directly onto Tenax TA sorbent tubes at a flow rate of 100 ml/min for 30 min. The flow rate during sampling was maintained using a calibrated flow adaptors. Volatiles collections onto sorbent tubes were carried out in duplicated to maintain the repeatability and reproducibility of sampling. Following sampling, sorbent tubes were tightly sealed with brass caps fitted with Teflon ferules to prevent losses of sampled volatiles and entries of contamination. Additionally, the sealed tubes were wrapped with clean aluminium foils and stored in cold storage at 5 °C before analysis to reduce environmental degradation and as a safety barrier to avoid ingression of humidity into the tubes.

Figure 3.11 Sorbent tube sampling of litter material using a flux hood technique.

3.4.1.2 Sorbent tube analysis

The primary stage of TD-GC-MS/O analysis of the collected sorbent tube samples is the thermal desorption (TD) of volatiles using a Markes Unity Thermal Desorber (Markes International Limited, UK). This unit is coupled to a gas chromatography-mass spectrometry/olfactory (GC-MS/O) system for chemical and sensory characterisation of the volatiles. Volatiles desorbed from the sorbent tubes were pre-concentrated onto a cold trap available in the thermal desorption unit before subjecting to rapid heating and injection onto the gas chromatography column for chemical elucidations. Chemical and sensory determinations of separated compounds were conducted with a mass spectrometer and human detectors.

Three main stages of thermal desorption of sorbent tube are outlined and discussed below:

a) Sorbent tube pre-purge

Tube pre-purge is an essential parameter to remove unwanted substances such as humidity and oxygen from tube before reaching the cold trap using carrier gas, helium (He). High humidity level along the transfer line pathway may damage the gas chromatography column whereas oxygen may react with volatiles during thermal desorption of sorbent tube contributing to oxidation of volatiles. During pre-purge, the cold trap and sorbent tube are set to trap at low temperature and 24 °C respectively to sustain volatiles organic compounds on cold trap and sorbent material before thermal desorption.

b) Sorbent tube desorption

Tube desorption is carried out to thermally desorbing the volatiles organic compounds collected during sampling onto the cold trap at a predetermined temperature. Temperatures used for tube desorption is a critical factor to be considered carefully to prevent degradation or breakdown of volatiles due to thermal impact. Temp 1 and Time 1 in the Figure 3.12 represent details of temperature and time required for tube to be thermally desorbed. Under circumstances of having highly concentrated samples, a split function is available to either introduce the entire or a part of volatiles onto the cold trap. Additionally, this feature also helps to recapture a certain amount of volatiles onto an additional sorbent tube for further studies.

c) Cold trap desorption

A general purpose graphitised cold trap (U-T11GPC Markes International, UK) with a dimension of 2 mm (diameter) by 60 mm (length) was fitted to the thermal desorption unit during this study to retrain volatiles released from sorbent tube during tube desorption. It pre-concentrates and releases most groups of volatiles in general. This trap can be cleaned easily to eliminate carryover from samples using

a trap heating feature available in the thermal desorption unit software. Volatiles retrained onto the cold trap are subsequently heated rapidly using a peltier cell to introduce the volatile vapour onto GC column. The trap low and trap high features indicate the initial and final temperatures of the cold trap respectively at a fix time (trap hold) during desorption of the volatiles. The rate of cold trap heating can be preset using values available in the trap heating rate feature. Ballistic heating accelerates cold trap heating from trap low to trap high temperature in a short period, preventing delays in volatiles release onto the GC column.

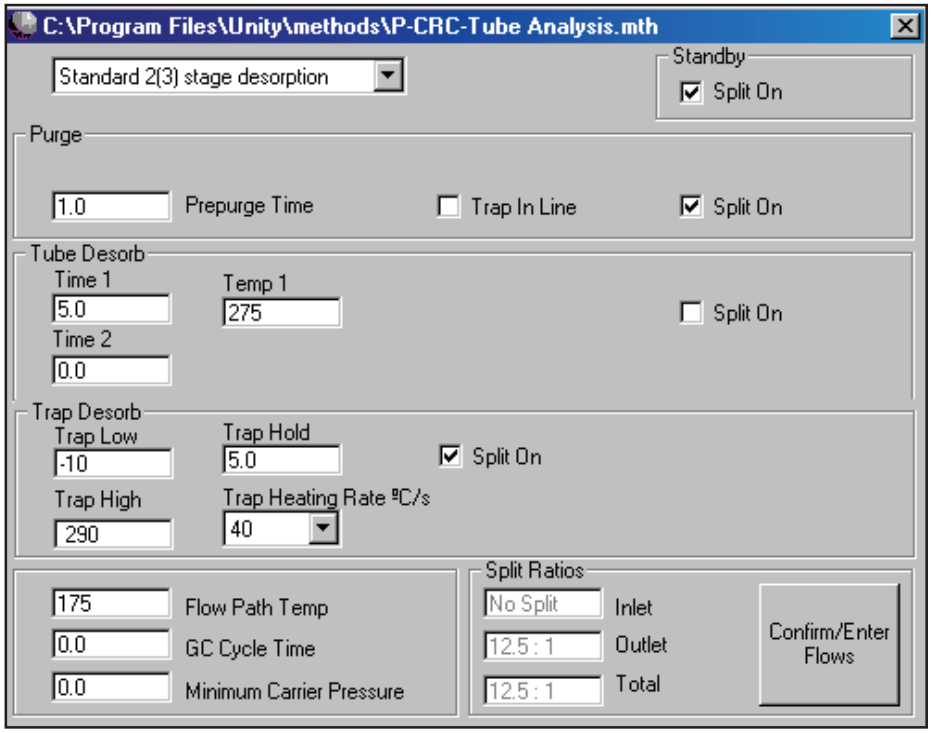


Figure 3.12 Sorbent tube operating parameters.

In this study, volatiles' vapour was split into a ratio of 12.5:1. Only 1 portion of split vapour was analysed with gas chromatography system. Recollection of volatiles onto a sorbent tube for further analysis can be initiated at this stage. Suitable flow path temperature should be employed for thermal desorption and transfer lines connecting to the gas chromatography system. Pathway lines set at extremely high temperature may cause breakdown of thermally unstable volatiles while transfer

lines with excessively low temperature may contribute to condensation of volatiles before reaching the gas chromatography column.

3.4.1.3 Sampling and operating parameters of sorbent tube analysis

Details for collection of volatiles onto sorbent tubes (Tenax TA) and thermal desorption of sorbent tubes loaded with volatiles into the thermal desorption unit are outlined in Tables 3.3 and 3.4.

Table 3.3 Volatile organic compounds sampling details for poultry litter.

Features	Values
Litter material	8 L
Sorbent material	Tenax TA
Sampling time	30 min
Flow rate	100 ml/min

Table 3.4 Sorbent tube desorption details for poultry litter sampling.

Features	Values
Sorbent tube pre-purge	1 min
Sorbent tube desorption	Time: 5 min Temperature: 275 °C
Cold trap desorption	Trap low: -10 °C Trap high:290 °C Trap hold: 5 min Trap heating rate: 40 °C/s Split ratio: 12.5:1
Flow path detail	Temperature: 175 °C

3.4.2 Development of direct dynamic headspace technique

3.4.2.1 Direct dynamic headspace sampling

Direct dynamic headspace sampling is a technique used to obtain vapour aliquot from sample matrix with minimum interferences such as dilution. It omits the use of sorbent material to collect gas vapour from the odour sources for TD-GC-MS analysis. Instead, a specially designed headspace sampler was used to pre-concentrate volatiles directly from the odorous sample onto a cold trap set in the thermal desorption unit. Sampling of volatiles using direct dynamic headspace sampler is simpler compared to sorbent tube volatiles collection as it eliminates the need for pre-conditioning and screening of sampling tubes as well as long periods of nitrogen gas spraging above the odour source.

The headspace sampler used in this study consists of two stainless steel inlets. One end of both inlets is attached to an empty stainless steel sorbent tube and the other to a sampling vessel (Figure 3.13). The empty stainless sorbent tube is placed on a peltier cell in the thermal desorption unit to connect the headspace sampler to the thermal desorption unit (Figure 3.14). The inlet line carrying sample vapour from sampling vessel to the cold trap for pre-concentration is insulated with Teflon as this stainless steel line is heated to prevent condensation of volatiles along the line before reaching the cold trap. Meanwhile the uninsulated stainless steel line is held at ambient temperature at all stages to carry in purge gas into the sampling vessel. The entire operation by direct headspace sampler is controlled with electronic pneumatic controller set in the thermal desorption unit via a booster heater (Markes International, UK). Approximately 100 ml of broiler litter was filled in an odour free sampling vessel before being sealed to the direct headspace sampler. Carrier gas was sparged through the broiler litter material to enhance the volatilisation of organic compounds into the headspace above the sample matrix. Condensed volatiles in the headspace were pre-concentrated directly onto the cold trap set in the thermal desorption unit for prior to desorption onto the gas chromatography column for odorants analysis.

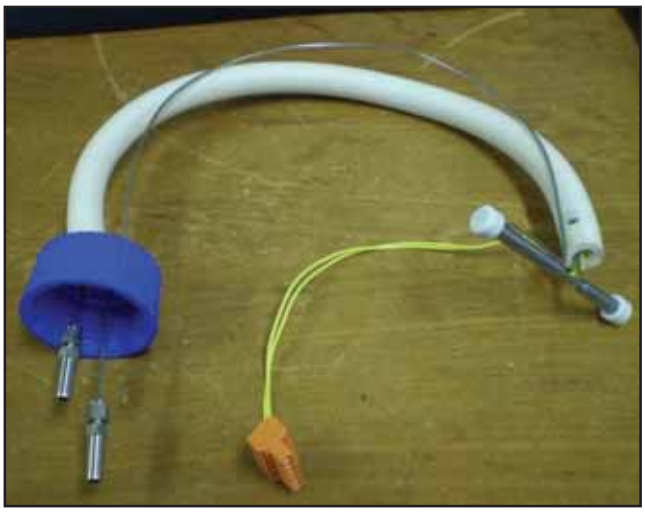


Figure 3.13 Headspace sampler used for dynamic headspace sampling (Markes International, UK).

Figure 3.14 Direct headspace sampler showing sample vessel and thermal desorption unit (Markes International, UK).

All sampling vessels were cleaned and rinsed thoroughly with hot water prior to use to prevent contamination. As a precaution, each sampling vessel was screened for contamination and background chromatogram to reduce interferences. Only sampling vessels with tight grip to the headspace sampler was utilised to prevent losses of volatiles during carrier gas purge and to maintain sufficient amount of pressure at the front inlet of the GC system. Unfit sampling vessel may contribute to leakage of volatiles into the atmosphere, concurrently causing improper operating condition for gas chromatography system due to mounting pressure at the front inlet. Additionally, headspace sampler inlets that become exposed to dirty sample matrix in the sampling vessel were packed with sufficient amount of quartz wool to filter dust emitting from sample during pre-purge and direct sampling stages. It is significantly important to maintain the cleanliness of these inlets at all point of time from ingression and condensation of contaminants along these lines as it is extremely difficult and involves tedious processes to clean up the inlets due to the small inner diameter area of the lines.

3.4.2.2 Direct dynamic headspace analysis

Figure 3.15 represents sampling stages involved in direct dynamic headspace technique that are outlined and discussed below:

a) Pathway line pre-purge

Headspace inlet lines and sampling vessel were pre-purged at a predetermined time with gas chromatography carrier gas at flow rate of 50 ml/min to remove humidity and oxygen before reaching the cold trap. This flow rate of gas was maintained using a needle valve for constant and fixed flow. Eliminations of high humidity and oxygen level along the transfer line pathway are essential to prevent impairment of GC column and oxidation of volatiles released during desorption respectively. During the pre-purge stage, the cold trap and Teflon insulated inlet of headspace sampler are held at a trap low temperature and 140 °C, respectively. At all stages, the uninsulated headspace sampler inlet, sampling vessel and broiler

litter sample were held at ambient temperature to achieve the aim of the project to sample volatiles at ambient environment with minimum interferences.

b) Direct sampling of volatiles

During direct sampling of odour, carrier gas of the gas chromatography was purged through the broiler litter sample sealed to the headspace sampler at a flow rate of 50 ml/min for a preset time. The carrier gas flows into the sealed sampling vessel through the uninsulated inlet and leaves carrying volatiles using the Teflon insulated inlet. Sparging carrier gas through litter material increases the volatilisation of volatiles into the gas phase (headspace) from the condensed phase (litter material); concurrently retraining the enriched volatiles in the headspace sampling vessel onto the cold trap set at the trap low temperature in the thermal desorption unit. While transferring volatiles from sampling vessel onto cold trap in the thermal desorption unit, the transfer lines were set at 140°C to prevent the condensation of volatiles along transfer lines besides constant flow rate of carrier gas.

c) Cold trap desorption

A general purpose graphitised cold trap (U-T11GPC Markes International, UK) was fitted into the thermal desorption unit to capture volatiles, especially compounds with C_4 to C_{30}. Volatiles pre-concentrated on the cold trap were subsequently heated rapidly using a peltier cell to introduce the compounds onto gas chromatography column. Initially, the cold trap was set to trap low temperature as low as -10 °C during pre-purge and direct sampling stages. The preset trap low temperature is suitable to capture most of the volatiles with low boiling point temperature on the cold trap. Subsequently, the cold trap was ballistically heated to reach trap high temperature desorbing all volatiles retrained onto gas chromatography column in a short period of time. The rate of cold trap heating can be preset using values available in the trap heating rate feature. Desorbed volatiles can be split into desired ratio using a split before reaching onto GC column, especially while handling highly concentrated aliquots that may overload or

contaminate the GC column and reduce peak resolution. In this study the split was not employed for broiler litter headspace sampling with an intention to determine all volatiles existing in the litter sample.

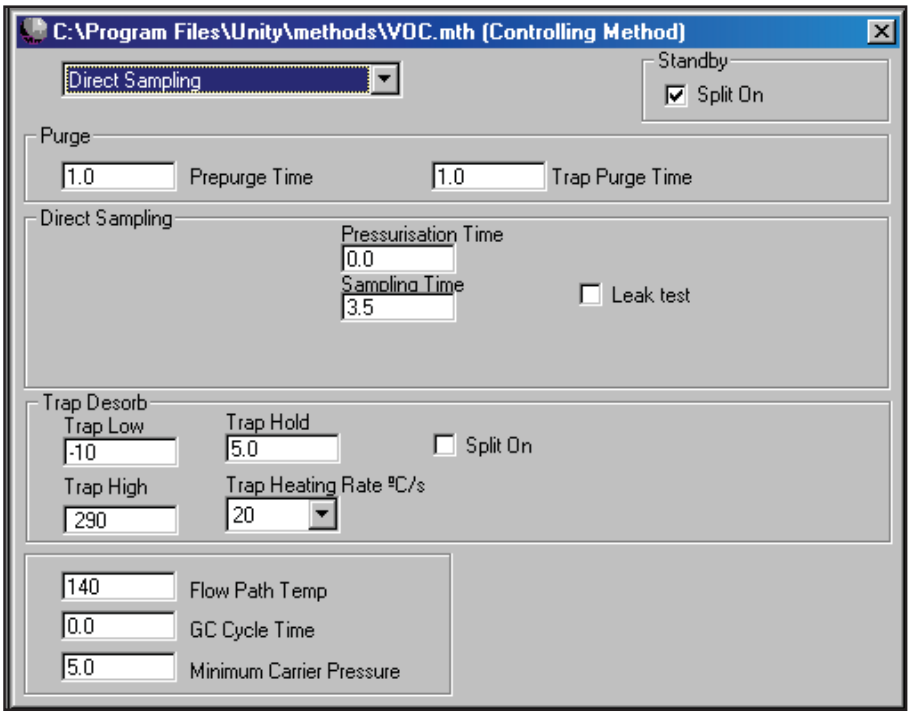


Figure 3.15 Direct dynamic headspace analysis operating parameters.

3.4.2.3 Sampling and operating parameters using direct dynamic headspace

Details involving direct dynamic headspace sampling of volatiles and the thermal desorption of the cold trap pre-concentrated with volatiles in the thermal desorption unit are outlined in Table 3.5.

Table 3.5 Direct dynamic sampling and analysis details.

Features	Values
Litter material	100 ml
Flow rate	50 ml/min
Pre-purge	1 min
Sampling time	3.5 min
Cold trap desorption	Trap low: -10 °C Trap high:290 °C Trap hold: 5 min Trap heating rate: 20 °C/s
Flow path detail	Temperature: 140 °C

3.5 Gas chromatography

Gas chromatography (GC) is a common technology used in many fields for analysis of substances. It provides routine analysis with high selectivity and sensitivity to determine and quantify organic substances.

3.5.1 GC operation and parameters

3.5.1.1 Carrier gas

Ultra high purity helium gas (BOC Gases, Sydney, Australia) was chosen as the carrier gas for all levels of GC analysis. This is significantly due to its inert and light molecular weight characteristics. In addition to this, the use of helium at all points during study is expected to assist operators to identify for leakages and interferences.

3.5.1.2 Column

The GC column employed for the separation of aliquot odorous volatiles has been limited to one type in this study (based on previous studies at the UNSW Atmospheric Emission and Odour Laboratory). A highly polar and long lasting polyethylene glycol column (HPInnowax, Agilent Technologies, North Ryde, Australia) with dimension of 0.25 mm x 30 m x 0.25 µm was selected due to its constant repeatability and reliability in compounds separation without co-elution. Besides its suitability for rugged analyses, this column also has high compatible applications with human olfactory detection port and mass selective detector, providing better peak separation and integration of low molecular weight molecules. Optimisation of carrier gas flow rate in gas chromatography column is often critical. Insufficiently determined flow rate may result in inaccurate elution time and incorrect operation of instrumental detector, especially when two different detectors are in application for the identification of compounds. In this study, the flow rate of the carrier gas was maintained at 1.6 ml/min for gas chromatography column for volatiles separation. However, modification of the carrier gas flow rate was required while splitting effluent from the GC column into the mass selective detector (MSD) and olfactory detection port (ODP) at a preset ratio using a splitter

connector (Figure 3.16). This effort is significantly important to prevent the ingression of atmospheric air into the instrumental system through the olfactory detection port's opened end, which may cause ineffective functionality of both detectors.

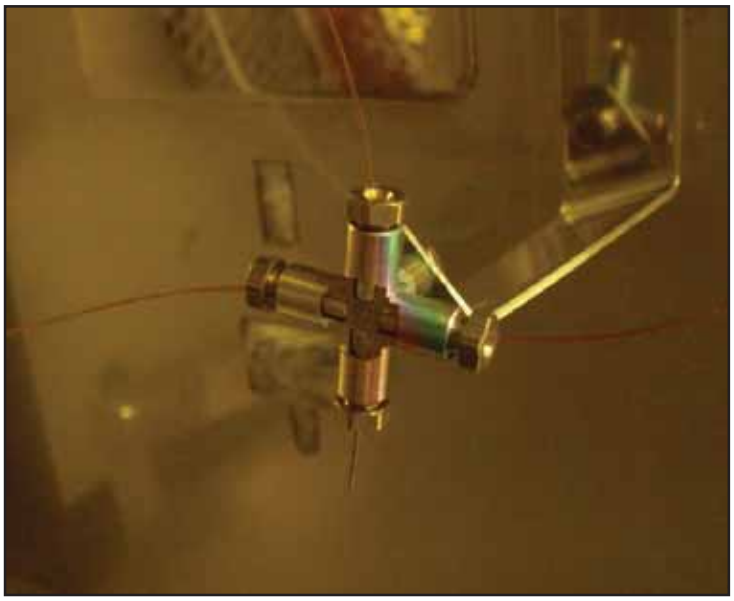


Figure 3.16 Splitting of GC column for simultaneous chemical (MSD) and olfactory (ODP) analysis.

3.5.1.3 Oven temperature

A polyethylene glycol column (HPInnowax) was chosen for the broiler litter odour study that has a maximum column temperature of 250 °C. The GC oven temperature setting therefore was set at the following setting: a) initial gas chromatography oven temperature was set and held at 50 °C for 2 min; b) the oven temperature was ramped at 5 °C/min till 125°C for 10 min and c) it was finally ramped at 10 °C/min till 200 °C for 2 min. The entire GC analysis took a total run time of 26.50 min for per sample. This estimate of time is an optimised period for human operators to conduct olfactory analysis at the olfactory detection port. Long experimental time frame may cause fatigue of olfactory detection port operators resulting in their inability to determine odorants.

3.5.1.4 Gas chromatography detectors

An important objective of this research is to evaluate odorants produced from broiler litter material simultaneously using olfactory and chemical analysis. To achieve this objective, GC was coupled to two different detectors as mass selective detector and olfactory detection port to assist in characterisations and quantifications of volatiles and odorants existing in the complex litter material.

3.5.1.4.1 Mass selective detector (MSD)

Among the varieties of detectors capable to be coupled with GC, MSD is the most widely and commonly used universal detector for quantitative and qualitative determination of chemical substances. Scan mode was employed in this study for the MSD allowing the identification of all compounds existing in the broiler litter odour within a preset range of m/z ion from 35 to 550. The MSD was functioning under the control of the Chemstation Software (Agilent Technologies, North Ryde, Australia). Identifications of separated chemicals were compared to the NIST02 database (National Institute of Standards and Technologies). Mass fragment patterns of species were simultaneously considered to confirm compounds identified by the NIST02 database. To maintain accuracy of the study, only compounds determined with peaks matching 80 percent and greater with the NIST02 database were reported in this study. Nevertheless, frequently and prominently occurring compounds with matches lower than 80 percent of quality were considered using retention time. Chemicals produced from broiler litter odour were carefully studied before a number of compounds were selected for confirmation of retention time and quantification.

3.5.1.4.2 Olfactory detection port (OPD)

Human sensory identification has been applied in comparison with results obtained from MSD analysis. For this purpose, an olfactory detection port (ODP) (Gerstel, Germany) was coupled to the GC column to simultaneously assess the effluent emerging from GC. The effluent was streamed from the GC to MSD and ODP at a split ratio of 2:3, which was predetermined at the initial temperature of the oven. An

electronic pneumatic control module of gas chromatography maintained the flow rate to both detectors as the gas chromatography oven temperature increased during analysis run time. Two human assessors were employed to evaluate the broiler litter odorants. Both assessors who were previously screened using n-butanol according to AS/NZS 4323.3.2001 standard varied in sensitivity with one assessor extremely sensitive and the other averagely sensitive. However, adequate amount of training was provided to both assessors in order to reduce errors and biasness during analysis.

The OSME human olfactory detection technique was successfully applied for determination of odorants in this study and the chromatogram produced using this method is called the “osmegram”. OSME sensory analysis studies volatiles without any series of dilution or modifications. It analyses volatiles in the actual form obtained from the source. The ODP system consists of an olfactory port and odour input device including a headset microphone and a control pad (Figure 3.17). The odour input device assists evaluators to record their responses of intensity and qualitative characters of perceived odorants at the olfactory port using the Gerstel software. Both intensity and qualitative characters of odorous species are equally vital to confirm the most dominating compound(s) in the sample matrix. During sample analysis, the Gerstel and Agilent Chemstation softwares were set to operate simultaneously to produce osmegram and total ion chromatogram respectively (Figure 3.18). These chromatograms can be laid on each other to determine odour potent volatiles and their qualitative characters and intensities.

Description of volatiles is essential to distinguish between odorous and non odorous chemical eluting from broiler litter material. Assessors were facilitated with a list of descriptor obtained from the Gerstel software to qualitatively characterise detected odorants. However, assessors were also allowed to record descriptions of odorants in their own words based on their daily experiences. One disadvantage of the Gerstel software is its incapability to convert the recorded odorants’ description into text form to be labelled on the total ion chromatogram. The assessors had to

playback the recorded description comments in order to key in the odorants characteristics manually. Four levels of odorants' intensities as low (1), medium (2), high (3), and very high (4) have been used by assessors to quantify the offensiveness of detected odorants. On the osmegram, the heights of perceived odorants vary depending on their recorded intensities.

Figure 3.17 Operator at the odour detection port (ODP) using headset microphone and a control pad for intensity ranking.

Figure 3.18 Operation of MSD and ODP outputs with chemstation.

3.5.1.5 Operating parameters for GC and ODP analysis

Details involving operation of the GC for volatiles separation and analysis and the setup and operation of the ODP for odorant analysis are outlined in Table 3.6.

Table 3.6 GC-MS/O operational details for GC, MSD and ODP analysis.

Details	Values
Column type	Polyethylene glycol
Column gas flow rate	1.6 ml/min
Oven temperature	Initial: 50 °C for 2 min. First ramp: 5 °C/min till 125 °C for 10 min Second ramp: 10 °C/min till 200 °C for 2 min
MSD temperature	250 °C
ODP temperature	280 °C

3.6 Instrument calibration

Broiler litter odour analyses using direct dynamic headspace and sorbent tube samplings revealed the existence of a large variety of volatiles, both odorous and non odorous compounds from the litter odour matrix. Calibration of these compounds is therefore required to confirm the retention times of the compounds and the efficacy of responses of the sampling and analysis system. The selection of the compounds was based on mixture of odorants detected via olfactory analysis and chemical abundance determined via mass spectrometry analysis.

Stock solutions consisting of fifteen pure odorous volatiles were prepared precisely in high performance liquid chromatography grade methanol (99%, Sigma Aldrich, Castle Hill) at 50, 100 and 250 parts per million of volume (ppmv). Stock solutions contained: acetone (99.5%, Sigma Aldrich, Australia), 2-butanone (99.5%, Supelco, US), 3-methyl-2-butanone (99.5%, Fluka, Europe), 2,3-butanedione (99.5%, Fluka, Europe), α-pinene (99%, Aldrich, Castle Hill), toluene (99.8%, Sigma Aldrich, US), dimethyl disulfide (99%, Aldrich, Castle Hill), 1-butanol (99%, Sigma Aldrich, US), limonene(97%, Sigma, US), 3-hydroxy-2-butanone (97%, Fluka, Europe), dimethyl trisulfide (98%, Aldrich, Castle Hill), acetic acid (99.7%, Sigma Aldrich, Castle Hill) and butyric acid (99%, Aldrich, Castle Hill).

3.6.1 Calibration of volatiles using sorbent tube technique

Screened Tenax TA sorbent tube was loaded with 1 µL of 50 ppm standard solution using a calibration rig that were concurrently sealed with brass caps fitted with Teflon ferules prior to analysis. Tubes loaded with stock solution were then thermally desorbed and analysed using the identical TD-GC-MS/O technique used in the study for broiler litter odour sampled on Tenax TA sorbent tubes. Calibrations were repeated using stock solutions of 100 and 250 ppmv concentrations, respectively.

3.6.2 Calibration of volatiles using direct headspace technique

Approximately 1 µL of stock solution was placed on the base of clean sampling vessel before instantly attaching to headspace sampler for direct TD-GC-MS-O analysis identical to broiler litter odour analysis. Calibrations of volatiles were repeated using stock solutions of 100 and 250 ppmv concentrations, respectively.

3.7 Supplementary litter analysis

3.7.1 pH analysis

pH values of litter samples were determined based on method described by Miles and co-workers and Turan and co-workers [158, 177]. Approximately, 150 g of distilled water was added on to 30 g of litter sample. Mixture was stirred and left to settle prior to the pH measurement using pH meter. The pH measurements were recorded in duplicates.

3.7.2 Litter moisture content

Litter moisture content was measured in the laboratory using an infrared moisture balance (Model F100, Kett, US). Approximately 0.5g of litter sample was used to record the moisture content. Data was recorded in duplicates.

3.8 Odour abatement analysis

Three different commercial materials commonly used in odour abatement systems were tested for odour emission reduction efficacy on the most odorous broiler litter materials collected during winter and summer. Activated carbon (Sigma Aldrich, Castle Hill), silica gel orange (Sigma Aldrich, Castle Hill) and zeolite (Sigma, US) were tested with wet litter samples collected at week 7 from the winter sampling and at week 6 from the summer sampling, respectively. As in previous tests, precautions were taken to prevent contaminations at all stages of experimentation. Odour and pH data of activated carbon, silica gel and zeolite were screened prior to mixing with litter materials.

3.8.1 Preparation of odour reduction sample bags

Ten 500 g of litter samples were prepared in odour free bags and mixed with 5, 10 and 25 percent of activated carbon, silica gel and zeolite, individually. Percentages of odour reducing materials added to the litter were calculated in relative to mass of broiler litter material in each bag. One 500 g litter sample bag was treated as a control.

3.8.2 Storage and analysis of odour reduction sample bags

Sample bags of litter mixed with odour reducing materials were placed in a ventilated fume hood with a flow rate of 0.5 m^3/s for 3 weeks at ambient temperature (approximate 23 °C) (Figure 3.19). Approximately, 100 ml of litter samples were taken from each of the sample bag for direct dynamic headspace TD-GC-MS/O analysis on weekly basis for three consecutive weeks to determine the effective of the odour abatement materials. The TD-GC-MS/O analysis conducted during odour abatement studies followed the procedure for TD-GC-MS/O analysis undertaken for the winter and summer broiler litter samples for odorants determination. Additionally, the, pH and moisture content values of each sample bags were recorded to concurrently compare their impacts on odorants produced and reduction in broiler litter material. All analysis (pH and moisture

content) were conducted in duplicates except for TD-GC-MS/O study that was treated as single replicate for each trial set.

Figure 3.19 Abatement sampling bags placed in the ventilated fume hood for odour reduction trials.

3.9 Statistical analysis

One way Anova was used to determine significance difference and impact of analysis with ($P<0.05$). Repeatability and reproducibility of replicated were analysed using two way Anova of Microsoft Office (Microsoft Excel 2007). To produce reliable correlation between instrumental and olfactory responses with reduced biasness, linest feature in Microsoft Excel 2007 was used to generate regression values.

CHAPTER FOUR

Analysis of Emissions from Poultry Litter

4.1 Introduction

Poultry litter is often highlighted to be the major source of odour associate with emissions in broiler production [207]. This study aims to assess this hypothesis using a laboratory scale odour analysis technique in order to provide a greater understanding of litter odour productions in tunnel ventilated broiler sheds. Previous studies on odour emissions from livestock vicinities suggest meteorological and production operations including manure handlings influence the odour emanation rates that are likely to cause annoyances to sensitive receptors living near animal facilities [12, 38, 208]. This study conducted a point source odour investigation using litters obtained from controlled environments within tunnel ventilated production sheds in Queensland, Australia. The research program emphasises to studying the impact that variables, such as bedding material type, broiler growth period, broiler body mass, season, litter pH and moisture content have on the emission of odours from broiler production sheds. One way Anova was used for statistical similarities between these variables and odour concentrations that was applied to determine significant variation, effect or difference at ($P<0.05$).

4.2 Olfactometry analysis of winter and summer litter

Odour variations in the litter material were estimated using dynamic dilution olfactometry analysis. Table 4.1 and Table 4.2 show the mean values of litter odour concentration, pH and moisture content obtained during the winter 2009 and summer 2010 sampling stages. Figure 4.1 illustrates the variation in the data odour concentrations detailed in Tables 4.1 and 4.2. During both sampling seasons, different types of bedding materials were in use to accommodate the broilers. Selecting bedding types often depends on the shed integrators decision that is usually based on the availability and cost of the materials. Pine wood and hard wood shavings were utilised as fresh bedding material on the sanitised floors of the ventilated sheds in winter and summer, accordingly. The application of fresh pine wood shavings as bedding produced a pleasant smell at the initial stage of sampling, attributed to the release of wood fragrant volatiles whereas no significant odour was perceived from the hard wood shavings that appeared dusty and drier than the winter bedding material. In addition, no significant changes were observed on the litter odour emission with the use of different bedding types as the emanation of odours can be observed to be generally associated with the increase with the presence of chickens (Figure 4.1) and could not be related to the source of bedding material. However, the odour emissions in the summer sampling do show that emissions are greater in the wet litter compared to similar odour concentration values of the winter wet litter.

Table 4.1 Winter broiler litter odour emissions, pH and moisture content variations.

Litter age	Litter type	Odour concentration (OU/m^3)	pH	Moisture content (%)
Week 0	Dry	1591 ± 222	7.54 ± 0.05	44.3 ± 3.7
Week 1	Dry	1421 ± 288	7.15 ± 0.3	27.4 ± 5.9
Week 2	Dry	6370 ± 2303	8.07 ± 0.45	25.6 ± 5.9
Week 3	Dry	10074 ± 1139	9.10 ± 0.01	21.7 ± 1.4
Week 4	Dry	19827 ± 397	9.01 ± 0.01	26.1 ± 3.0
Week 5	Dry	20294 ± 3809	8.86 ± 0.01	27.8 ± 2.3
Week 6	Dry	20356 ± 4150	8.82 ± 0.01	27.7 ± 3.1
Week 7	Dry	20100 ± 1341	8.65 ± 0.03	25.7 ± 4.2
Week 8	Dry	4612 ± 435	8.41 ± 0.01	22.1 ± 0.3
Week 0	Wet	1539 ± 304	6.50 ± 0.49	41.7 ± 1.06
Week 1	Wet	2910 ± 329	7.38 ± 0.16	35.0 ± 10.8
Week 2	Wet	15090 ± 1628	8.22 ± 0.27	41.9 ± 14.2
Week 3	Wet	18451 ± 1740	8.77 ± 0.02	42.0 ± 12.0
Week 4	Wet	39593 ± 8009	8.16 ± 0.01	53.4 ± 2.1
Week 5	Wet	76059 ± 8201	5.65 ± 0	62.8 ± 5.8
Week 6	Wet	43394 ± 10088	7.63 ± 0	45.0 ± 10.8
Week 7	Wet	115372 ± 22883	7.13 ± 0.01	56.6 ± 9.2
Week 8	Wet	93311 ± 21443	7.16 ± 0.01	58.0 ± 1.0

Table 4.2 Summer broiler litter odour emissions, pH and moisture content variations.

Litter age	Litter type	Odour concentration (OU/m^3)	pH	Moisture content (%)
Week 0	Dry	604 ± 168	6.40 ± 0.14	28.8 ± 3.8
Week 1	Dry	1557 ± 124	6.30 ± 0.14	21.7 ± 4.2
Week 2	Dry	2260 ± 424	6.60 ± 0.28	30.8 ± 3.2
Week 3	Dry	1920 ± 217	7.86 ± 0.17	30.3 ± 5.5
Week 4	Dry	10040 ± 563	8.20 ± 0.3	25.1 ± 0.9
Week 5	Dry	83344 ± 26738	8.26 ± 0.06	29.7 ± 5.5
Week 6	Dry	53782 ± 5799	8.63 ± 0.04	23.5 ± 1.3
Week 7	Dry	79328 ± 16619	8.35 ± 0.35	29.2 ± 4.7
Week 8	Dry	45369 ± 6320	8.40 ± 0.47	27.5 ± 0.8
Week 0	Wet	812 ± 135	6.32 ± 0.01	29.0 ± 4.0
Week 1	Wet	1635 ± 373	6.91 ± 0.01	21.2 ± 1.2
Week 2	Wet	2161 ± 350	7.17 ± 0.04	33.9 ± 7.5
Week 3	Wet	2093 ± 495	8.70 ± 0.28	27.1 ± 2.1
Week 4	Wet	8721 ± 949	8.50 ± 0.25	30.1 ± 7.6
Week 5	Wet	30818 ± 21398	7.98 ± 0.08	23.0 ± 2.4
Week 6	Wet	104379 ± 9843	8.10 ± 0.15	28.7 ± 7.4
Week 7	Wet	42686 ± 4603	8.52 ± 0.21	35.9 ± 9.6
Week 8	Wet	49506 ± 7365	8.70 ± 0.13	30.2 ± 8.3

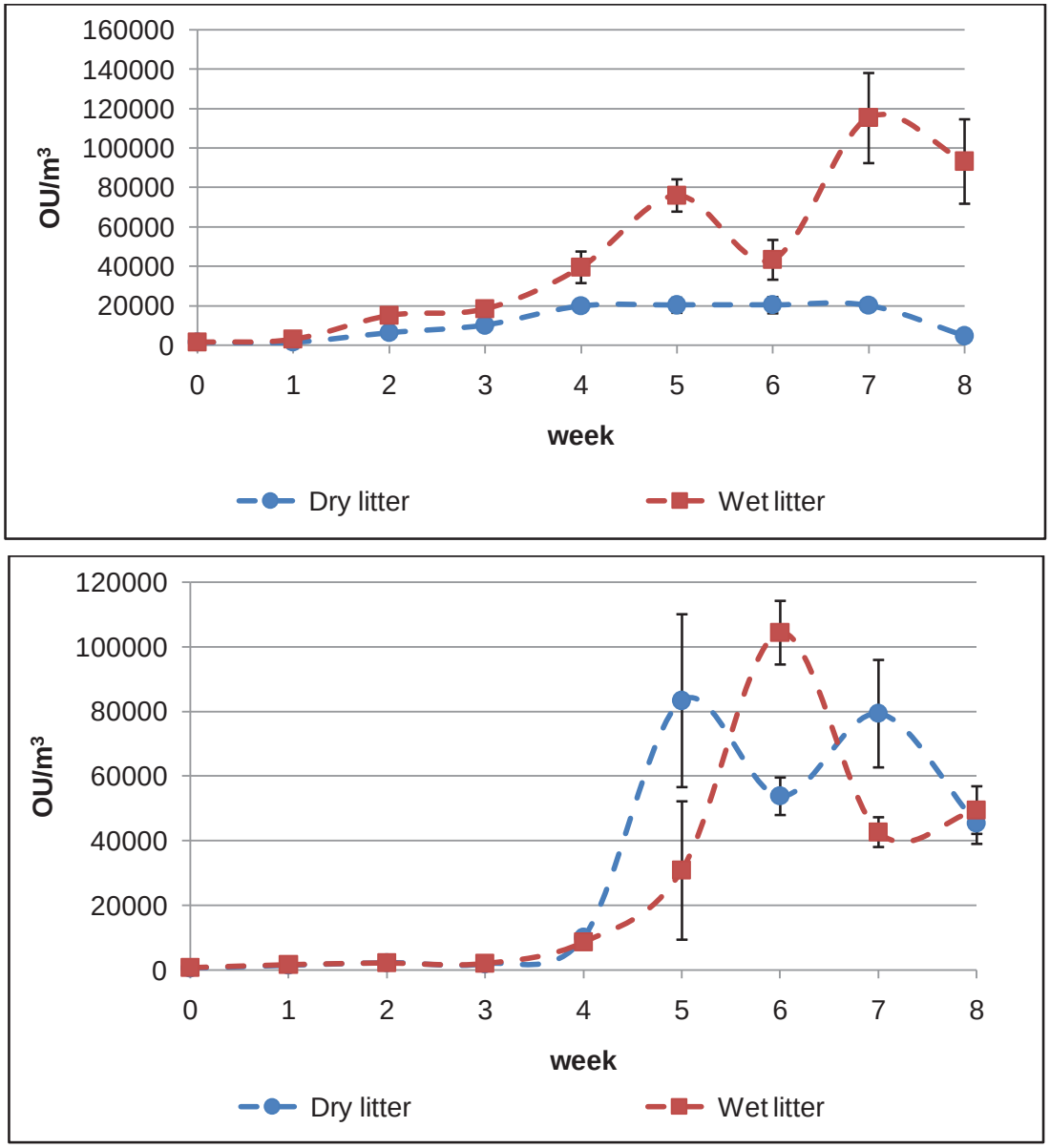


Figure 4.1 Litter odour concentration variation across growth cycle showing winter (top) and summer (below).

It is important to know the quantity of odour emanating from an odour emitting source within an area at a period of time prior to quantification of emission rates at the outlet of facilities. Point sources emissions suggest and assist with emission rates estimation at the outlets of the facilities. In addition, it is at these point sources like litter surfaces, where the odour mitigating strategies should be implemented rather than at the odour venting outlets (i.e. the fan exhausts). Litter odour emission rates were calculated based on odour concentration data obtained from Table 4.1 and Table 4.2 and the parameters used during flux hood odour sampling, that are detailed in Equation 4.1, with OER = odour emission rate (OU/m^2min), C_{OU} = odour concentration (OU/m^3), Q = flux hood flow rate (L/min) and A = area closed by flux hood (m^2), radius of flux hood = 0.2m.

$$OER = C_{OU}\, Q / A \qquad \text{(Equation 4.1)}$$

Litter odour emission rates of respective litter types and sampling climates are shown in Table 4.3 with the variations being illustrated in Figure 4.2. The result obtained from the winter and summer litter odour analysis (Figure 4.2) shows high odour emission rates up to 4500 OU/m^2min were observed for the litter samples when the emission rates were determined by directly sampling from above the broiler litter material. Among all litter samples, winter wet litter was observed to exhibit highest emission rate.

Table 4.3 Estimations of odour emissions rates of winter and summer litters.

Litter age	Odour emission rate, OU/m^{2}min			
	Dry litter	Wet litter	Dry litter	Wet litter
Week 0	63	61	24	32
Week 1	57	116	62	65
Week 2	254	601	90	86
Week 3	401	735	76	83
Week 4	789	1576	400	347
Week 5	808	3028	3318	1227
Week 6	810	1727	2141	4155
Week 7	800	4593	3158	1699
Week 8	184	3715	1806	1971

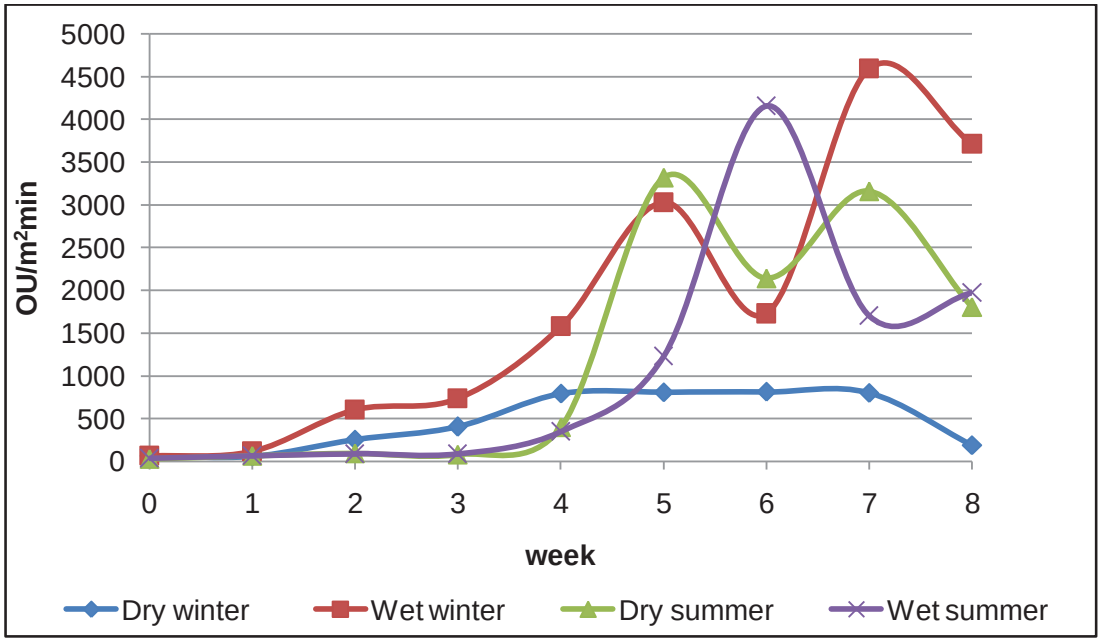


Figure 4.2 Variations in odour emissions rates for winter and summer litters.

In comparison to previous odour concentration studies from broiler facilities, Dunlop and co-workers estimated 122 to 1142 OU/m^3 [179], Jiang and Sands reported 50 to 1000 OU/m^3 [157], Robertson and co-workers reported 1300 to 2300 OU/m^3 [209], Amon and co-workers reported 500 to 2080 OU/m^3 [190] and Misselbrook and co-workers reported 1000 OU/m^3 [96] that are significant lower than the values obtained from the current study. However, direct comparison of odour concentrations and/or odour emission rates with the published data are rather complex as different sampling techniques and source of emission were used that created different levels of benchmarking for determining odour emission rates. The higher odour concentration and/or emission rate reported in this study from the litter material however does support the suggestion that litter material is a major source of odours that are emitted from broiler sheds.

4.3 Variations in odour emissions due to wet and dry litter

During winter sampling (Table 4.1), odour concentrations from the dry and wet litters increased from week 1 with the introduction of birds into the shed. Dry litter odour concentration generally remained low during entire production process. It emitted the least amount of odour concentration with the highest reading detected after week 6 of production at 20356 OU/m^3. Whereas the winter wet litter escalated in emission beginning from week 3 with a rapid increase observed from week 6 marking the highest emission in week 7 at 115372 OU/m^3. This magnitude was approximately five times higher than the highest recorded by the dry litter of winter. Meanwhile, the emissions in the summer litter samples remained comparatively low with only a significant increase noticed after 4 weeks. In contrast to the winter litters, summer dry litter's emission escalated rapidly from week 4, with the highest odour concentration occurring in week 5 at 83344 OU/m^3 before decreasing in week 6. The dry litter emission however increased for a second time from week 6 to week 7 with an odour concentration of 79328 OU/m^3 being observed. The summer wet litter sample exhibited a slightly different emission trend, as the odour concentration was observed to increase from week 4 with the highest odour concentration occurring in week 6 at 104379 OU/m^3. It was noticeable that the

summer wet litter emitted low magnitudes of odours in comparison to summer dry litter except in week 6. Nevertheless, no significant difference in emission was observed between the summer wet and dry litters as their magnitudes exhibited similar strengths.

Analysis of variance was used to further confirm that the magnitude of odour emission variations from the studied litters where similarities ($P>0.05$) between seasons (summer and winter) and litter types exist, except when comparing the dry with the wet winter litters, which showed a greater variation in emission. This observation is probably due to the controlled environment and/or similarity between the tunnel ventilated sheds chosen to study, thus reducing the seasonal impact on odour emission variation. Odour emissions developed substantially with the introduction of young broiler chicks into the shed and onto the fresh bedding. As observed (Figure 4.2), litters were found to become more odorous while progressing through the growth of birds ($P<0.05$), even though the emanations varies in rate and period of increase [210].

The initial increase in litter odour emissions during winter and summer samples (except in the summer wet litter), occurred during the first five weeks of chicken growth in which the broiler gained significant body mass. The increase in chicken mass also resulted in increased accumulation of excreta on the bedding material in addition to spillage from feed material and water. A second increase in litters emissions was also detected after the first removal of chicken at weeks 5-6 and maybe attributed to a further development in the body mass of remainder birds and an increase in the accumulation of excreta on the soiled litters [183]. This explanation could not be applied to the observation that the highest odour concentration occurred in the summer wet litter in week 6, which was after the reduction in bird numbers. Further physical, chemical and microbiological analysis of litter is required to understand the role that these processes play in the formation and emission of odours from soiled litter. Linear regression analysis (Figure 4.3)

shows correlations of the impact of bird body mass on litter odour concentration for respective seasons.

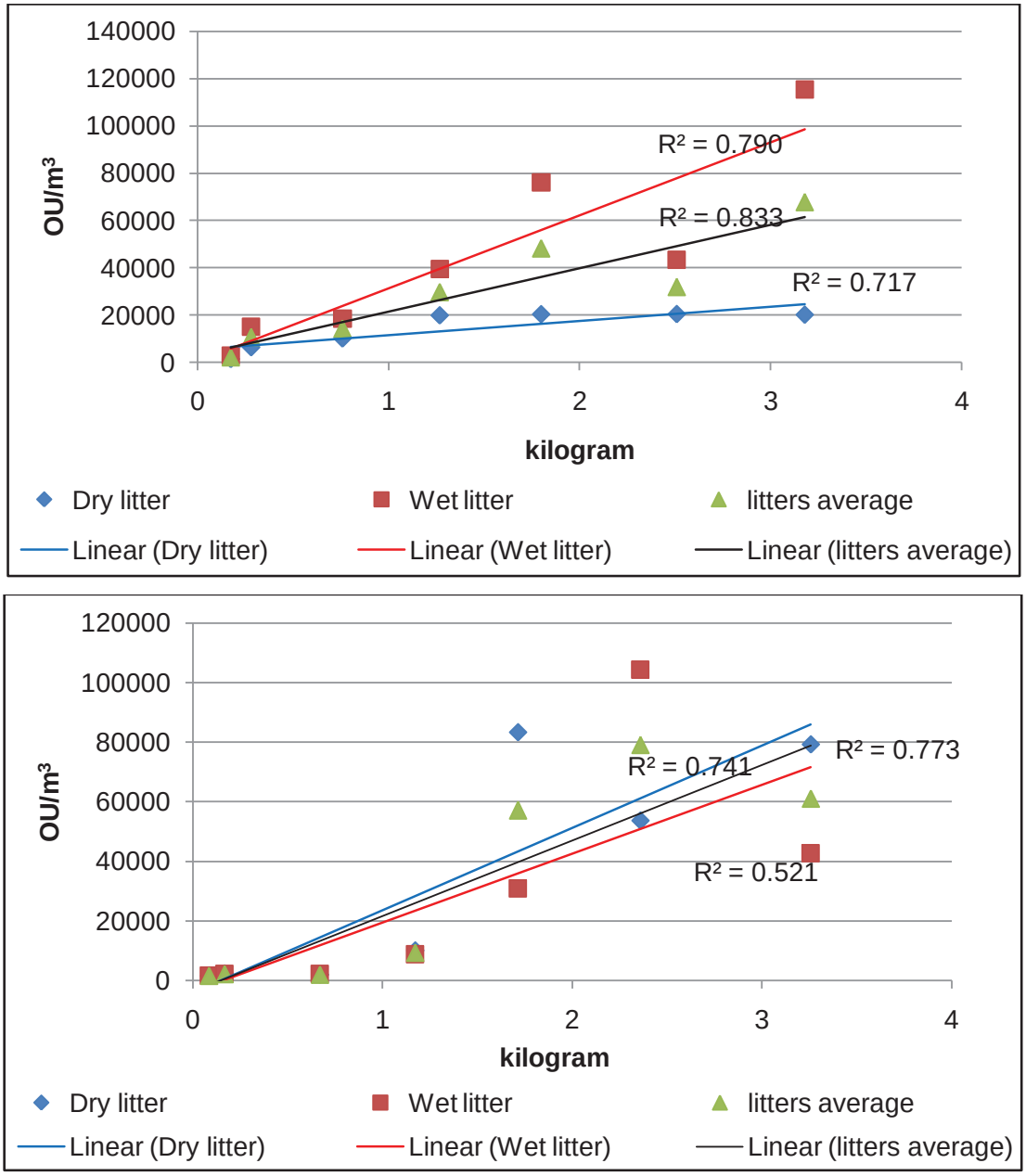


Figure 4.3 Correlation of odour concentration (OU/m^3) with increasing body mass of broiler chickens during winter (top) and summer (below) litter sampling.

The results showed that strong correlations were produced and that generally larger birds generate more odours. It is expected that with increased body mass, the chickens also excreted more manure onto the litter and that this most likely to provided a more suitable platform for microbial activities within the bedding material for substantial increase in odour emissions. In this study, chicken body mass again was observed to be one of the important factors influencing the emissions of odours from the litter compared to total number of birds within sheds that often targeted as a major cause to increase in emission rates. Generally, this observation that a greater number of chickens will result in a greater emission of odours is supported by the current results, however, the odour analysis of the summer wet litter samples suggests that the number of birds and the emission rates are not as strongly linked to each other (R^2 = 0.52) as in the other litters. It is also interesting that this shed (i.e. summer wet litter samples) contained the least number of chickens but generated the highest odour emission. This finding suggests that the physical, chemical and microbial conditions of the litter play an important part in the formation and emission of odours. Further studies are needed to better understand the litter conditions that resulted in greater release of odours from the soiled bedding material.

4.4 Variation in moisture and litter pH in summer and winter litter

Moisture content and pH values were two physical parameters of litters that were routinely measured during litter odour studies. The data recorded on litter moisture content and pH values during winter and summer sampling campaigns are illustrated in Figure 4.4. Litter and pH values recorded during this study matched the ranges published in previous studies [158, 188, 211]. Apparently, no significant difference was observed in moisture content of litters between seasons and type, except for winter wet litter that varied and exhibited higher range of moisture, especially from week 4 to 5 and week 7 to 8. The water content in litter is frequently reported as a prominent factor to be associated with odour generation and transportation from one medium to another [183, 207]. Moisture content maintained between 25 to 35 % is suggested to reduce offensive odour emission

and dust formation from litter materials [158]. The variations in moisture content are often influenced by the number of birds, ambient temperature, facility humidity, birds' health, drinker management and ventilation rates. In addition, large birds covering or insulating the litter surface increase the capability of litter to sustain water content within the litter [158].

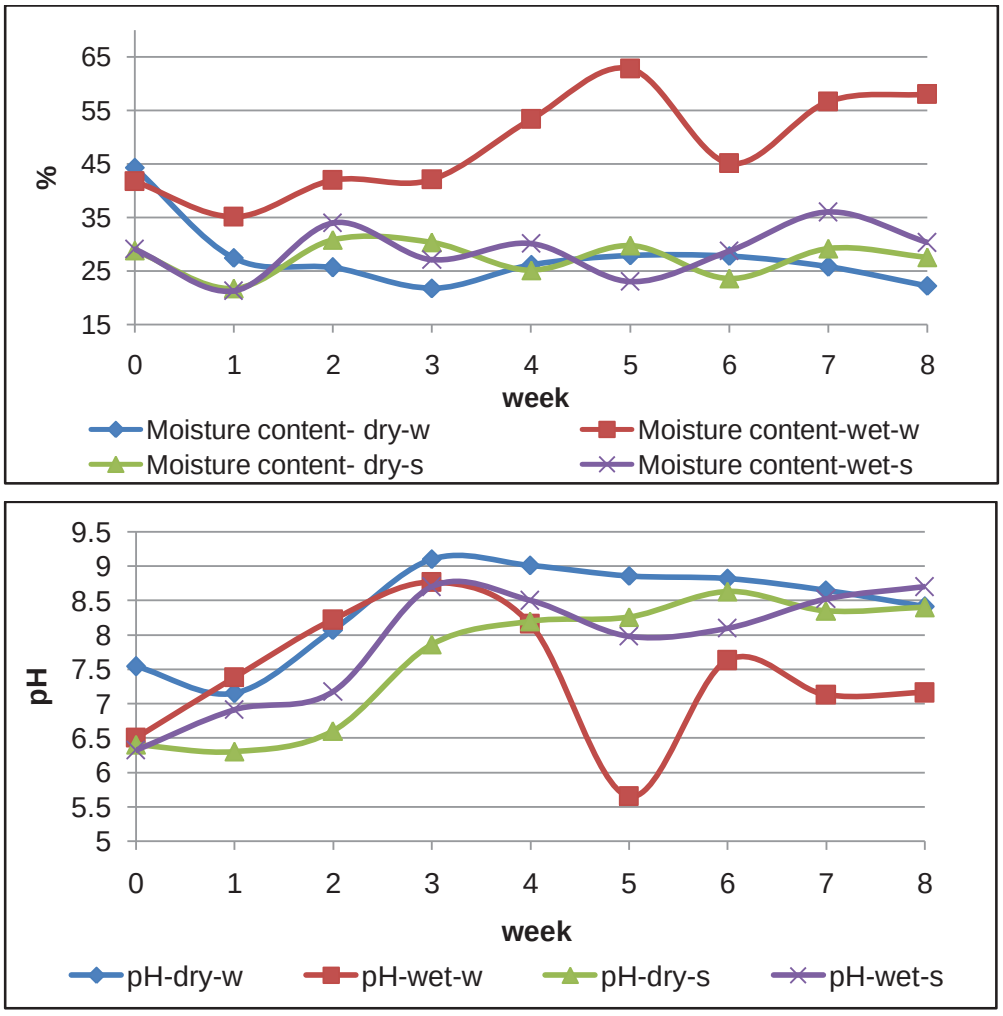


Figure 4.4 Variations in litter moisture contents (top) and pH (below) in winter and summer litters.

The results show that higher moisture content was detected along broiler drinker lines than along the middle sections of the tunnel ventilated shed. In winter, caking of the litter was observed to be more predominating, especially for the prominently wet litter samples. Removal or cracking of caked litters further enhanced litter odour emission during sampling. During the summer litter sampling, due to low moisture content, the litters were observed to be dusty and had non-caking appearance.

The highest moisture content recorded during the winter and summer sampling was for the wet litter in weeks 5 and 7, at 62.8 % and 35.9 % respectively whereas litters generally exhibited pH values from 6 - 9.5, except for the winter wet litter that recorded 5.65 as its lowest value. The analysis of variance of the litters also revealed a noticeable change in moisture content and pH values between the dry and wet winter litters ($P<0.05$). The literature suggests that wet litters with moisture content of 38.4% and above will assist in the formation of litter cakes as well as modify the pH of the litter pH that causes increases in odour emissions [158, 188, 211].

The results of analysis of litter moisture content and pH against odour concentration over the seasonal broiler production cycle are illustrated in Figure 4.5, 4.6, 4.7 and 4.8 accordingly, showing distinguishable trends in the dataset from which further analysis via linear regression analysis were attempted to obtain a clearer understanding of these variations that are displayed in Figure 4.9 and Figure 4.10. Moisture content values for the litters were initially higher, which subsequently reduced in week 1 most likely the result of evaporation during the introduction of young broilers that requires higher shed temperatures. In addition, smaller size of chickens at initial sampling stages causes exposure of large litter area surface to facility temperature that substantially further enhanced drying of litters. Wet winter litter appeared to be very damp in week 5 and parallel with the generation of odour concentration. Whereas, the dry winter litters exhibited a higher range of moisture content in week 0 (40-43 %) than expected, this is

probably due to inappropriately managed of the fresh bedding prior to application in the shed. The wet winter litter moisture content exhibited similar trend towards odour concentrations that simultaneous increase or decrease with odour concentrations (Figure 4.5).

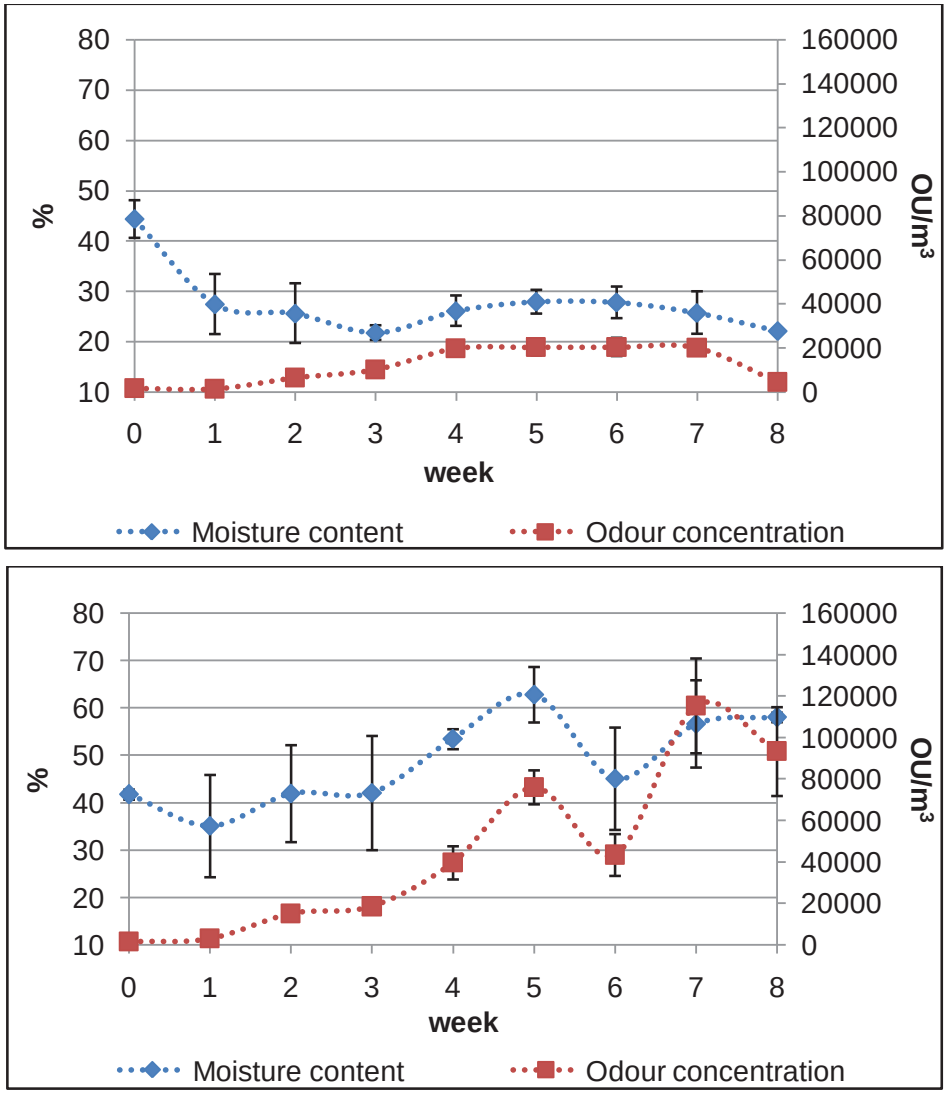


Figure 4.5 Variation of moisture content with odour concentration in winter dry (top) and wet (below) litters.

In comparison to the winter litters, the summer litters variation was minimal with no general trend towards odour concentrations (Figure 4.6). Both litters sustained low moisture content within 20 to 35 % throughout sampling periods. A partial trend with odour concentration was exhibited by the dry summer litter from week 4 to week 8 but no significant trend was observed for the wet summer litter.

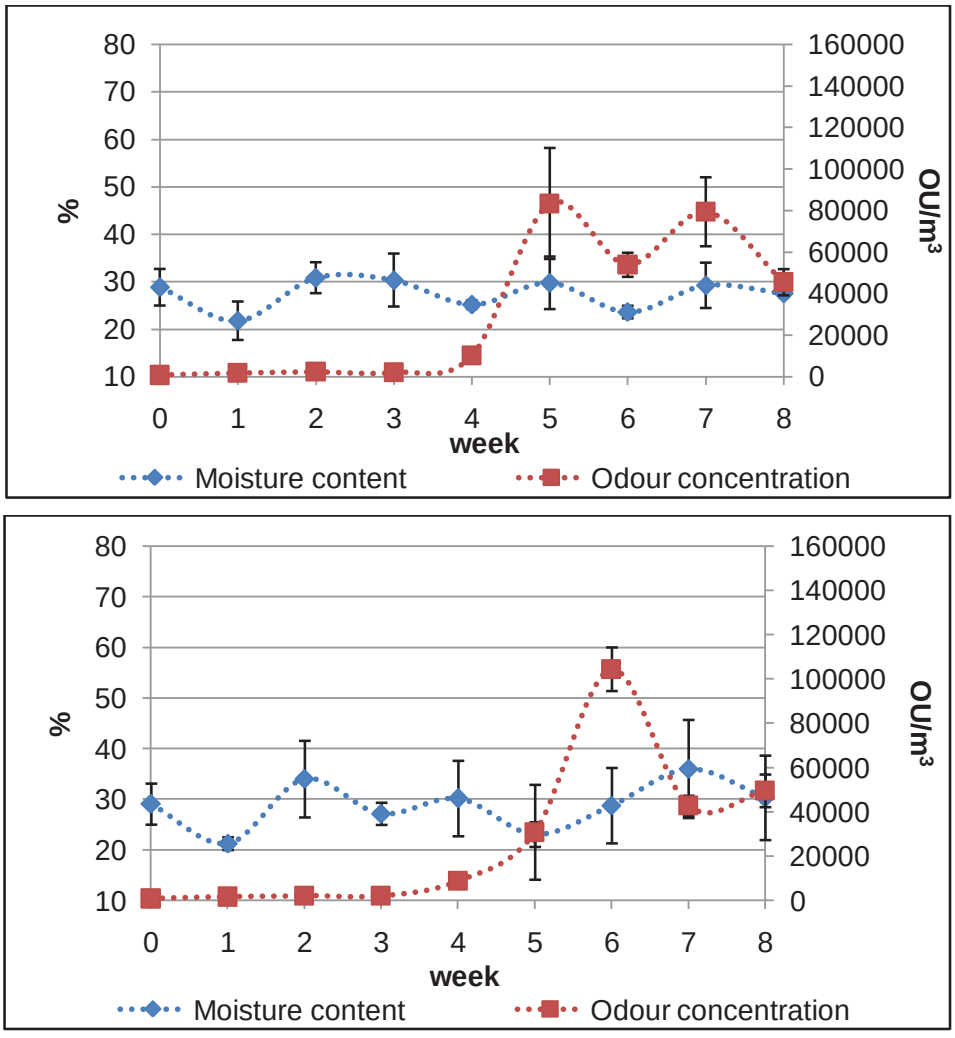


Figure 4.6 Variation of moisture content with odour concentration in summer dry (top) and wet (below) litters.

The pH estimations obtained from sampling periods correlated well with previously published data [188], increases in litter pH from the initial to the post harvest weeks ranged from 6.5 to 8.5 depending on materials used as the litters. The dry winter litter pH values progressed comparably with odour concentrations before decreasing from week 4 to week 7. Whereas the wet winter litter displayed a consistent trend, decreasing in pH values with increasing odour concentrations throughout the broiler growth cycle (Figure 4.7). During the sampling stages, the lowest pH was recorded for the wet winter litter in week 5, which was probably attributed to the association of highest moisture content and greater deposition of manure in litter that caused acidic characteristics in the litter [158].

The initial litter pH values for the summer litters (Figure 4.8) exhibited similar values to the winter litters even though the litter material types used in both seasons were different. During summer, the dry litter pH increased from week 1 with increase in odour concentration until week 5 when the highest value detected in week 6, corresponding to a decrease in odour concentration. Meanwhile the summer wet litter, increased from its initial pH value until week 3 before decreasing in week 4 that can be related to an increase in litter odour concentration.

Figures 4.9 and 4.10 illustrate the association of litter pH and moisture content of litters with odour concentrations throughout the broiler growth cycle. Reasonably strong coefficients of correlation were obtained for the winter litters samples compared to the summer litters. Sufficient correlation between moisture content and odour concentration were identified in the wet winter litters while dry winter litter showed better association between pH and odour concentration. Considerably low or no correlations for pH and moisture content with odour concentration were observed in the summer litters except for dry summer litter that showed a low correlation for pH with odour concentrations. Neither pH nor moisture content was found corresponding with odour concentrations in the wet summer litter.

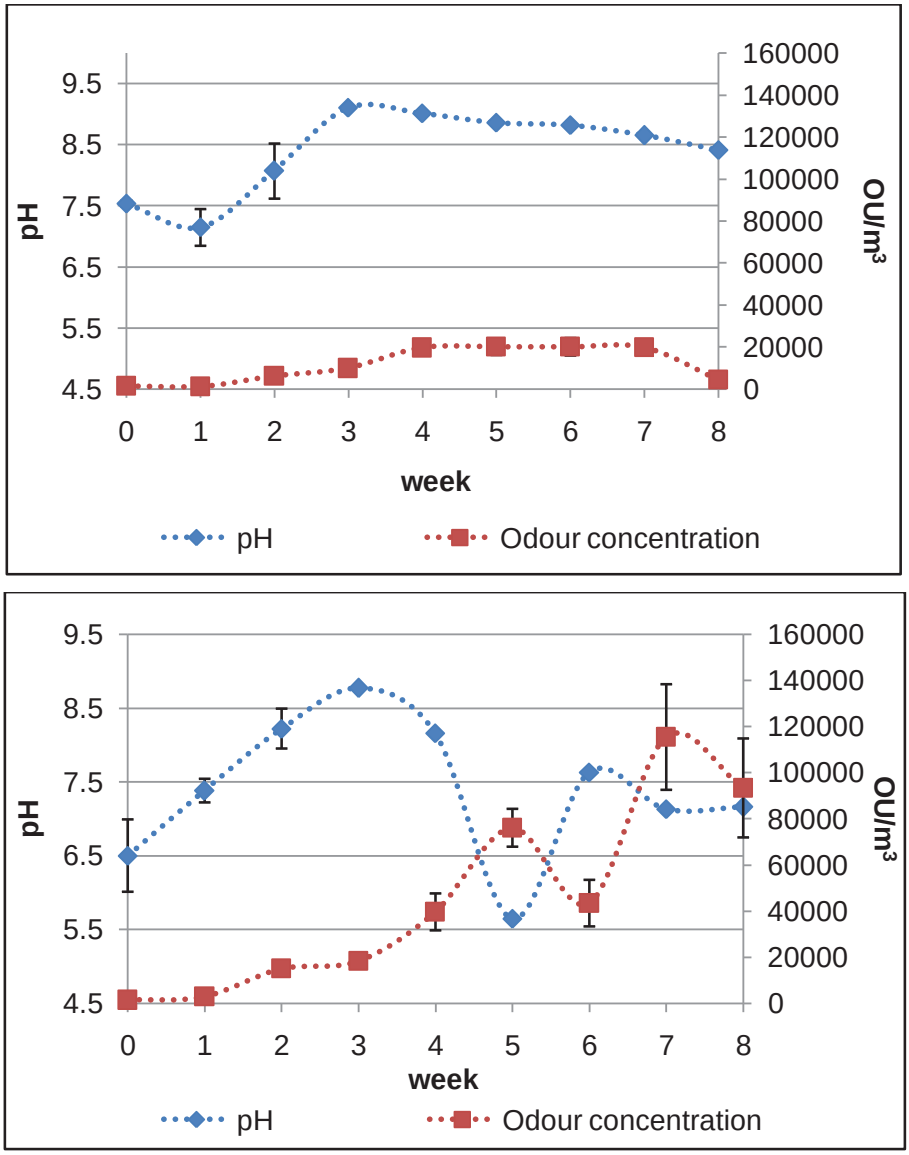


Figure 4.7 Variations in pH with odour emission for winter dry (top) and wet (below) litters.

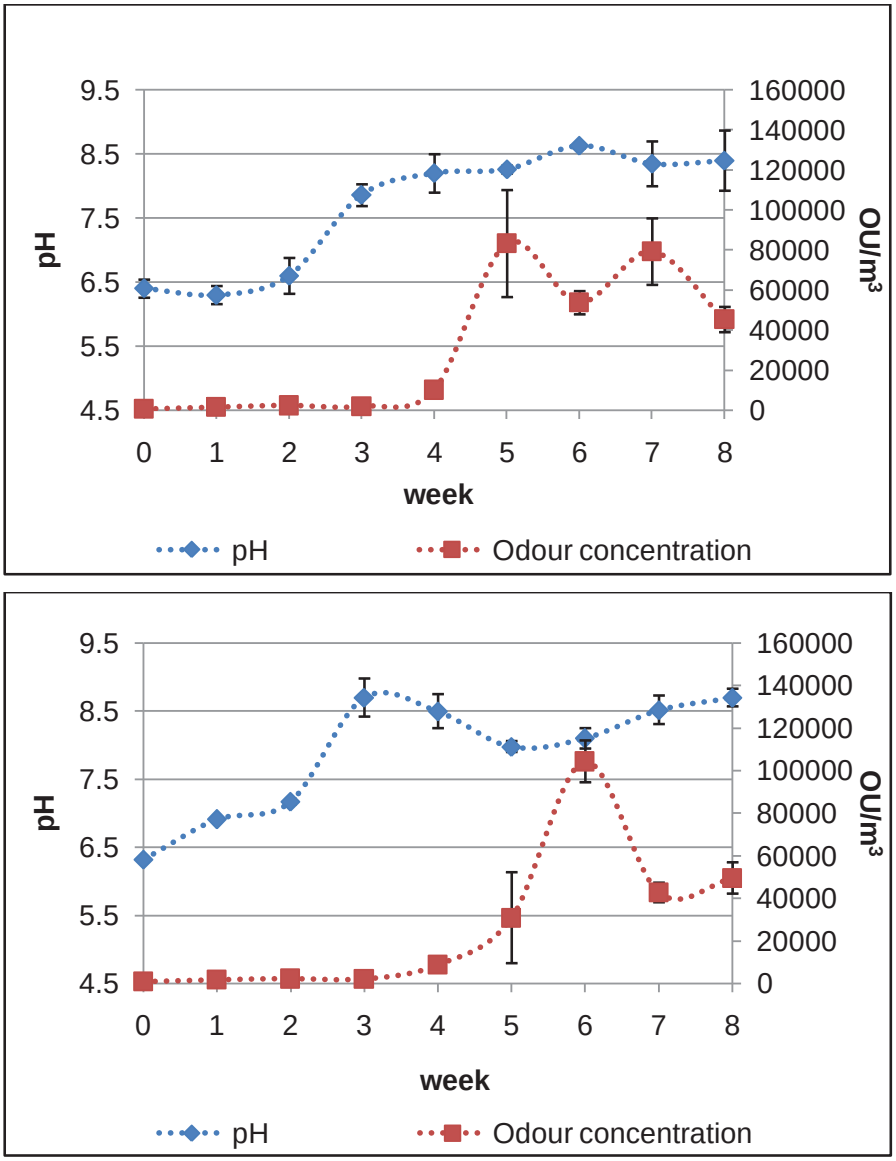
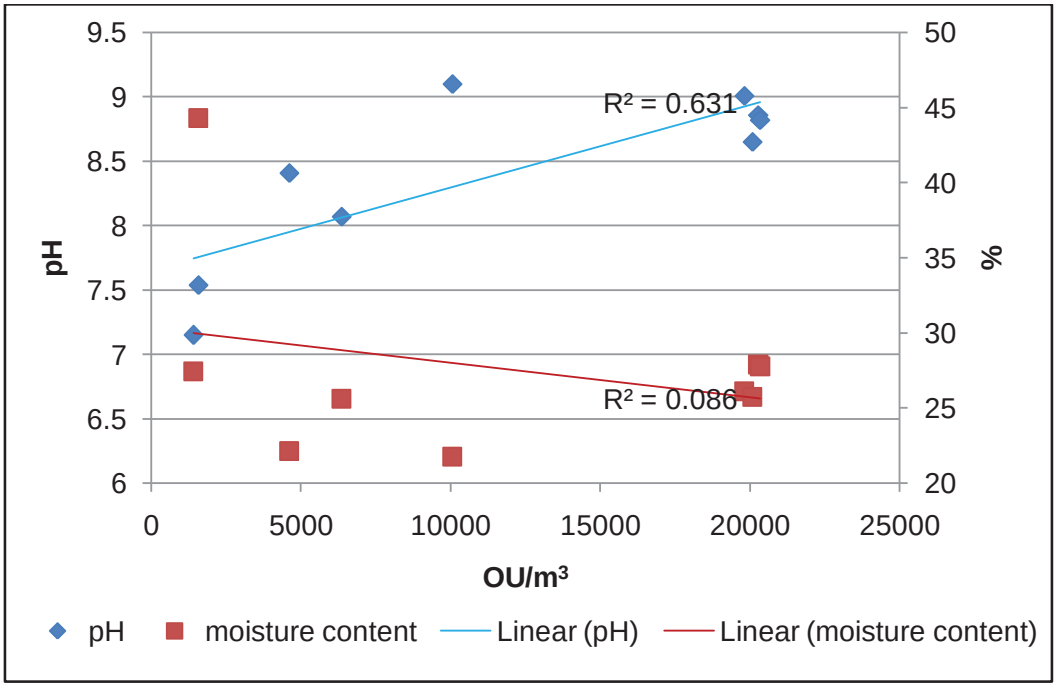


Figure 4.8 Variations in pH with odour emission for summer dry (top) and wet (below) litters.



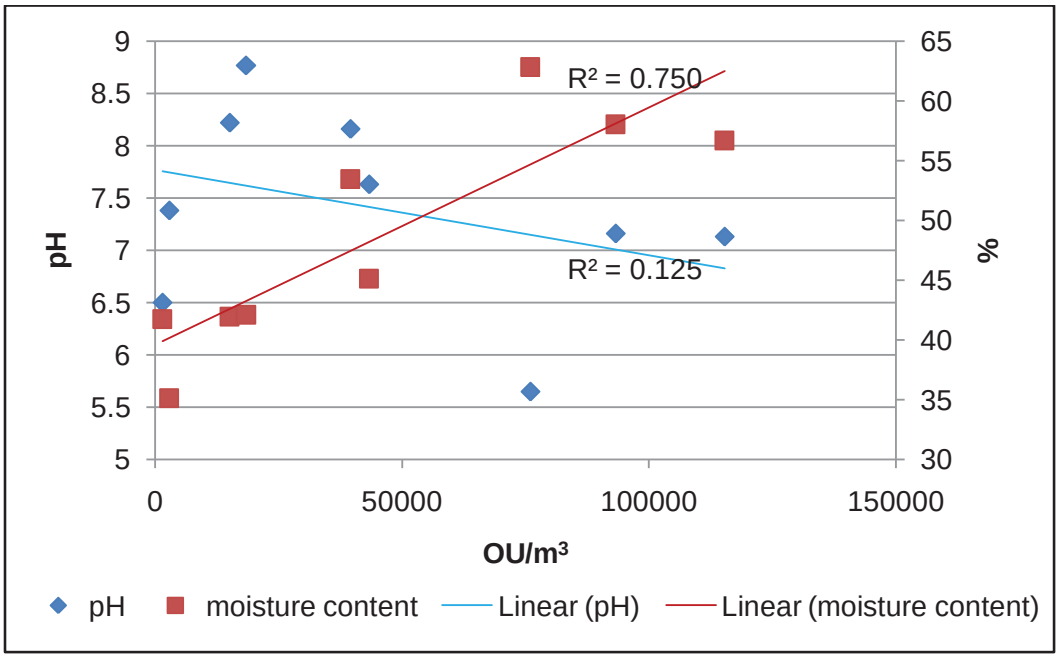


Figure 4.9 Correlation of moisture content and pH with winter dry (top) and wet (below) litter odour concentrations.

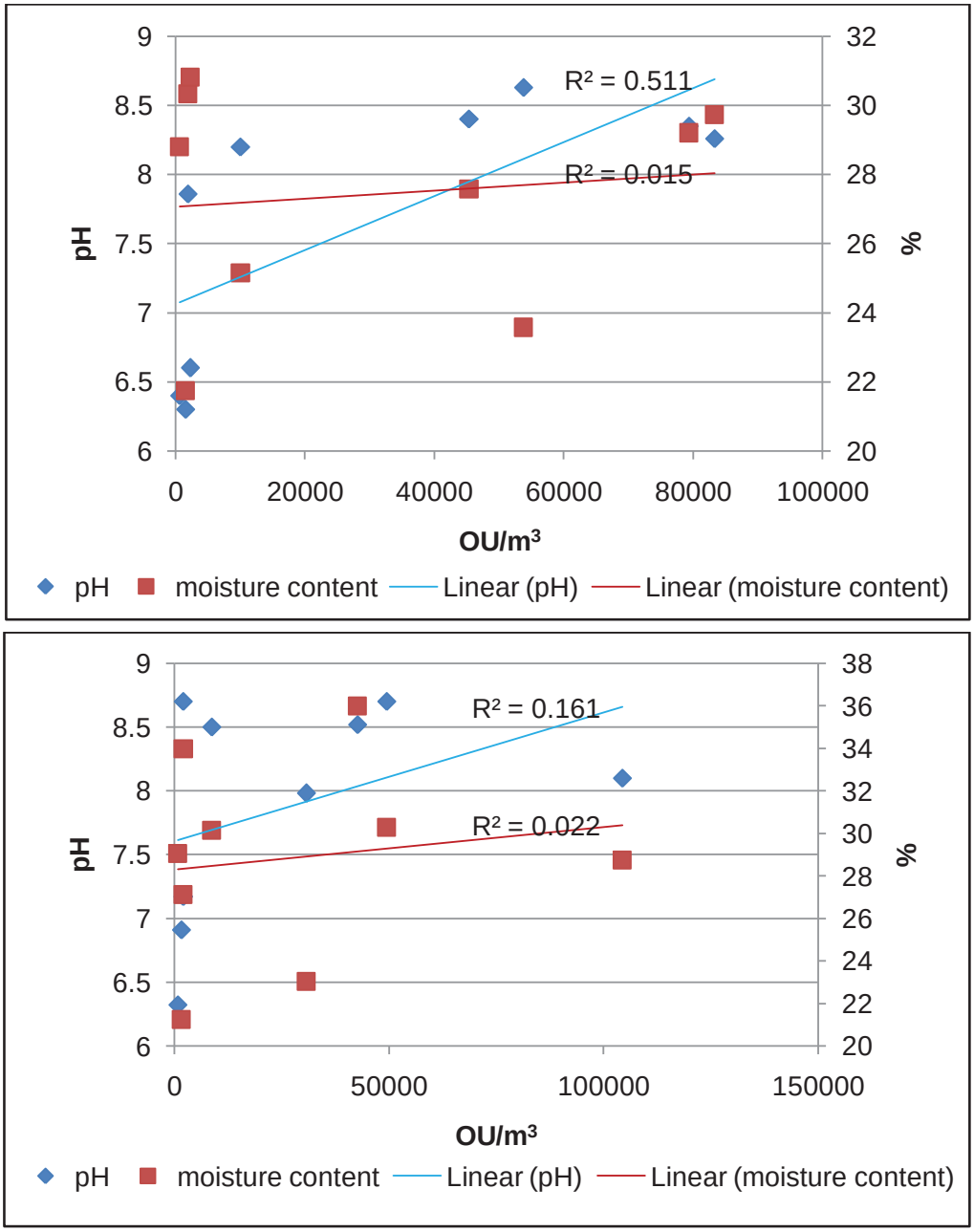


Figure 4.10 Correlation of moisture content and pH with summer dry (top) and wet (below) litter odour concentrations.

4.5 Summary

Dynamic dilution olfactometry analysis was successfully conducted on winter and summer broiler litter odour samples, providing the dynamicity of emissions during broiler production cycle. In general, both climate (summer and winter) litters showed rapid increase in odour concentration (and odour emission rates) from week 1 to week 5 except for the wet summer litter, which progressed at steady increase throughout the broiler growth. Odour concentration obtained for the winter litters ranged from 1421 to 20356 OU/m^3 in the dry litter and from 1539 to 115372 OU/m^3 in the wet litter. Meanwhile during the summer sampling, the dry and wet litters exhibited odour concentrations ranging from 604 to 83344 OU/m^3 and from 812 to 104379 OU/m^3, respectively. The greatest amount of odour emission encountered during the sampling study for the winter and summer litter was from the caked wet broiler litter that sustained high amount of water and low pH value. Maturing birds and deposition of manure and other biological fluids and solids substantially transformed the water content and pH of the litters, which subsequently altered the physical, chemical and microbial properties of the bedding material and the emission of odours.

Among the variables investigated, bird's body mass corresponded strongly with odour concentrations for both sampling seasons. Wet winter litter moisture content exhibited an adequate correlation with the odour concentration whereas dry litter showed a better association between the litter pH and the odour concentration. No significant impacts for season, bedding types and the number of birds on odour concentration were identified during the investigation. As previously reported in the literature, this study suggests that odour concentration (and therefore emission rate) can be minimised with proper maintenance of the litter moisture content and drinker systems as these systems were observed to be the most likely cause of the wet litter during winter sampling. Alternatively, the shortening of the length of production cycle to five weeks instead of seven weeks will further prevent the formation of odorous emissions, concurrently reducing manure depositions and litter pH amendments.

CHAPTER FIVE

Chemical Analysis of Emission from Broiler Litter

5.1 Introduction

The chemical composition of odorous emissions from broiler production and in general poultry operations is limited. Most livestock studies have focused on piggery and dairy emissions and have measured the chemical composition as the emission is ventilated from the facilities and not at the source point. This study aims to perform headspace thermal desorption-gas chromatography-mass spectrometry/olfactory (TD-GC-MS/O) analysis on winter and summer broiler litters to determine the key odorants responsible of obnoxious odour emissions in the tunnel ventilated broiler sheds. Volatiles from litters were collected by employing sorbent tubes and direct dynamic headspace sampling prior to characterisation using TD-GC-MS/O analysis. This study will provide information on the development of headspace TD-GC-MS/O method using selected standard solutions for speciation of broiler litter odorants. Only odorants with substantial odour intensity levels of respective collections are discussed herein relating their significance with dynamic dilution olfactometry assessment obtained from the previous chapter. In addition, complete lists of volatiles that exhibit a strong odour quality throughout the sampling campaigns, comparing sampling technique and litter material types across the broiler growth cycle of winter and summer climate and their chemical structures are shown in Appendix A, Appendix B and Appendix C accordingly. Appendix D and Appendix E display calibration results of sorbent tube and direct headspace sampling using external standard solution.

5.2 Development of headspace TD-GC-MS/O analysis

5.2.1 Laboratory calibration of headspace TD-GC-MS/O technique

A direct headspace sampler coupled to a TD-GC-MS/O was validated for efficacy in chemical speciation, repeatability and reproducibility to monitor variations in volatiles at ambient environment. The assessment was anticipated to provide information on the sample quantity and extraction time in order to identify the breakthrough sampling time during direct headspace sampling. Simultaneously, the validation of direct headspace technique was compared with sorbent tube extraction under identical GC conditions using standard solutions consisting of common odorants reported in poultry facilities. The calibration curves obtained for the responses by the analytical instrument for the standard mixtures are shown in Appendix D and Appendix E for sorbent tube and direct dynamic headspace, respectively. As a basic requirement to determine background noise, all sorbent tubes and direct sampling vessels were screened thoroughly for contamination before use. Figure 5.1 and Figure 5.2 show the spectra of blank samples and the chemicals encountered from background analysis are shown in Tables 5.1 and 5.2.

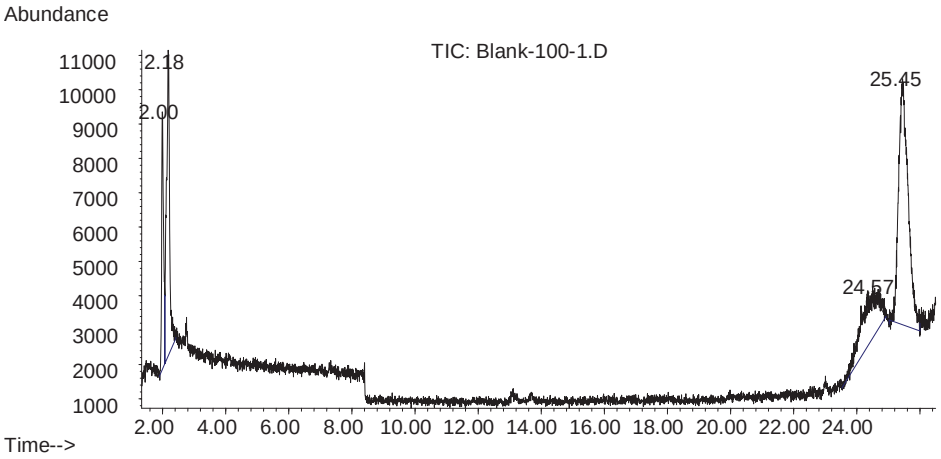


Figure 5.1 TIC of blank Tenax TA sorbent tube.

Table 5.1 Volatiles of blank Tenax TA sorbent tube.

Retention time (min)	Compounds
2.00	Ethylene oxide
2.18	Carbon dioxide

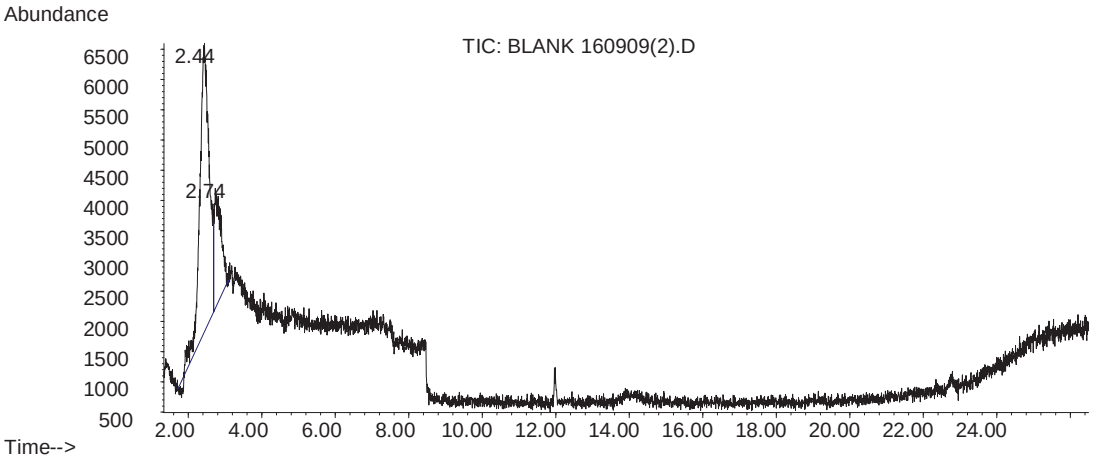


Figure 5.2 TIC of empty direct sampling vessel.

Table 5.2 Volatile obtained from empty direct sampling vessel.

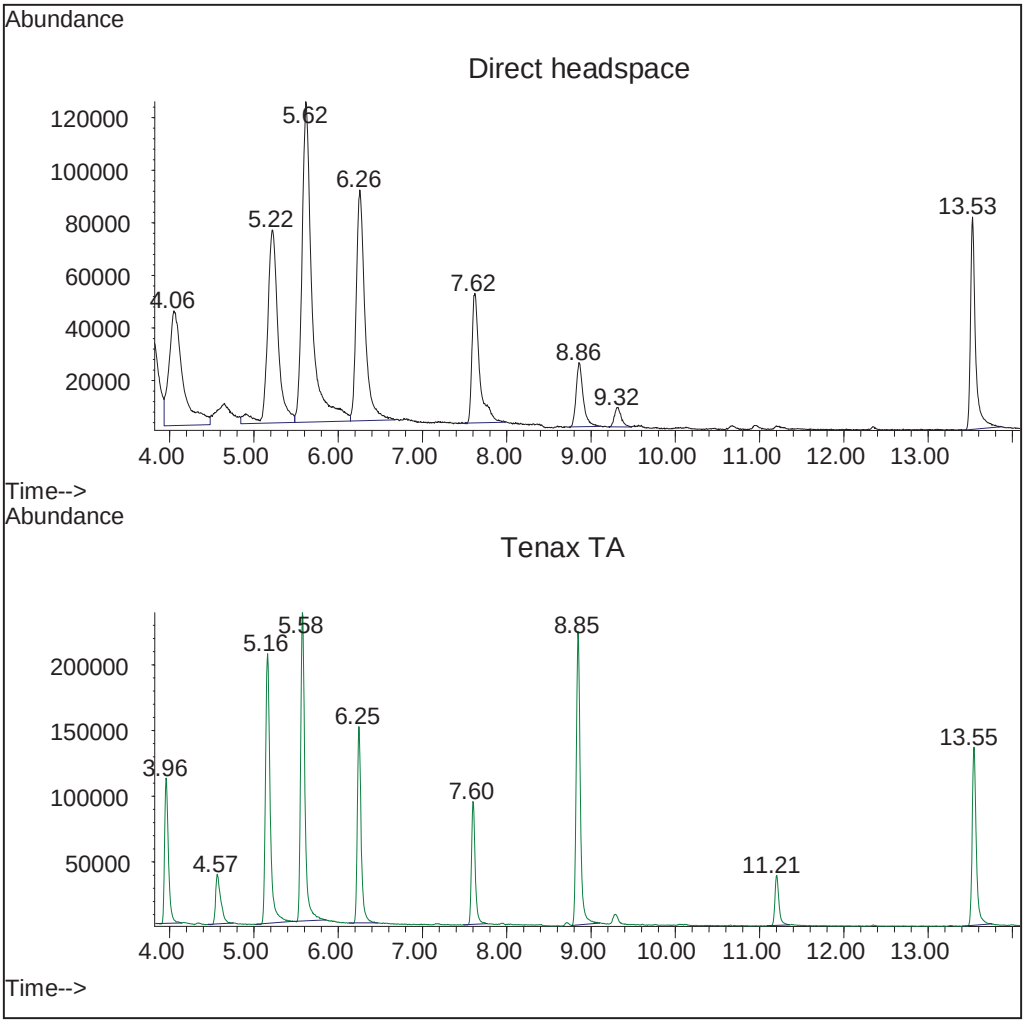
Retention time (min)	Compounds
2.44	Carbon dioxide

For direct headspace extraction, volatiles were swept using purge gas onto the cold trap for 3.5 min. The pre-concentration time chosen showed sufficient extraction of the sample with post blank tests revealing high recovery of volatiles. Shorter extraction time employed on standard solution provided for poor matching of volatiles identified by the mass-spectrometry library. Meanwhile, longer sample extraction with direct headspace sampling contributed to overloading of volatiles onto the cold trap and the GC system. This was visible with poorly separated 'shark fin' shaped volatile peaks noticed on the total ion chromatogram of GC. However, the extraction time is highly subjected to changes depending on the rough estimation of sample concentration, especially for environmental based samples.

Both sampling techniques were observed to successfully discriminate all chemicals tested during validation stage at varying concentrations. Using the direct headspace, all volatiles were determined effectively at concentration as low as 50 ppmv except for acetone, 3-hydroxy-2-butanone and butanoic acid that required higher concentrations. Two important aspects owing to this circumstance are a) further dilution with purge gas during sampling of volatiles onto the cold trap that reduce the concentration of substance and increase the detection limits in the GC system and b) the co-efficiency of a substance to volatilise from a condensed sample phase to the headspace gas phase. The sorbent tube method revealed all chemicals at concentration of 50 ppmv. It is important to note that the volume of samples injected between sampling procedure differed attributed to varying sample pre-concentration technique on the cold trap, hence both extraction techniques are inadequate to be compared directly for chemical quantitative information.

The extracting techniques can therefore be compared for volatiles qualitative information. The occurrence of elucidating volatiles' retention time from the GC system appeared to be consistent between the sampling methods, also presenting the reliability of the GC system in responding to the chemicals tested. Figure 5.3 shows comparatively similar occurrence of odorants' retention times between the

two sampling techniques used. The analysis of variance showed adequate repeatability of the extraction methods with insignificant differences (P>0.05) traced (Figure 5.4). In addition, the GC-MS/O system responded efficiently in discriminating the variation in volatiles abundances (Figure 5.5) and perceived odour intensity corresponding to differing standard solution concentrations.



Retention time (min): 4.06 =3-methyl-2-butanone, 4.57 = 2,3-butanedione, 5.22 = alpha pinene, 5.62 = toluene, 6.26 = dimethyl disulfide, 7.62 = 1-butanol, 8.86 =limonene, 11.21 = 3-hydroxy-2-butanone, 13.53 = dimethyl trisulfide

Figure 5.3 Spectra of standard solution with significant similarity in retention times of volatiles.

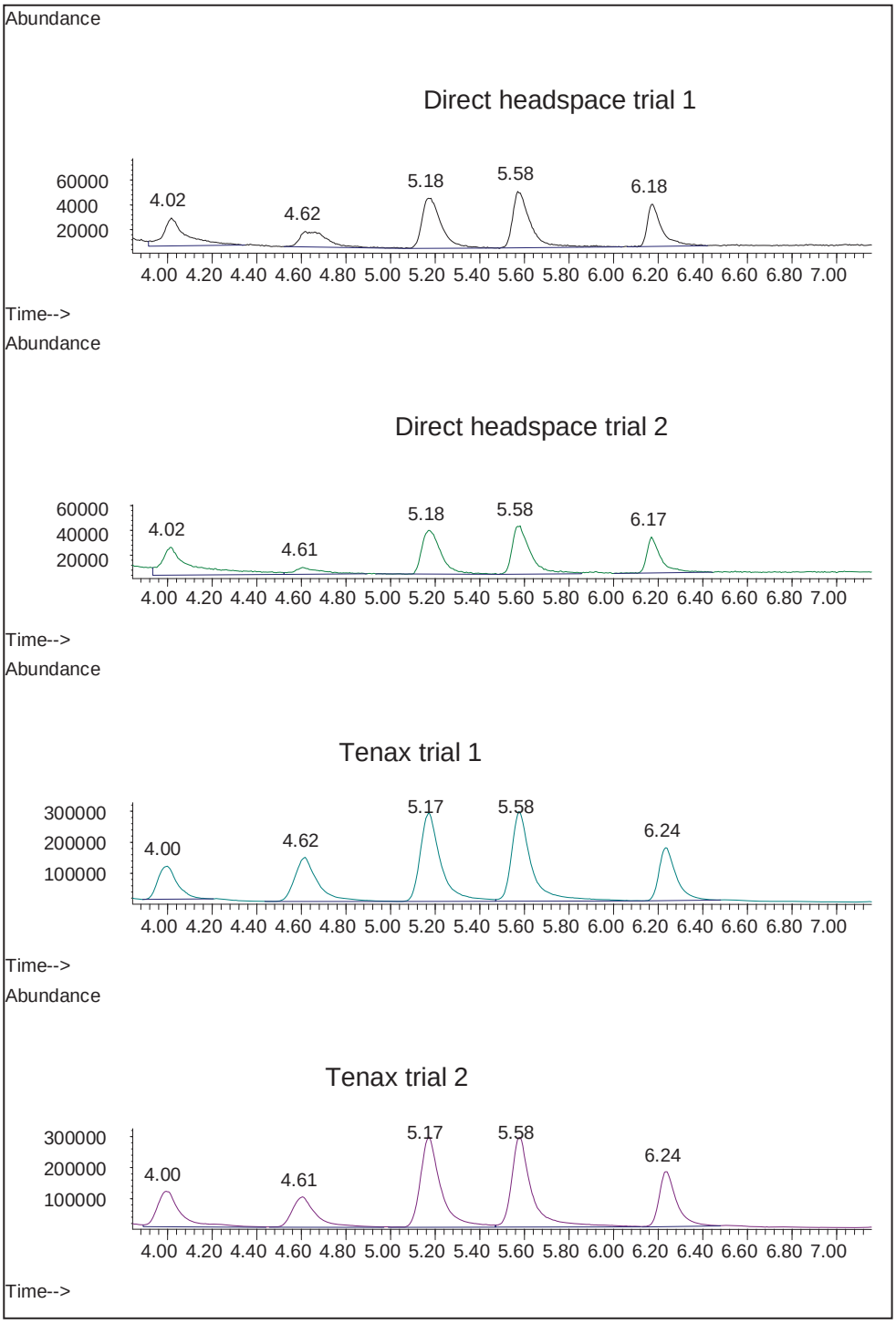
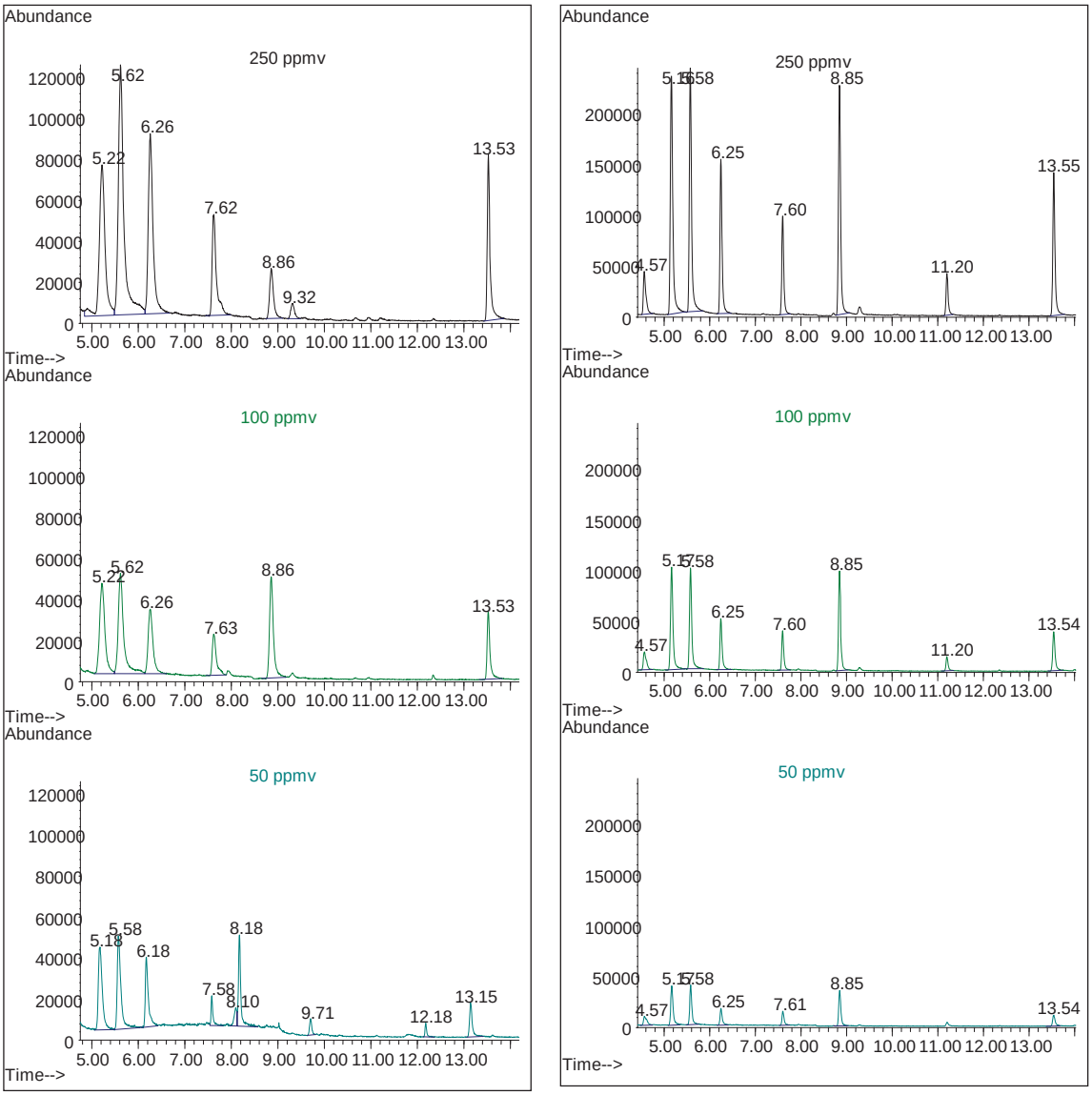


Figure 5.4 Consistency in volatiles retention time and abundance reflecting on the reliability of sampling and analysis system obtained using 50 ppmv standard solutions.



(a) Direct headspace

(b) Tenax TA

Figure 5.5 TICs of standard solutions with significant differences exhibited with increases in standard solution concentrations (P<0.05).

Table 5.3 shows comparison of olfactory responses for standard solution via direct headspace sampling and sorbent tube under identical GC-MS/O parameters. The olfactory responses produced for both sampling technique provided similar description of odorants but varied in terms of intensity attributed to varying abundance of respective chemicals sampled. During the olfactory assessment, intensification in the strength of perceived odorants with increases in the concentration of the volatiles is not essential for all volatiles as some odorants require larger difference in concentrations to exhibit changes in their perceived odour intensities. Procedure used to determine volatiles of potential odorants is shown in Figure 5.6 and Figure 5.7. The total ion chromatograms are overlaid with olfactory responses (osmegram) to match odorants according to overlapping retention times.

Table 5.3 Olfactory responses of standard solutions obtained for direct headspace and sorbent tubes (Tenax TA).

Compounds	Olfactory responses					
	50 ppmv		100 ppmv		250 ppmv	
	Direct	Tenax	Direct	Tenax	Direct	Tenax
acetone						
2-butanone			solvent		solvent	solvent
3-methyl-2-butanone		solvent			chemical	sweet solvent
2,3-butanedione		rotten cabbage	rotten cabbage	rotten vegetable		rotten vegetable
alpha.-pinene	smoky solvent	pinene	pine	pine	pine	pine
toluene	solvent	solvent	pleasant chemical	solvent		solvent
dimethyl disulfide	chemical	smoky	chemical	smoky	chemical	foul
1-butanol	smoke		solvent	alcohol	foul	foul
limonene	citrus	lemonish	solvent	alcohol	foul	lemonish
3-hydroxy-2-butanone		ash	musty	ash		musty
dimethyl trisulfide	putrid, ferment	putrid, ferment	putrid, ferment	putrid, ferment	putrid, ferment	putrid, ferment
acetic acid	vinegar	foul	smoke	vinegar	vinegar	foul
butanoic acid	rancid	cheesy, rancid	rancid	cheesy, rancid	rancid	cheesy

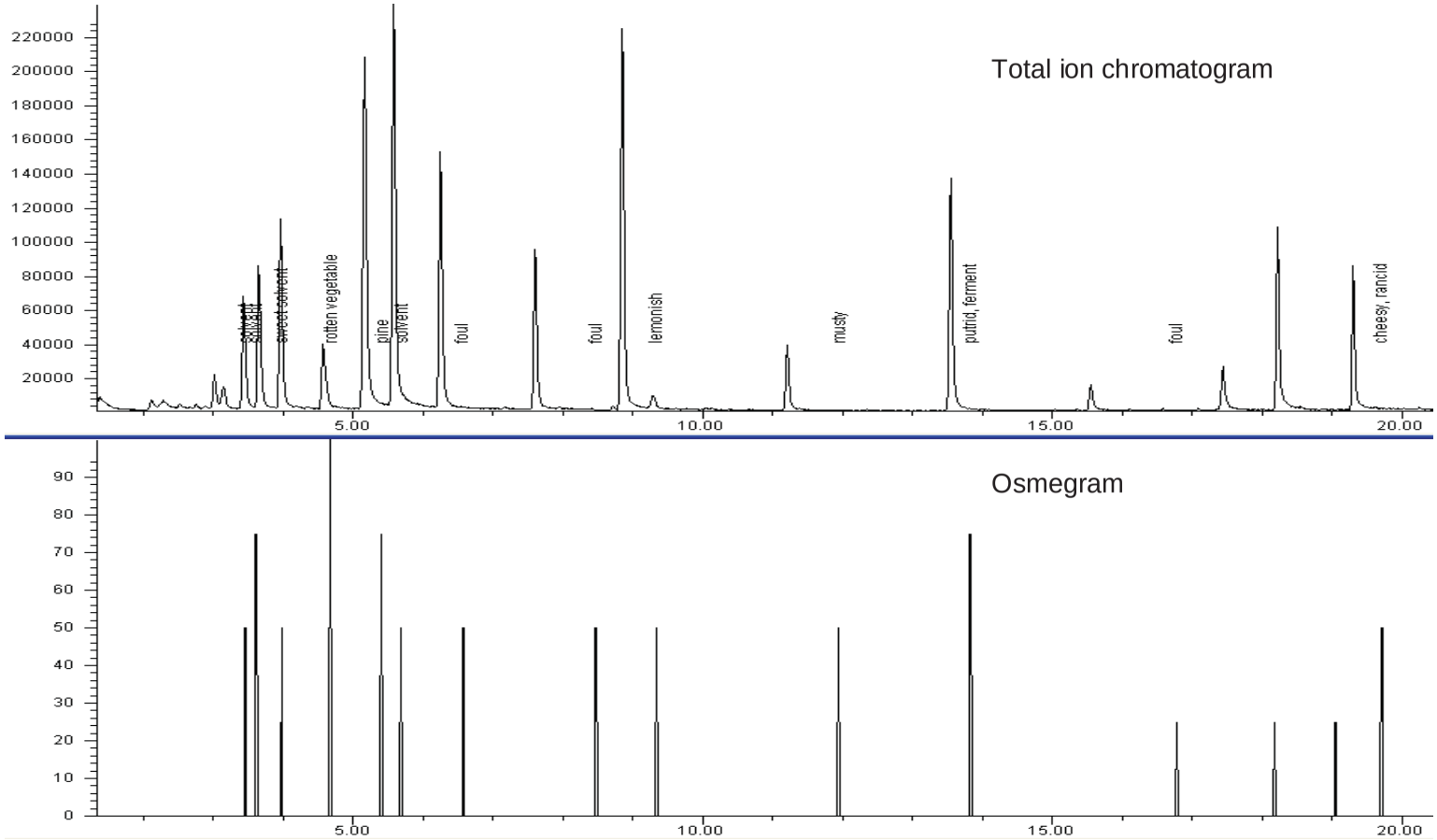


Figure 5.6 Comparison of TIC and osmegram identifying potential volatiles with odour properties of standard solution using Tenax TA sorbent tube method with descriptions of respective volatiles noted on TIC.

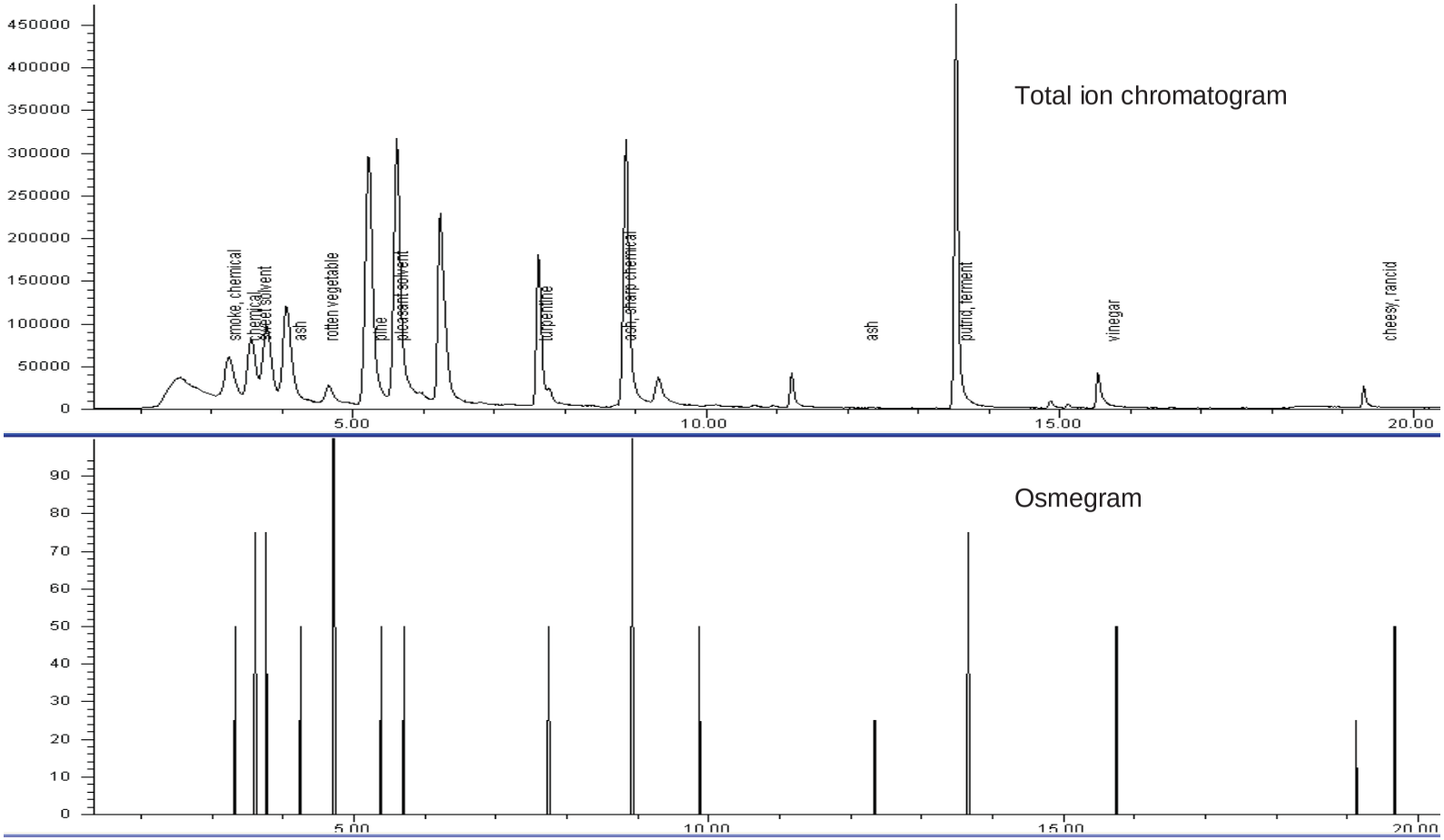


Figure 5.7 Comparison of TIC and osmegram identifying potential volatiles with odour characteristics of standard solution using direct headspace extraction with descriptions of respective volatiles noted on TIC.

5.2.2 Broiler litter odour sampling

Owing to repeatability and reproducibility demonstrated during the sampling and analysis technique validation, both direct headspace and sorbent tube extraction methods coupled to TD-GC-MS/O system were implemented in this study to characterise the odorants from broiler litter samples. In addition, the effort is anticipated to provide information on the selectivity of chemicals captured using varying sampling techniques since livestock odour contains complex mixture of odorous and non odorous substances.

5.2.2.1 Direct dynamic headspace sampling

The direct dynamic headspace sampler validation provided a simpler and rapid platform to analyse volatiles emitting from the headspace of broiler litters. The significant advantage of the direct headspace is the potential of the technique to collect volatiles released from odour source with minimal sample preparation than of the use of solvents in liquid extraction that tends to reduce the absolute identification of volatiles emitting from a matrix as some diluents potentially retain volatiles. Instead, direct headspace sampling employed herein to pre-concentrate volatiles directly from the litter sample onto cold trap at ambient temperature eliminates the need for solvent extraction during the collection of volatiles. This allow for a robust extraction and speciation of numerous volatiles from litter in original form without any alteration made on sample matrix besides reduction in the time required for volatiles collections prior to GC analysis.

During application of direct headspace extraction for litters, volatilisation of chemicals was enhanced using an inert gas flow into the sampling vessel allowing increase of chemicals into the sample headspace, especially to improvise identification of volatiles existing in small quantities and concentrations in samples. Adequate sealing between the sampling vessel and headspace sampler was ensured to preventing leaking and losses of volatiles into the atmosphere during gas purge. Approximately, 175 ml of headspace gaseous sample from 100 ml of litter was pre-concentrated onto the cold trap in 3.5 min. This volume may appear to be small but suitable for highly concentrated or large amount of samples in order to prevent volatiles

condensation along the instrumental pathway and to reduce volatiles' volume breakthrough episodes. The flow rate for the purge gas was set to 50 ml/min was observed to be sufficient for litters study as no turbulent or dust was produced in the sampling vessel that concurrently avoided clogging of headspace sampler and cold trap. This was further confirmed with post blank testing conducted that appeared to be free of sample volatiles or contamination. One disadvantage identified for the direct headspace method was the difficulty in analysing excessively wet samples that subsequently increases humidity in the headspace of sample vessel. Extremely wet samples may not be suitable for direct headspace sampling on the graphitised cold trap used for study as the cold trap has the tendency to collect moisture during pre-concentration stage, thereby reducing the resolution of GC-MS chromatogram. Probably application of reduced sample volume and time may allow the study of immensely wet samples using direct headspace sampler.

5.2.2.2 Sorbent tube sampling

Extraction of volatiles using sorbent tube promotes collection of emission samples at ambient field conditions that are influenced by meteorological aspects. The sorbent tube features allow transportation of volatiles from sampling sites for analysis in the laboratory and flexibility in sample storage periods of up to a month during restricted analysis time. In this study, sorbent tube packed with Tenax TA was selected for volatiles collection attributed to its suitability in collecting a wide range of chemical compounds. Prior to sampling volatiles on the sorbent tube, the sample matrix was purged with high purity nitrogen gas for 25 min at a flow rate of 5 L/min to enhance uniformity of volatiles in the headspace above sample during pre-concentration. Immense care was taken to optimise the purge gas flow to prevent turbulent that dumps dust and other particulate matters into the sorbent tubes. The flow rates of sorbent tube and sampling pump were calibrated adequately to maintain high quality control throughout volatile collection. The flow rate features of sorbent tube collections are significantly important to determine variations in volatiles qualitatively and quantitatively. Approximately 3 L of litter odour was pre concentrated on Tenax TA each time. Tubes loaded with volatiles were sealed

tightly and wrapped with aluminium to avoid ingression of contaminants. Sealed sorbent tubes were refrigerated prior to sampling. Sorbent tubes involves two stages of thermal desorption before introducing the volatiles onto GC column for separation and identification.

5.2.3 Broiler litter odour analysis technique (TD-GC-MS/O)

Samples obtained from headspace extractions were pre-concentrate on a general graphitised carbon cold trap placed in the thermal desorption unit. The introduction of analytes onto GC column occurred in either single stage or two stages thermal desorption procedure, depending on method of volatiles collected. Since direct headspace concentrates volatiles directly onto the cold trap, this technique only requires single stage thermal desorption which is at the cold trap to release the trapped volatiles into the GC system. Meanwhile for sorbent tube collection, volatiles trapped onto sorbent material were desorbed to be pre-concentrated onto the cold trap where a second thermal desorption occurs to introduce volatiles onto GC column. A temperature elevated flow path connection consisting of fused silica was used to link the thermal desorption unit and the GC-MS/O system. Increased temperature and appropriate carrier gas flow rate are required to transfer volatiles onto GC column while reducing the condensation of analytes along the transfer pathway. However, extreme precaution was practised during temperature setting at all levels during thermal desorption processes to prevent oxidation of volatiles attributed to exposure to high temperature.

5.2.4 Headspace TD-GC-MS/O analysis of broiler litter odorants

The benefit of using GC-MS/O is the identification of volatiles responding to chemical abundance and olfactory responses simultaneously. The solvent free extraction techniques were observed to sustain the original composition of litter materials while preventing formations of artefacts. In addition, the collaborated sampling and analysis techniques significantly exhibited prominent discrimination of volatiles from dry and wet litter samples with varying physical conditions throughout broiler production in winter and summer climates, resulting in identification of a diverse range of volatiles and odorants (Figure

5.8). The duplication of litter samples collected during direct headspace and sorbent tube revealed adequate repeatability and reproducibility of volatiles (Figure 5.9) with analysis of variance demonstrating insignificant difference ($P>0.05$). The occurrence of volatiles was observed to be consistent in each replicates collected of similar litter samples.

In general, direct headspace sampling is to determined odour emission directly from potential odour source at its generation point. Point source volatiles generated in a facility are often predicted to be greater in number of volatiles and their abundances compared to other sections of a production and at receptor point due to degradation and dilution of chemicals. This is evident with the results obtained between sorbent tube and direct headspace. The direct headspace sampling demonstrated a greater quantity of volatiles that had at least a 10 times greater integration of peak area of odorants captured than that observed for sorbent tube extraction even though a greater volume of samples were introduced on GC column than with direct headspace sampling (Figure 5.10). During direct odorant sampling, the shorter period of gas purge at a low flow rate in a sealed vessel could have prevented dilution and improved the diffusion of odorants from the solid litter phase to the gas phase that was concurrently concentrated onto cold trap in the thermal desorption unit. Whereas the application of long period of gas purge at high flow rate to enhance uniformity of volatiles in the litter headspace may have caused the dilution of volatiles' concentration prior to loading of volatiles on sorbent bed.

Another limitation that should be taken into consideration resulting in low abundance of chemical speciation is the two stages of thermal desorption of samples collected using sorbent tube that may have degraded thermally unstable volatiles. Speciation of a greater number of volatiles from direct headspace sampling was not essential throughout the sampling stages. Instead this technique was more efficient in providing information of dominate volatiles in the litter that may contribute to odorous emission. Such information would be beneficial in selecting appropriate odour abating strategies in animal production facilities. Figure 5.11 shows an example of Tenax tube at week 5 for a wet litter

sample where the chromatogram is characterised by more ketones and alcohols, observed at the beginning of the TIC from 3 to 4.5 min, whereas the direct headspace sampling shows the greater domination of ketones (at 3-4 min and 12 min) and volatiles fatty acids (at 13 -17 min) in line with wet litter pH condition obtained for week 5. The volatiles fatty acids were identified using Tenax but at immensely lower concentration at similar retention time as direct headspace sampler.

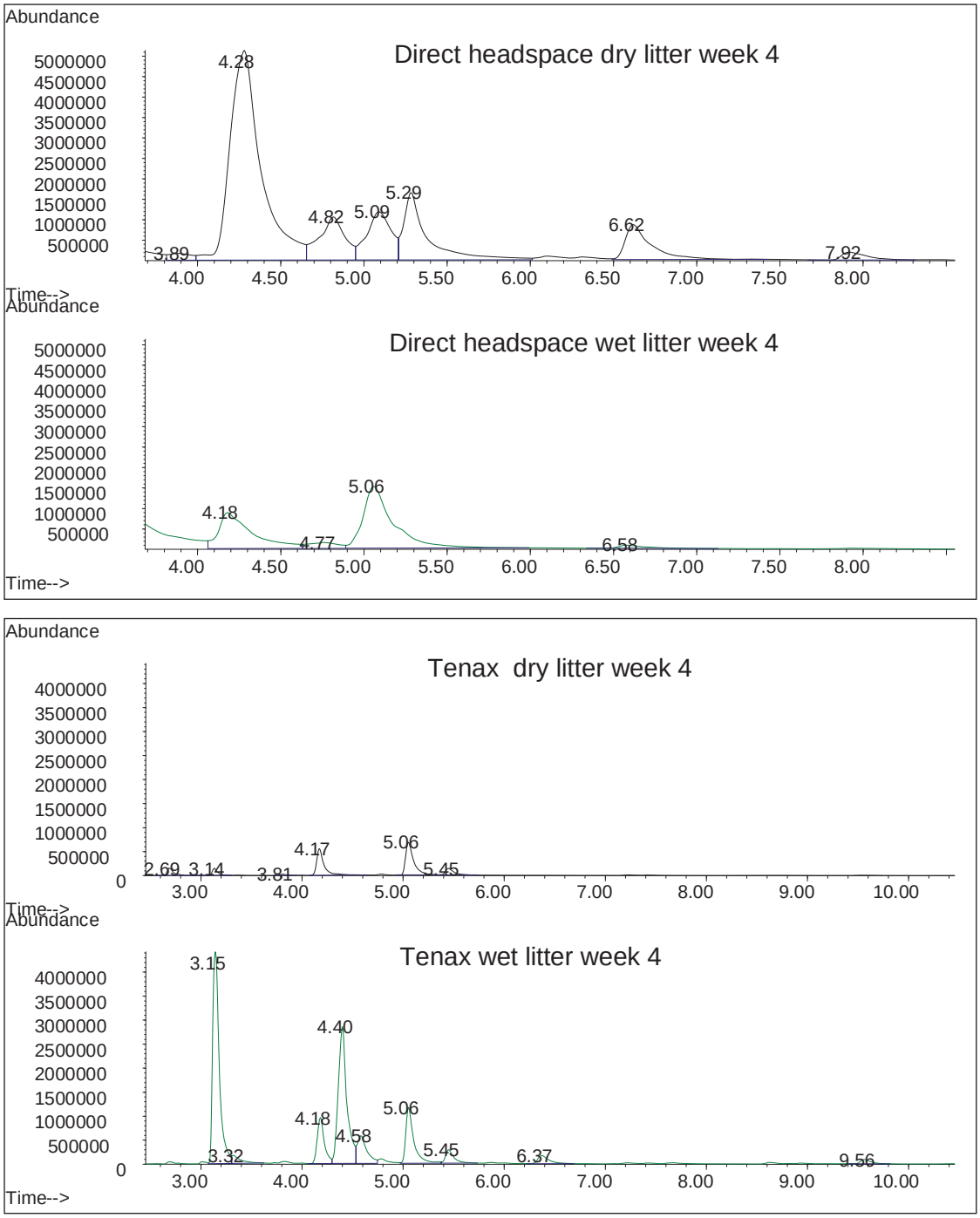


Figure 5.8 TICs present variations of dry and wet litter using direct headspace (top) and Tenax tube (below).

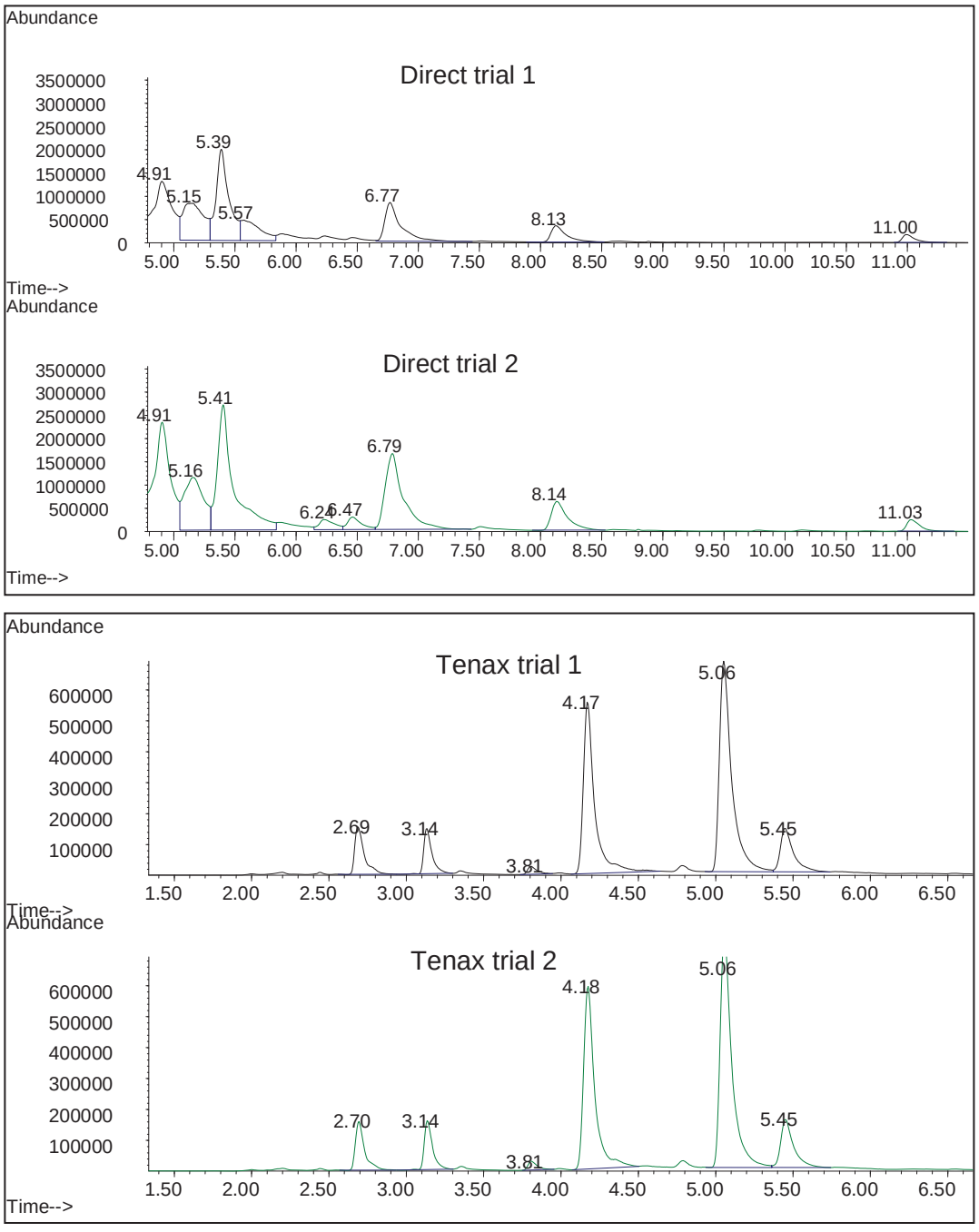


Figure 5.9 Comparison of sampling and analysis system for repeatability and reproducibility using broiler litter materials using direct headspace (top) and Tenax tube (below).

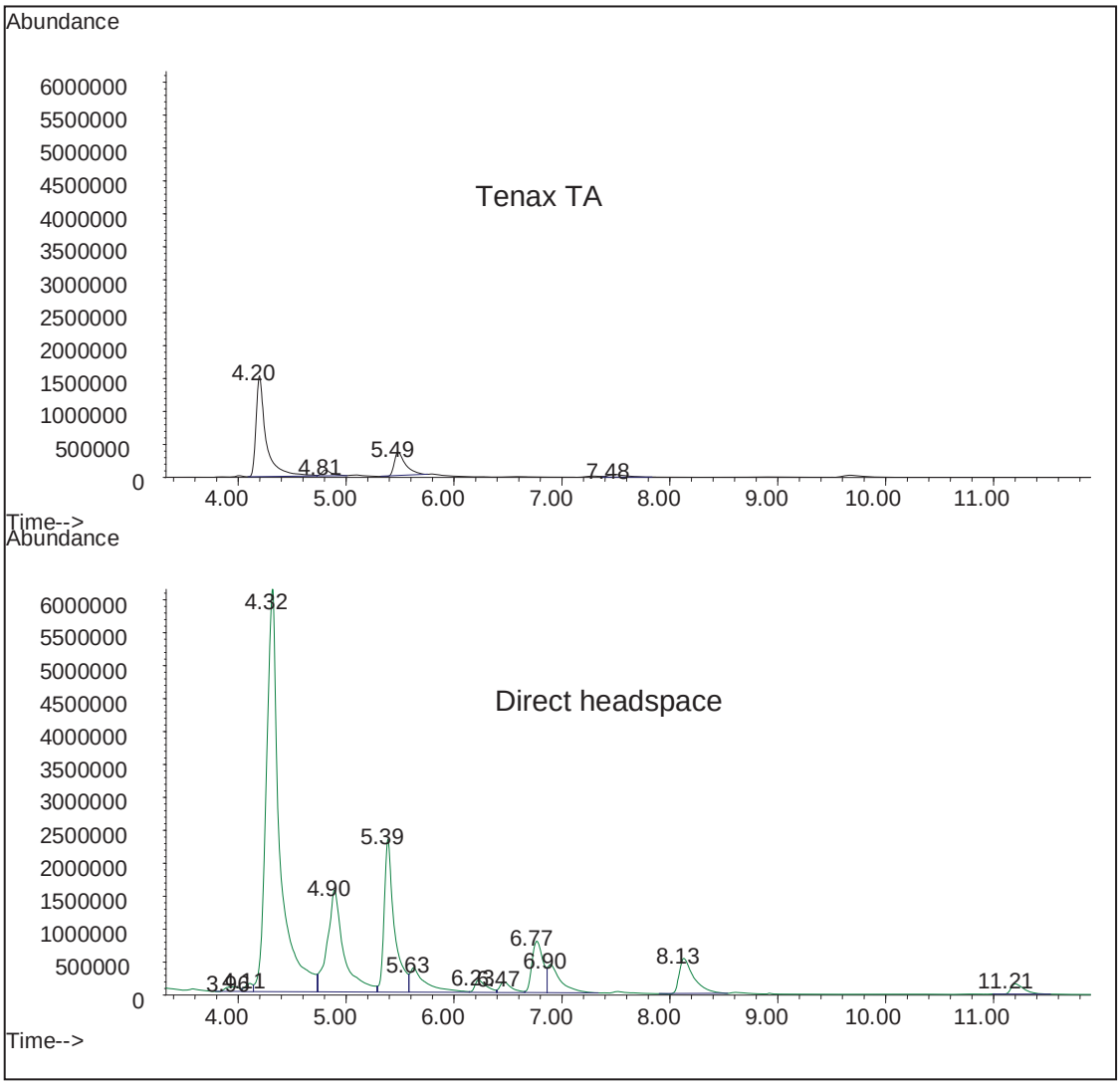


Figure 5.10 Comparison of abundance of dry litter odorants obtained for sorbent tube and direct headspace extraction.

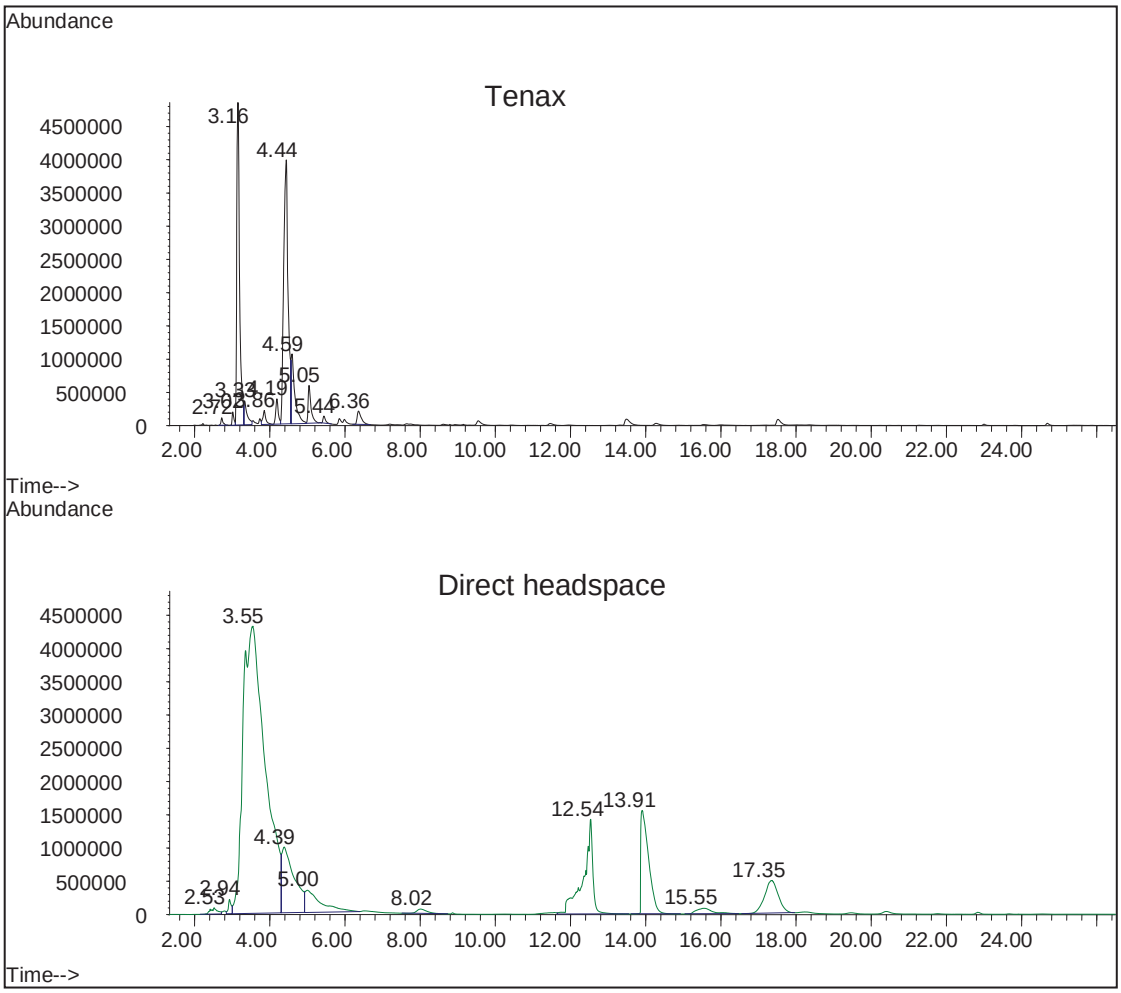


Figure 5.11 Comparison of spectra from wet litter of week 5 obtained from sorbent tube and direct headspace.

The coupling of olfactory responses data (osmegram) with total ion chromatogram yields valuable discrimination between volatiles generated with odorous or non odorous quality that can be linked to odour occurrence. One limitation of this technique is the lack of information for the overall odour concentration as the olfactory port assessment is a response due to characterisation of odour compounds as a separated technique than as a composed set. In general, the olfactory description and intensity of litter volatiles observed to transform from pleasant and mildly pleasant to obnoxious and strongly obnoxious while progressing through broiler growth period and litter types. Increases in the strength of perceived offensive odorants from litters were anticipated with the existence of birds and accumulation of biological fluids and solids by the broilers. The odorants studies revealed a range of odorous compounds with low odour threshold limits that were identified at the olfactory detection port below the detection limits for the instrument or matched poorly with mass spectrometry library. For example methanethiol and 3-hydroxy-2-butanone are reported at trace compounds and identified at some stages due to prominent putrid and musty odour description of respective compounds at maximum rating on odour intensity scale for both winter and summer litters.

The application of direct headspace sampling for olfactory analysis generally showed the determination of more odorants at higher odour intensity perceived in line with greater abundance of volatiles concentrated onto cold trap than for sorbent tube extraction (Figure 5.12). Variation in volatiles abundance is known to simultaneously affect the odorants' characteristics and perceived odour intensity [36, 119]. Odorants rated using direct headspace sampling were prominently higher than for Tenax sorbent tube owing to large abundance of volatiles concentration (Figure 5.13).

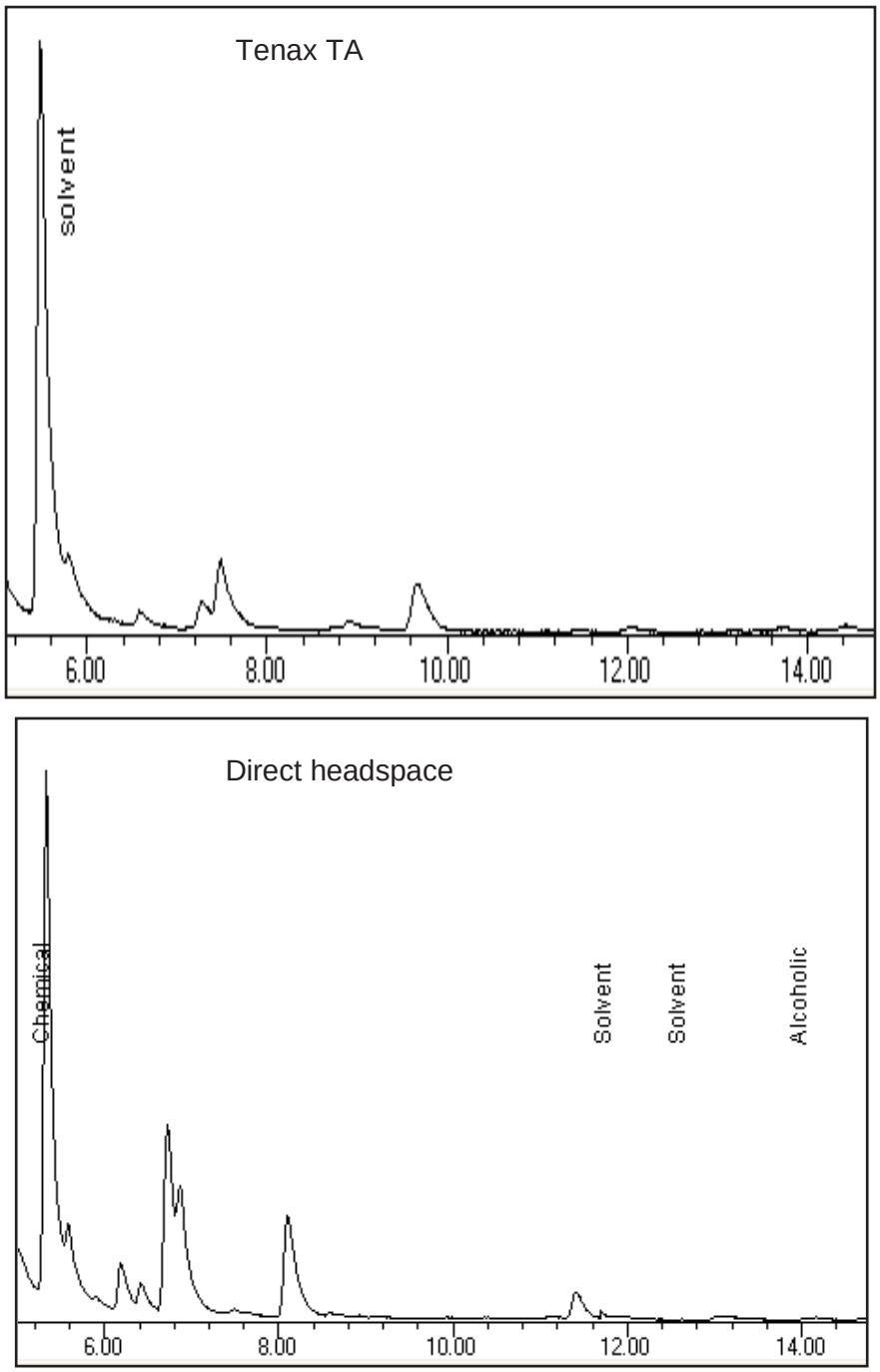


Figure 5.12 Comparison of a winter week 1 dry litter odorants showing characterisation for sorbent tube and direct headspace.

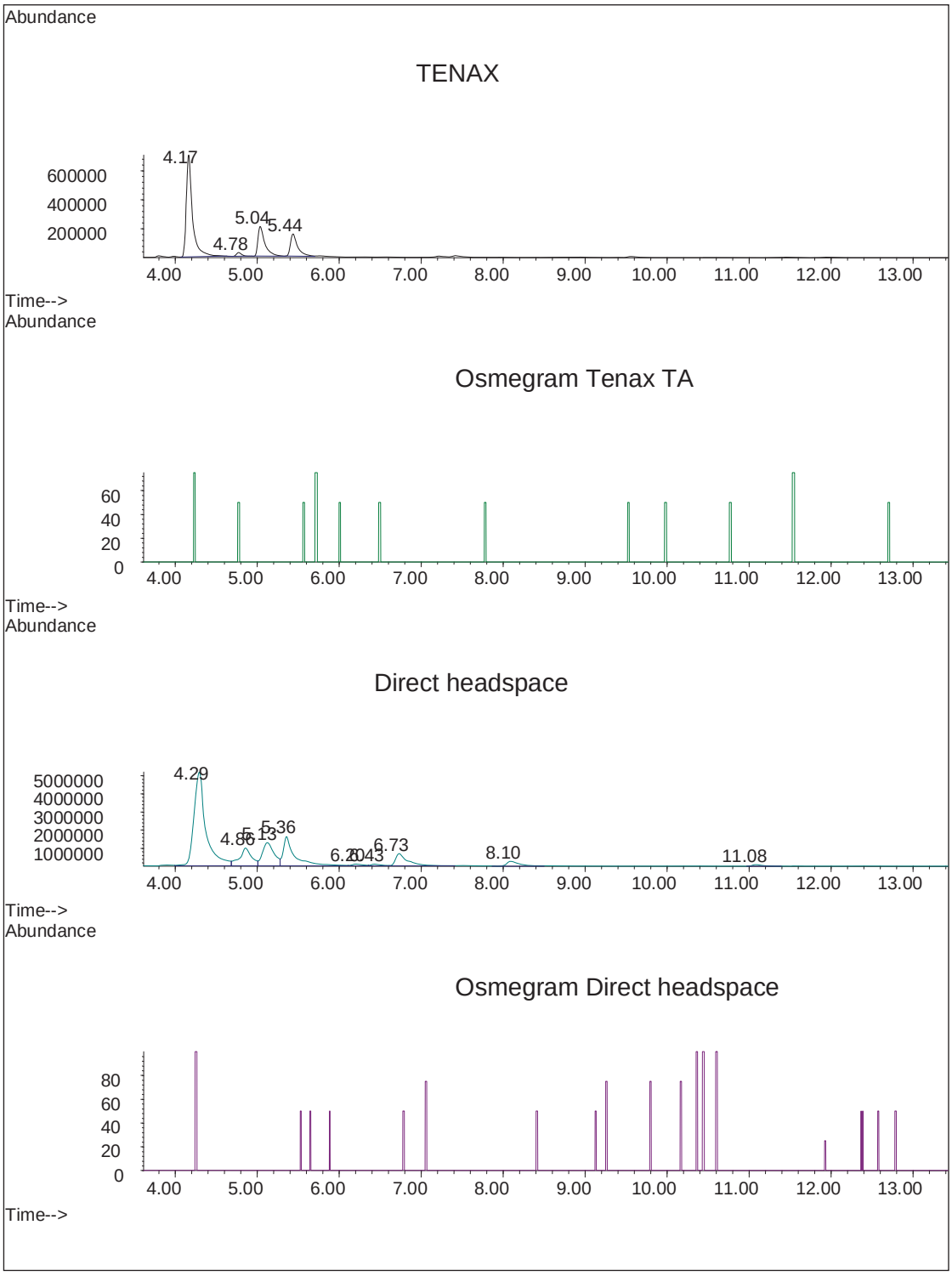


Figure 5.13 Comparison of spectra and osmegram for winter dry litter obtained for sorbent tube and direct headspace. The osmegram of the direct headspace shows greater number of odorous compounds rated at higher intensity than for the Tenax sorbent tube.

For example, limonene is perceived at higher abundances to produce a plastic or petrol like odour, whereas it emanates a chemical like odour at lower abundances from the winter litters. Solvent and rotten vegetable like odours were produced for 2,3 butanedione at low and high abundances, respectively from summer litters. This circumstance is shown in Figure 5.14 which displays the varying description and intensity at the initial and final stages of respective peak volatiles on total ion chromatogram.

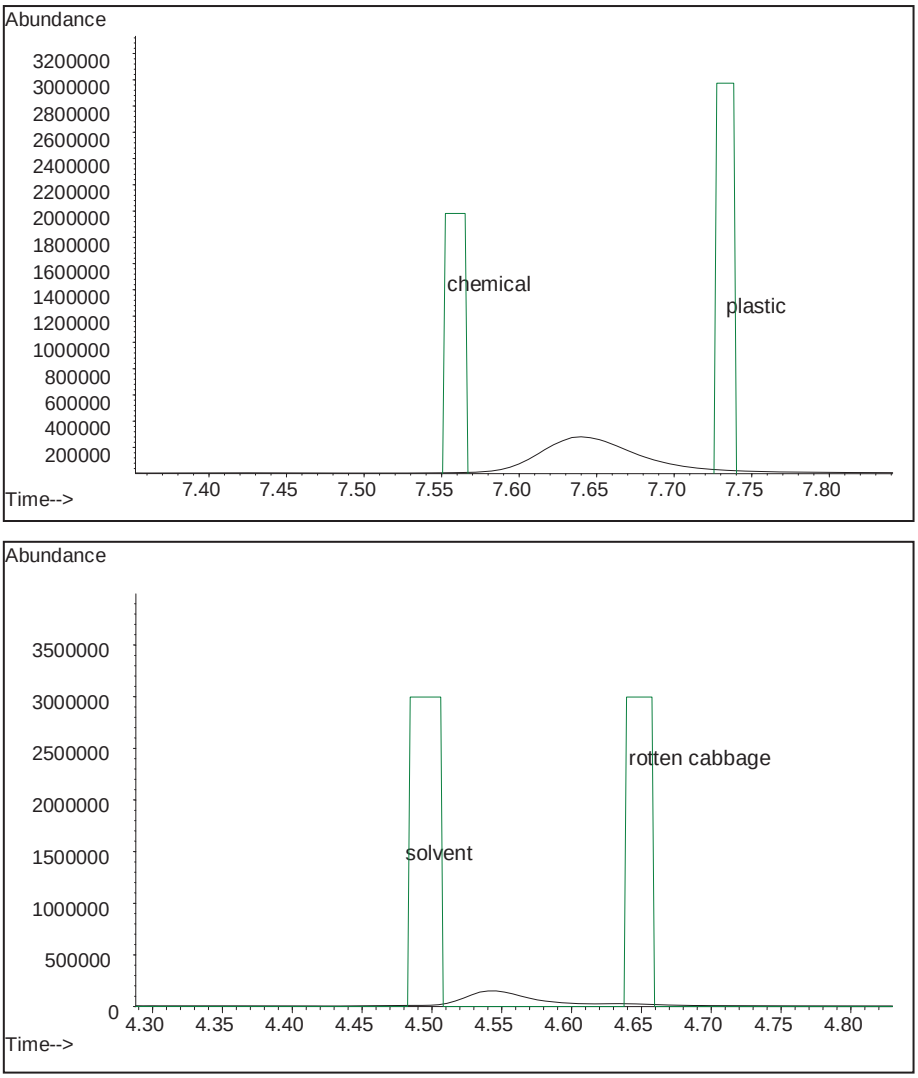


Figure 5.14 Variations in odorants description and intensity attributed to concentration of volatiles presented in limonene (top) and 2,3-butanedione (below).

During the olfactory evaluation two panellists were employed with different olfactory sensitivities (based on n-butanol) in order to characterise the emissions. The operator with a greater olfactory sensitivity (i.e. low butanol detection) was able to identify a greater number of odorants than the operator with a normal or average olfactory sensitivity. This resulted in a large variation in the olfactory results obtained of litter olfactory analysis (Figure 5.15).

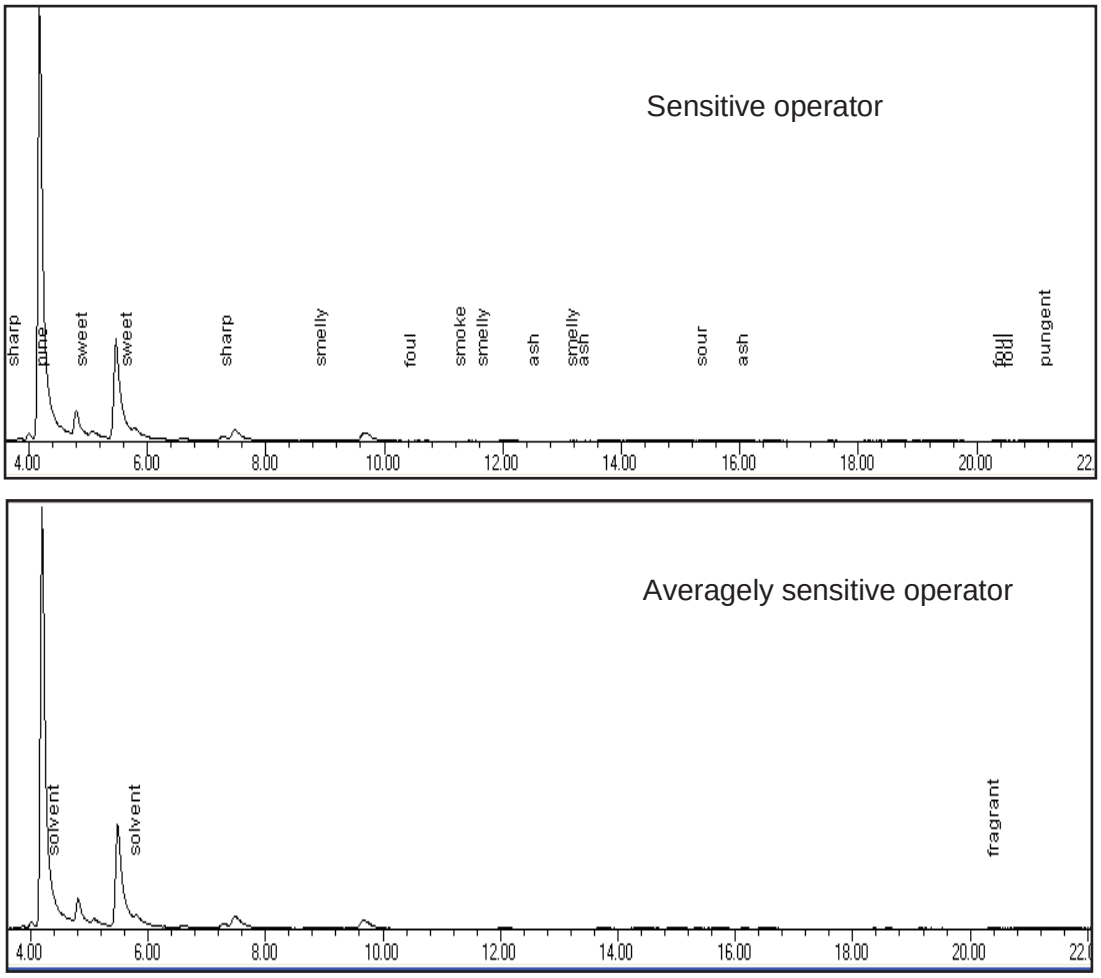


Figure 5.15 Difference in olfactory panellists response for dry winter litter.

While assessing human reaction efficacy corresponded to odour detected, both operators responded efficiently towards perceived odorants. In most cases, operators were observed to respond to perceived odour by pressing the odour indictor button while simultaneously recording the odour description. Figure 5.16 shows a part of total ion chromatogram overlapped with olfactory responses. Olfactory responses often fall directly above volatile peak on total ion chromatogram as observed at 4.17 min and 5.45 min or at the beginning or end of chemical peaks as marked at 4.83 and 5.17 min. Nevertheless, the overlap is often highly subjective and influenced by the operator's ability and experience to detect and make a swift judgement of perceived response.

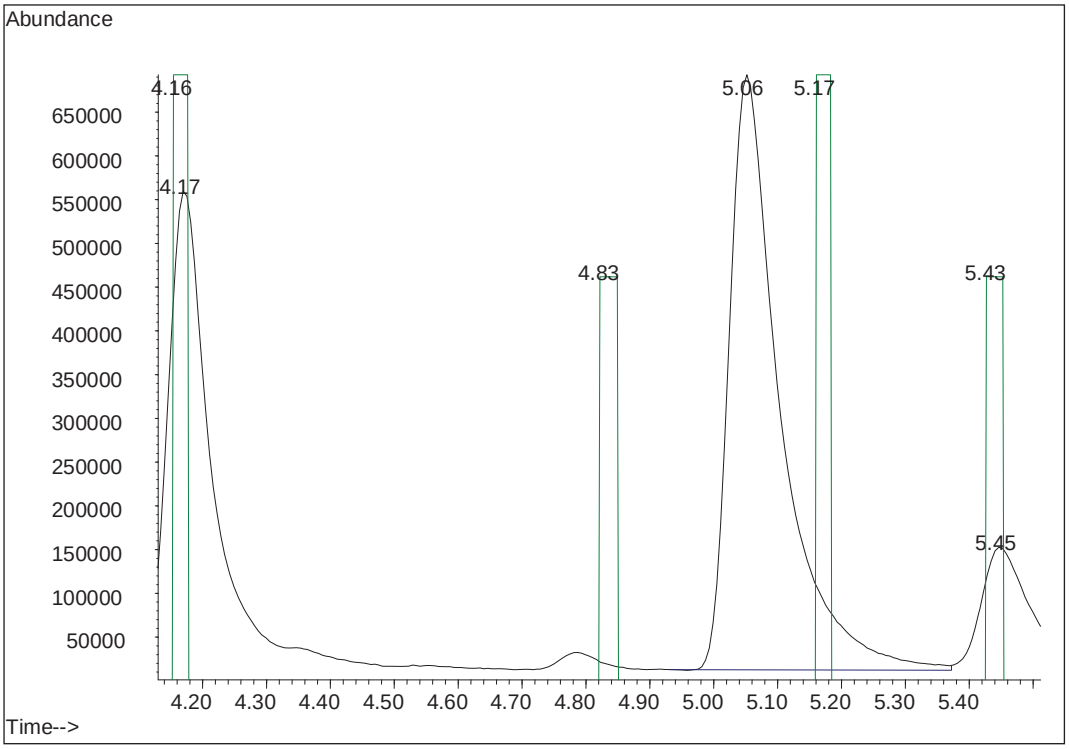


Figure 5.16 Overlay of TIC and osmegram displaying the efficacy in operator's olfactory responses.

Several delays in responding speed by the operators were accepted and noticed during analysis and are most likely attributed to time required for the operators to evaluate the perceived odorants in terms of intensity and identifying suitable odour descriptor, especially for newly experienced odorants (Figure 5.17). Significant delays in olfactory awareness were prominent for low abundant volatile elucidating after the elution of highly intense odorants. This often caused an overloading of operator sensory response resulting in low sensitivity and slower response to compounds eluting afterwards [36]. In addition, longer olfactory exhalation in operator during analysis also may cause some delays in odour response.

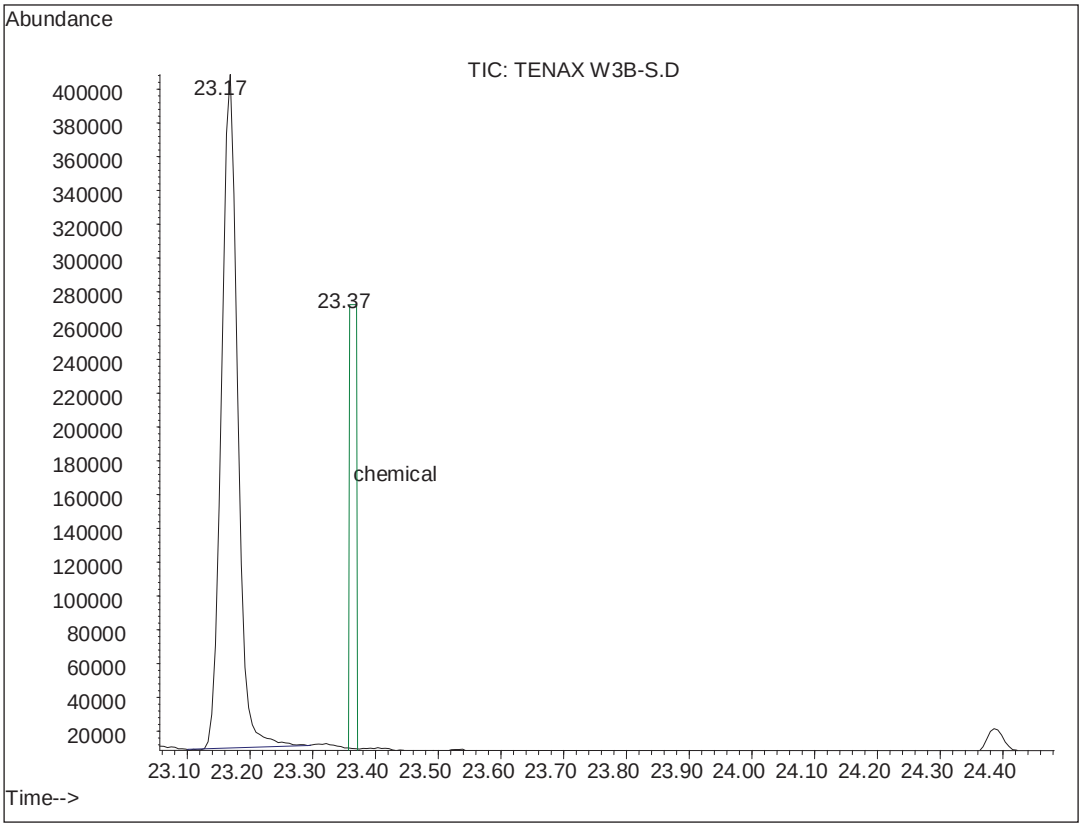


Figure 5.17 Delay in operator's response observed for volatile determined at 23.17 min with olfactory response delayed at 23.37 min.

During some olfactory assessment, more than one rating of an odorant was noticed. This observation could be attributed to underestimation or overestimation of detected odour strength by the operator, usually between the initial and final stage of an elucidating volatile (Figure 5.18). Hence, multiple responses were obtained at the same points of peak exhibiting the effort of operator to correctly rate the odour intensity on the osmegram scale.

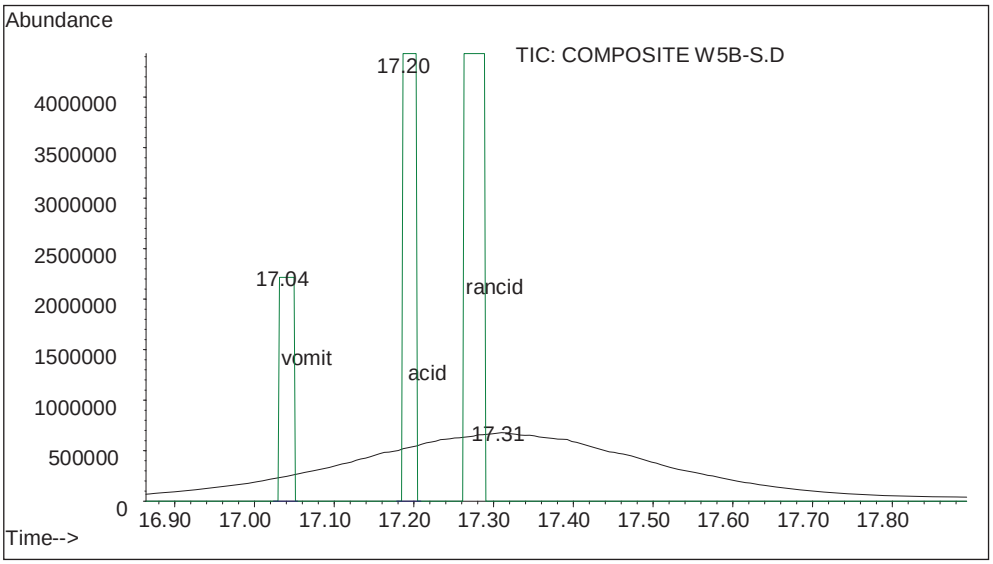


Figure 5.18 Multiple olfactory responses obtained of butanoic acid from winter wet litter on TIC using direct headspace.

Greater sensitivity by human olfactory assessment over chemical analysis is evident during this study. During GC-MS/O analysis, the operators were able to detect and characterise odorants perceived when no peaks were available or with low match on total ion chromatogram (Figure 5.19). This was especially noticed for extremely low odour threshold volatiles like sulfur and nitrogen containing compounds and volatile fatty acids. However, this effect may not be related to delays in operator's response since similar episodes were repeated prominently at particular retention times, type of odour materials and between operators (Figure 5.20).

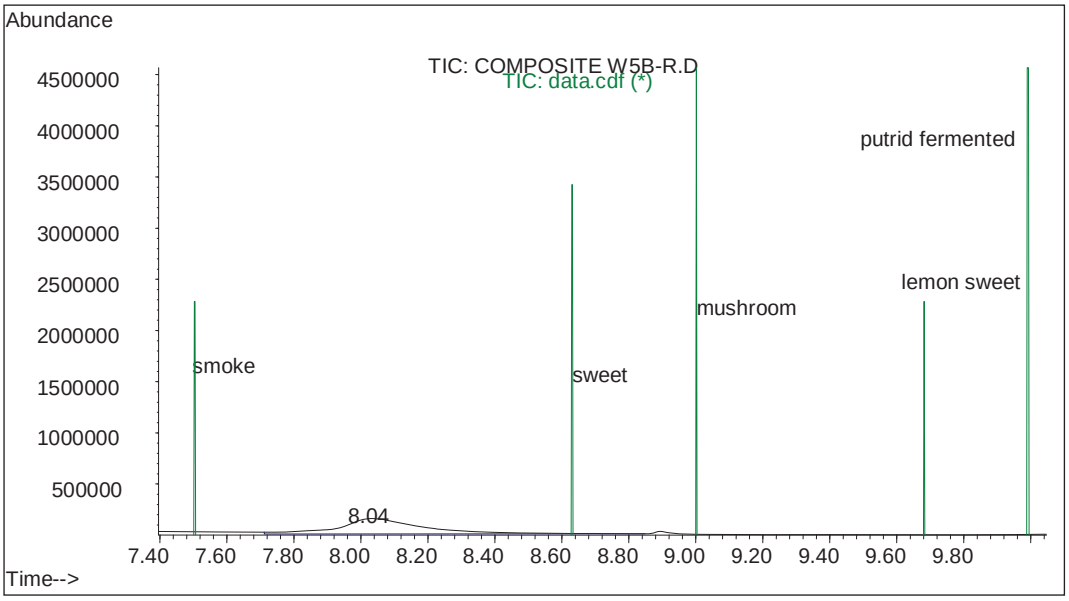


Figure 5.19 Overlay of TIC and osmegram presenting on greater ability to detect odorants in human olfactory than of instrument.

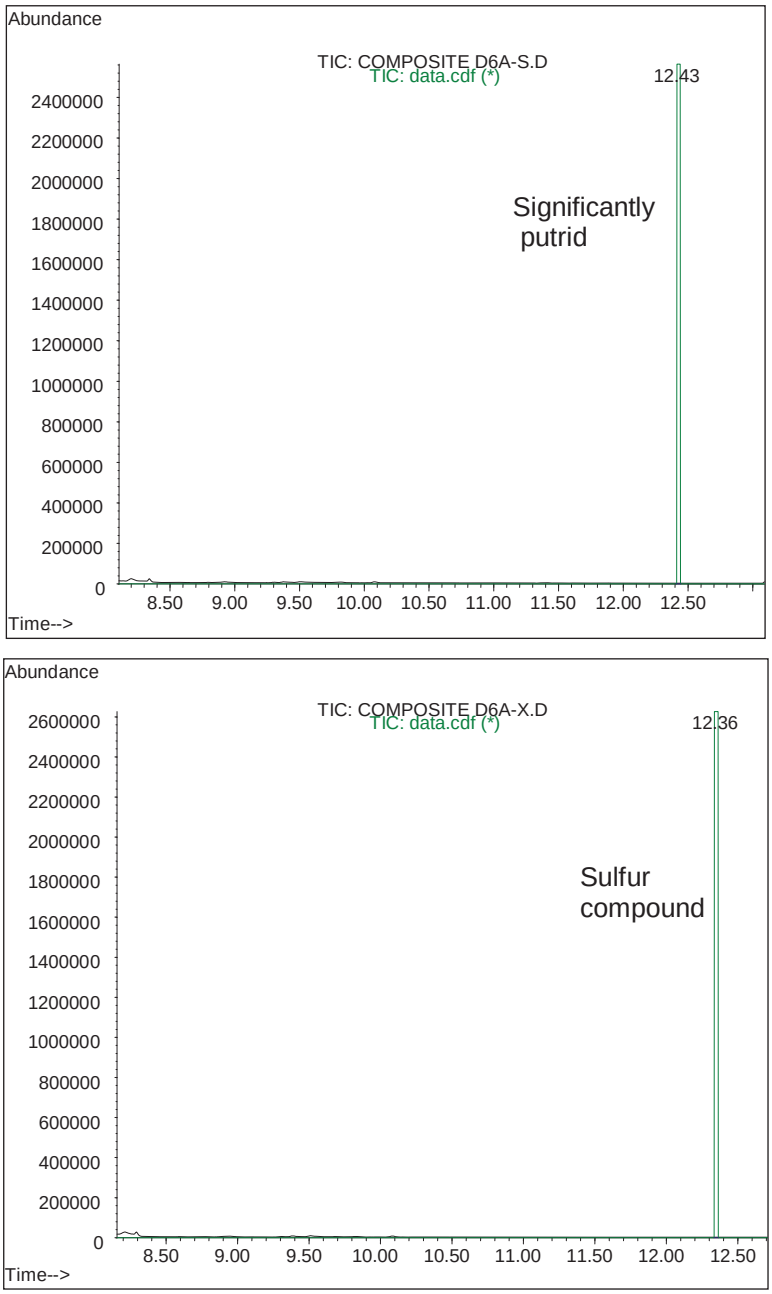


Figure 5.20 Comparison of consistency in detecting low odour threshold volatiles between sensitive (top) and averagely sensitive operators. The overlaid TICs with osmegram show noticeable low detection of an odour at 12.50 min using human nose characterised as highly offensive rate with no instrumental information available.

5.3 Summary of headspace TD-GC-MS/O method

The headspace sampling coupled to TD-GC-MS/O provided both chemical and sensory responses analysis that had repeatability and reproducibility with synthetic solutions and broiler litter materials with minimal experimental preparation required. The solvent free methods employed were observed to provide substantial responses with concentration of samples and consistently recorded volatiles occurrences and odorants characteristics while discriminating chemicals from varying materials without alteration of samples. These aspects are extensively important in comparing variations in volatiles obtained for environmental samples that have complex matrix and are often shown to have a diverse range of chemicals.

Competency assessment of a combination of headspace sampling coupled to TD-GC-MS/O has demonstrated high efficiency of analysis for this methodology as a tool to study broiler litter odorants and to evaluate potential odour abatement strategies. Changes in sampling and analysis parameters are required, depending on the nature of studied materials. The comparison of direct headspace and sorbent tube samplings revealed sufficient information on the impacts of sampling technique parameters' on the chemical and sensory responses. However, limitations in human sensory and analytical instrumentation must be taken into account while employing these techniques to reduce bias and inappropriately analysed data.

5.4 Characterisation of broiler litter

Broiler litters volatile characterisation was performed for winter and summer samples using the developed headspace sampling technique coupled to TD-GC-MS/O and sorbent tube sampling using Tenax TA. The litter samples were collected from tunnel ventilated broiler sheds, transported to UNSW and sampled under ambient conditions in order to provide chemical and olfactory speciation of odours emitting from the sample materials. A full set of odorants determined from winter and summer dry and wet litters are summarised in Table 5.4 to Table 5.11. Details on significant odorants characterised and their intensities between sampling techniques, litter types and seasons during the broiler growth periods are provided in Appendix A and Appendix B.

5.4.1 Winter litter characteristics

While progressing through the broiler production cycle, the winter dry and wet litters exhibited large variation in terms of appearance, moisture content, pH values and odour intensity and quality. Table 5.4 to 5.7 highlight the odorant profiles for the different sampling techniques and litter samples (wet and dry).

5.4.1.1 Week 0 - 2

Litter samples collected in week 0 were from sanitised floor sheds spread with fresh pine shaving as the bedding material. The samples appeared unsoiled and friable with no birds existed in the shed during collection (Figure 5.21). As a result of natural emanation from fresh bedding of pine shaving, terpenes were observed to dominate the odour emissions. Hence, the odour produced was described as more pleasant than offensive. In week 1, approximately 43000 young broilers (7 days old) were transferred onto the clean bedding material (Figure 5.22). Small black particles of manure were visible on the pine shaving due to manure being excreted from the broilers, resulted in the detection of acetic acid and dimethyl disulfide (Figure 5.23). Nevertheless, the total number of volatiles captured from the headspace techniques declined compared to the previous week, which was most likely attributed to losses of volatiles during evaporation and drying of litter as the temperature was elevated in the shed conditions. More terpenes were detected, however in reduced concentrations.

Figure 5.21 Pine wood shaving used in the tunnel ventilated broiler shed during winter broiler production.

Figure 5.22 Large number of young broilers transferred on fresh bedding material in week one.

Figure 5.23 Manure appeared within fresh bedding in week one

As the broilers grow and gain body weight, the litter becomes further soiled with subsequent increase in manure excretion and size, resulting in a rise in the pH values in week 2. Extreme extraction of manure occurred on wet litter that transformed the physical appearance from a yellow to brown blackish colour which concurrently heightened the odour offensiveness with the presence of dimethyl trisulfide identified from sorbent tube technique. Direct headspace detected the presence of more odorants in line with changes in litter properties. While analysing odorants individually, although the headspace method recorded odorants at a higher level of intensities, their odour characteristics remained relatively less offensive in week 2, except for acetone, 2,6-dimethyl-2,4,6-octatriene and alpha dimethylstyrene.

5.4.1.2 Week 3 - 5

The dry litter obtained from the tunnel ventilated broiler shed started to exhibit alkaline characteristics with a further increase in the litter pH. The sorbent tube sampling recorded an increased number of volatiles consisting of sulfur compounds, volatile fatty acids and ketones. This was especially significant for the wet litter that demonstrated greater perceived odour intensity. Meanwhile, strong odour intensity was perceived of litter materials even though a decline in the volatiles detected for both dry and wet samples using direct headspace sampling. Wet litter obtained after week 4 sustained excessively high level of moisture content compared to dry litter resulting in an intensification of volatile's

offensiveness. The direct headspace sampling revealed maximum strength of the perceived volatiles intensity on scale corresponding mainly to the presence and increase in the abundance of sulfur compounds. In week 5, winter wet litter was caked and generated highly obnoxious emission as a result of further deposition of water content (Figure 5.24). In comparison to week 4, wet litter pH decreased immensely from 8.15 to 5.65, exhibiting acidic nature. The litter odour was identified to contain a high abundance of sulfur containing compounds, ketones and volatile fatty acids perceived at greater intensity. The presence of volatiles fatty acids in the wet litter corresponded with the low litter pH condition.

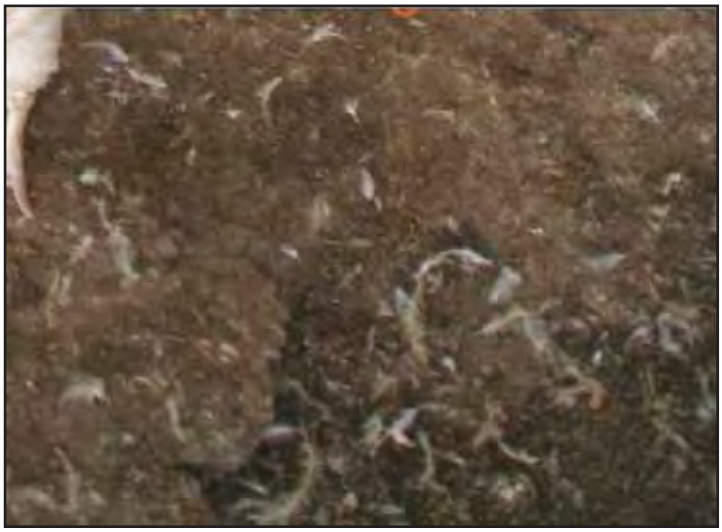


Figure 5.24 Caked winter wet litter of week 5.

5.4.1.3 Week 6 - 8

Approximately 20000 broilers were harvested from the shed at week 6, substantially decreasing the litter moisture content and increasing the pH value of winter wet litter. The odour was dominated by sulfides and butanoic acid with some terpenes determined from the litter. The peak area of the methanethiol perceived in litter using direct headspace is not noted in the odorants results table due to low instrumental match but is reported as a trace compound based on a previous match of its retention time and substantial odour description and strength. In the final weeks of the broiler growth cycle, the remainder birds gained the maximum body mass in week 7 before completely being removed from the sheds (Figure 5.25). With continuous biological fluid excretion, winter

wet litter heightened in humidity once again after week 6. The unpleasantness of wet litter continued to rise with increase in volatiles abundance. Domination of dimethyl trisulfide, ketones and alcohols was noted for the wet litter using sorbent tube sampling. In week 8, soiled litters were collected with all birds removed from the sheds. The breaking of the thick caked litter heightened the emission resulting in the identification of the most number of analytes for the dry and wet litters using sorbent tube sampling. A mixed trend in volatiles abundance was observed in comparison to week 7 with less offensive odour characteristics for the analytes. Direct headspace exhibited similar trends to sorbent tubes with a lesser number of volatiles been determined.

Figure 5.25 Fully grown birds ready for harvest.

Table 5.4 Volatiles obtained from dry winter litter using sorbent tubes.

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	Min	max		
Aromatic hydrocarbons				
1-methylethyl-benzene	2.01E+06	8.14E+06	2	Solvent(3)
butylated hydroxytoluene	2.06E+05	2.49E+05	2	
ethylbenzene	1.37E+06	3.21E+06	2	Foul(2)
m-xylene	4.29E+06	4.29E+06	1	Fruity(2)
o-cymene	9.97E+04	4.21E+06	4	Smoke-gas (2)
o-xylene	5.11E+06	5.11E+06	1	Fruity(2)
allyl anisole	1.34E+06	1.34E+06	1	Sewer(2)
Phenol	1.53E+05	8.78E+05	6	Sweet/foul(2-3)
p-xylene	1.55E+06	6.40E+06	2	fragrant(2)
Styrene	5.93E+04	1.51E+05	2	Foul(2)
Toluene	1.30E+06	2.01E+06	3	Solvent/pungent(2-3)
Alcohols				
2-ethyl-1-hexanol	3.44E+05	4.07E+06	4	Chemical/fragrant(2-3)
2-butanol	9.74E+05	9.43E+06	3	Fragrant/chemical(2-3)
isopropyl alcohol				Fragrant(3)
Sulfur compounds				
dimethyl disulfide	3.21E+06	6.27E+07	8	Chemical/manure(2-3)
dimethyl sulfide	2.34E+05	1.04E+06	5	Mold(2)
dimethyl trisulfide	1.41E+05	2.24E+06	7	Sharp putrid(3-4)
Volatile fatty acids				
acetic acid	2.38E+05	2.50E+06	4	Acid/vinegar(2-3)
butanoic acid	1.18E+05	4.23E+06	3	Solvent/rancid(2-4)

n= frequency of compound repeated in the 9 weeks of sampling

Table 5.4 Volatiles obtained from dry winter litter using sorbent tubes (cont).

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	Min	max		
Ketones				
2-butanone	3.84E+06	2.99E+07	7	Fruity/solvent(2-3)
3-hydroxy-2-butanone	7.70E+05	3.21E+06	2	
3-methyl-2-butanone	1.39E+06	4.54E+06	5	Alcoholic/fruity solvent (2-3)
3-octanone	2.55E+05	7.05E+05	4	Sweet/resin(2)
Acetone	6.60E+06	1.12E+07	8	Solvent(2-3)
Terpenes				
.beta.-phellandrene	2.24E+05	9.60E+07	4	Fragrant/fruity(1-2)
.beta.-pinene	3.47E+06	1.62E+08	9	Fragrant/resin(2)
3-carene	4.59E+06	4.59E+06	1	
alpha pinene	1.09E+07	3.73E+08	9	Pine(2-4)
alpha.terpinolene	2.42E+06	2.42E+06	1	
alpha.thujene	2.63E+05	2.63E+05	1	
camphene	5.34E+05	3.27E+07	9	Solvent/fruity/chemical (2-3)
Limonene	7.53E+05	1.96E+07	8	Sweet solvent/petrol (2-4)
gamma-terpinene	1.44E+06	1.44E+06	1	Sweet(2)
Sabinene	1.66E+07	1.66E+07	1	
Terpinene	8.10E+05	8.10E+05	1	Solvent(2)
Tricyclene	5.84E+05	8.97E+07	3	Solvent(2)
Others				
2,4-pentadienenitrile	3.42E+05	7.53E+05	6	Plastic/foul(2-3)
Octane	2.49E+05	6.40E+05	3	Solvent/gas/chemical(2)
2-methyl furan	1.29E+05	1.45E+06	6	Ethery(3)

Table 5.5 Volatiles from wet winter litter using sorbent tubes.

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Aromatic hydrocarbons				
1-methylethyl-benzene	2.50E+06	7.73E+06	2	Solvent(3)
Anisole	1.66E+05	4.22E+05	2	
butylated hydroxytoluene	1.42E+05	2.52E+05	3	
m-xylene	9.84E+06	9.84E+06	1	Sweet solvent(3)
o-cymene	3.19E+05	7.52E+06	7	Soap-foul(2)
o-xylene	2.09E+06	2.09E+06	1	Varnish(3)
allyl anisole	2.59E+05	2.29E+06	3	Sweet/Chemical/ Varnish(3)
p-cresol	1.44E+05	2.51E+05	2	Smoke/foul(2)
Phenol	2.21E+05	4.54E+06	6	Foul(1)
Alcohols				
3-methyl-1,5-Pentanediol	4.03E+06	4.03E+06	1	
1-Butanol	3.39E+06	7.03E+07	6	Sweat/mold(3)
3-methyl-1-butanol	8.92E+06	2.09E+07	2	
2-ethyl-1-hexanol	6.08E+05	4.65E+06	4	Fragrant(3)
4-methyl-1-pentanol	3.86E+06	3.86E+06	1	Solvent(2)
1-propanol	3.27E+07	4.24E+07	3	Floral(2-3)
2-methyl-1-propanol	4.74E+06	4.74E+06	1	
2,3-butanediol	9.84E+05	9.84E+05	1	
2-butanol	2.69E+07	5.71E+08	7	Fragrant/chemical(3)
2-pentanol	7.59E+06	7.59E+06	1	
3-octanol	1.09E+06	1.15E+06	2	Sweet/chemical(2)
isopropyl alcohol	4.00E+07	4.00E+07	1	
1-Octen-3-ol	5.12E+05	5.94E+05	2	
1-Dodecanol	1.12E+05	1.12E+05	1	

Table 5.5 Volatiles from wet winter litter using sorbent tubes (cont).

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Aldehydes				
butanal	9.12E+05	9.12E+05	1	Ash(2)
pentanal	6.63E+05	6.63E+05	1	
Sulfur compounds				
dimethyl disulfide	8.72E+06	7.18E+07	8	Chemical/manure(2-4)
dimethyl sulfide	1.64E+05	4.04E+05	4	
dimethyl trisulfide	5.37E+05	3.99E+06	7	Sharp putrid/rotten (3-4)
2,4-dithiapentane	1.78E+05	1.47E+06	4	Rancid(2)
Volatile fatty acids				
acetic acid	5.97E+05	1.38E+07	7	Vinegar/pungent/ rancid(2-3)
butanoic acid	3.98E+05	1.21E+07	6	Sweetish ether/rancid(3-4)
propanoic acid	2.20E+05	1.86E+06	6	Foul/rancid(2-3)
2-methyl- propanoic acid	8.97E+05	9.34E+05	2	
Ketones				
2-butanone	6.30E+06	4.31E+08	8	Fruity/ sweet solvent/(2-4)
2-hexanone	5.29E+06	5.29E+06	1	
3-hydroxy-2-butanone	3.10E+06	4.51E+07	6	Foul/chemical(2-3)
3-methyl-2-butanone	4.24E+06	3.84E+07	4	Chemical/ash(3)
3-octanone	4.79E+05	3.70E+06	6	Paint/chemical/garbage(2)
6-methyl-2-heptanone	1.01E+06	1.01E+06	1	Sweet solvent(3)
acetone	1.93E+06	9.13E+06	7	Solvent(2)
1-(2-furanyl)-ethanone	1.42E+06	3.39E+06	2	Chemical(2)
verbenone	2.69E+05	5.76E+05	2	
camphor	0.00E+00	0.00E+00	2	Foul(2)

Table 5.5 Volatiles from wet winter litter using sorbent tubes (cont).

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Terpenes				
.beta.-phellandrene	1.60E+08	1.60E+08	1	
.beta.-pinene	1.27E+07	2.26E+08	9	Solvent /Resin(2)
3-carene	5.65E+06	5.65E+06	1	
alpha pinene	2.90E+07	4.69E+08	9	Pine(2-4)
alpha.terpinolene	5.00E+06	5.00E+06	1	Soap(2)
alpha.thujene	8.93E+05	2.35E+06	5	
camphene	4.37E+06	3.43E+07	7	Solvent/fruity/ chemical(2-3)
caryophyllene	2.20E+06	2.20E+06	1	
limonene	1.10E+06	3.28E+07	8	Chemical/plastic(2-4)
gamma-terpinene	8.97E+06	8.97E+06	1	Foul(2)
sabinene	2.04E+06	3.32E+06	2	Plastic(4)
terpinene	5.46E+05	1.78E+06	2	Solvent(3)
tricyclene	9.10E+05	3.19E+06	2	Solvent(2)
Others				
(ethoxymethyl)-oxirane	5.18E+05	5.18E+05	1	Sweet chemical(3)
2,4-pentadienenitrile	1.61E+05	4.50E+06	7	Solvent(2-3)
3-pentenenitrile	2.74E+06	2.74E+06	1	Putrid(2)
ethyl acetate	1.74E+06	1.04E+07	4	Fruity(2-3)
octane	3.85E+05	5.91E+05	4	Chemical(2)
2-methyl furan	2.29E+05	4.13E+05	4	Chemical(2)

n= frequency of compound repeated in the 9 weeks of sampling

Table 5.6 Volatiles obtained from dry winter litter using direct headspace.

Compounds	Peak area			Range of odour descriptions and intensities (1-4)
	min	max	n	
Aldehydes				
2-methyl-3-phenyl-propanal	1.86E+06	1.86E+06	1	Fresh/green(2)
4-(1-methylethyl)-benzaldehyde	1.20E+07	1.20E+07	1	
Aromatic hydrocarbons				
1-butenyl-benzene	2.08E+06	2.08E+06	1	
1-methoxy-4-methyl-2-(1-methylethyl)-benzene	5.52E+06	5.52E+06	1	Solvent(2)
2-butenyl-benzene	2.08E+06	2.08E+06	1	
2-methyl-5-(1-methylethyl)-phenol	5.04E+07	5.04E+07	1	Solvent(2)
(2-methyl-1-propenyl)-Benzene	3.88E+05	1.00E+08	4	
alpha dimethylstyrene	2.32E+05	5.04E+07	7	Chemical(3)
m-cresol	5.04E+07	5.04E+07	1	Sharp(2)
m-cymene	1.24E+06	2.42E+07	3	Sweet/smoke(2-3)
methyl eugenol				
o-cresol	1.86E+06	1.86E+06	1	
o-cymene	2.39E+06	6.70E+08	7	Solvent/plastic/ smoke(1-3)
allylanisole	5.88E+05	5.04E+07	4	Acid/foul(2)
p-cresol	2.22E+06	2.22E+06	1	Aromatic(3)
phenol	1.93E+04	4.57E+05	5	
styrene	4.11E+06	4.11E+06	1	

Table 5.6 Volatiles obtained from dry winter litter using direct headspace (cont).

Compounds	Peak area			Range of odour descriptions and intensities (1-4)
	min	max	n	
Ketones				
1-(4-methylphenyl)-ethanone	5.04E+07	5.04E+07	1	Paint(3)
2-butanone	4.46E+07	3.76E+08	3	
acetone	4.99E+06	1.44E+08	6	Fragrant/smoke/ chemical(2)
isopinocamphone	3.34E+06	3.34E+06	1	
menthone	7.29E+06	7.29E+06	1	
camphor	4.88E+05	1.00E+06	2	Rotten grass(2)
Sulfur compounds				
dimethyl disulfide	2.99E+07	1.77E+08	7	chemical/manure/ earthy/sulfur(2-3)
Volatile fatty acids				
acetic acid	7.85E+05	4.32E+06	5	Foul/acid(2-3)
butanoic acid	3.23E+05	2.89E+06	4	Chemical/putrid(2-4)
propanoic acid	2.08E+05	2.08E+05	1	

Table 5.6 Volatiles obtained from dry winter litter using direct headspace (cont).

Compounds	Peak area			Range of odour descriptions and intensities (1-4)
	min	max	n	
Terpenes				
.alpha.-caryophyllene	2.93E+06	2.93E+06	1	
.alpha.-phellandrene	9.86E+06	2.43E+08	5	Ash/citrus/sweet solvent/sulfur(2-3)
.beta.-phellandrene	2.03E+06	1.16E+08	3	
.beta.-Pinene	1.06E+07	5.25E+08	7	Fruity/spice/ wet smoke(2-3)
2-carene	2.94E+06	7.68E+08	4	
3-carene	2.91E+07	5.04E+07	2	
alpha. terpinene	1.24E+07	3.80E+08	4	Citrus/plastic(3)
alpha.pinene	2.72E+07	1.32E+09	9	Wood fragrant/ pine(2-4)
camphene	4.77E+06	1.02E+09	8	Corniferous/ chemical(2-3)
limonene	5.13E+06	1.00E+08	8	Solvent/fragrant(2-3)
gamma.terpinene	3.82E+06	5.04E+07	4	Solvent/fragrant(2-3)
sabinene	4.37E+07	1.82E+08	2	
tricyclene	6.27E+06	1.00E+08	4	Acid/fruity(2)
Others				
2,4-pentadienenitrile	3.02E+05	4.91E+05	3	Rubber/solvent(2-3)
2,6-dimethyl-2,4,6-octatriene	1.02E+06	5.04E+07	4	Sulfur/sewer(2-4)

n=frequency of compound repeated in the 9 weeks of sampling

Table 5.7 Volatiles from wet winter litter using direct headspace.

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Alcohols				
1,3-butanediol	2.00E+07	9.00E+07	3	Sweet(3)
4-methoxy- 1-butanol	2.00E+06	2.00E+06	1	
2-(vinyloxy)-ethanol	5.00E+06	1.00E+08	3	Solvent(2)
2-butanol	3.00E+08	3.00E+08	1	Alcoholic(2)
phenylethyl alcohol	9.13E+05	9.13E+05	1	Sweet chemical(3)
Aldehydes				
4-(1-methylethyl)-benzaldehyde	3.00E+06	3.00E+06	1	Chemical(3)
butanal	5.00E+07	5.00E+07	1	
Aromatic hydrocarbons				
1-methoxy-4-methyl-2-(1-methylethyl)-benzene	4.00E+06	4.00E+06	1	Foul(4)
2-methyl-5-(1-methylethyl)-phenol	1.00E+06	1.00E+06	1	Moth ball(2)
alpha dimethylstyrene	7.92E+05	5.00E+07	8	Fragrant(1)
m-cresol	4.07E+05	4.07E+05	1	
m-cymene	3.00E+07	3.00E+07	1	Earthy(2)
methyl eugenol	2.00E+06	4.00E+06	2	
o-cymene	4.00E+06	2.00E+08	6	Aromatic/rubber (2-3)
allylanisole	3.97E+04	2.00E+07	6	Fresh/solvent/foul (2-3)
p-cresol	4.02E+05	1.00E+06	3	Smoke(2)
phenol	2.61E+05	2.00E+07	6	
styrene	5.00E+06	5.00E+06	2	
thymol	1.00E+06	1.00E+06	1	Hospital(3)
Indole	4.19E+05	4.19E+05	1	

Table 5.7 Volatiles obtained from wet winter litter using direct headspace (cont).

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Ketones				
1-(4-methylphenyl)-ethanone	4.00E+06	4.00E+06	1	Chemical(3)
3-hydroxy-2-butanone	1.00E+07	3.00E+08	5	Chemical/smoke/ burnt sugar/rancid(2)
1-methoxy-2-propanone	4.00E+07	4.00E+07	1	Foul(2)
2-butanone	2.00E+08	2.00E+09	6	butanol/sweet solvent/chemical(2-4)
acetone	1.00E+07	3.00E+08	8	Gas/rubber/ alcohol(2-4)
isopinocamphone	1.00E+06	2.00E+08	3	Foul/solvent/ fragrant/(2)
camphor	1.00E+06	2.00E+06	3	Foul-fresh(2-3)
Sulfur compounds				
dimethyl disulfide	5.00E+07	2.00E+08	5	Chemical/putrid (2-4)
methanethiol	1.26E+05	3.83E+05	2	Putrid/sulfur(2-4)
Volatile fatty acids				
acetic acid	6.46E+05	2.00E+08	6	Sweat/acid/urine (2-4)
butanoic acid	1.00E+06	1.00E+08	4	Dry manure/chemical/ rancid(2-4)
4-methyl-pentanoic acid	7.00E+06	7.00E+06	1	Sharp(3)
propanoic acid	9.98E+05	2.00E+07	2	bacon/rubber(2-4)

Table 5.7 Volatiles obtained from wet winter litter using direct headspace (cont).

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Terpenes				
.alpha.-caryophyllene	9.00E+06	9.00E+06	1	Garbage(3)
.alpha.-phellandrene	2.00E+07	3.00E+08	4	Fruity solvent/burnt wood(2-3)
.beta.-Pinene	3.00E+07	4.00E+08	7	Perfume/chemical/ wet smoke(2-4)
2-carene	1.00E+07	1.00E+07	1	
3-carene	2.00E+07	2.00E+07	1	
alpha. terpinene	1.00E+07	3.00E+08	3	Chemical/alcohol (2-4)
alpha.pinene	1.00E+08	1.00E+09	7	Alcohol/pine (2-4)
camphene	3.00E+07	8.00E+08	5	Sweet solvent/spice/ chemical(2-3)
limonene	1.00E+07	1.00E+08	8	Solvent/fruity/ plastic(2-4)
gamma.terpinene	7.00E+06	5.00E+07	3	
sabinene	3.00E+08	3.00E+08	1	Solvent(3)
tricyclene	1.00E+07	6.00E+07	2	Sweet(2)
Others				
1-methoxy-2-methyl-propane	5.00E+06	5.00E+06	1	
2,3-dimethyl-oxirane	2.00E+07	2.00E+07	1	
2,4-pentadienenitrile	9.99E+05	9.99E+05	1	rotten(4)
2-pentene	2.00E+07	2.00E+07	2	Solvent(3)
2,6-dimethyl-2,4,6-octatriene	2.00E+06	2.00E+08	4	Sulfur/sewer(2-4)

n= frequency of compound repeated in the 9 weeks of sampling

5.4.2 Summer litter

In comparison to the winter litter samples collected, the summer litters demonstrated smaller variations in physical amendments, odour emissions, moisture and pH values throughout broiler growth cycle. Table 5.8 to Table 5.11 highlight the odorant profiles for the different sampling techniques and litter samples (wet and dry).

5.4.2.1 Week 0 - 2

Litters from week 0 were from cleaned floor shed covered with hard wood chips (Figure 5.26) as the bedding material with no birds. The samples were unsoiled and odourless during this period of sampling. Volatiles samplings revealed aromatic hydrocarbons in low abundances and odour intensity. In week 1, approximately 41000 young broilers (at 7 days old) were transferred onto the cleaned shed floor. No significant difference was noticed for dry and wet litter. The odorants' intensities remained steady even though acetic acid, acetone and toluene were detected at higher abundances in the litters. Unlike the winter litters, the litter appeared insignificantly soiled with broilers gaining body mass. In week 2, the sorbent tube showed increases in the volatiles captured with relatively low odour intensities, dry summer litter generated a greater number of volatiles than of wet summer litter. In comparison to the winter litters, both dry and wet litters exhibited low moisture content and pH values as low as 7, which was in agreement with the presence of low abundance of acetic acid in the initial three weeks of production.

Figure 5.26 Fresh hardwood shaving used for bedding during summer broiler production.

5.4.2.2 Week 3 – 5

In week 3, sulfur containing chemicals were characterised using the direct headspace sampling, however the intensity of the offensive remained insignificant. In the subsequent week, the odour strength was elevated in the dry litter samples. In week 5 (Figure 5.27) the litter become slightly soiled, this resulted in the dry litter odour exhibited the occurrence of alcohols, sulfur compounds and ketones whereas for the direct headspace sampling the highest intensity for the offensive odorants come from the wet litter. Ketones and sulfur compounds were found in greater abundance using direct headspace than for sampling via sorbent tubes. The summer dry litters showed an increase in pH values and were observed to sustain a greater percentage of moisture content than of wet litters.

Figure 5.27 Summer's week 5 soiled litter

5.4.2.3 Week 6 - 8

There was a reduction in the level of analytes being detected from the summer litter samples that was in agreement with the removal of large number birds in week 6. In contrast with the bird harvest, an increase in wet litter's moisture content was recorded in week 6 with ketones and sulfur compounds being determined to dominate the odour in terms of offensive qualities. This observation corresponded with the caking of the wet litter in week 6 (Figure 5.28). As the bird's maximum body mass occurred, the accumulation of soiled litter in week 7 resulted a strong domination of sulfur compounds being exhibited from both the dry and wet litter. This observation continued into week 8 with reduced abundance. The pH and moisture content values for the litters were observed to remain steady in the last 3 weeks of production.

Figure 5.28 Caking of wet litter during week 6.

Table 5.8 Volatiles obtained from dry summer litter using sorbent tube.

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Alcohols				
2-ethyl-1-hexanol	4.96E+05	1.46E+06	5	Sweet solvent/pungent(2)
4-(1,1-dimethylethyl)-cyclohexanol	5.05E+05	1.17E+06	8	Rancid/alcohol(1-2)
1-Butanol	3.19E+06	3.19E+06	1	Chemical(2)
2-Butanol	7.10E+05	8.29E+07	2	Solvent(2)
Ketones				
3-hydroxy-2-butanone	1.88E+07	1.88E+07	1	Musty/chemical(3)
2,3-Butanedione	5.06E+05	5.38E+06	5	Rotten vegetable/pungent(2-4)
2-Butanone	1.64E+06	1.65E+08	5	Sweet solvent/ chemical(2-3)
3-Octanone	2.78E+05	2.78E+05	1	
Acetone	1.82E+06	1.84E+07	9	Solvent/chemical(2-3)
Acetophenone	2.48E+05	1.80E+06	8	Solvent/glue(2)
Sulfur compounds				
Dimethyl disulfide	1.49E+06	3.72E+07	6	
Dimethyl sulfide	1.64E+05	2.01E+06	6	Solvent/chemical(2-3)
Dimethyl trisulfide	3.90E+05	1.70E+06	5	Ferment/rotten(3-4)

Table 5.8 Volatiles obtained from dry summer litter using sorbent tube (cont).

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Aromatic hydrocarbons				
.alpha.-methylstyrene	7.06E+05	2.31E+06	8	Smoke/burning rubber(2-3)
1,2,4-trimethyl-benzene	1.03E+05	2.25E+05	7	Citrus/chemical/ musty(2)
Benzene	1.65E+05	1.65E+05	1	
Butylated hydroxytoluene	7.46E+06	1.93E+07	8	Glue/chemical/ foul(2-3)
Phenol	2.35E+05	8.90E+05	9	Medicinal/solvent/ smoke(1-2)
p-Xylene	1.49E+05	8.10E+05	4	Chemical(2)
Styrene	8.13E+04	8.13E+04	1	Mild chemical(2)
Toluene	4.54E+05	5.96E+06	6	Alcohol(3-4)
Terpene				
alpha guaiene	1.93E+05	2.31E+05	2	Foul(1)
D-Limonene	1.12E+05	2.43E+05	2	Foul(2)
Volatile fatty acid				
Acetic acid	5.28E+05	6.18E+05	4	Sewer/vinegar(2-3)
Other				
2,4-Pentadienenitrile	3.98E+05	9.45E+05	2	Sewer(2)
Trimethylamine	2.62E+05	1.14E+06	3	Sharp(2)

n= frequency of compound repeated in the 9 weeks of sampling

Table 5.9 Volatiles obtained from wet summer litter using sorbent tube.

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Alcohols				
2-ethyl-1-hexanol	5.01E+05	1.59E+06	9	Fragrant/smoke/sharp (2)
4-(1,1-dimethylethyl)-cyclohexanol	5.16E+05	1.13E+06	6	Foul/solvent(2)
1-Butanol	1.31E+07	1.31E+07	1	Plastic(3)
2-Butanol	1.21E+06	6.02E+07	2	Solvent(2)
Aldehydes				
Benzaldehyde	1.50E+05	1.50E+05	1	Earthy/solvent(1)
Ketones				
3-hydroxy-2-butanone	8.66E+06	8.66E+06	1	Musty(3)
2,3-Butanedione	6.93E+05	6.56E+06	5	Rotten vegetable/pungent(2-4)
2-Butanone	3.29E+06	1.42E+08	5	Moth ball/sweet solvent(2)
3-methyl-2-butanone	1.79E+06	2.04E+06	2	Foul(2)
3-Octanone	1.41E+05	2.43E+05	5	
Acetone	1.21E+06	2.25E+07	9	Solvent/soil/chemical (2-3)
Acetophenone	1.20E+05	1.65E+06	7	Solvent/chemical(2)
Sulfur compounds				
Dimethyl disulfide	1.56E+06	3.36E+07	6	
Dimethyl sulfide	1.33E+05	2.28E+06	6	Solvent/chemical(2-3)
Dimethyl trisulfide	9.25E+04	8.77E+05	5	Ferment/rotten(3-4)

Table 5.9 Volatiles obtained from wet summer litter using sorbent tube (cont).

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Aromatic hydrocarbons				
.alpha.-methylstyrene	8.23E+05	2.52E+06	6	Chemical/irritant(2)
1,2,4-trimethyl-benzene	1.06E+05	2.70E+05	7	Citrus/chemical/musty (2)
Butylated hydroxytoluene	7.39E+06	1.71E+07	6	Solvent/chemical/foul (2)
Phenol	1.74E+05	8.94E+05	9	solvent/chemical/ smoke(2)
p-Xylene	1.50E+05	6.73E+05	5	Gas/pungent(2-3)
Styrene	9.92E+04	9.92E+04	1	Foul(2)
Toluene	3.15E+05	1.17E+07	6	Pleasant solvent(2-3)
Terpenes				
alpha guaiene	1.16E+05	3.75E+05	3	Rancid(1)
D-Limonene	8.72E+04	2.11E+05	4	Chemical/plastic(2)
Volatile fatty acids				
Acetic acid	1.68E+05	3.68E+05	4	Sewer/vinegar(2)
Others				
2,4-Pentadienenitrile	3.20E+05	4.33E+05	3	Plastic/glue(2)
Trimethylamine	4.19E+06	4.19E+06	1	Foul(2)

n= frequency of compound repeated in the 9 weeks of sampling

Table 5.10 Volatiles obtained from dry summer litter using headspace.

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Terpenes				
.alpha.-Pinene	9.96E+05	1.93E+06	3	Fragrant(2)
.beta.-Pinene	4.41E+05	4.41E+05	1	
alpha selinene	2.83E+05	2.83E+05	1	Foul(2)
Ketones				
2,3-butanedione	2.17E+06	7.47E+06	2	Rotten vegetable/solvent(2-3)
2-butanone	2.60E+07	6.51E+07	3	Sweet solvent/chemical/foul(2-4)
3-methyl-2-pentanone	2.22E+06	5.93E+06	2	
acetone	2.47E+06	1.85E+08	8	Fragrant/alcohol/foul(2-4)
Volatile fatty acids				
Acetic acid	1.27E+05	7.93E+05	9	Smoke/earthy/chemical (1-2)
Sulfur compounds				
Dimethyl trisulfide	4.52E+04	1.97E+05	3	Rotten(3-4)
Dimethyl disulfide	6.03E+06	4.30E+07	6	Chemical/manure/ sulfur (1-3)
Dimethyl sulfide	5.20E+06	2.81E+07	5	Sulfur/sewer(2-3)

Table 5.10 Volatiles obtained from dry summer litter using headspace (cont).

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Aromatic hydrocarbons				
1-ethyl-3-methyl-benzene	1.13E+05	1.69E+05	3	
1,3,5-trimethyl-benzene	9.24E+04	1.31E+05	7	Glue/musty(1-2)
Butylated hydroxytoluene	1.37E+05	3.06E+05	3	Earthy/ethery(1-2)
Phenol	1.40E+05	5.78E+05	4	Chemical(2)
p-xylene	1.96E+05	2.44E+06	4	Smoke/dry manure(3)
Styrene	1.33E+05	1.33E+05	1	
Toluene	1.02E+06	4.85E+06	6	Chemical(1-2)
Others				
Trimethylamine	5.02E+06	1.66E+07	3	Putrid(3-4)
Trichloromethane	3.71E+06	3.71E+06	1	

n= frequency of compound repeated in the 9 weeks of sampling

Table 5.11 Volatiles of wet summer litter using direct headspace.

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	max		
Alcohols				
2-butanol	2.36E+07	2.36E+07	1	Alcohol(3)
Aldehydes				
3-methyl-butanal	9.55E+06	1.45E+07	2	Pungent(3)
Ketones				
2,3-butanedione	7.13E+06	7.49E+07	3	Rotten vegetable/pungent (2-4)
2-butanone	3.21E+07	8.56E+08	3	Pungent(3)
3-hydroxy-2-butanone	3.45E+05	2.64E+06	2	Foul(2)
3-methyl-2-butanone	1.34E+07	1.34E+07	1	
3-methyl-2-pentanone	4.70E+06	1.57E+07	3	Pungent(4)
Acetone	1.82E+07	6.13E+08	6	Solvent/manure(2-4)
Acetophenone	1.63E+05	1.63E+05	1	Smoke(2)
Volatile fatty acids				
Acetic acid	1.04E+05	7.59E+05	9	Smoke/chemical/ Vinegar (2-3)
Sulfur compounds				
Dimethyl trisulfide	5.90E+04	7.52E+05	4	Rotten(3-4)
Dimethyl disulfide	4.68E+06	1.08E+08	6	Manure/sulfur(2-4)
Dimethyl sulfide	8.07E+06	3.44E+07	5	Rotten/putrid(2-4)

Table 5.11 Volatiles of wet summer litter using direct headspace (cont).

Compounds	Peak area		n	Range of odour descriptions and intensities (1-4)
	min	**max**		
Aromatic hydrocarbons				
1-ethyl-3-methyl-benzene	5.67E+04	1.43E+05	3	
1,3,5-trimethyl-benzene	7.52E+04	1.46E+05	7	Green/smoke(1-2)
Butylated hydroxytoluene	3.64E+04	5.31E+04	2	Chemical(1)
Phenol	2.76E+05	2.79E+06	3	Smoke(2)
p-xylene	1.22E+06	4.79E+06	3	Sharp/putrid(3-4)
Styrene	1.15E+05	2.86E+05	4	
Toluene	9.05E+05	1.46E+06	2	Sharp(2)
Others				
2,4-Pentadienenitrile	5.27E+04	5.27E+04	1	Fishy(2)
Trimethylamine	9.48E+06	2.22E+07	2	Putrid(2-4)
Trichloromethane	4.18E+06	7.37E+06	4	

n= frequency of compound repeated in the 9 weeks of sampling

5.4.3 Variation in the broiler litter volatiles

From the broiler litter odorant investigation, large quantities of chemicals and odorants were determined from litter materials by employing both chemical and sensory techniques (TD-GC-MS/O). Figure 5.29 illustrates the variations in number of chemicals obtained between the dry and wet litters for winter and summer climates. Approximately 85 % of dry and 69 % of wet winter litters' volatiles were characterised as odorants using Tenax TA tube with only 57 % of dry and 67 % of wet winter litter volatiles captured as odorants using direct headspace sampler. The summer litters recorded higher percentages of odorants differing from 71 % to 92 % between the two sampling techniques and the litter types. The higher percentages of odorants observed in the summer litters were most likely due to fewer volatiles being produced. In comparison, winter litters were identified to release the greater number of volatiles with a large variation in chemical functionalities than summer litters employing both sampling methods.

While the birds maturing, production and domination of volatiles been emitted from the litters were transformed in terms of chemical functionality. The abundance, odour description and intensity were most likely due to natural transformation process depending on the rate of microbial degradation occurring within the litter materials. The diversity of chemical functionalities for the litter samples are depicted in Figure 5.30. Domination of aromatic hydrocarbons and terpenes in the winter litters and aromatic hydrocarbons and ketones in summer litters were observed. At the initial stage, winter litter odorants exhibited emissions primarily containing terpenes and aromatic hydrocarbons prior to the formation and emission of unpleasant odours that consisted of alcohols, ketones, volatile fatty acids and sulfur containing compounds. This olfactory change is due to the transfer of birds onto the bedding material. In contrast, aromatic hydrocarbons, ketones, sulfur and nitrogen compounds were largely produced in the summer litters with no major volatile fatty acids characterised other than acetic acid.

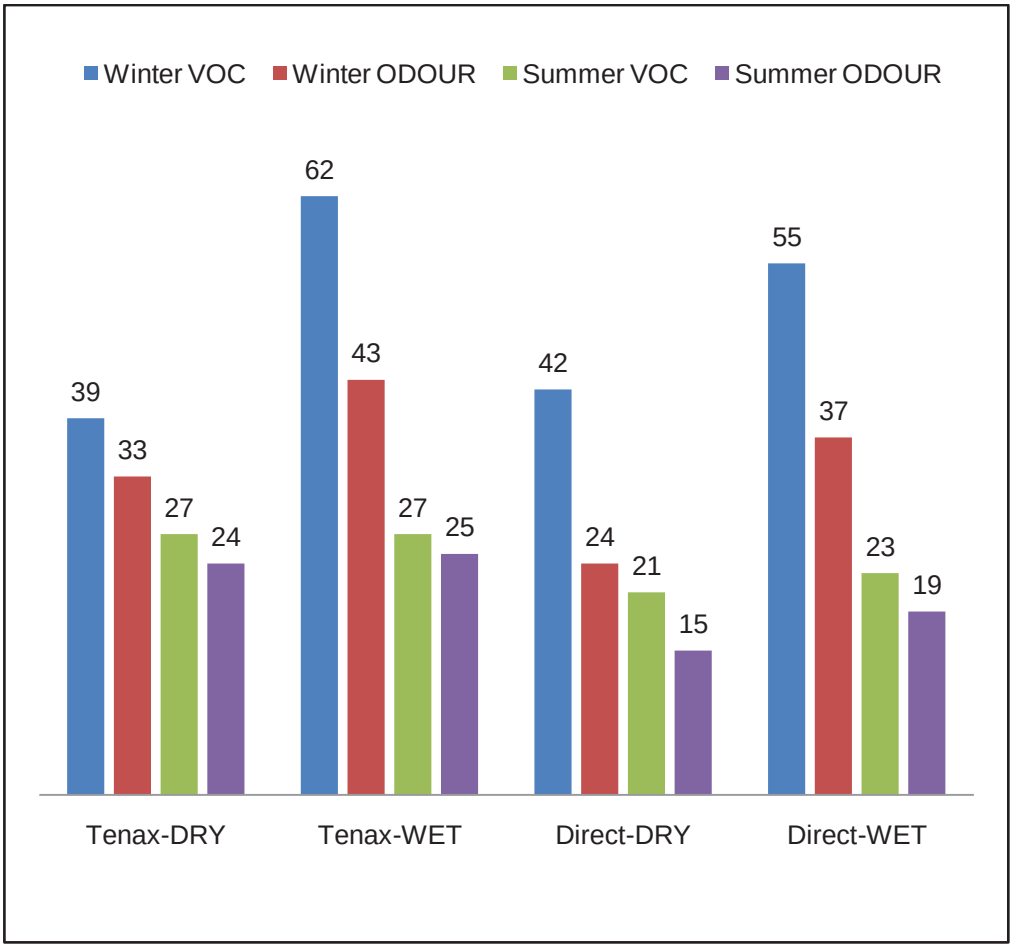
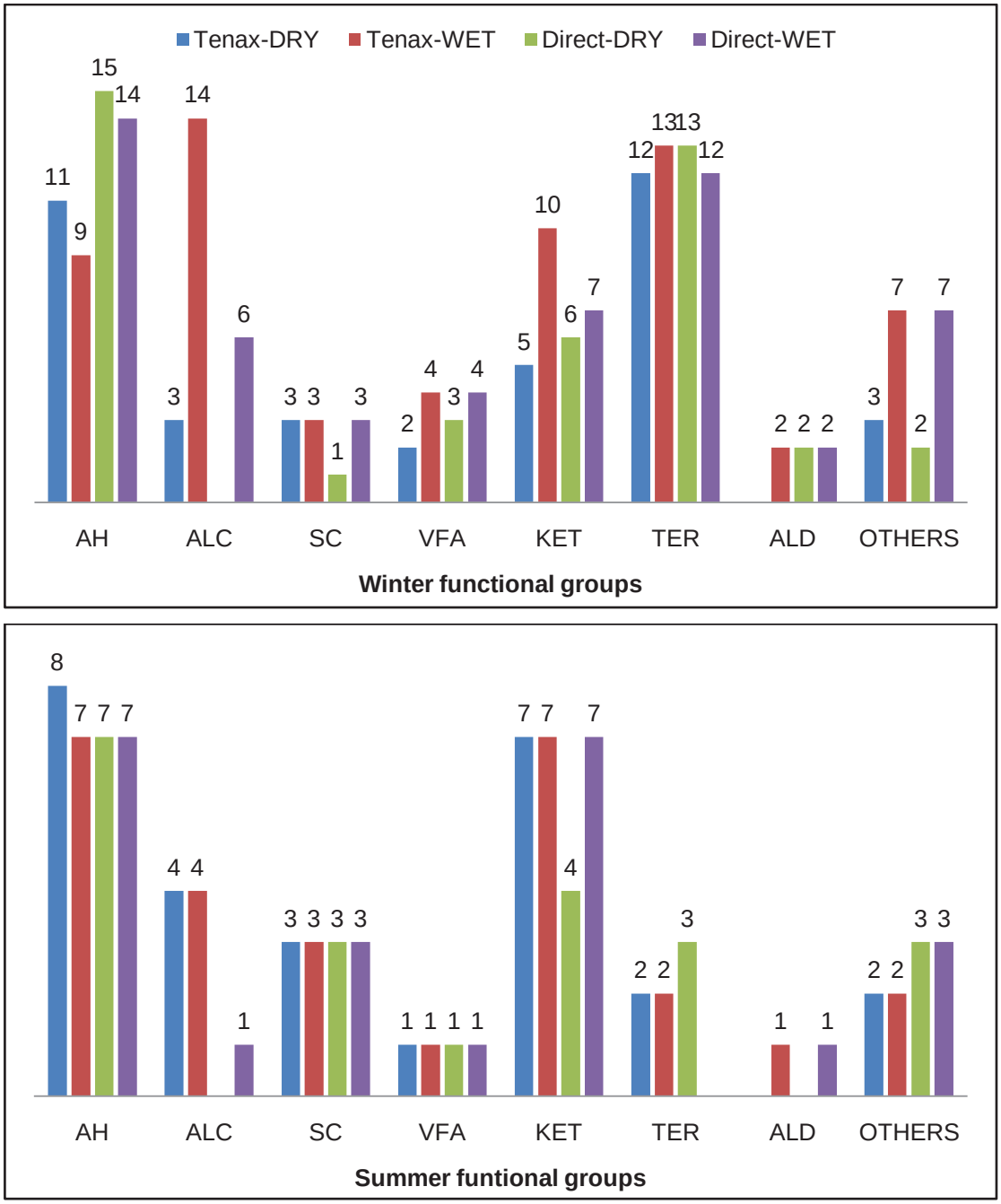


Figure 5.29 Comparison of volatiles and odorous volatiles detected from winter and summer samples with Tenax TA tubes and direct headspace samplings.



AH=aromatic hydrocarbons ALC= alcohols SC=sulfur compounds VFA= volatile fatty acids KET= ketones TER=terpenes ALD =aldehydes

Figure 5.30 Variation of chemical functionalities from winter (top) and summer (below)

5.4.4 Broiler litter odorants

The chemicals and odorants identified from different litters were observed to vary with the physical and chemical properties of the litters. From this study, a variety of odorous species were collected during broiler litter analyses that are expected to influence the global litter odour that could be released from the poultry shed. At the initial stage of sampling, the litters appeared unsoiled releasing acceptable pleasant odour during the winter study. Meanwhile the summer litters were noticeably non odorous at the early stages of sampling. The extensiveness of perceived litter odours were found to increase gradually with the introduction of birds and the soiling of the fresh beddings with biological solids and fluids. The biodegradation process by micro-organisms in soiled litter under aerobic and anaerobic conditions produced varying odour potent chemicals, mainly of alcohols, volatile fatty acids, sulfur compounds, ketones, terpenes and aromatic hydrocarbons groups. The detections of large amounts of terpenes and aromatic hydrocarbons at the initial stages can be attributed to natural occurrence of these chemical groups from plant materials used in the bedding. In addition, odorants belonging to these varieties of functionality can be disregarded as obnoxious odour since the odour quality was reasonably pleasant or less offensive, whereas ketones, volatile fatty acids, sulfur and nitrogen containing compounds produced higher scale of odour intensity with prominent unpleasant odour characteristics. It is noteworthy that mostly all odour descriptions collected for odorants through the headspace TD-GC-MS/O matched significantly with published odorants qualities from a variety of research area [35-36, 59, 146,151]. Some small differences existed in odour characterisation vocabulary attributed to variation in concentration and experience of sensory evaluating operators.

5.4.4.1 Volatile fatty acids

The volatiles fatty acids are low threshold odorants mainly formed by degradation of plant fibre material and proteins under anaerobic conditions. Two potential pathways of volatile fatty acid productions include hydrolysis of carbohydrates in plant materials and deamination of amino acids [5, 21]. The short chained volatiles fatty acids such as acetic, propanoic and butanoic acids

were found abundantly in the winter samples, which are likely to be the product of hydrolysis process carried out on carbohydrates existed in the fresh bedding plant materials. Only two branched volatiles acids, 2-methyl propanoic and 4-methyl pentanoic acids were detected herein, anticipated of deamination of protein in the broiler manure. In addition, generation of volatiles fatty acids are also feasible from the oxidation of primary alcohol. For example, 1-butanol is oxidised into butanoic acid via oxidation of butanal. Among the volatile fatty acids characterised, propanoic and butanoic acid demonstrated higher degree of offensiveness than acetic acid. The presence of large amount of volatile fatty acids in week 5 for the wet litter is in agreement with litter pH recorded of the respective week. Olfactory responses categorised volatile fatty acids as highly offensive odorants exhibiting descriptions varying from sharp, urinal, vinegar, rancid, rubbery and cheesy.

5.4.4.2 Sulfur containing compounds

Sulfur compounds including methanethiol, dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide and 2,4-dithiapentane varied largely in the winter and summer litter samples across the full growth cycle. Manures accumulation provided the primary platform for the production of sulfur volatiles via two biochemical pathways: a) hydrolysis of sulfurous amino acids under anaerobic conditions that releases sulfidic compounds and b) sulfate reduction in urine through assimilatory or dissimilatory reactions producing sulfide, water and carbon dioxide. Chemically, methanethiol detected in the litters during the analysis could have been the parent compound to generate the other sulfides such as the dimethyl sulfide, dimethyl disulfide and dimethyl trisulfide [21, 212] and provides better understanding of emissions prominent to sulfur containing compounds of litters. In the summer litters, sulfides were observed to dominate the odorants produced. The characterisation of sulfur compounds from the litters was conducted at high caution owing to the limitation of the cold trap used for volatile pre-concentration in the thermal desorbing unit towards monoterpenes and sulfur compounds. Further work is needed to better characterise reduced sulfur compounds being formed and emitted from in different litters.

During the sulfur odorants analysis, 2,4-dithiapentane was identified in the winter wet litter. This substance has not previously been reported in poultry litter odour. The 2,4-dithiapentane has a distinctive sulfur compound often related to truffle flavour in food and flavour sciences. In the animal waste odour study by Cai and co-workers, the chemical was first reported from swine waste using GC/O technique, demonstrating a skunk like odour [147]. The sorbent tube technique used herein captured 2,4-dithiapentane at a retention of 9.34 min at reasonably high abundance with rancid odour quality that was mildly rated, with string MS library match quality of 91 %. The highest odour offensive rating for sulfur compounds was obtained for dimethyl sulfide, dimethyl trisulfide and methanethiol. These compounds are described as rotten, putrid and ferment when perceived at low peak area abundances, proving their low odour threshold characteristics. Whereas, odour description for dimethyl disulfide remained at an acceptable level such as chemical like odour compared to the other sulfur compounds even though it was recorded at maximum level on the odour scale at some stages.

5.4.4.3 Ketones

Both winter and summer litters demonstrated the generation of a variety of ketones that varied between seasons. Major ketones identified from litters included: 2-butanone, 3-hydroxy-2-butanone and 2,3-butandione with significant odour characteristics as solvent, sweet chemical and earthy, musty or mushroom that were less offensive in odour quality than of other chemical functionalities. The productions of ketones are mainly the result of the oxidation of secondary alcohol as shown in Figure 5.31. This includes the oxidation of 2-butanol producing 2-butanone and the subsequent oxidation on 2,3-butandediol and 3-hydroxy-2-butanone generating 2,3-butanedione. The domination of 2-butanol and 2-butanone in week 5 and 7 for the winter wet litters and 3-hydroxy-2-butanone and 2,3-butanedione for the summer wet litter in week 6 (both obtained through sorbent tube and direct headspace sampling) further confirmed the likely hood that the ketones production pathway in the litter material can be described as in Figure 5.31.

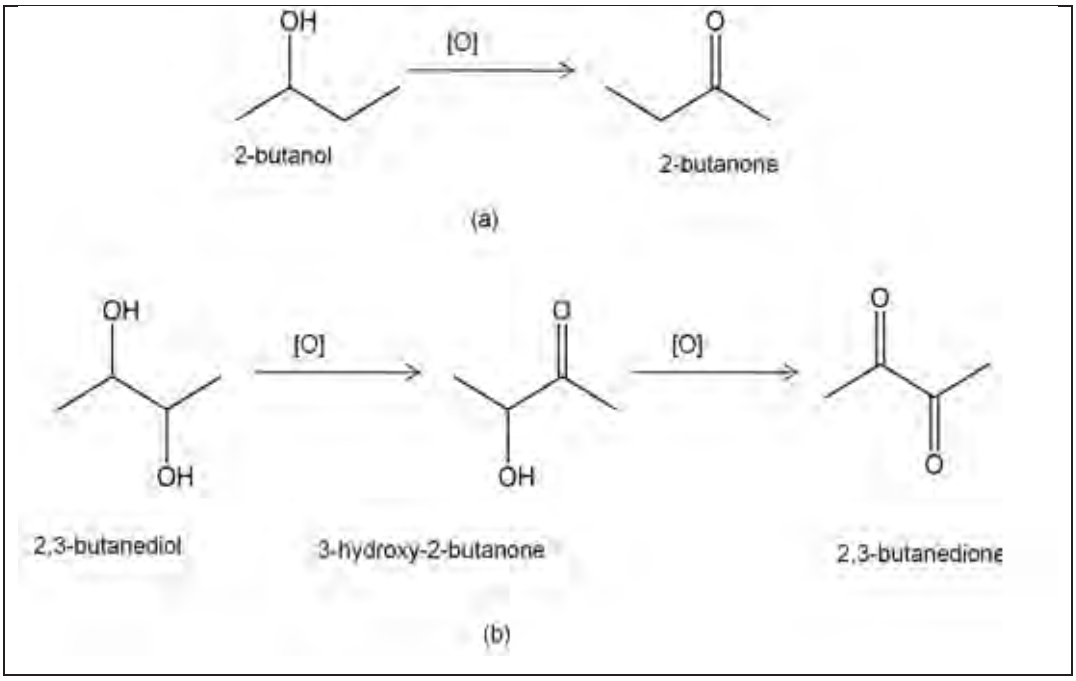


Figure 5.31 Production mechanism of a) 2-butanone and b) 2,3-butanedione based on alcohols.

5.4.4.4 Phenol and cresols

Continuous accumulation of manure in the litters allows for the production of aromatic hydrocarbons such as phenol, indole, toluene and cresols. During the winter litter study, phenols and cresol were detected from week 3 and progressing throughout the broiler growth cycle. Whereas in the summer litters, the occurrence of phenol at the initial stage (week 0) was unexpected since fresh hard wood shaving was utilised as the bedding material. These compounds are produced via microbial degradation of the manure involving deamination and decarboxylation of aromatic amino acids [5]. Although the phenol and cresol exhibit medicinal, aromatic or pleasant odour quality at the initial stages of sampling, gradually these compounds demonstrated nauseating odour characters with increase in concentrations that caused annoyance [21].

5.4.4.5 Nitrogen containing compounds

Two nitrogen containing compounds were identified in the litters as 2,4-pentadienenitrile and trimethylamine, both were observed in the winter and summer litters, except that no trimethylamine was obtained in winter litters. The 2,4-penradienenitrile smell is transformed from processed rubber sheet, fishy,

glue and turpentine while the trimethylamine shows a more offensive putrid and fishy like odour across the production cycle. These odorants most probably have originated from the manure and urine that are great sources of urea collected on bedding material. Volatile nitrogen compounds are produced via decarboxylation of amino acids or amination of aldehydes. The trimethylamine produced herein is most likely a product of the decarboxylation of amino acids in the manure and broiler feed since no aldehydes were detected in the summer litter materials. Previous reports of the identification of 2,4-pentadienenitrile for poultry litter odour is also scanty and overall insufficient information is available for this compound.

5.4.5 Integration of TD-GC-MS/O selected odorants with dynamic olfactometry odour concentrations

One of the key objectives of the sampling conducted using dynamic olfactometry analysis (Chapter 4) and TD-GC-MS/O analysis is to incorporate the global odour concentration from the litters to the list of odorants identified in litter emissions in order to determine the influence of individual chemicals on the occurrence of odour annoyance. As numerous volatiles of different chemical functionalities have been identified from broiler litters, only selected odorants were demonstrating an impact on the human olfactory as detected by TD-GC-MS/O. The major chemical functionalities chosen for linearity analysis were based on the frequency of occurrences and intensity of the odour responses observed throughout the production cycle. These chemical groups included: volatile fatty acids, ketones, phenolic compounds, sulfur and nitrogen containing compounds from winter week 7 and summer week 6 for wet litters.

In general, the compounds that were characterised as highly offensive were detected to elevate abundance during the increase in odour concentration events, as shown in Figures 5.32 and 5.33 for volatile fatty acids and sulfur compounds from winter litter. High odour emissions were noticed in week 5 and week 7 that also exhibited high volatilisation of volatile fatty acids and sulfur compounds. However, it is often a difficult task to establish direct relationship between volatiles abundances (or concentrations) with odour emission

concentrations due to the existence of unique interaction between numerous volatiles in an odour at different concentrations. Additionally, the selectivity of volatiles, trend in production and emission of volatiles and the impact of various environmental aspects will also impact the ability to develop relationships between chemical abundance and the total odour emission.

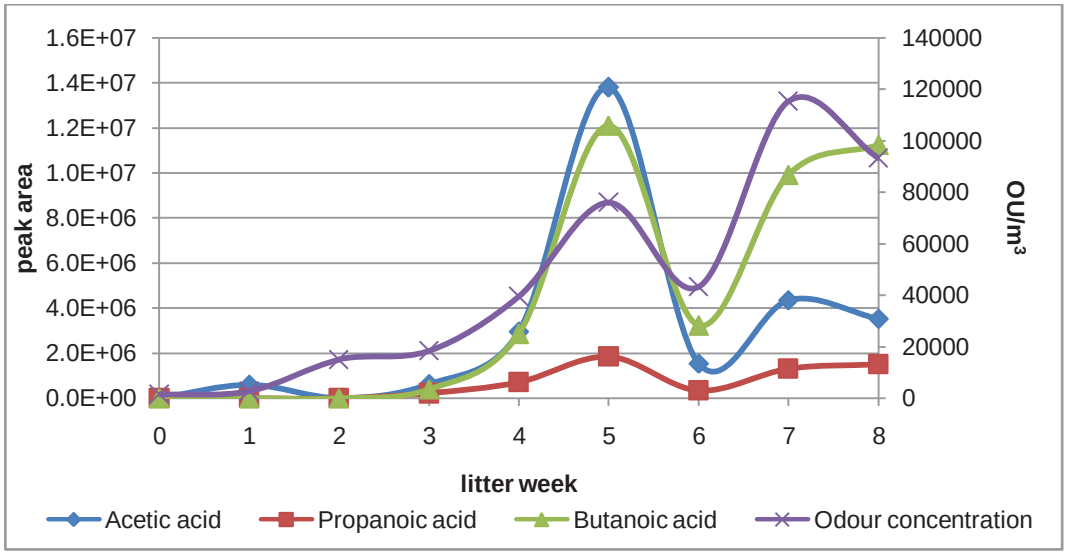


Figure 5.32 Dynamicity of volatile fatty acids for wet winter litter. Productions of the acids were visibly noticed to affect the odour concentrations during weeks 5 and 7.

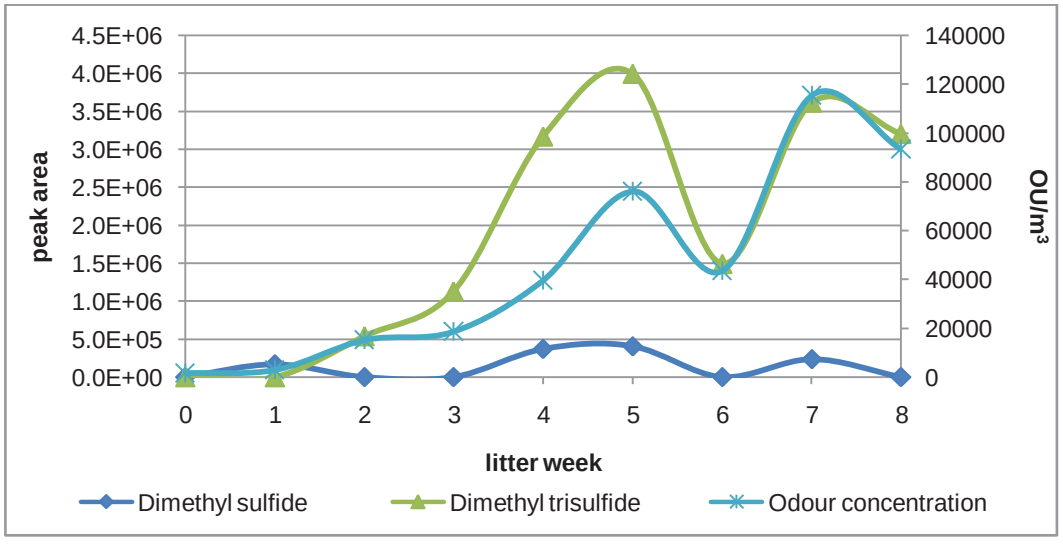


Figure 5.33 Dynamicity of sulfur compounds for wet winter litter. Similar to volatile fatty acids, the sulfur compounds produced some impact on the odour emission at weeks 5 and 7.

As a preliminary attempt, the correlations of dominate odorous volatiles in term of abundances with odour concentrations obtained through dynamic olfactometry analysis were used to generate regression values. The linearity curves attained for individual odorants using sorbent tube and direct headspace sampling of winter and summer litters are shown in Table 5.12 and Table 5.13 respectively. Reasonably good regressions were obtained for propanoic acid, butanoic acid, dimethyl trisulfide and 2,4-pentadienenitrile using sorbent tubes. Meanwhile only average correlations were exhibited for ketones, phenol and 2,4-dithiapentane. For the direct headspace sampling, no correlations were achieved except for 2-butanone, phenol and cresol. This circumstance is majorly anticipated with extreme production of respective volatiles during highest odour concentration weeks that appeared as outliers in comparison to other emission weeks [213]. The eliminations of these extreme peak areas for individual volatile fatty acids and ketones produced improved regressions ranging from 0.8 to 0.91 for direct headspace sampling that was in agreement with sorbent tube sampling results. Fewer key odorants identified at reasonably distributed peak areas promoted simplicity in correlating efforts between the volatiles and the odour emission concentration in summer wet litter. The Tenax tube demonstrated good regression with 2-butanone, 2,3-butanedione, dimethyl sulfide and toluene. Meanwhile the direct headspace sampling revealed better relationships with acetone, 2-butanone, 2,3-butanedione, phenol and trimethylamine.

Table 5.12 Correlations between winter odour emissions and volatiles abundances.

Compounds	r^2	
	Tenax	**Direct**
acetic acid	0.349	0.11
propanoic aicd	0.799	0.102
butanoic acid	0.869	0.127
acetone	0.595	0.001
2-butanone	0.505	0.575
3-methyl-2-butanone	0.466	
3-hydroxy-2-butanone	0.303	0.144
dimethyl sulfide	0.132	
dimethyl trisulfide	0.784	
2,4-dithiapentane	0.562	
dimethyl disulfide	0.103	0.057
methanethiol		0.001
phenol	0.578	0.612
cresol		0.693
2,4-pentadienenitrile	0.71	

Table 5.13 Correlations between summer odour emissions and volatiles abundances.

Compounds	r^2	
	Tenax	Direct
acetic acid	0.275	0.443
acetone	0.346	0.776
2-butanone	0.764	0.649
2,3-butanedione	0.91	0.713
dimethyl sulfide	0.799	0.481
dimethyl trisulfide	0.495	0.117
dimethyl disulfide	0.438	0.175
phenol	0.399	0.798
toluene	0.757	-
trimethylamine		0.679

As the individual compounds tested for correlation produced some uncertainties, further studies as grouped compounds based on chemical functionalities were conducted. The attempt generated improved regression relationships of some odorants as showed in Figures 5.34, 5.35 and 5.36 for the winter litters. Figure 5.37 shows the correlation of the total peak area for ketones, sulfur and volatiles fatty acids with odour concentration, which produced only an average regression (R^2=0.56). Whereas, an improved correlation with odour concentrations in the winter litter was measured using only the total peak area of sulfur and volatile fatty acids, as shown in Figure 5.38.

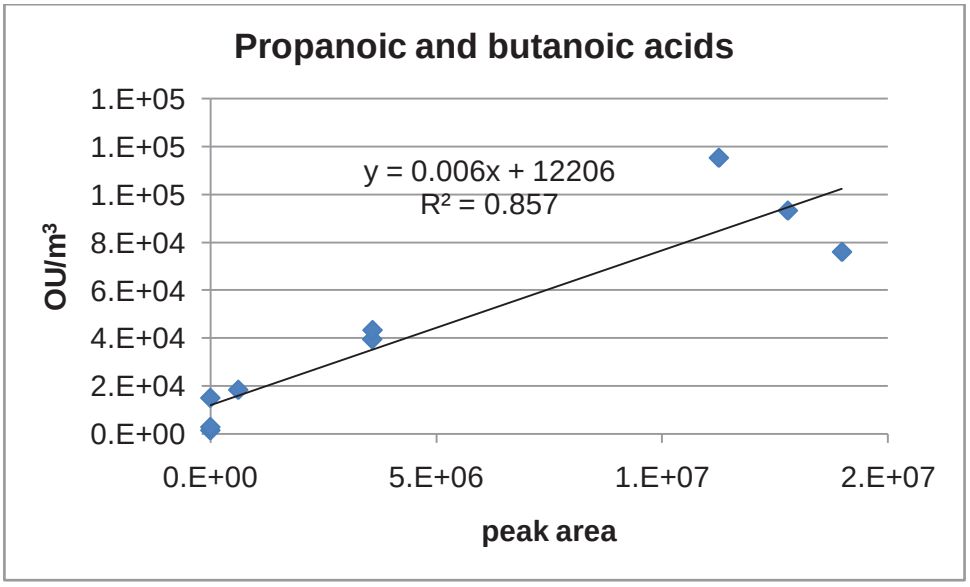


Figure 5.34 Correlation of concentration of determined volatile fatty acids of wet winter litter.

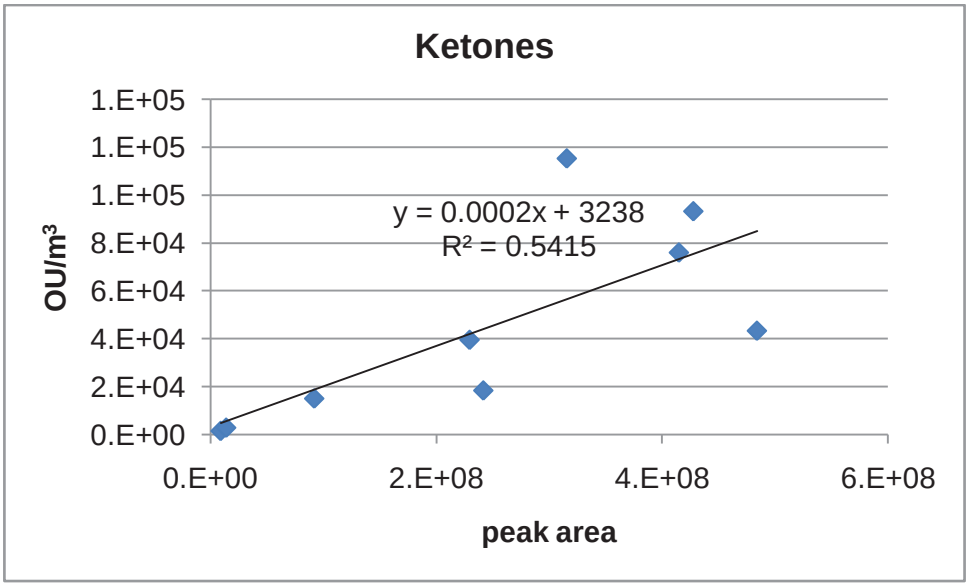


Figure 5.35 Correlation of odour concentration determined of all ketones in winter litter with Tenax.

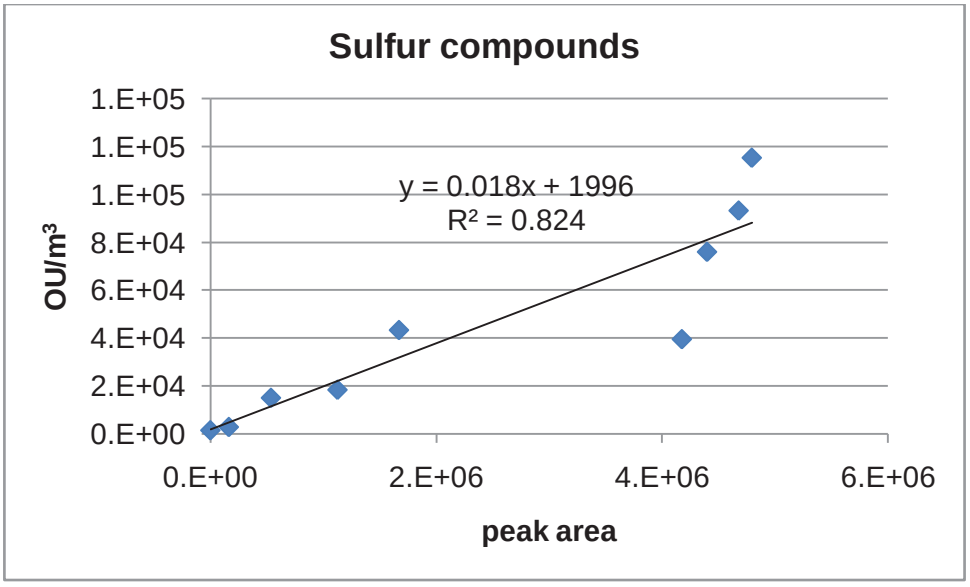


Figure 5.36 Correlation of odour concentration determined of all sulfur compounds except for dimethyl disulfide in winter litter with Tenax.

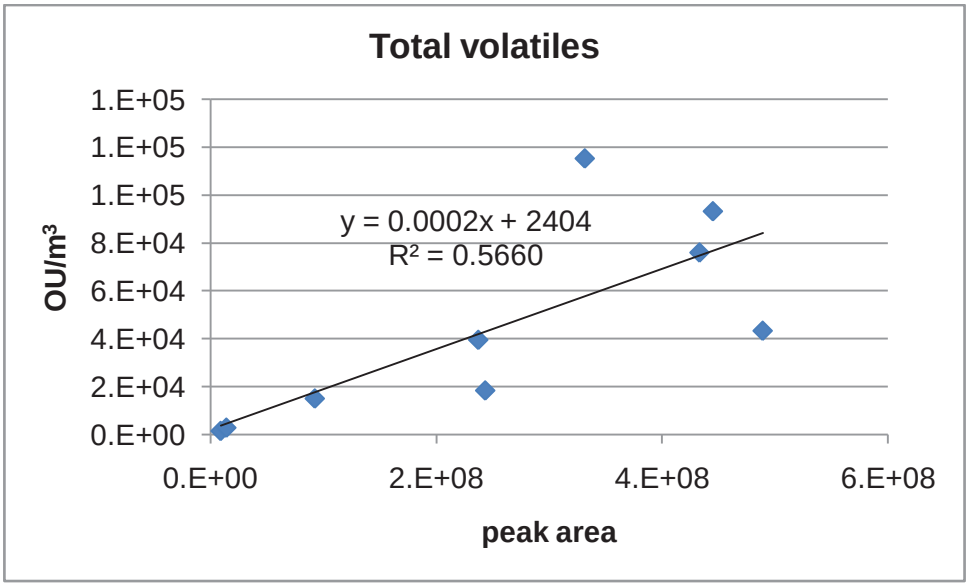


Figure 5.37 Average correlation of odour concentration determined of ketones, volatile fatty acids and sulfur compounds in winter litter with Tenax.

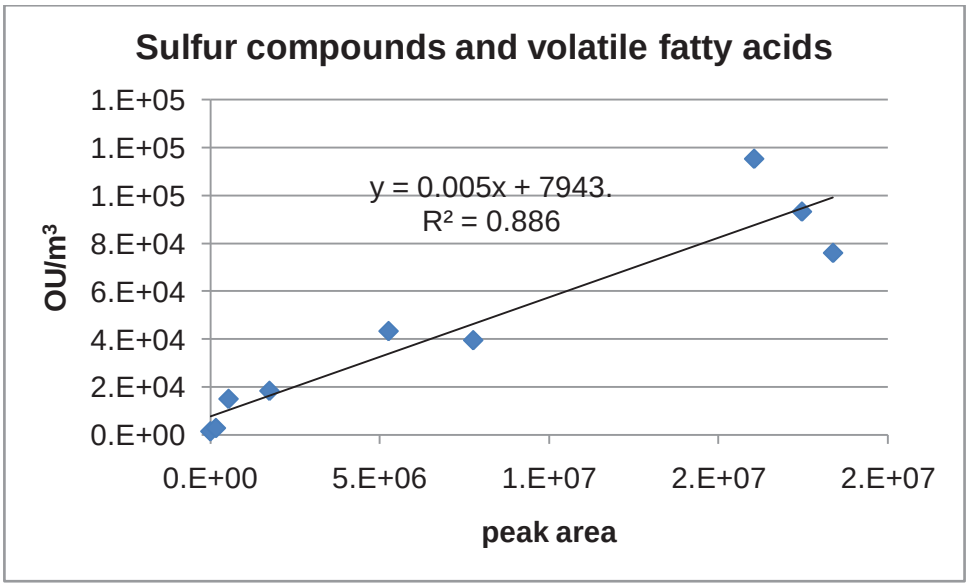


Figure 5.38 Fairly good correlation obtained of odour concentration determined of sulfur compounds and volatile fatty acids in winter litter.

For summer litter, grouped peak area of all ketones, phenolic compounds and sulfur compounds except for dimethyl disulfide was observed to show an increased impact on odour concentrations than as individual compounds (Figure 5.39, Figure 5.40 and Figure 5.41, respectively). The sum of ketones, sulfur and phenolic chemicals also showed a good correlation with odour emission concentrations (Figure 5.42). Some uncertainty appeared in the correlation analysis can be attributed to the exclusion of selective volatiles due to insignificant odour intensity, frequency and abundance. In addition, limitations existed within the sampling and analysis that could have further enhanced on the ambiguity of the linearity test.

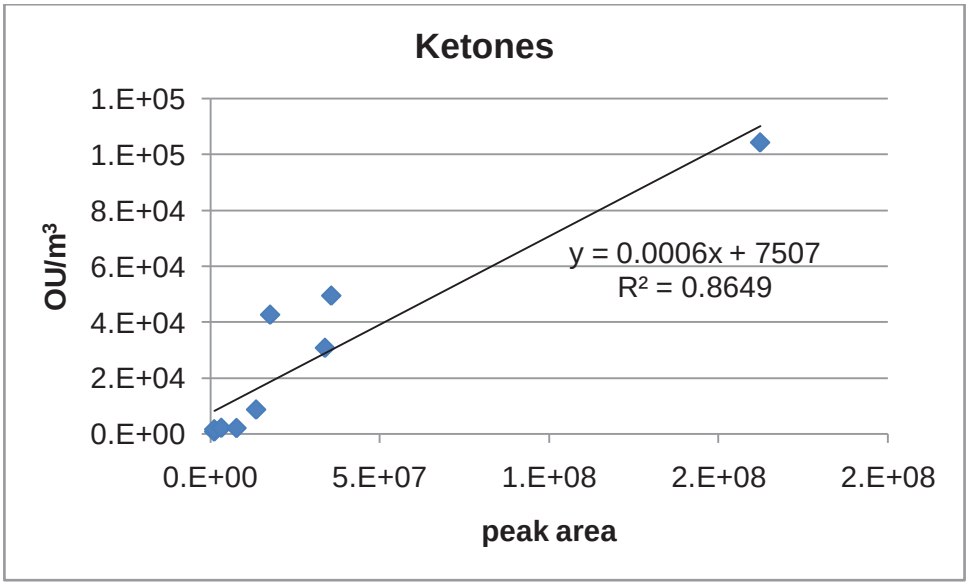


Figure 5.39 Correlation of odour concentration determined of acetone, 2-butanone and 2,3-butandione summer litter with Tenax.

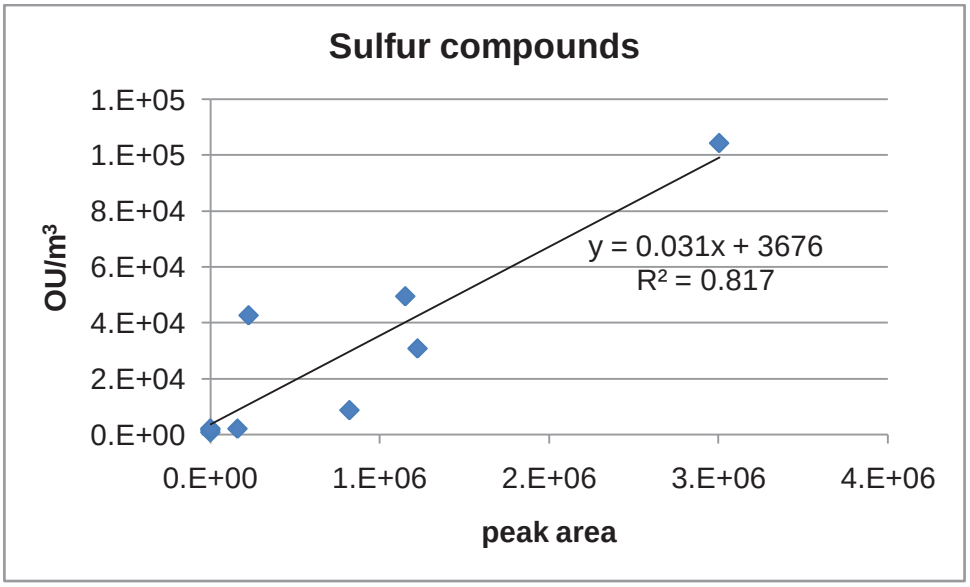


Figure 5.40 Correlation of odour concentration determined of dimethyl sulfide and dimethyl trisulfide in summer litter with Tenax.

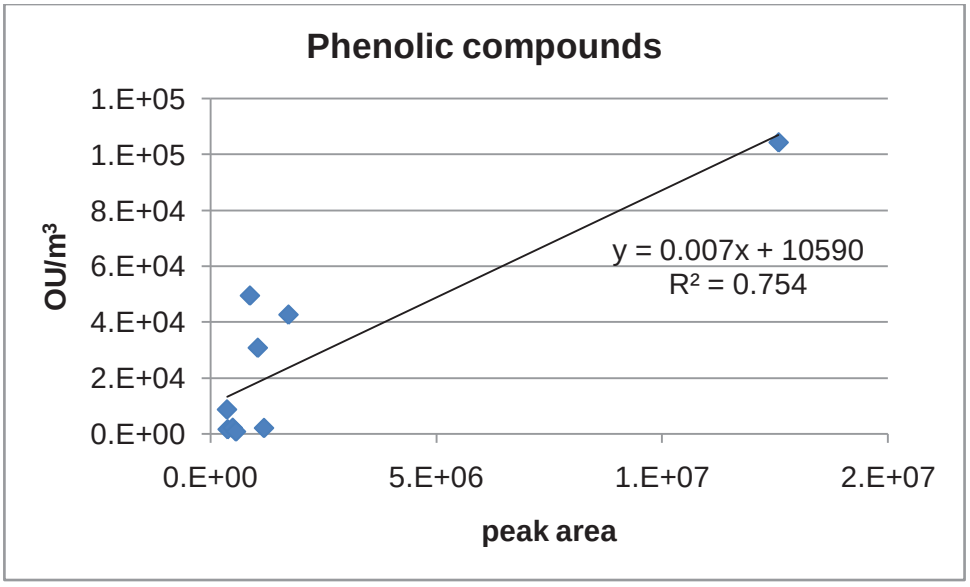


Figure 5.41 Correlation of odour concentration determined of phenol and toluene in summer litter with Tenax.

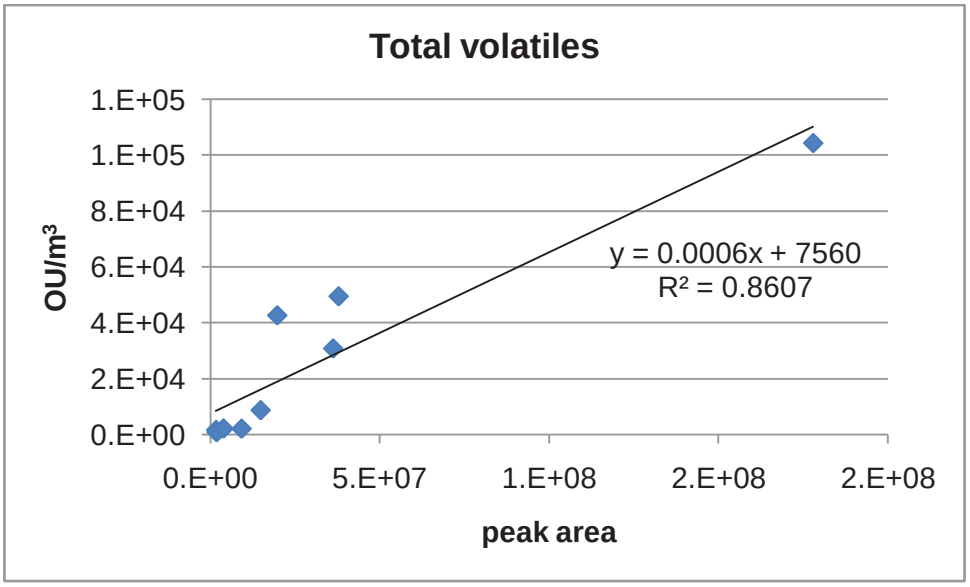


Figure 5.42 Fairly good correlation obtained of odour concentration determined of all ketones, sulfur and phenolic compounds obtained of summer litter

According to the correlation analysis, identified single odour peak area can be used to predict the impact of the particular odorant for global odorous emissions; however, this technique is not feasible at all time due to the limitations that existed within the experimental design. Instead, correlating the sum of grouped chemicals or the peak area of all volatiles identified provides a better understand of the interaction between volatiles in varying odour emission concentrations in complicated environmental conditions, especially for odour control management. From the linearity study, a fairly good correlation was obtained between winter odour emission and volatiles fatty acids and sulfur compounds. Whereas, the summer litter odour was observed to vary with trimethylamine, ketones and sulfur compounds. In both seasons, dimethyl disulfide showed weaker effect on odour impact.

5.5 Summary of broiler litter odorants characterisation

Litter odorants characterisation was one key objective of the study program. The use of sorbent tube and direct headspace to collect volatiles associated with TD-GC-MS/O analysis facilitated in speciation of a diverse range of volatiles and odorants. The analysis has shown that the key chemicals include: ketones, terpenes, sulfur and nitrogen compounds, volatile fatty acids, alcohol, aromatic hydrocarbon and aldehydes. Table 5.14 and 5.15 summarises the volatiles with distinct odour characteristics in both winter and summer litters. The concentrations of odorants determined directly from the litters were generally higher than for sorbent tube sampling due flow of inert purge gas into the sealed sampling vessel that allowed increase of chemical volatilisation into the sample headspace. In addition, adequate sealing between the sampling vessel and headspace sampler prevented leaking and losses of volatiles into the atmosphere during gas purge. This suggests strongly that odours are predominately generated from litter bedding, released into the production shed environment and transported to local receptors. The results also show that the variations in volatiles emitting from the litters depend significantly on the maturing birds that accumulate excreta and impact of environmental conditions within the litters. Ketones, volatile fatty acids, sulfur and nitrogen compounds that are released from litters exhibited highly offensive odour quality and intensity that subsequently categorised these chemical groups as major odour annoyance causing odorants.

Table 5.14 Odorants with significant characteristics of winter litters.

Compounds		
Aromatic hydrocarbons	**Alcohols**	**Ketones**
alpha dimethylstyrene	2-ethyl-1-hexanol	2-butanone
m-cymene	2-butanol	3-hydroxy-2-butanone
p-cresol	isopropyl alcohol	acetone
o-cymene	1-Butanol	3-octanone
1-methylethyl-benzene	1-propanol	6-methyl-2-heptanone
1-methoxy-4-methyl-2-(1-methylethyl)-benzene	1,3-butanediol	1-(4-methylphenyl)-ethanone
toluene	phenylethyl alcohol	acetone
phenol		camphor
o-cymene	**Sulfur compounds**	3-methyl-2-butanone
allylanisole	dimethyl disulfide	1-(4-methylphenyl)-ethanone
	dimethyl trisulfide	
Terpenes	methanethiol	**Aldehydes**
alpha pinene	2,4-dithiapentane	4-(1-methylethyl)-benzaldehyde
camphene		
limonene	**Others**	**Volatile fatty acids**
gamma.terpinene	2,4-pentadienenitrile	acetic acid
.alpha.-phellandrene	2,6-dimethyl-2,4,6-octatriene	butanoic acid
.beta.-Pinene	2-methyl furan	propanoic acid
alpha. terpinene	2-pentene	isocaproic acid
sabinene	(ethoxymethyl)-oxirane	2-methyl- propanoic acid
.alpha.-caryophyllene	3-pentenenitrile	
2-carene	ethyl acetate	
3-carene		

Table 5.15 Odorants with significant characteristics of summer litters.

Compounds		
Ketones	**Aromatic hydrocarbons**	**Sulfur compounds**
3-hydroxy-2-butanone	.alpha.-methylstyrene	Dimethyl sulfide
2,3-Butanedione	Butylated hydroxytoluene	Dimethyl trisulfide
2-Butanone	Toluene	Dimethyl sulfide
Acetone	p-xylene	
3-methyl-2-pentanone		**Aldehydes**
		3-methyl-butanal
Volatile fatty acid	**Alcohols**	
Acetic acid	2-butanol	**Others**
	1-Butanol	Trimethylamine

CHAPTER SIX

Odour abatement trials and analysis

6.1 Introduction

Odour annoyance from livestock production can reduce the quality of life in nearby residences and can become a threat to the long term sustainability of the poultry industry in Australia. Additionally, odours impacts have been reported to contribute to some adverse human health in local receptors [162,183]. As a result, measures to control emissions at farm sources are a possible mechanism to reduce the impact by these emissions on local population. In additional to direct emission of odours from poultry productions, poultry sheds also produce large quantities of spent litter for storage and land application at the end of each production cycle, which currently results from the preference by operators to use fresh bedding material for new broiler batch. As litter and odour generations from broiler farms are inevitable, amelioration of litter properties may alleviate offensive odorous emission while providing opportunity to reuse spent litter as bedding for new broiler batch.

Two basic odour control approaches can be applied for emission reductions are:

a) reduction of moisture content within the litter material
b) litter odour adsorption using potential odour adsorbents.

This chapter will provide information on the impact of adding activated carbon, silica gel and zeolite as an adsorbent on litter moisture content, pH and the abatement of odorous compounds. Wet litter samples collected at week 7 from the winter sampling and at week 6 from the summer sampling were used as the test litter for the abatement trials. One way Anova was used for the statistical analysis, with significant reduction, affect or differences determined at ($P<0.05$).

6.2 Sorbent material characteristics

6.2.1 Activated carbon

Activated carbon molecule contains graphitised black materials of coal, coconut shell, wood and peat. It is available commercially in the form of powder and granules. Granulated activated carbon is preferred as an adsorbent of organic and non polar materials over powdered activated carbon due to its large internal surface area and unique internal porous structure that provide high efficacy in volatiles trappings. The activated carbon is frequently marketed as an efficient and potent material for numerous water and gas phase applications, mainly as a packed in filters in the form of a media to adsorb pollutants from waste air stream and surface and groundwater.

6.2.2 Silica gel

Silica gel is a non-toxic, porous and vitreous granule or bead. This chemically inert substance has a wide range of applications in many areas such as drying agents and the adsorption of volatiles due to its extensive adsorption rate at different humidity levels. Common use of silica gel is as a desiccant in laboratories to control moisture content, preventing decaying or spoilage of samples.

6.2.3 Zeolite

Zeolite is a polar micro-porous solid adsorbent that consists of neutrally charged silica and negatively alumina. Zeolite is used widely in a variety of industries, including petrochemical, refrigeration and agriculture as a drying and carbon dioxide removing agents in the air. The high absorbency of moisture and selective odorants in zeolite is the result of its porous structure and its molecular sieve and ionic bonding properties.

6.3 Effect of adsorbent addition on litter appearance

Considerable physical changes were observed in the tested poultry litters treated with adsorbents (Figure 6.1). Throughout the analysis stages, all treated litters appeared drier and more friable than the control litter. Additionally, significant growth of fungi was also noticed on the surface of control litter set. The physical appearance of dried treated litters corresponded adequately with moisture content data obtained through adsorption study. A comparison of adsorbents showed that the application of activated carbon and silica gel to the poultry produced a drier and less odorous litter than for the addition with zeolite. Application of zeolite onto the litter was observed to be less effective as it generated dust particles during the sampling and analysis stages.

Untreated litter

Litter with activated carbon

Litter with silica gel

Litter with zeolite

Figure 6.1 Appearance of treated and untreated litters during abatement trial.

6.4 Effect of adsorbent addition on litter moisture content

Figure 6.2 shows the moisture content variations during the abatement trials for the winter and summer litters, respectively. Similar moisture content reduction trends were observed within the treated litters for both seasons. The moisture content in all sets reduced considerably while progressing through the experiment stages, however, the rates of moisture content varied between different tested adsorbents. In general, a steady decrease in moisture content was noted in the winter treated litters. Silica gel exhibited the prominent efficacy in trapping moisture compared to activated carbon and zeolite. This is evident with no moisture detected in the litters with 10 % and 25 % of silica gel in week 3 winter set. In comparison to the winter litter sets, the adsorbents were noticed to perform more efficiently in the summer litters sets, probably due to the low initial litter moisture at the start of the trial. Low water content in starting litter material could have improved and lessened the efforts of the adsorbents in decreasing the litter moisture. From the trials, the total removal of water was obtained from all litters with activated carbon and silica gel from week 1 to 3. In contrast, higher moisture content was detected in litter sets with zeolite in comparison to the control and other treated litter samples. In both the winter and summer trials, litters with zeolite generally sustained more water content than other adsorbing materials which confirms zeolite as a substance with high affinity in binding water molecules that concurrently saturates the environment [187].

Additionally, consideration must be given to the impact of fume hood exhaust fan on the litters' moisture content during the adsorbent trials. The fume hood had a continuous air flow rate of 0.5 m^3/s which during the abatement trials this flow environment could have favoured higher water evaporation rates from the litters than without ventilation. This is evident by the observation that the moisture was decreasing in the control litters with the constant flow of air in the fume hood. Statistically, significant reduction in moisture content were obtained between trial periods ($P<0.05$) and insignificant reduction differences were recorded between the adsorbent materials for the winter trial sets. The summer

trial sets revealed effective reduction of moisture content between the adsorbents materials.

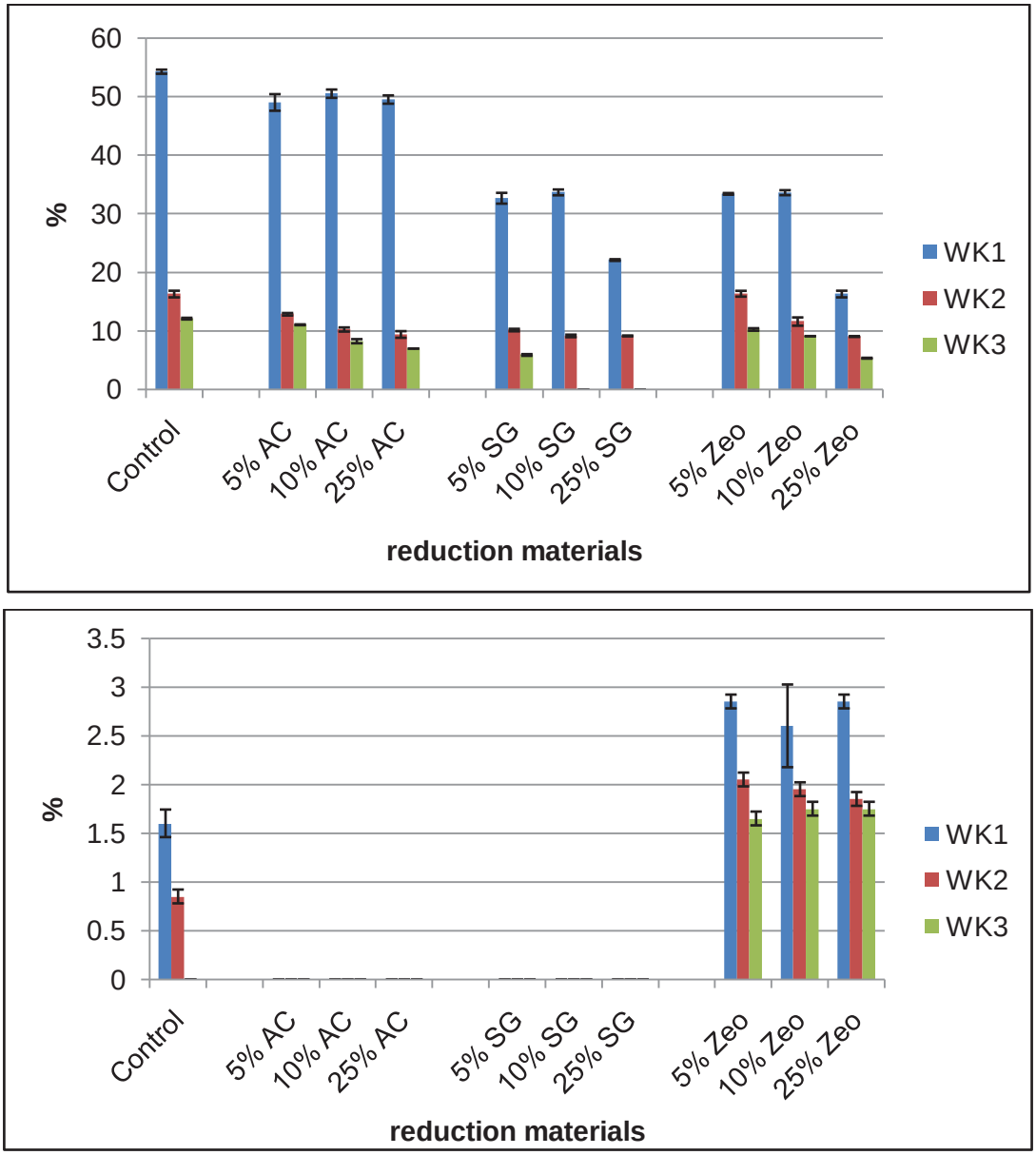


Figure 6.2 Variations in moisture content obtained during abatement trials for winter (top) and summer (below) litters with the addition of activated carbon (AC), silica gel (SG) and zeolite (Zeo).

6.5 Effect of adsorbent addition on litter pH

Figure 6.3 shows the pH variations obtained for the winter and summer abatement trials. All litter sets exhibited alkaline characteristics during the study periods. The pH values for the winter litters increased from previous weeks with values ranging from 6.5 to 9.4. The most significant increase in litter pH was observed for the winter litter treated with 25 % silica gel (25 % SG), transforming from acidic conditions in week 1 to alkaline in week 2. Summer litters varied a little with pH decreasing from week 1 into week 2 before subsequent increase in week 3. The summer abatement trial sets displayed a greater scale of pH values than the winter sets that ranged from 8.2 to 9.7. The highest pH values obtained were for litters with zeolite compared to activated carbon and silica gel from both seasons. Analysis of variance revealed insignificant difference in litter pH values between the tested adsorbents but with significant variation between study weeks for the winter litter. In contrast, significant variation in litter pH was observed between adsorbents compared to the abatement trial period.

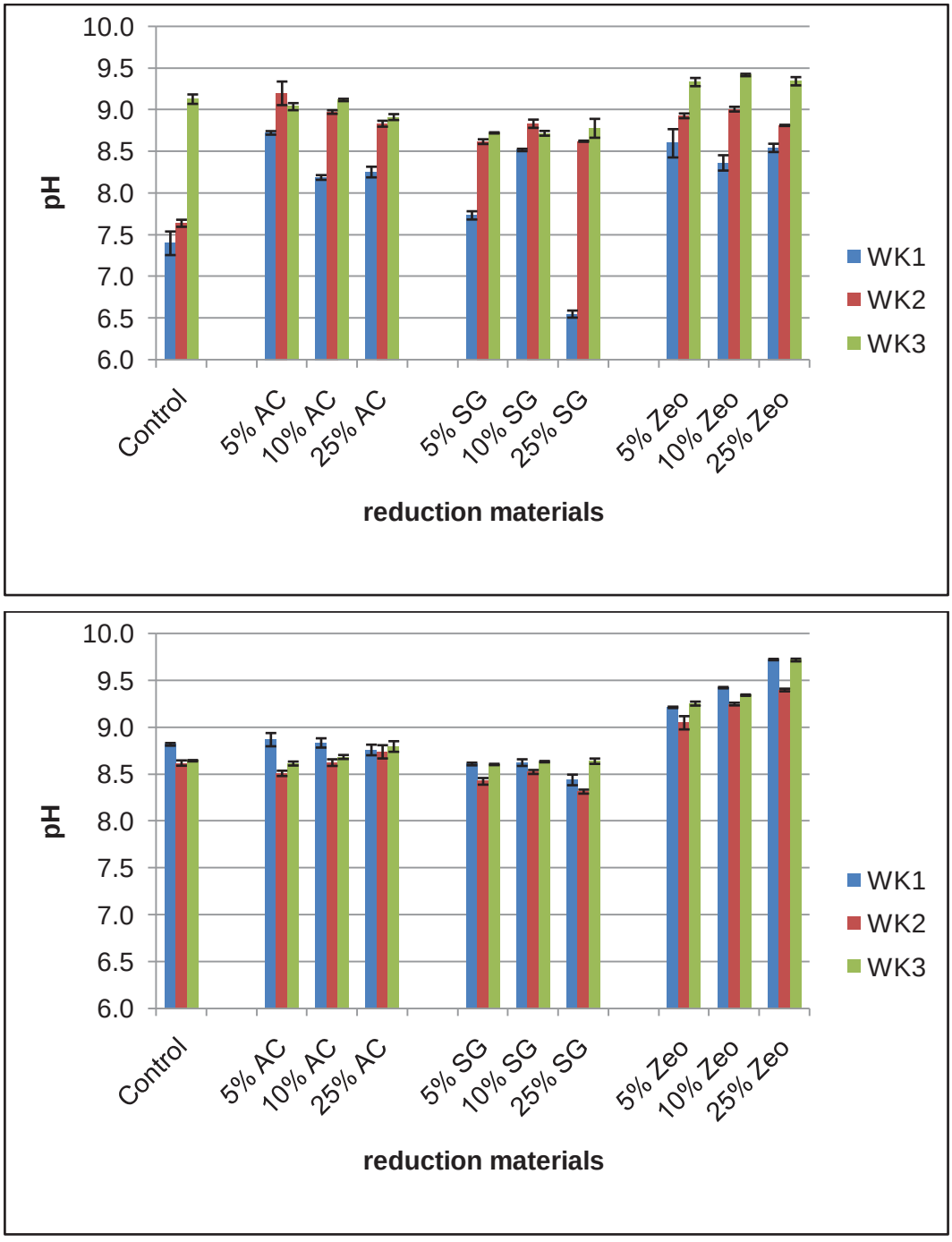


Figure 6.3 Variations of pH in treated winter (top) and summer (below) litters with the addition of activated carbon (AC), silica gel (SG) and zeolite (Zeo).

6.6 Effect of adsorbent addition on volatile emissions

The abatement trials attempted to provide an understanding on the potential application of litter odour adsorbing products. Results obtained from abatement trial generally suggest reductions of volatiles in all the treated litter sets in comparison to control litter. Some treated litters were observed to release higher yield of volatiles than the control set in the initial stages of trials (i.e. week 1), which could be attributed to the heterogenic characteristic of litters and the random selection of samples from sample bags. However, this statement is not applicable at all periods of the analysis especially when more significant reductions of volatiles were observed.

A pungent or nose piercing odour was perceived from all the litter sets, which could be attributed to the generation of ammonia in the summer and winter litter for the adsorbent trials. The release was sensed at greater intensity with a decrease in the litter moisture content and lasted until the end of abatement trials. Between trials set, the higher intensity for ammonia was perceived from the litters treated with zeolite. Drying litters with high pH values will enhance ammonia release from the litter surface due to lack in binding agent like water [214, 215]. Further quantification of the ammonia emission is not discussed herein as the analytical parameters for this study were set to focus on volatile organic compounds determinations.

In general, activated carbon and silica gel performed more efficiently in adsorbing volatiles from the litters than zeolite. Seven highly odorous compounds were observed to respond arbitrarily with the application of the selected adsorbents (Figure 6.4 to Figure 6.11). The adsorption of trimethylamine (TMA) was observed with litter treated with activated carbon and silica gel. No TMA was identified in week 2 of litters with 25 % of activated carbon and 10 % and 25 % of silica gel. Application of 5 % and 25 % of zeolite showed increase in the volatilisation of TMA compared to the control litter before decreasing in week 2 and being completely removed for 10 % and 25 % of zeolite noticed in week 3.

The adsorption efficacies with the addition adsorbents were noticed instantly for sulfur containing compounds, ketones and volatiles fatty acids. Complete adsorption of ketones for winter litters treated with activated carbon and silica gel were observed from week 1 to week 2 than for zeolite in week 3. In contrast, summer litters amended with silica gel were found to emit acetone in week 2. Volatile fatty acids were reduced in week 2 with none being detected in week 3 using all adsorbents. However, excessive volatilisations of acetic acid and butanoic acid were noticed from the winter litters with 25 % silica gel and zeolite in week 1, which is most likely a result of low moisture content in litter that assisted diffusion of volatile fatty acids into the headspace of sample [216]. Water soluble volatiles within wet matrix are likely to be present in lower quantity in air that subsequently reduces volatilisation. Similar conditions were existed for dimethyl disulfide for the summer litters treated with 10 % and 25 % of silica gel and zeolite, respectively. Complete removal of dimethyl trisulfide was obtained for all adsorbent within week 1. Irregularly and indefinitely interaction between adsorbents and toluene from litter were noticed with unknown adsorbing trend. Complete eliminations of toluene were obtained for 5 % and 10 % of activated carbon and zeolite for the winter litter and 10 % and 25 % of activated carbon and 10 % of zeolite for the summer litter. Significant reductions of TMA, acetone, 2-butanone, 2,3-butanedione, acetic acid, butanoic acid, dimethyl disulfide and dimethyl trisulfide were obtained over the adsorption trial period for the adsorbent used, except for toluene. Variation analysis revealed similar adsorbents with different ratio of application on the litter contributed to insignificant reduction of volatiles. Instead, noticeably decreases in volatilisation were obtained for the application of 5 % and 10 % activated carbon, silica gel and zeolite but not for 25 % for each of the adsorbents.

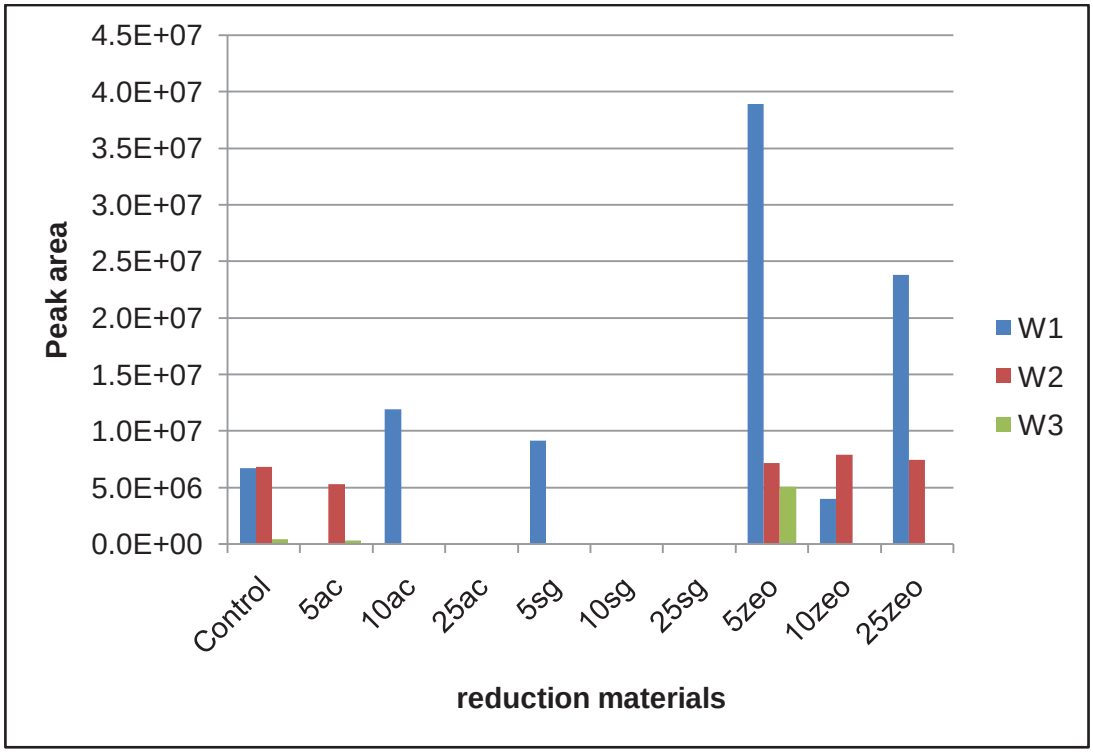


Figure 6.4 Volatilisation of trimethylamine from winter litters with the addition of activated carbon (AC), silica gel (SG) and zeolite (Zeo) at weeks 1, 2 and 3 (W1, W2, W3).

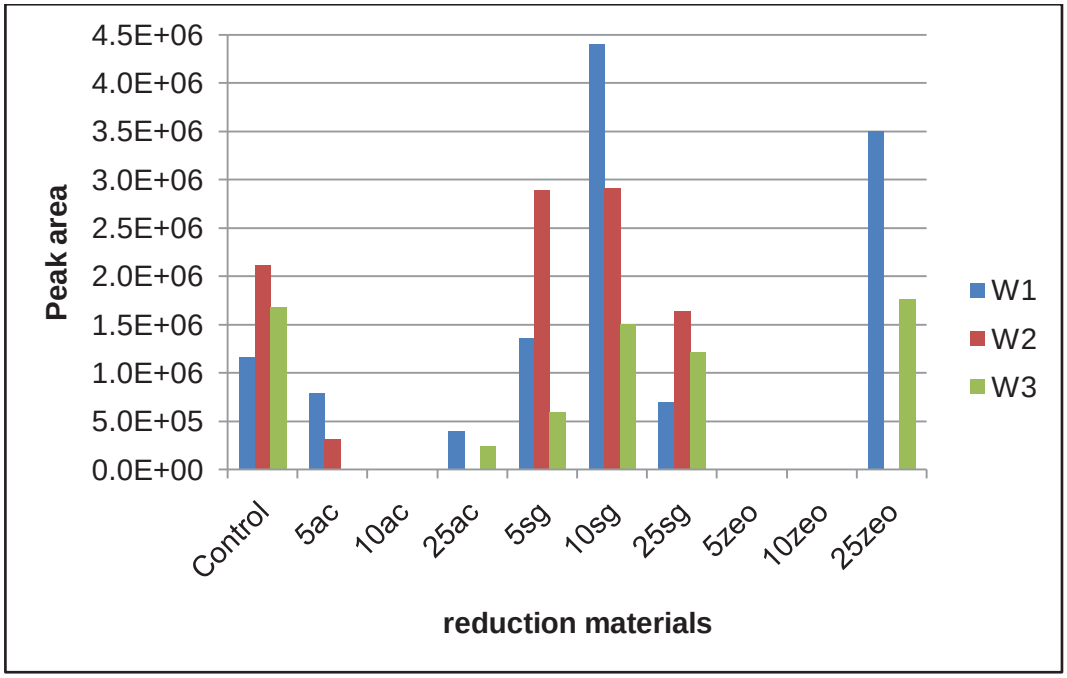


Figure 6.5 Volatilisation of toluene in the winter litters with the addition of activated carbon (AC), silica gel (SG) and zeolite (Zeo) at weeks 1, 2 and 3 (W1, W2, W3).

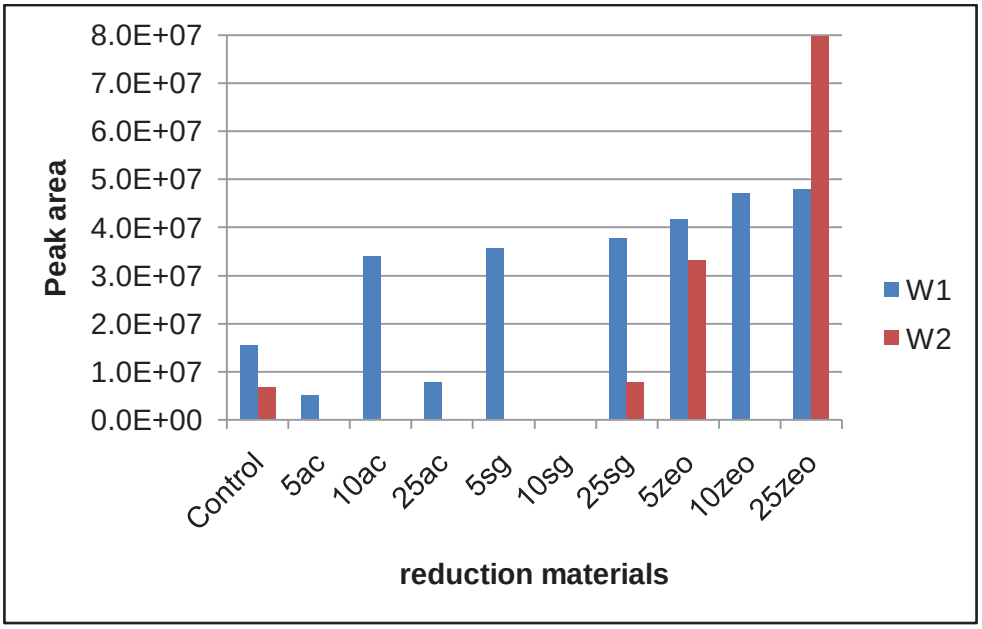


Figure 6.6 Adsorption of acetone in winter litter using activated carbon, silica gel and zeolite at weeks 1 and 2. No acetone was detected in week 3.

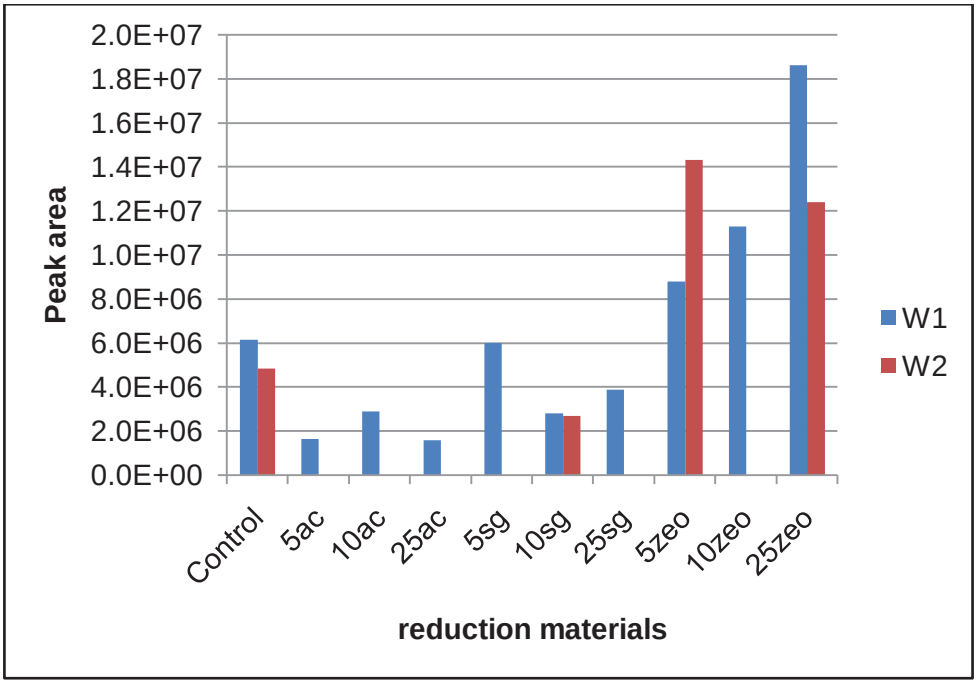


Figure 6.7 Adsorption of 2-butanone in winter litter using activated carbon, silica gel and zeolite at weeks 1 and 2. No butanone was detected in week 3.

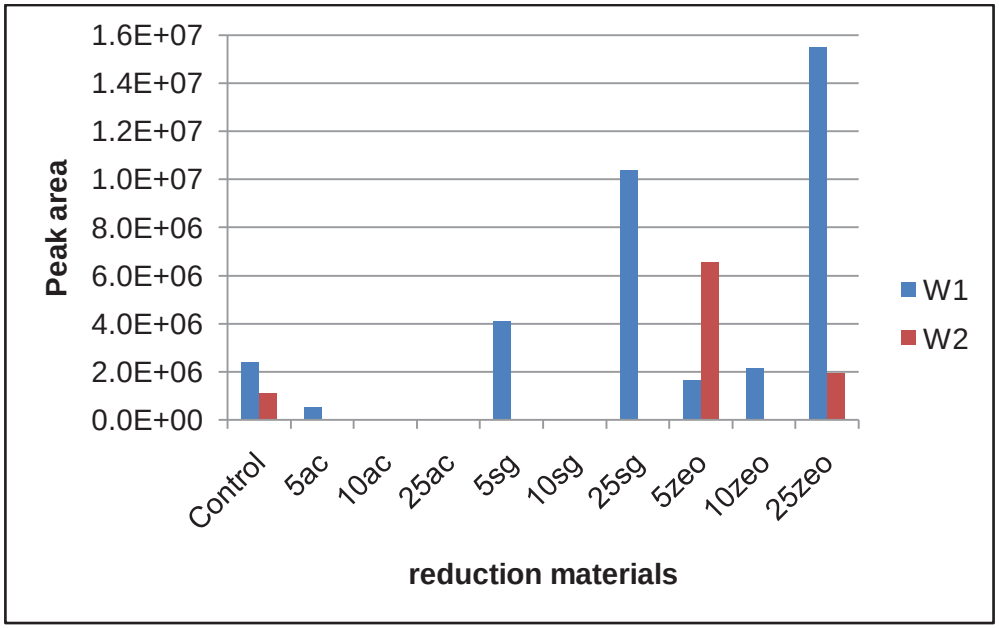
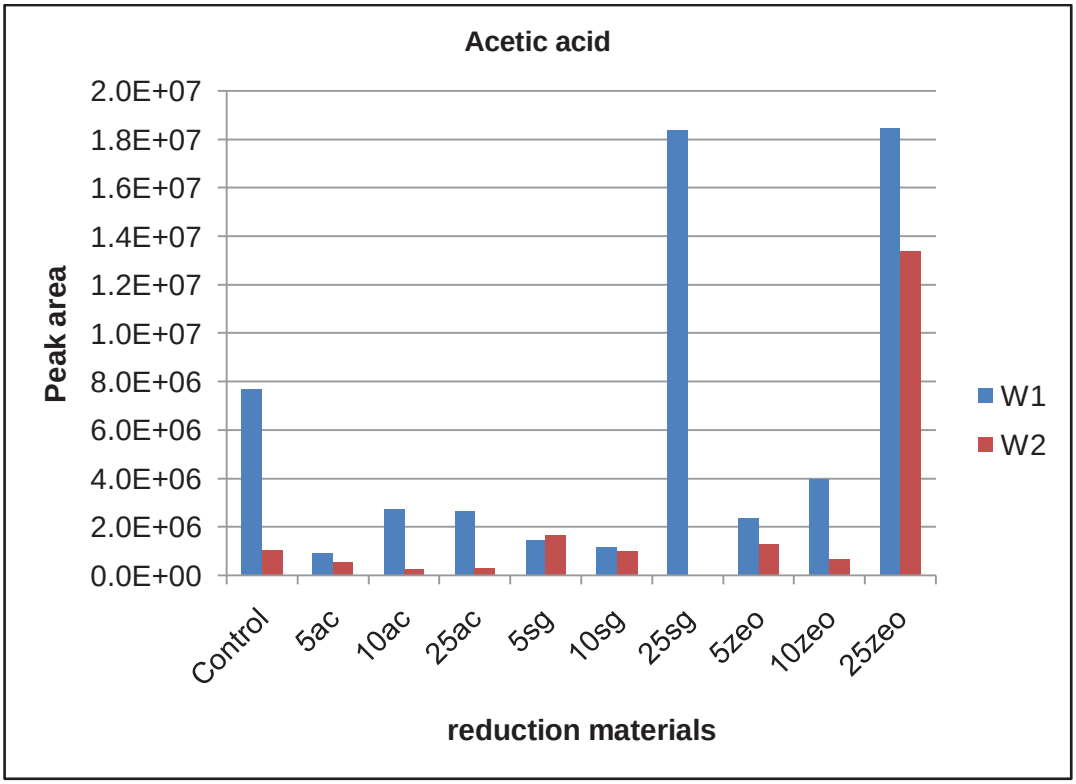


Figure 6.8 Adsorption of 2,3-butanedione in winter litter using activated carbon, silica gel and zeolite at weeks 1 and 2 (W1, W2).



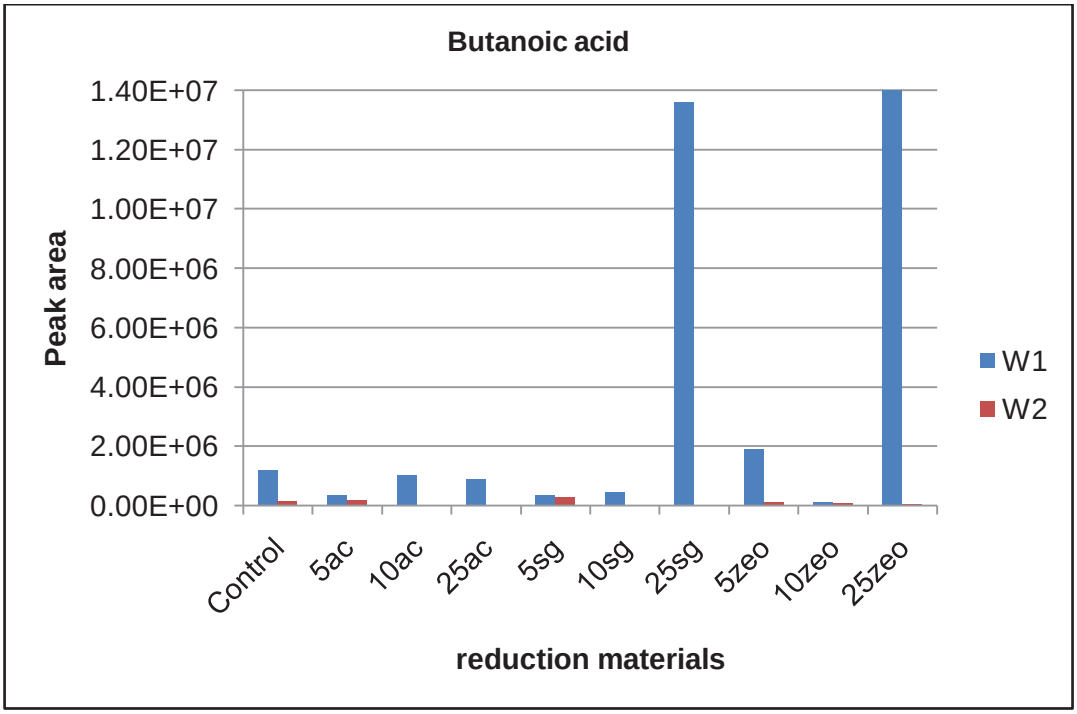


Figure 6.9 Variations in the emission of volatile fatty acids determined in winter litters with the addition of activated carbon (AC), silica gel (SG) and zeolite (Zeo) at weeks 1 and 2 (W1, W2).

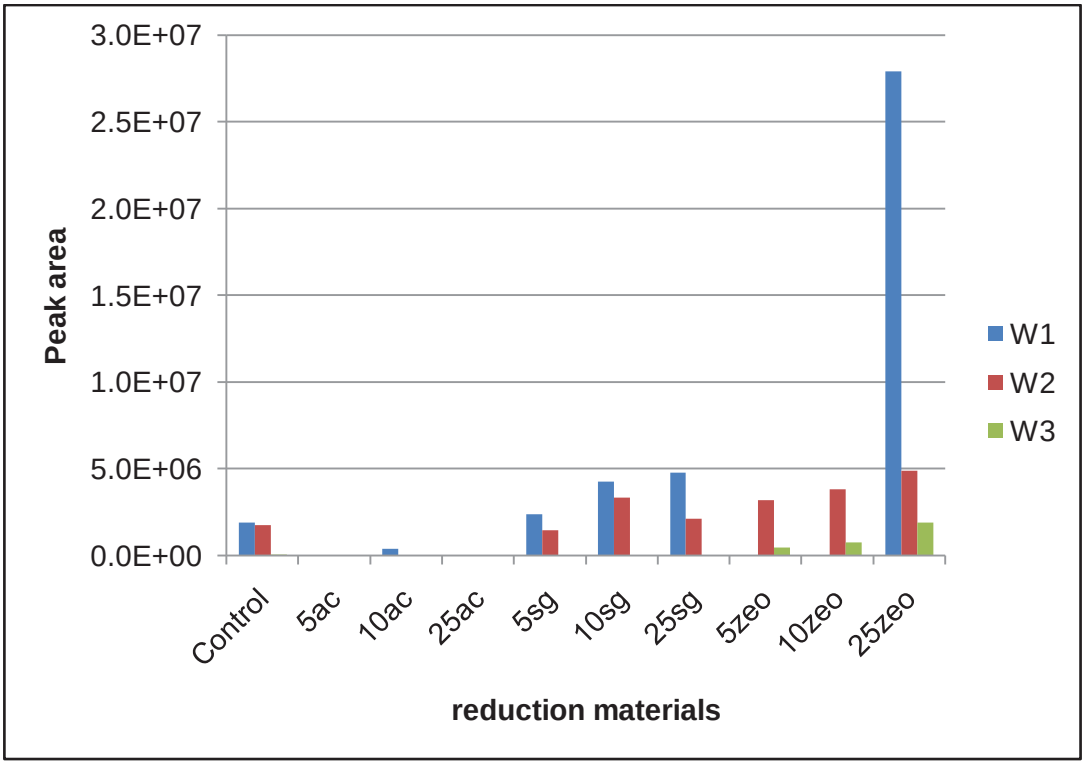


Figure 6.10 Adsorption of acetone in summer litter using activated carbon, silica gel and zeolite at weeks 1, 2 and 3 (W1, W2, W3).

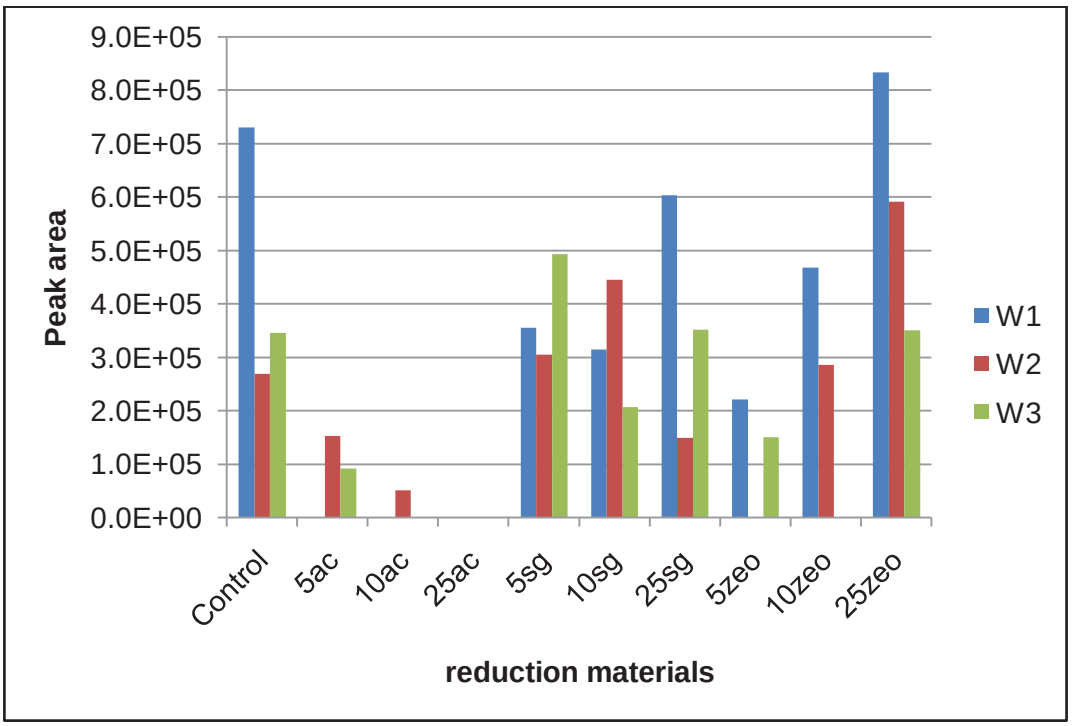


Figure 6.11 Variations in the emission of toluene determined in summer litters with the addition of activated carbon (AC), silica gel (SG) and zeolite (Zeo) at weeks 1, 2 and 3 (W1, W2, W3).

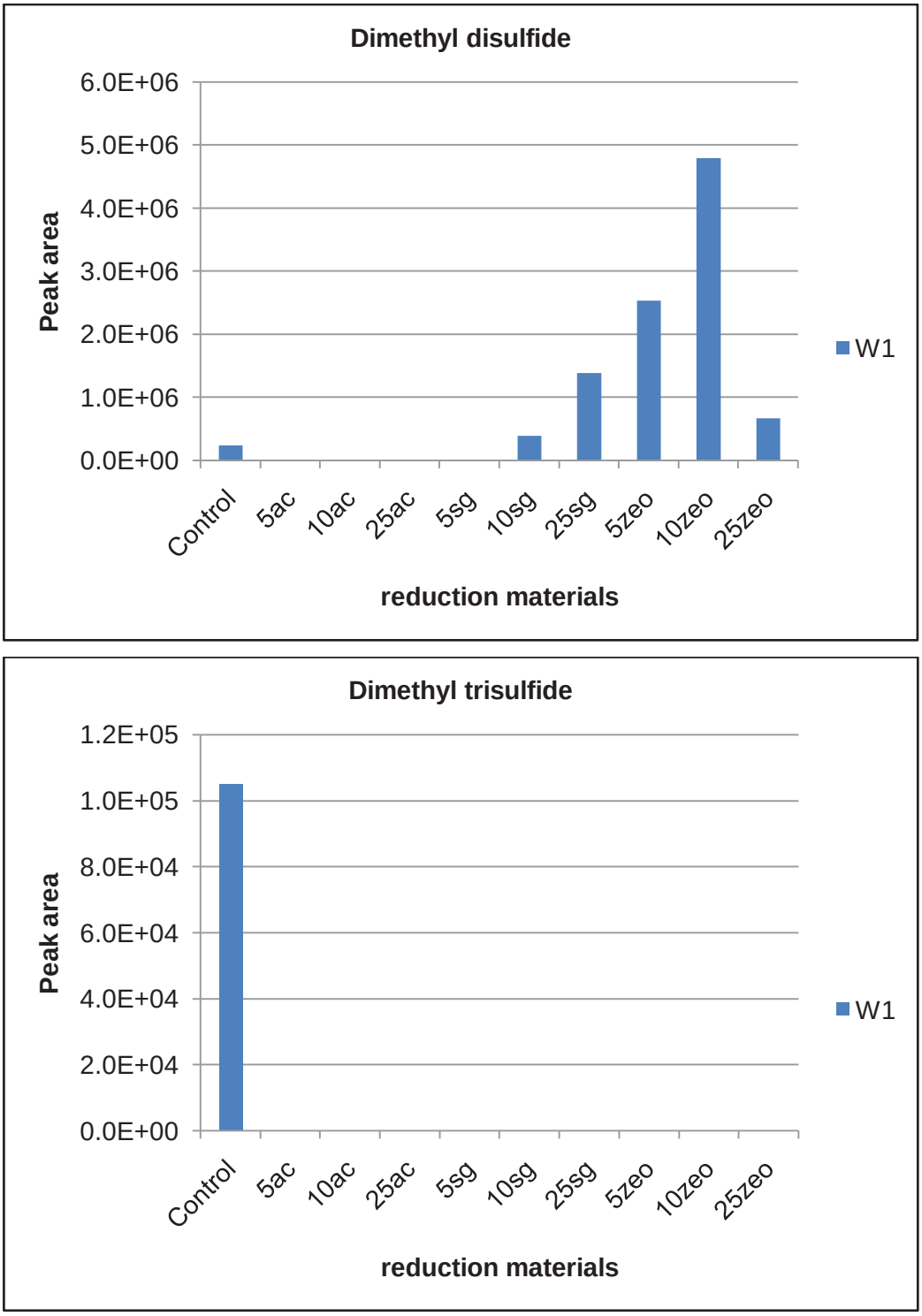


Figure 6.12 Variation in volatilisation of dimethyl disulfide (top) and dimethyl trisulfide (below) in summer litter with the addition of activated carbon (AC), silica gel (SG) and zeolite (Zeo) after one week 1 (W1).

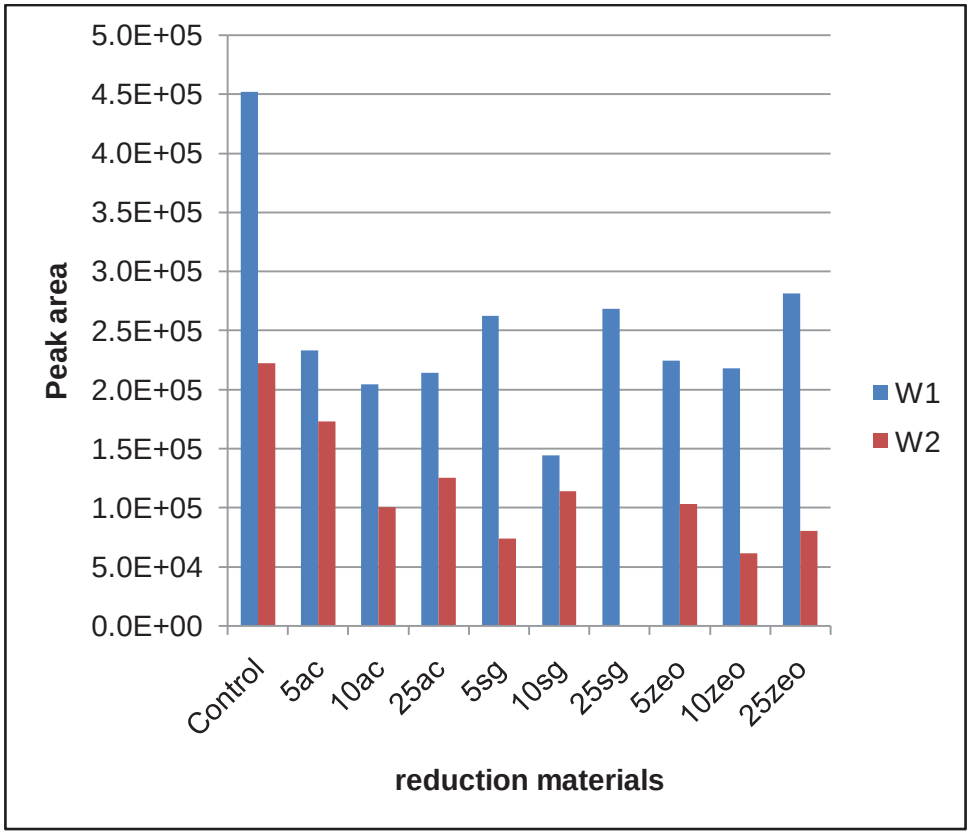


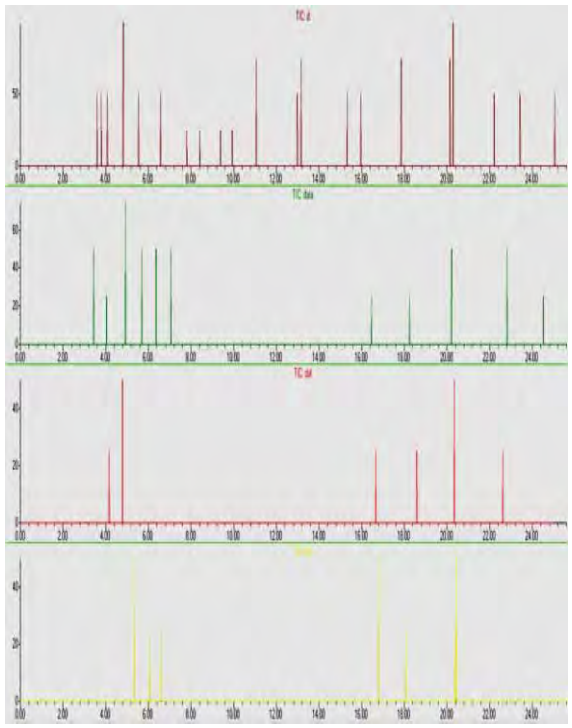
Figure 6. 13 Volatilisation of acetic acid in summer litter with the addition of activated carbon (AC), silica gel (SG) and zeolite (Zeo) at weeks 1 and 2 (W1, W2).

6.7 Effect of adsorbent addition on sensory analysis

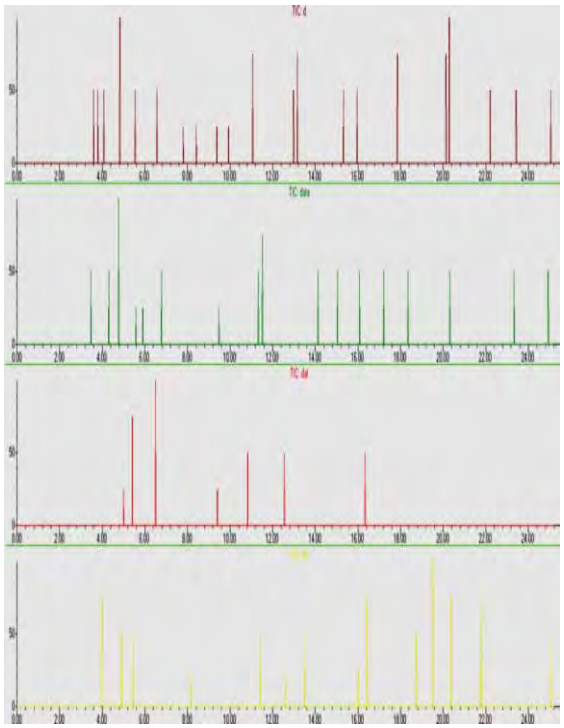
Figure 6.14 and 6.15 shows the sensory response of panellist during direct TD-GC-MS/O analysis of the winter treated litters. Analysis of variance suggested significant difference in intensity of volatiles perceived between the adsorbents. Odour was only perceived from the litters in the first week of abatement for the winter litters. Meanwhile, no odour was detected from the summer treated litters.

Fewer human olfactory responses were observed for litters applied with activated carbon than for the trials with silica gel and zeolite. Reductions in number of odour responses and their intensities were observed with increases in the ratio of activated carbon used in the litters. Perceived intensities of volatiles from the litters treated with silica gel were relatively greater than for activated carbon but lower than zeolite. The litter with silica gel exhibited similar trend to activated carbon, i.e. decreases in odour response and intensity with increases in ratio of silica gel applied on litter. In contrast, decrease in odour response with insignificant decreases in odour intensity was observed with greater application of zeolite to the litter.

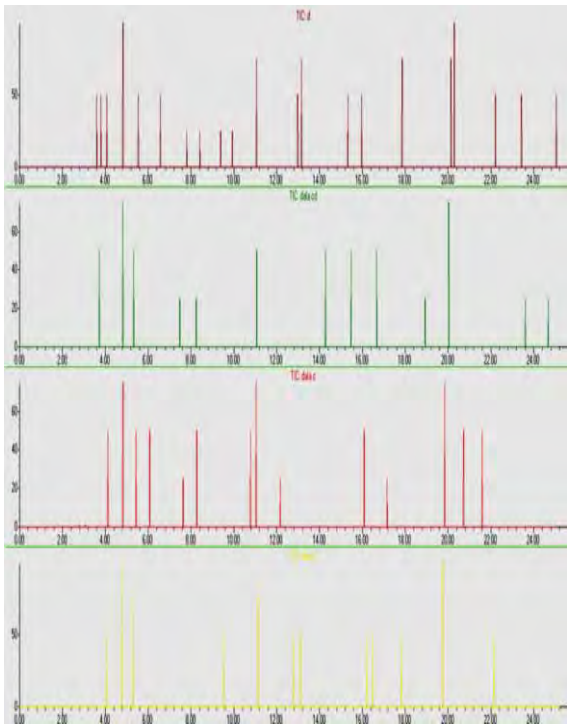
A disadvantage observed from abatement trial conducted was emission of ammonia which was not studies in this project. Olfactory response for ammonia emissions perceived from the litters abatement trials were not displayed in the osmegram due to the instrumental setting focussed mainly on identification of volatile organic compounds. Even though substantial reduction in volatile organic compounds' intensities were obtained using the different adsorbents, the overall reduction in odour hedonic tone was not achieved due to the pungency characteristic in odour caused by the ammonia release.



Activated carbon

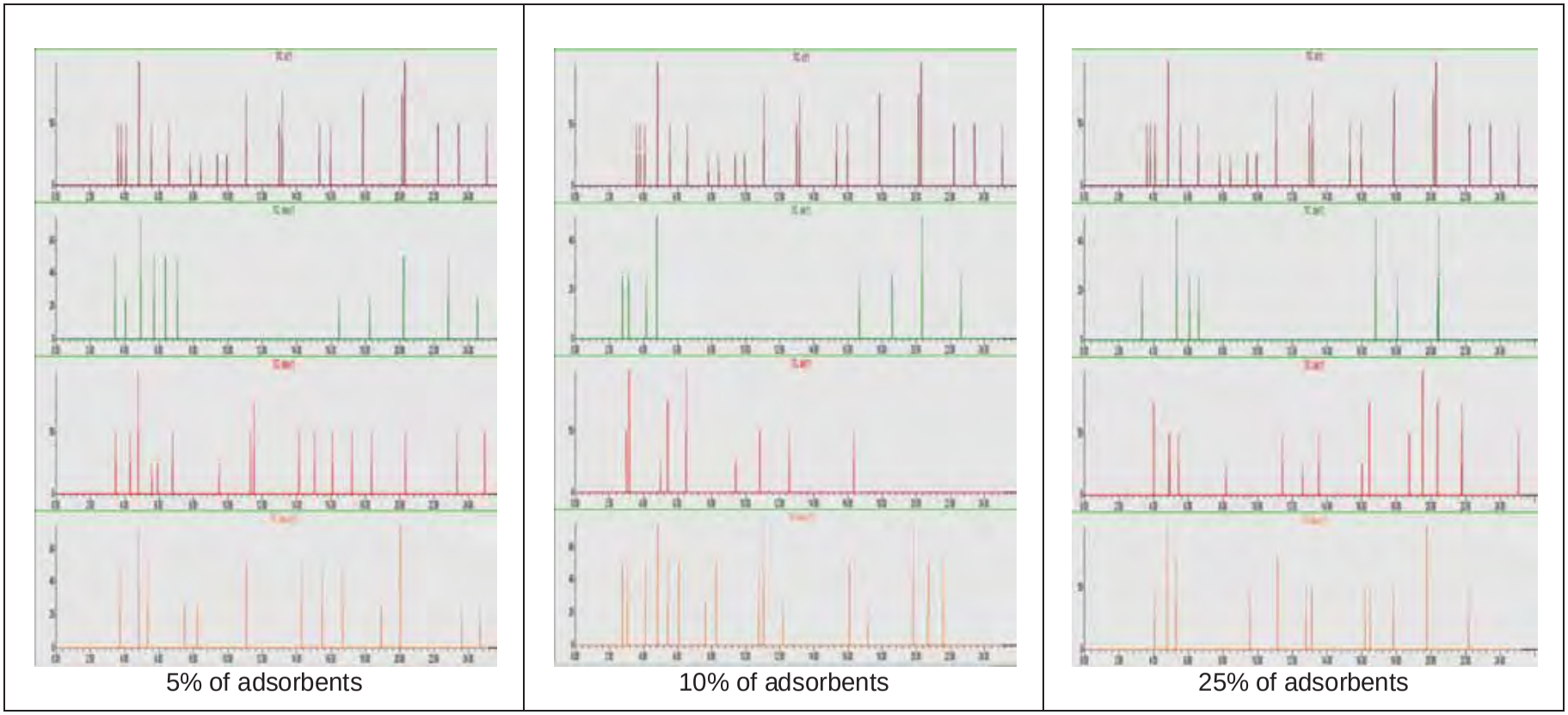


Silica gel



Zeolite

Figure 6.14 Osmegrams showing olfactory and intensity responses for control litter (top) followed by litters treated with 5, 10 and 25 % of adsorbents.



5% of adsorbents | 10% of adsorbents | 25% of adsorbents

Figure 6.15 Osmegrams showing olfactory and intensity responses for control litter (top) followed by litters treated with activated carbon, silica gel and zeolite at 5, 10 and 25 %, respectively.

6.8 Summary

The assessment of activated carbon, silica gel and zeolite as a potential odour reducing strategy directly applied on odorous litters showed a mixed trend of chemical and sensory responses. The heterogeneous condition of the litter particles in contact with the reduction materials and the exposed surface area during the storage under ventilation and samplings stages may have resulted in some of the varied reduction patterns. In general, all adsorbents decreased litter moisture content, increase litter pH and reduce volatilisation of organic compounds at diverse rates across trial periods. Physical changes were visible in the treated litters than control sets. Based on the chemical and sensory responses obtained, activated carbon and silica gel exhibited prominent adsorptions or reductions in litter volatiles. The results revealed noticeable efficacy for activated carbon and silica gel with interactions on excessively wet litter found in winter litter conditions, which is often a major problem in sheds generating anaerobically produced volatiles. The litters treated with activated carbon and silica gel appeared remarkably drier and friable than the controls. Performance of zeolite was found to be comparative, but less effective. However, decrease in odour hedonic tone was unachievable mainly due to emission of ammonia from trial sets. Therefore, before considering the application of odour control products within a broiler production shed, it is advised to apply appropriate litter management practices within the shed conditions to avoid or reduce the generation of odours at source point. It is also evidence from the trials that no one product is capable of reducing or removing all volatiles presents in the emission of odours from poultry shed litter.

CHAPTER SEVEN
Conclusion and recommendation

7.1 Introduction

At many instances, litter used as the bedding material is suggested as the major contributor to the offensive emissions in these broiler facilities. Hence, this study's primarily aim was to develop and apply headspace TD-GC-MS/O analysis to the characterisations of odorants in the gaseous emissions from dry and wet litters during winter and summer seasons.

The application of direct dynamic headspace and sorbent tube samplings resulted in a rapid and robust pre-concentration of volatiles which subsequently assisted in the chemical speciation with significant repeatability and reproducibility using GC-MS and human olfactory analysis. Furthermore, the elimination of solvents as volatile extractant allowed minimal amendment of the litter sample and degradation of volatiles, providing a comprehensive understanding of odorants present in the litter gaseous emanations. However, the utmost advantage of this sampling and analysis methodology carried out was the association of mass spectrometry and olfactory port analysis in detecting odour potent volatiles of numerous compounds characterised from the litters.

From the diverse list of compounds obtained from the headspace TD-GC-MS/O sampling and analysis, only prioritised odorants with significant odour quality and intensity were integrated with simultaneously conducted dynamic olfactometry in order to determine the impact of particular offensive species on the total litter emission as a single or functional group of compounds. Finally, three selected commercially available additives were assessed for their efficacy as odour adsorbing materials employing direct dynamic headspace TD-GC-MS/O analysis. The abatement study exhibited selectivity in reduction of compounds volatilisation

depending on type and quantity of additive material mixed within the litter and period of experimentation.

7.2 Objectives and outcomes

The primary objective of developing and applying the headspace TD-GC-MS/O to assess the composition of odorants from broiler litter samples collected from tunnel ventilated broiler shed in Australia was successfully achieved. Both direct headspace and sorbent tube techniques revealed high reliability for volatiles sampling prior to pre-concentration and thermal desorption. The solvent free methodology provided substantial TD-GC-MS/O responses corresponding to the sample's properties that efficiently discriminate chemicals encountered from varying litter materials, which is extensively important in comparing variations in volatilisation at differing broiler production stages and identifying odour potent volatiles. Nevertheless, during the application of the TD-GC-MS/O analysis, some limitations in human sensory and analytical instrument responses must be taken into consideration to reduce bias.

Often animal or poultry production facilities are understood to operate under simple working mechanism that could easily implement odour abatement techniques within the production as odour controlling strategies in comparison to other agricultural or food industries. However, abating poultry odour is not an easy task to be performed in the intensive animal operation facilities. The complexity in the composition of the odour produced within broiler tunnel ventilated sheds was revealed using TD-GC-MS/O analysis with numerous volatile organic compounds consisting of terpenes, volatile fatty acids, ketones, sulfur and nitrogen containing compounds, aromatic hydrocarbons, aldehydes and alcohols identified from the litter gas phase. Although the cold trap used for volatile pre-concentration in this study does not favour the speciation of sulfur components, frequently occurring methanethiol, dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide and dithiapentane in winter and summer litter samples were carefully characterised with high match quality and mass fragmentation.

The diversity in litter volatiles were found to rely significantly on maturing birds and changing litter properties with ketones, volatile fatty acids and sulfur and nitrogen compounds contributing the most offensive odour quality and intensity. The accumulation of manure and the spillage of water onto bedding materials substantially were observed to change the moisture content and pH estimation of litter that subsequently affected the litter odour emanation compositions and rates. The existence and domination of sulfur and volatile fatty acids within the winter litters and ketones, sulfur and phenolic compounds within the summer litters were determined to be odour annoyance contributing volatiles for the respective seasons. These findings were in agreement with increases noted in odour emission concentrations data obtained from dynamic dilution olfactometry results with the volatilisation of specified odorous homologues. In this study, unlike methanethiol, dimethyl sulfide and dimethyl trisulfide, the dimethyl disulfide was categorised as a less offensive odorant with merely chemical like odour, although rated at a higher odour intensity at some analysis stages during the production cycle.

Odour abatement trials attempted during the study to determine the efficacy of litter odour abatement materials showed mixed trends in the potential of activated carbon, silica gel and zeolite as odour controlling additives. These observations can be attributed to the heterogeneity in the litter particles in contact with the reduction materials and the exposed surface area during storage under ventilation and samplings stages. In general, all the adsorbents tested decreased the litter moisture content, increased the litter pH and reduced the volatilisation of organic compounds at diverse rates across the trial periods. From the TD-GC-MS/O responses for the trials, the activated carbon and silica gel exhibited prominent adsorptions or reductions in litter volatiles besides producing visibly drier and friable litter than for control and zeolite trial sets. However, decrease in odour hedonic tone was not achieved mainly due to the pungency in the odour produced from the release of ammonia from all trial sets.

7.3 Recommendation

The benefit in associating the headspace odour sampling technique and analysis methodologies (i.e. chemical and olfactory analysis) was evident throughout the study, especially while evaluating the efficacy of the odour reducing or controlling additives. Like in food and flavour research areas, more advanced applications involving chemical and sensory detectors should be encouraged in the livestock research fields to improve our understanding on complex odours.

However, some aspects of the direct headspace technique introduced herein require further modification. Currently, the study reports on dominating broiler litter odorants describing and quantifying on their odour quality and intensity in which some olfactory stimulating offensive volatiles with low yield or rating are not discussed herein due to infrequent occurrence and/or low match by the instrumental detector. In addition, the frequent appearance of sulfur containing compounds from the litters as volatile/odorant justifies the need for more research studies with precise sampling and suitable pre-concentration and analysis techniques for these highly liable compounds.

Firstly, future work should focus in improvising the flexibility of the current TD-GC-MS/O methodology in assessing and quantifying volatiles of all ranges from broiler litters as chemical and olfactory quantification of odorants in order to provide efficient evaluation of abatement systems. Secondly, since no individual product tested exhibited absolute reduction of the nuisance odorants produced, combination of additives should be tested at laboratory scale and at farm scale as it could be more effective in decreasing hedonic tone and odour intensity. This attempt could be further extended with efficacy trials conducted in real field condition as direct application onto bedding material or media loaded in an adsorption filter fitted at the ventilation exhaust.

Finally, some aspects affecting litter odour formation and emission remained unclear. This is evident with the highest odour emission rate recorded with removal

of birds from summer wet litter and some ambiguities displayed in the association of litter pH and moisture content with odour concentrations. Further analysis of broiler litter and its odour is recommended to determine the absolute influence of these physical/chemical and microbial variables in the formation and emission of litter odours.

7.4 Conclusion

The primary aim of the study that being to develop a direct headspace TD-GC-MS/O technique for assessing and correlating the chemical and olfactory responses of key odorants produced from bedding materials collected at poultry sheds managed under Australian climates was successfully achieved. The application of the headspace TD-GC-MS/O method for litters collected during winter and summer sampling campaigns provided extensive lists of odour potent volatiles responsive to odour annoyance of respective seasons. The presence of sulfur and volatile fatty acids for winter litters and ketones, sulfur and phenolic compounds for summer litters were determined to be the odorants contributing the most olfactory annoyance. Laboratory scale abatement trials conducted using commercial additives exhibited higher potential of activated carbon and silica gel as efficient odour adsorbing or reducing materials compared to zeolite. However, decrease in odour hedonic tone was not achieved due to production of ammonia from the trial sets. The research objectives listed at the initial stage of the project were successfully attained providing better knowledge of odour emissions from litter materials collected from tunnel ventilated broiler sheds at ambient temperature.

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APPENDIX A

Weekly winter litter odorants

Table A-1 Winter week 0 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
Octane				4.87E+05	burnt	2
Acetone	1.00E+07			9.13E+06	sweet	2
Tricyclene	3.04E+06	solvent	2	3.19E+06	solvent	2
alpha pinene	3.73E+08	Wood	2	4.69E+08	pine	2
Camphene	3.27E+07			3.43E+07	chemical	2
.beta.-pinene	1.62E+08	Fruity	2	2.26E+08	resin	2
3-carene	4.59E+06			5.65E+06	sweat	2
Limonene	1.96E+07			3.28E+07	chemical	2
.beta.-phellandrene	9.60E+07	Fruity	2	1.60E+08		
gamma-terpinene	1.44E+06	Sweet	2	8.97E+06	smelly	2
o-cymene	4.21E+06	Smoky	2	7.52E+06	Soapy	2
alpha.terpinolene	2.42E+06			5.00E+06	Soapy	2
alpha.thujone				5.05E+05	Fruity	2
Camphor				1.23E+06	Smoky	2
Caryophyllene				2.20E+06	Smoky	2
allyl anisole	1.34E+06	Smelly	2	2.29E+06	Sweat	2

Table A-2 Winter week 1 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
2-methyl furan	1.17E+06	ether	3			
alpha pinene	8.97E+07	pine	4	3.82E+07	pine	4
limonene	3.80E+06	sweet solvent	2	1.26E+06	chemical	3
sabinene				3.32E+06	plastic	4
acetic acid				5.97E+05	vinegar	3

Table A-3 Winter week 2 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
alpha pinene	4.65E+07	pine	3	9.46E+07	pine	3
.beta.-pinene	1.34E+07	fragrant	3	2.69E+07	resin	2
3-hydroxy-2-butanone				3.10E+06	solvent	3
dimethyl trisulfide	3.30E+05	sharp sewer, rotten	3	5.37E+05	putrid, rotten	3

Table A-4 Winter week 3 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
2-butanone	1.06E+07	fruity solvent	2	2.27E+08	foul	3
alpha pinene	3.50E+07	Pine	3	5.86E+07	pine	3
2-butanol				1.06E+08	solvent	2
camphene	2.01E+06	Solvent	3	7.25E+06	fragrant, chemical	3
dimethyl disulfide	2.62E+07	Manure	3	2.84E+07	solvent	3
.beta.-Pinene				1.91E+07	resin	3
1-butanol				3.39E+06	alcohol	3
limonene	1.74E+06	petrol, chemical	3	1.35E+06	fragrant	1
alpha.thujene				8.93E+05	paint	3
2,4-pentadienenitrile				8.79E+05	solvent	3
3-hydroxy-2-butanone	3.21E+06	Garbage	3	7.76E+06	solvent	2
dimethyl trisulfide	7.17E+05	sharp putrid, rotten	4	1.13E+06	putrid, rotten	3
propanoic acid				2.20E+05	foul	3
butanoic acid	1.18E+05	sweetish ethery	2	3.98E+05	rancid	3

Table A-5 Winter week 4 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
alpha pinene	3.04E+07	Pine	3	5.07E+07	pine	3
2-butanol				1.83E+08	solvent	3
camphene	1.97E+06	solvent	3	8.24E+06	solvent	3
.beta.-pinene	1.05E+07	sharp resin	2	2.13E+07	resin, chemical	3
1-butanol				1.64E+07	foul	3
limonene	9.43E+05	petrol, chemical	3	2.36E+06	petrol, chemical	3
dimethyl trisulfide	1.57E+06	sharp putrid, rotten	3	3.17E+06	putrid, rotten	4
2-ethyl-1-hexanol				8.19E+05	fragrant	3
phenol	3.20E+05	sweet solvent	3	1.23E+06	foul	2

Table A-6 Winter week 5 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
ethyl acetate				1.04E+07	fruity	3
2-butanone	2.99E+07	fruity solvent	4	4.15E+08	sweet solvent	4
3-methyl-2-butanone	4.54E+06	fruity	3			
alpha pinene	1.90E+07	pine	2	3.03E+07	pine	3
2-butanol	9.43E+06	chemical	3	5.71E+08	solvent	3
dimethyl disulfide	6.27E+07	solvent	3	6.00E+07	chemical	3
.beta.-pinene	8.98E+06	chemical	3	1.56E+07	resin	2
limonene	7.53E+05	sweet solvent	4	5.53E+05	plastic solvent	3
dimethyl trisulfide	2.24E+06	putrid, ferment	3	3.99E+06	putrid, rotten	3
acetic acid	2.50E+06	acid, vinegar	2	1.38E+07	rancid	3
2-ethyl-1-hexanol	4.07E+06			4.65E+06	fragrant	3
propanoic acid				1.86E+06	rancid	3
butanoic acid	4.23E+06	rancid	4	1.21E+07	rancid	4

Table A-7 Winter week 6 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
toluene	2.01E+06	pungent, foul	3			
limonene	1.02E+06			1.14E+06	plastic	3
dimethyl trisulfide	3.14E+05	putrid, rotten	3	1.49E+06	putrid, rotten	2

Table A-8 Winter week 7 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
2-butanone	2.42E+07			2.80E+08	fruity solvent	3
isopropyl alcohol				4.00E+07	fragrant	3
3-methyl-2-butanone	3.78E+06	floral	2	1.77E+07	chemical	3
alpha pinene	2.17E+07	pine	3	5.41E+07	pine	3
2-butanol				2.50E+08	solvent	3
camphene	1.10E+06	chemical	2	6.62E+06	fragrant	3
1-butanol				2.20E+07	moldy	3
limonene	9.66E+05	foul	2	3.21E+06	plastic	4
(ethoxymethyl)-oxirane				5.18E+05	sweet	3
3-hydroxy-2-butanone				1.82E+07	chemical	3
dimethyl trisulfide	5.56E+05	putrid, rotten	3	3.62E+06	putrid, rotten	4
allyl anisole				2.59E+05	sweet	3

Table A-9 Winter week 8 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
acetone	6.64E+06	solvent	3	1.93E+06	solvent	2
2-methyl furan	1.29E+05	ether	3			
2-butanone	1.32E+07	fruity solvent	3	3.42E+08	fruity solvent	3
3-methyl-2-butanone	1.40E+06	fruity	2	3.84E+07	ash	3
alpha pinene	1.09E+07	pine	3	7.37E+07	pine	3
2-butanol	9.74E+05	fragrant	2	1.13E+08	fragrant	3
dimethyl disulfide	1.30E+07	solvent	3	1.20E+07	chemical	4
1-butanol				7.03E+07	putrid	3
1-methylethyl-benzene	8.14E+06	solvent	3	7.73E+06	solvent	3
p-xylene	6.40E+06			9.84E+06	varnish	3
6-methyl-2-heptanone				1.01E+06	sweet solvent	3
3-pentenenitrile				2.74E+06	putrid	3
3-hydroxy-2-butanone				4.51E+07	solvent	2
dimethyl trisulfide	1.41E+05	putrid, rotten	3	3.20E+06	putrid, rotten	3
2-ethyl-1-hexanol	3.44E+05	fragrant	3			
butanoic acid				1.13E+07	sweetish ether	3
allyl anisole				4.50E+05	varnish	3

Table A-10 Winter week 0 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
.alpha.-pinene	1.32E+09	Pine	4	1.27E+09	perfume	4
alpha fenchone	4.15E+08	Fruity	4			
Camphene	1.02E+09	Coniferous	3	7.57E+08	Spice	3
.beta.-Pinene	5.25E+08	Citrus	4	3.77E+08	perfume	2
.alpha.-phellandrene	2.43E+08	Citrus	3	2.63E+08	solvent	3
alpha terpinene	3.80E+08	Solvent	3	2.60E+08		
Limonene	5.04E+07	Plastic	3	5.57E+07	Plastic	4
Sabinene	1.82E+08			3.21E+08	solvent	3
gamma terpinene	5.04E+07	Plastic	3	4.71E+07		
o-cymene	6.70E+08	Plastic	3	1.68E+08	aromatic	3
Caryophyllene	2.93E+06			9.48E+06	Smelly	3
1-methoxy-4-methyl-2-(1-methylethyl)-benzene				3.78E+06	solvent	3
Unknown					garbage	4
ally anisole	5.04E+07			2.23E+07	Grassy	3

Table A-10 Winter week 0 litter odorants determined using direct headspace (cont).

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
4-(1-methylethyl)-benzaldehyde	1.20E+07			3.05E+06	chemical	3
1-(4-methylphenyl)-ethanone	5.04E+07	Paint	3	4.06E+06	chemical	3
2-methyl-5-(1-methylethyl)-phenol	5.04E+07	solvent	2	1.30E+06	hospital	3
Thymol				1.19E+06	hospital	3

Table A-11 Winter week 1 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
.alpha.-pinene	3.11E+08	pine	3	7.59E+08	pine	3
camphene	1.08E+08	solvent	3	1.45E+08	solvent	2
dimethyl disulfide				7.70E+07	putrid	3
.alpha.-phellandrene	1.17E+07			2.64E+07	putrid	3
alpha terpinene	1.24E+07			2.47E+07	alcohol	4
Limonene	3.01E+07	foul	3			
o- cymene	3.00E+07	solvent	1	6.24E+07	foul	3
alpha dimethylstyrene				1.42E+07	burnt	4
isopinocamphone				2.02E+08	foul	3

Table A-12 Winter week 2 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
acetone				1.25E+08	rotten	4
.alpha.-pinene	6.55E+08	pine	4	7.76E+08	pine	3
beta pinene	2.34E+08	smelly	4	3.75E+08	solvent	3
.alpha.-phellandrene	2.12E+07	sweet	2	2.17E+07		
alpha terpinene	2.77E+07	plastic	3		fruity	3
limonene	9.09E+07			1.07E+08	citrus	3
gamma terpinene	2.03E+07			2.46E+07	stale	2
2,6-dimethyl-2,4,6-octatriene	2.86E+06	smelly	4	3.21E+06	putrid	4
alpha dimethylstyrene	1.01E+07	ferment	4	7.20E+06	ferment	4
camphor	4.88E+05	foul	3	1.20E+06	sharp	3
Isopinocamphone	3.34E+06			2.52E+06	foul	4
allyl anisole	5.88E+05	foul	2	1.36E+06	solvent	4

Table A-13 Winter week 3 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
.alpha.-pinene	6.60E+08	pine	3	4.37E+08		
1,3-butanediol					alcohol	3
allyl anisole	4.49E+07			8.77E+05	manure	3

Table A-14 Winter week 4 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
acetone	1.40E+08	foul	2	3.20E+08	rubber	4
.alpha.-pinene	4.20E+08	pine	3	1.00E+08	pine	4
dimethyl disulfide	8.00E+07	earthy	2	1.70E+08	sulphur	4
o-cymene	3.00E+07	smoke	3	3.60E+06	rubber	4
methanethiol				3.83E+05	putrid	4
acetic acid				6.46E+05	urinal	4

Table A-15 Winter week 5 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
acetone	1.31E+08	alcoholic	3	1.39E+07		
2-butanone				2.03E+09	sweet chemical	4
2-butanol				3.23E+08	alcoholic	4
dimethyl disulfide	1.77E+08	putrid	2	1.26E+08	chemical, paint	4
methanethiol				1.26E+05	putrid, ferment	4
acetic acid	4.32E+06	vinegar	2	1.67E+08	acid	4
propanoic acid	2.08E+05			1.81E+07	rubber	4
butanoic acid	2.89E+06	foul	2	1.33E+08	vomit, acid cheesy	4
4-methyl-pentanoic acid				7.22E+06	sharp acid	3

Table A-16 Winter week 6 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
2-butanone	3.76E+08	sweet chemical	2	1.30E+09	sweet chemical	4
.alpha.-Pinene	2.12E+08	wood fragrant	3	4.65E+08	wood fragrant	2
.beta.-pinene	4.20E+07	wet smoke	3	1.33E+08	wet smoke	4
methanethiol	trace	sulfur	4	trace	rubber, pungent	4
butanoic acid	3.23E+05	cheesy	4	1.37E+06	cheesy	4

Table A-17 Winter week 7 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
2-butanone	4.46E+07			1.32E+09	sweet chemical	3
limonene				2.38E+07	wet smoke	3
2,4-pentadienenitrile				9.99E+05	rubber	4
methanethiol	trace	rubbery	2	trace	faecal	4
acetic acid	7.93E+05			9.48E+06	chlorinous chemical	4
butanoic acid	1.01E+06	putrid	2	9.80E+06	cheesy sourish	4
p-cresol				5.83E+05	sweet chemical	4

Table A-18 Winter week 8 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
2-butanone	7.28E+07			8.35E+08	sweet chemical	4
.alpha.-pinene	4.11E+07	chemical	3	2.84E+08		
camphene	4.77E+06	chemical	3			
dimethyl disulfide	2.99E+07	sewer	3			
Methanethiol	trace	foul	2	trace	rubber	4
butanoic acid	2.86E+06			6.91E+06	cheese sourish	3
phenol	4.57E+05	smoke	2	1.82E+07	plaster, medicinal	4

APPENDIX B

Weekly summer litter odorants

Table B-1 Summer week 0 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
1,2,4-trimethyl-benzene	1.99E+05	foul	2			
2-ethyl-1-hexanol	1.46E+06	foul	2	9.17E+05		
.alpha.-methylstyrene	1.97E+06	vomit	2			
butylated hydroxytoluene	1.93E+07	pleasant solvent	2			
phenol	3.35E+05	medicinal	1	5.70E+05	pleasant chemical	2

Table B-2 Summer week 1 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
acetone	2.35E+06	chemical	2	1.23E+06	Putrid	2
limonene				8.72E+04	plastic	2
acetic acid	5.43E+05	foul	2	2.53E+05	Putrid	2
alpha guaiene	1.93E+05	foul, sour	1	3.75E+05	Foul	2
phenol	3.89E+05	chemical	2	3.85E+05	smoke	2

Table B-3 Summer week 2 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
acetone	1.82E+06	foul	2	3.30E+06	solvent	2
limonene	1.12E+05	foul, sour	2			
3-Octanone		alcoholic	2	1.73E+05	solvent	2
1,2,4-trimethyl-benzene	1.56E+05	chemical	2	1.22E+05	mushroom	2
2-ethyl-1-hexanol	1.21E+06	foul	2	5.11E+05	soil	2
acetophenone		glue, nail polish	2	1.20E+05	pleasant smell, caramel	2
.alpha.-methylstyrene	1.44E+06	foul	2			
butylated hydroxytoluene	1.60E+07	glue	2			
phenol	4.45E+05	smoke	2	1.83E+05	smoke	2

Table B-4 Summer week 3 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
dimethyl sulfide	1.64E+05	sulphur	2	1.60E+05	ash	2
acetone	2.51E+06			7.79E+06	soil	2
dimethyl disulfide	1.49E+06	chemical,	2	1.56E+06	gassy chemical	2
limonene				1.69E+05	chemical	2
2,4-pentadienenitrile	3.98E+05			3.20E+05	plastic	2
1,2,4-trimethyl-benzene	2.25E+05	citrus	2	2.65E+05	fragrant	2
acetic acid	5.74E+05	foul	2	2.73E+05	vinegar	2
2-ethyl-1-hexanol	1.24E+06	pleasant smell	2	1.59E+06	fragrant	2
benzaldehyde		gas, chalky	2			
acetophenone	1.41E+06	alcoholic solvent	2	1.65E+06	foul	2
4-(1,1-dimethylethyl)-cyclohexanol	5.30E+05	alcoholic solvent	1	7.53E+05	pleasant smell	2
.alpha.-methylstyrene	2.31E+06	pleasant, caramel	2	2.52E+06	chemical	2
butylated hydroxytoluene	7.46E+06	rat like smell	2	7.39E+06	chemical	2
phenol	4.55E+05	foul	2	3.31E+05	chemical	2

Table B-5 Summer week 4 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
dimethyl disulfide	3.52E+07	chemical	3	9.77E+06	chemical	3
3-octanone	2.78E+05	putrid	3	1.41E+05	earthy	2
2,4-pentadienenitrile	9.45E+05	putrid	2	3.66E+05	glue, turpentine	2
3-hydroxy-2-butanone					musty	3
dimethyl trisulfide	7.79E+05	fermented	4	2.66E+05	ferment	4
acetic acid		sewer	3			
acetophenone	7.02E+05	putrid	3	7.58E+05	foul	2
butylated hydroxytoluene	1.61E+07	foul	3	1.71E+07	chemical	2

Table B-6 Summer week 5 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
dimethyl sulfide	2.01E+06	foul	3	3.46E+05	foul	2
acetone	1.48E+07	foul solvent	3	2.25E+07	solvent	3
2,3-butanedione	5.38E+06	rotten vegetable	4	1.48E+06	rotten vegetable	4
2-butanol	8.29E+07	foul chemical	3	1.21E+06	foul	2
propanol	5.96E+06	alcoholic	4	6.76E+05		
dimethyl disulfide	3.72E+07	foul	3	2.33E+07	foul chemical	2
3-hydroxy-2-butanone	1.88E+07	musty, chemical	3		musty	2
dimethyl trisulfide	1.70E+06	putrid	4	8.77E+05	putrid	4
acetic acid	6.18E+05	vinegar	3	1.68E+05	mild acid	2
acetophenone	3.88E+05	foul solvent	3	3.17E+05	solvent	2
butylated hydroxytoluene	8.47E+06	solvent	2	8.05E+06	solvent	3

Table B-7 Summer week 6 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
2,3-butanedione	1.55E+06	foul	2	6.56E+06	rotten vegetable	3
dimethyl disulfide	2.36E+07	chemical	3	2.17E+07	chemical	3
3-hydroxy-2-butanone		musty	3	8.66E+06	musty, earthy	3
dimethyl trisulfide	9.55E+05	putrid, rotten	4	7.24E+05	putrid	4

Table B-8 Summer week 7 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
2,3-butanedione	5.06E+05	rotten cabbage	3	6.93E+05	putrid	2
3-hydroxy-2-butanone				Trace	earthy	3
dimethyl trisulfide	3.90E+05	putrid	3	9.25E+04	rotten	3

Table B-9 Summer week 8 litter odorants determined using Tenax tube.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
3-hydroxy-2-butanone	trace	musty	3	trace	musty	3
dimethyl trisulfide	5.14E+05	rotten	3	5.25E+05	rotten	3

Table B-10 Summer week 0 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
Acetone	2.84E+06	sweet solvent	2			
trichloromethane					Pleasant	2
Toluene	1.17E+06	chemical	2			
acetic acid	5.48E+05	foul	2	1.92E+05	Chemical	1
alpha selinene	2.83E+05	foul	2			
butylated hydroxytoluene	3.06E+05	earthy	2	3.64E+04	Aromatic	2
Phenol	5.78E+05	chemical	2			

Table B-11 Summer week 1 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
acetone	5.63E+06	fragrant	2			
.alpha.-pinene	1.93E+06	fragrant	2			
toluene	2.39E+06	pleasant solvent	2	9.05E+05	sharp	2
1,3,5-trimethyl-benzene	1.13E+05	glue	2	1.01E+05	green	1
acetic acid	2.65E+05	chemical	2	1.34E+05	wet smoke	1
butylated hydroxytoluene	1.60E+05	pleasant smell	2			

Table B-12 Summer week 2 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
toluene	1.09E+06	chemical	1	1.46E+06	foul	2

Table B-13 Summer week 3 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
dimethyl sulfide				1.02E+07	foul	2
trichloromethane				7.37E+06	chemical	2
dimethyl disulfide	6.03E+06	putrid	2	9.06E+06	putrid	2
1-ethyl-3-methyl-benzene	1.27E+05			1.43E+05	putrid	2
1,3,5-trimethyl-benzene	1.24E+05	smoky	2	1.36E+05	smoky	2
acetic acid	3.98E+05	smoky	2	1.04E+05	smoky	1

Table B-14 Summer week 4 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
acetone	4.96E+07	alcoholic	2	1.82E+07	foul	2
2-butanone	2.69E+07	sweet solvent	2			
dimethyl disulfide	1.30E+07	chemical	2	4.68E+06	manure	2
1,3,5-trimethyl-benzene	9.34E+04	alcoholic	2	8.47E+04		

Table B-15 Summer week 5 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
trimethylamine	1.66E+07	putrid	3	9.48E+06	putrid	3
dimethyl sulfide	2.81E+07			3.44E+07	sulphur	4
acetone	1.85E+08			4.66E+08	ferment	4
2-butanone	6.51E+07	foul	3	4.79E+08	sweet chemical	3
2,3-butanedione	2.17E+06			3.57E+07	sharp	3
3-methyl-butanal				9.55E+06	pungent	3
3-methyl-2-pentanone	2.22E+06			1.13E+07	pungent	4
2-butanol				2.36E+07	rotten	4
dimethyl disulfide	4.30E+07	manure, putrid	3	1.08E+08	chemical	4
p-xylene	2.30E+06			1.22E+06	sharp smoky	4
dimethyl trisulfide	4.52E+04	rotten	4	1.92E+05	putrid, rotten	4
acetic acid	7.93E+05	chemical	2	7.59E+05	rancid	3

Table B-16 Summer week 6 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
2-butanone	2.60E+07	solvent	2	8.56E+08	Sweet	3
2,3-butanedione	7.47E+06	solvent	3	7.49E+07	sweet solvent, rotten vegetable	4
dimethyl disulfide	2.96E+07	chemical	3	3.33E+07	chemical	3
p-xylene	2.44E+06	foul	3			
dimethyl trisulfide				1.23E+05	Rotten	4

Table B-17 Summer week 7 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
dimethyl sulfide				2.06E+07	putrid	4
acetone	1.28E+08	foul	3	2.54E+08	foul solvent	4
dimethyl disulfide	3.10E+07	manure	3	3.16E+07	foul	3
dimethly trisulfide	1.97E+05	putrid	4	7.52E+05	putrid	3

Table B-18 Summer week 8 litter odorants determined using direct headspace.

	Dry litter			Wet litter		
Compound	**Peak area**	**Description**	**Intensity**	**Peak area**	**Description**	**Intensity**
dimethyl sulfide	9.19E+06			8.07E+06	Rotten	3
dimethyl trisulfide	9.39E+04	Rotten	3	5.90E+04	Rotten	3

APPENDIX C

Chemical structures of volatiles determined from winter and summer litter materials

Figure C-1 Chemical structures of alcohols obtained of litter.

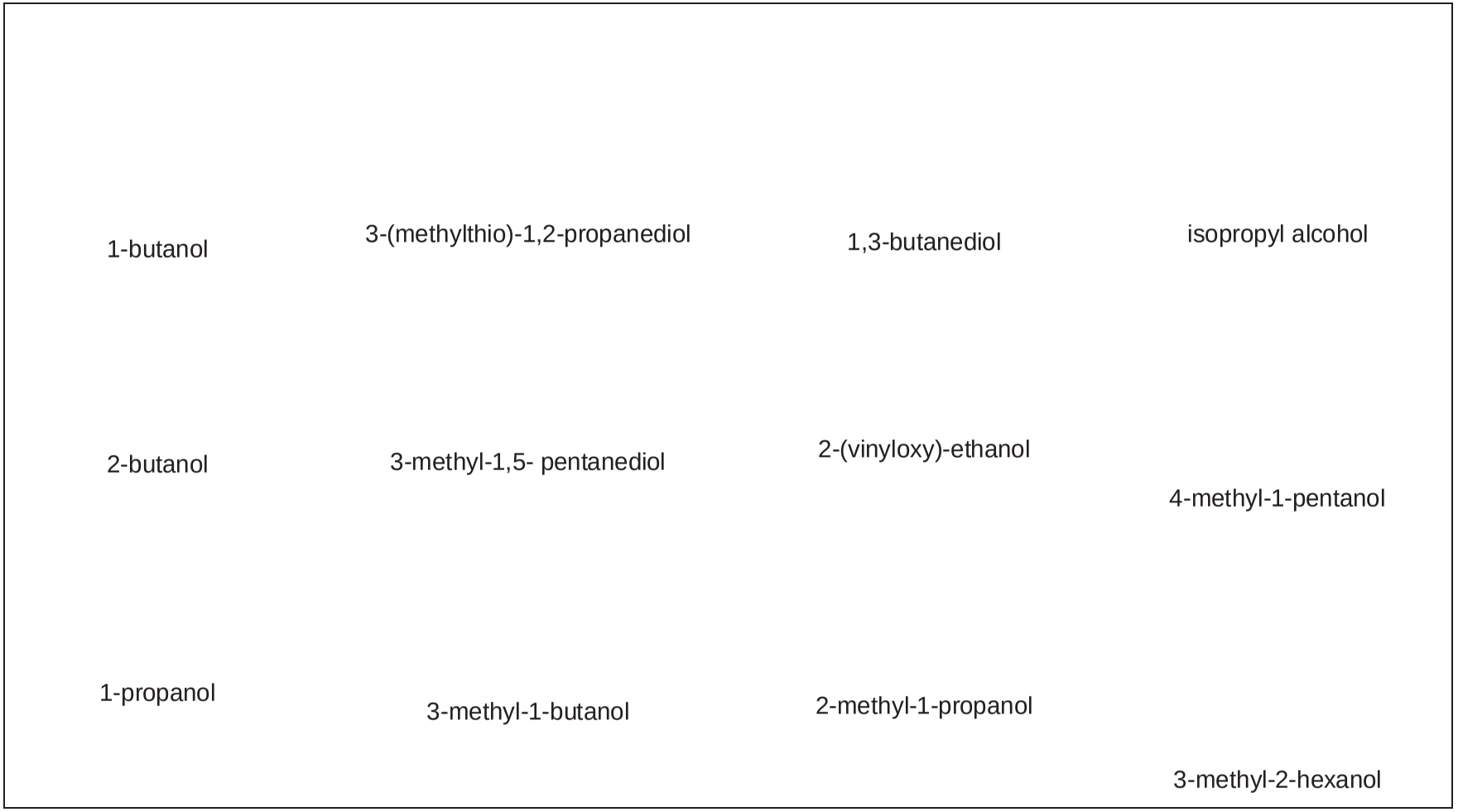


Figure C-1 Chemical structures of alcohols obtained of litter (cont).

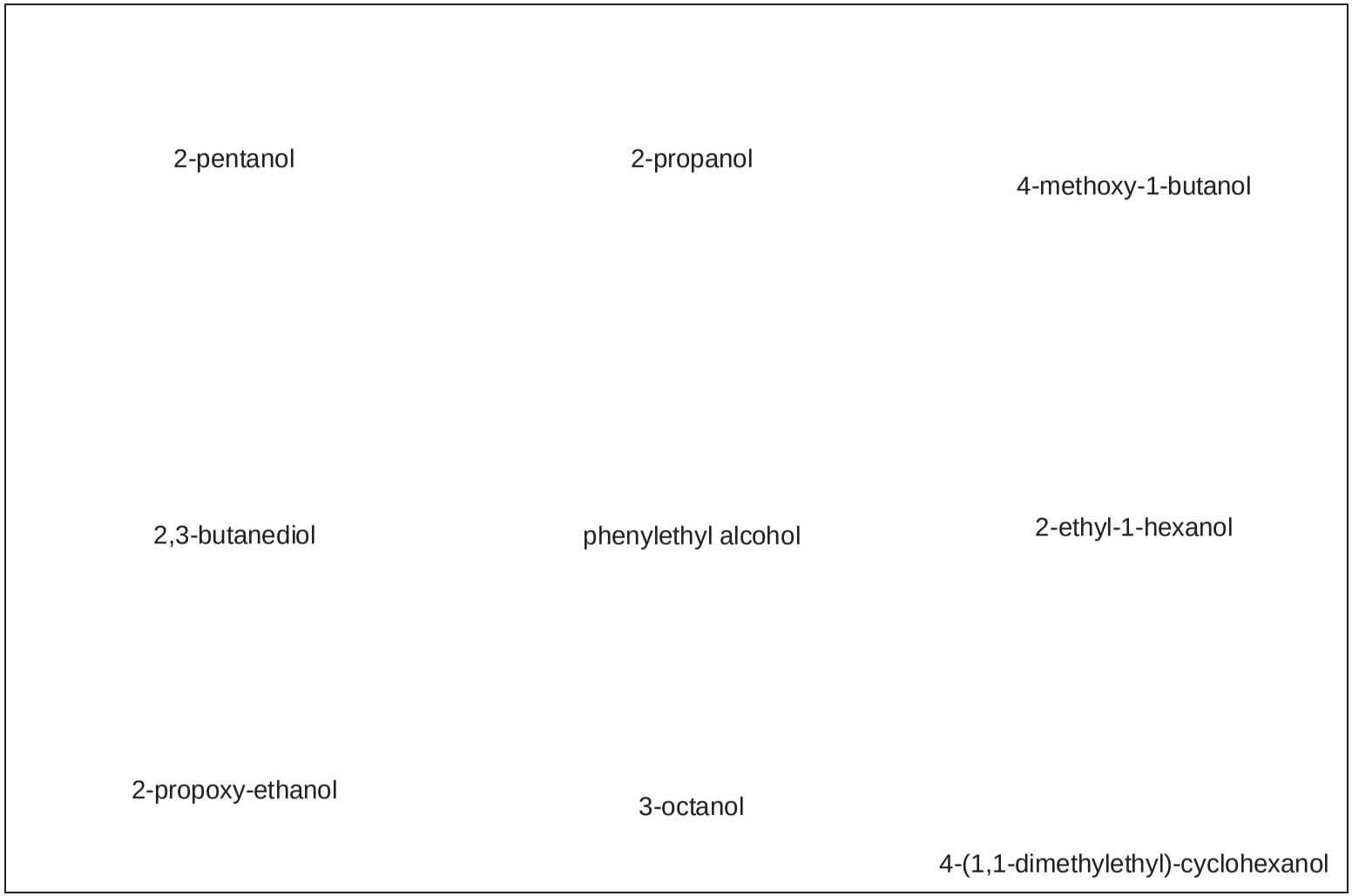


Figure C-2 Chemical structures of sulfur compounds obtained of litter.

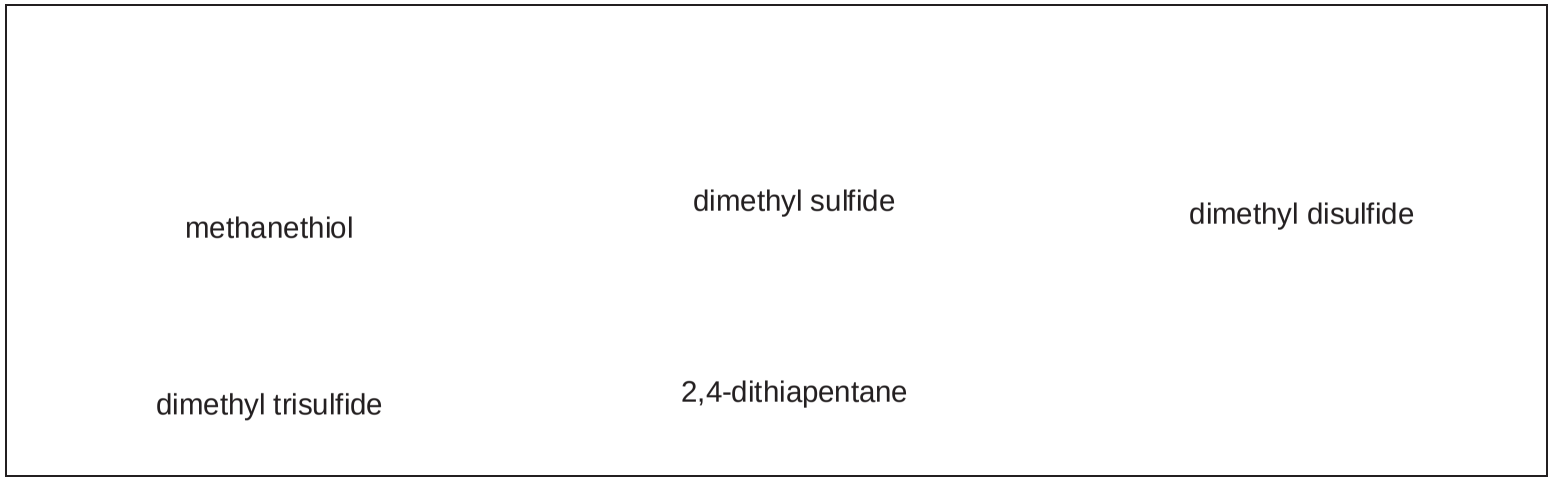


Figure C-3 Chemical structures of volatile fatty acids obtained of litter.

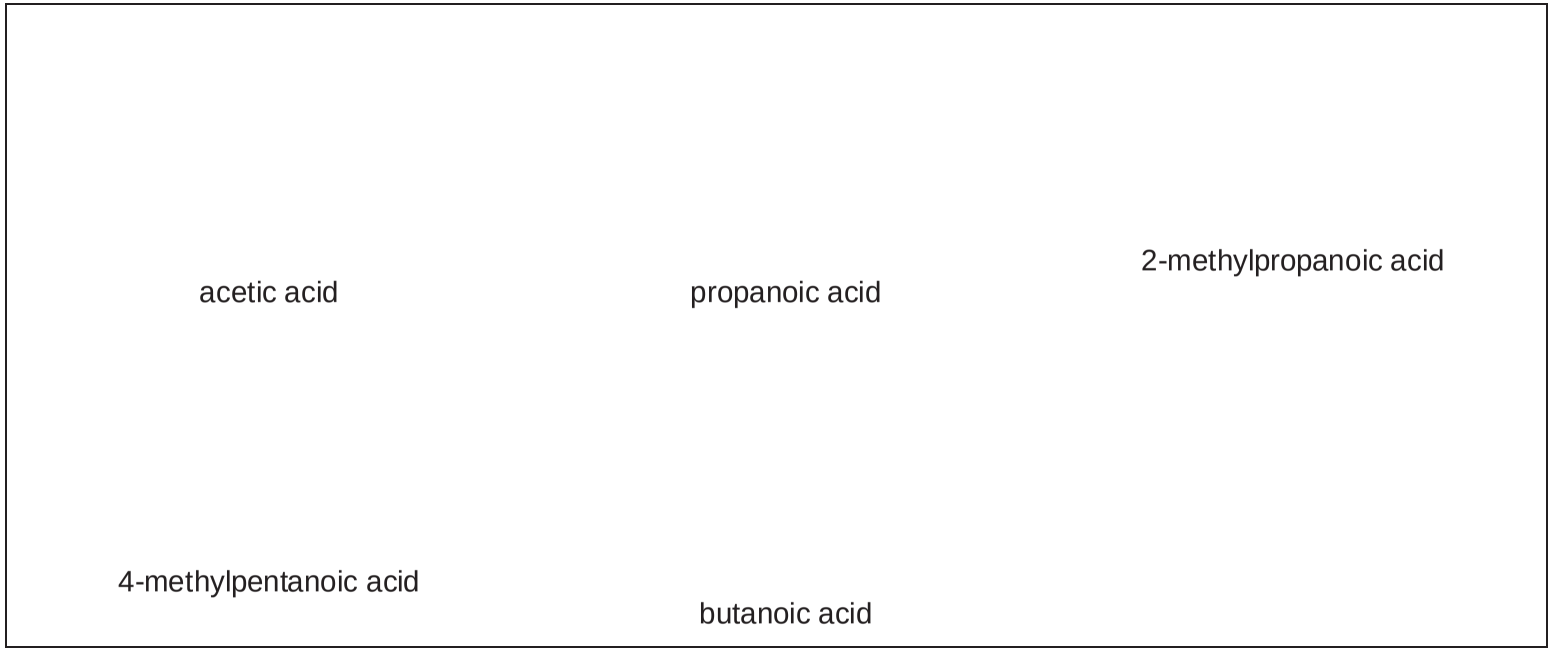


Figure C-4 Chemical structures of ketones obtained of litter.

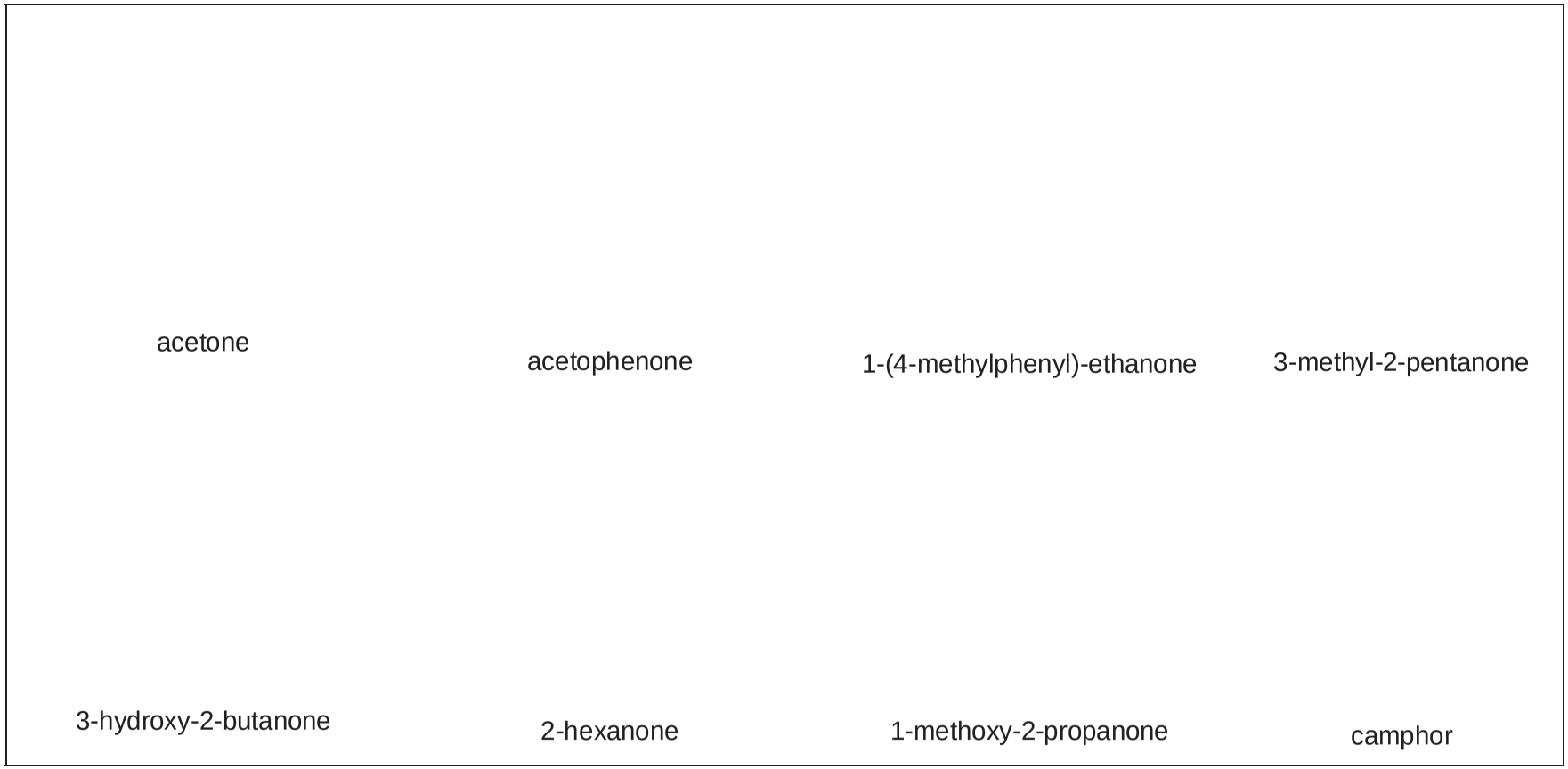


Figure C-4 Chemical structures of ketones obtained of litter (cont).

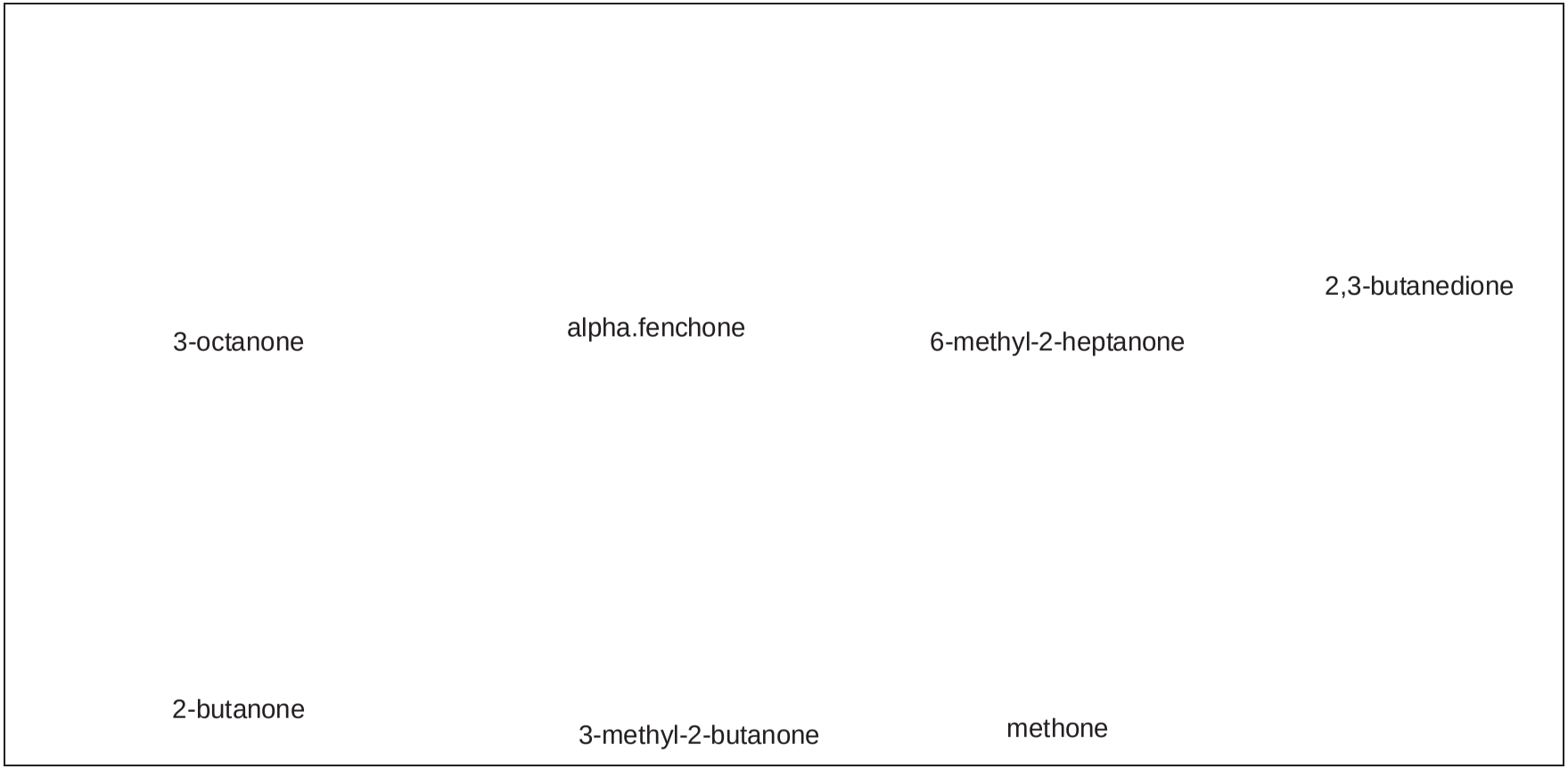


Figure C-5 Chemical structures of terpenes obtained of litter.

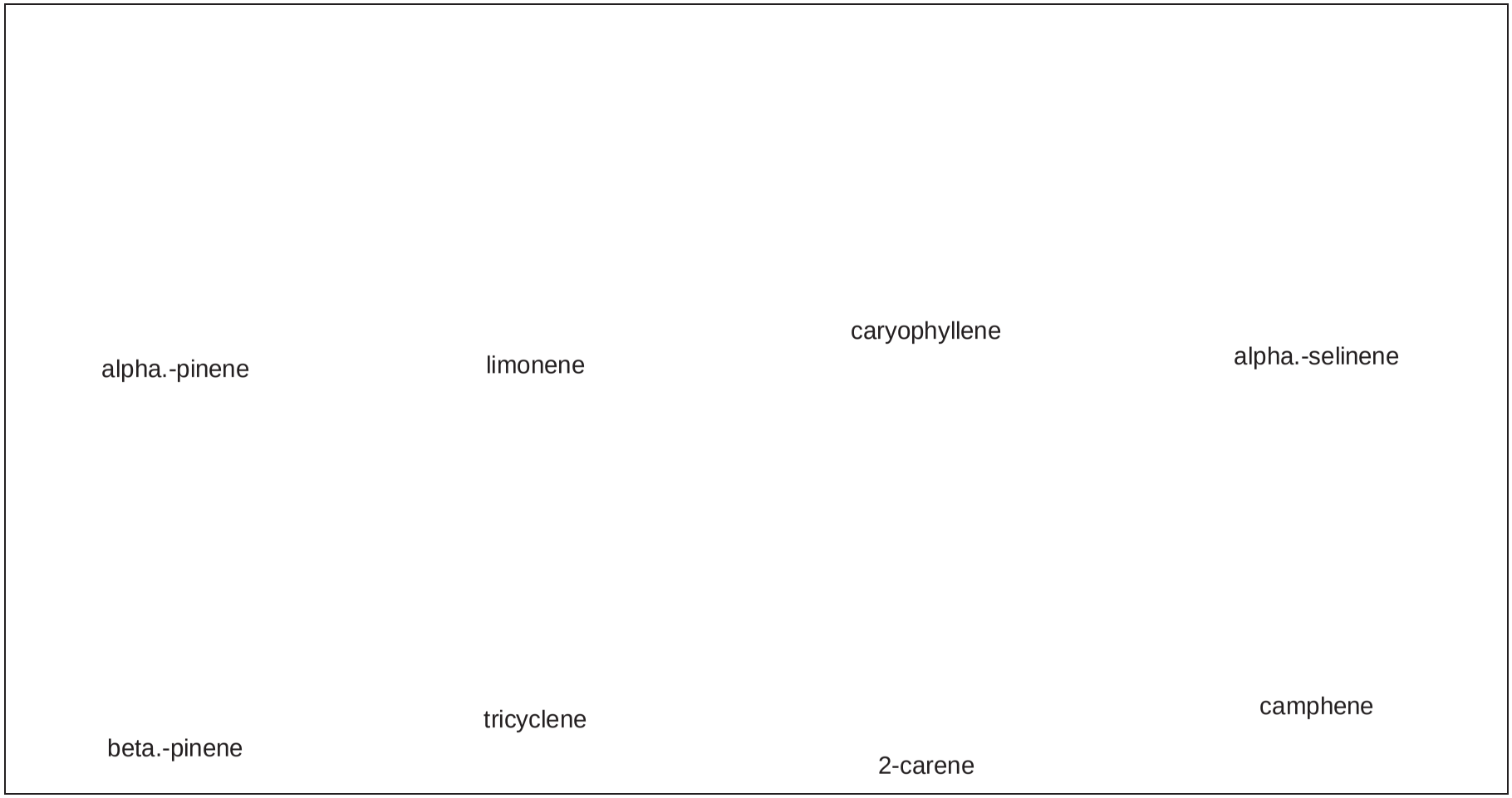


Figure C-5 Chemical structures of terpenes obtained of litter (cont).

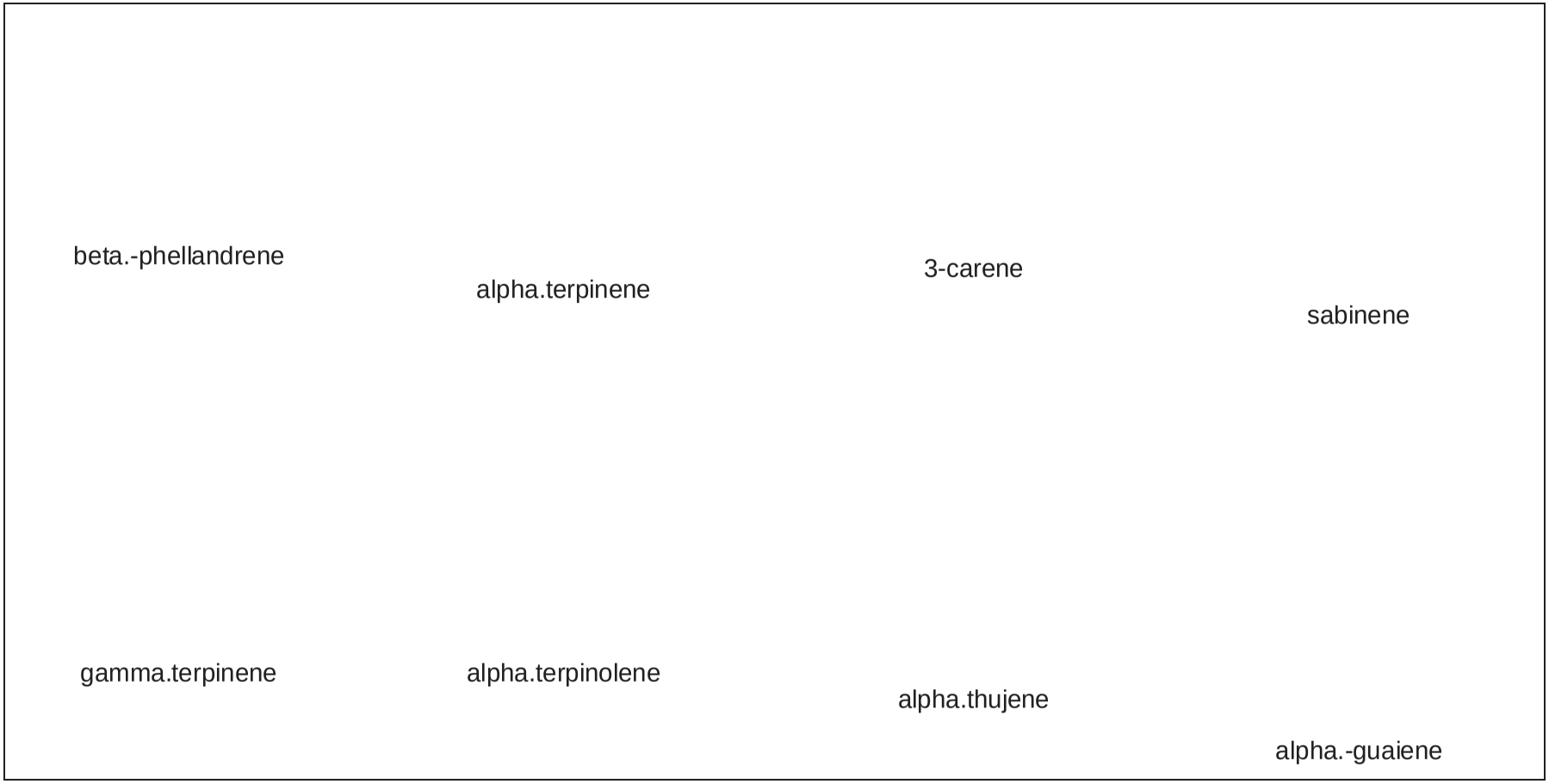


Figure C-6 Chemical structures of aromatic hydrocarbons obtained of litter.

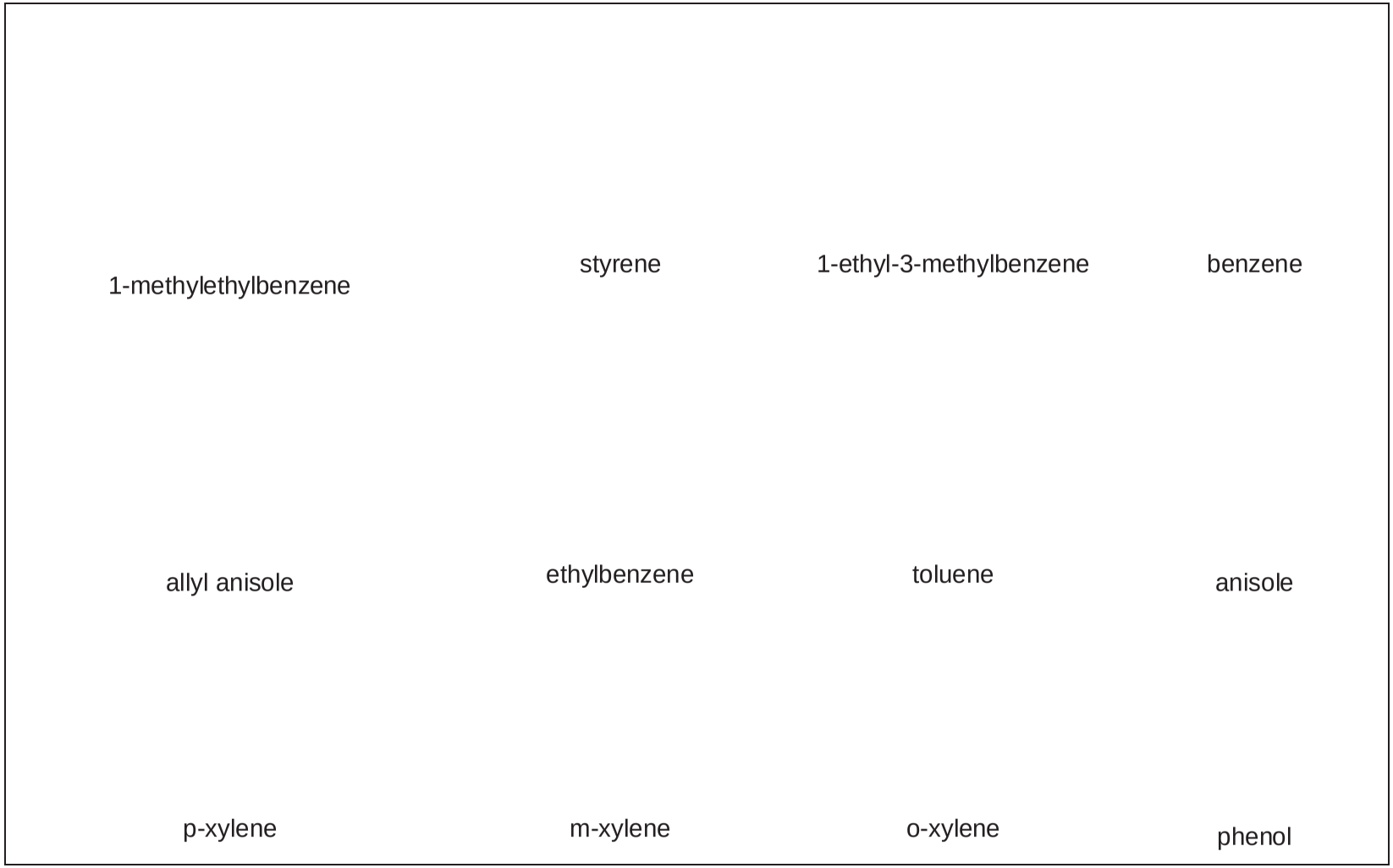


Table C-6 List of aromatic hydrocarbons (cont).

p-cresol	m-cymene	1,2,4-trimethylbenzene	alpha.-methylstyrene
butylated hydroxytoluene	o-cresol	1,3,5-trimethylbenzene	thymol
p-cymene	2-methyl-5-(1-methylethyl)-phenol	m-cresol	cymene

Table C-6 List of aromatic hydrocarbons (cont).

dimethylstyrene	1-methoxy-4-methyl-2-(1-methylethyl)-benzene
2-butenylbenzene	methyleugenol

Figure C-7 Chemical structures of aldehydes obtained of litter.

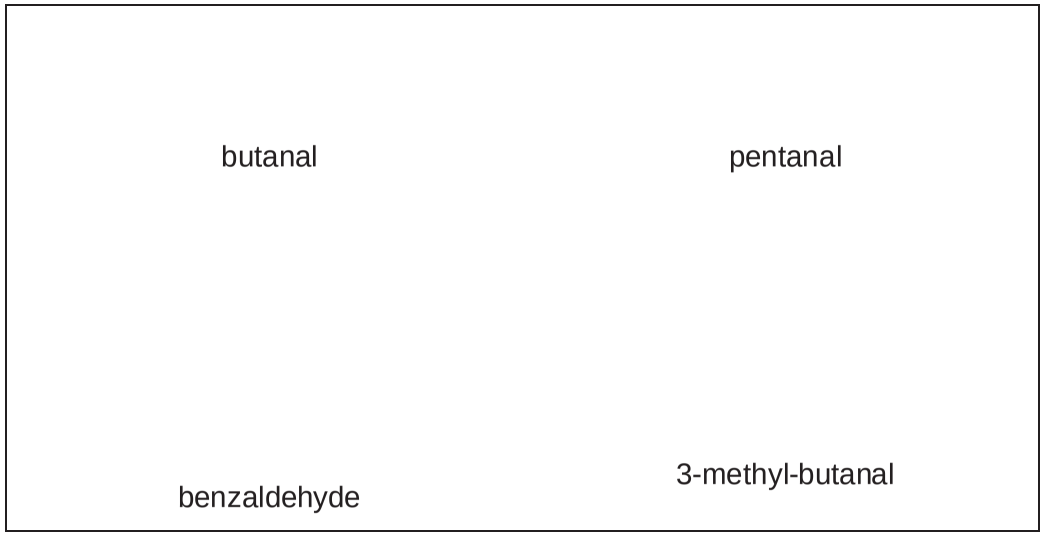
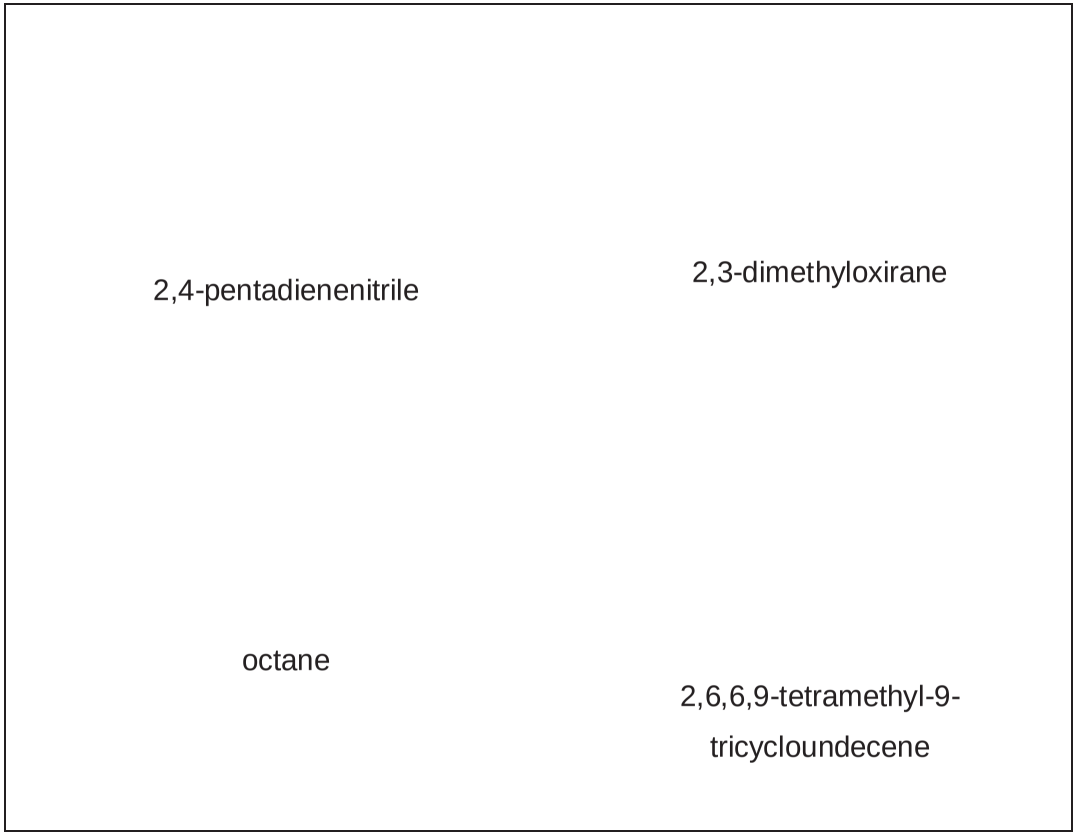


Figure C-8 Chemical structures of other homologues from litter.

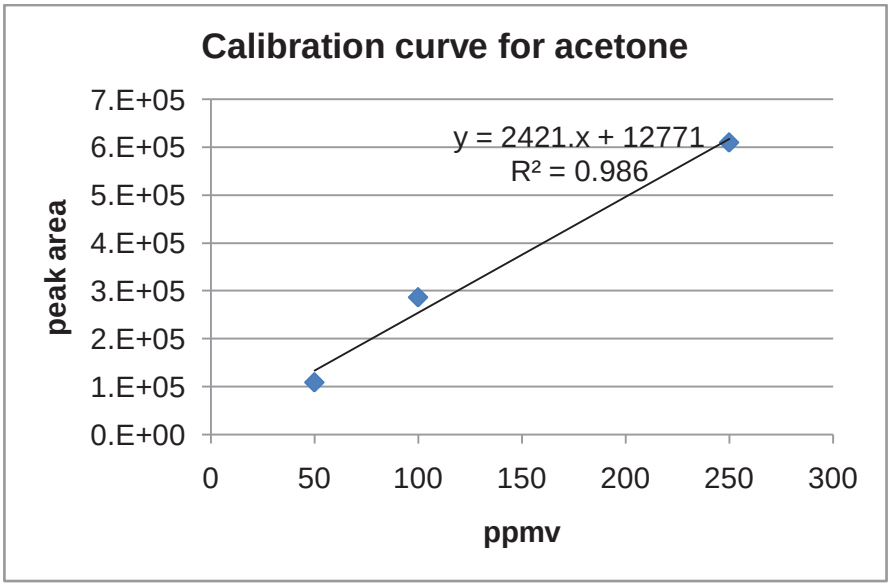
(ethoxymethyl)oxirane	indole	2,6-dimethyl-2,4,6-octatriene	trimethylamine
3-pentenenitrile	1-methoxy-2-methylpropane	2-pentene	trichloromethane
ethyl acetate	2-(1,1-dimethylethyl)-3-methyloxirane	1,3,3-trimethyldiaziridine	2-methylfuran

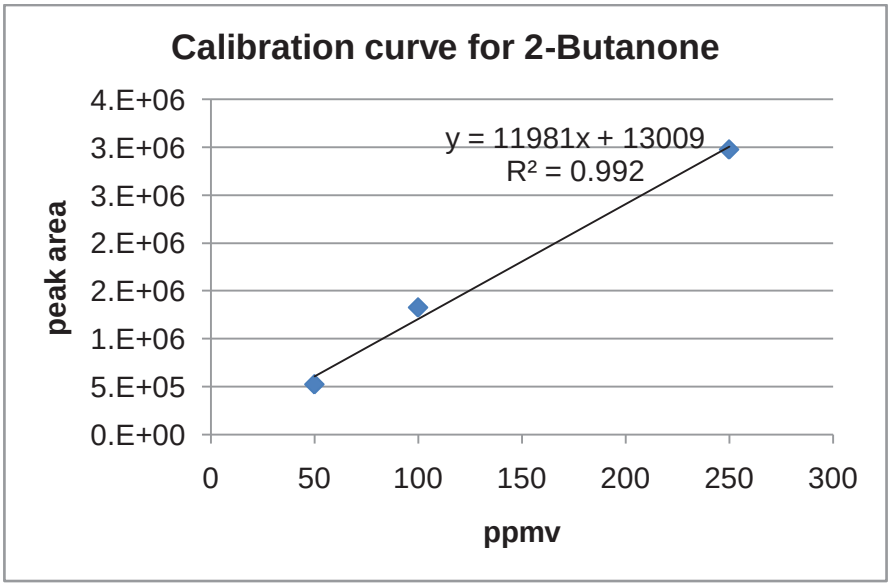
Figure C-8 Chemical structures of other homologues from litter (cont).

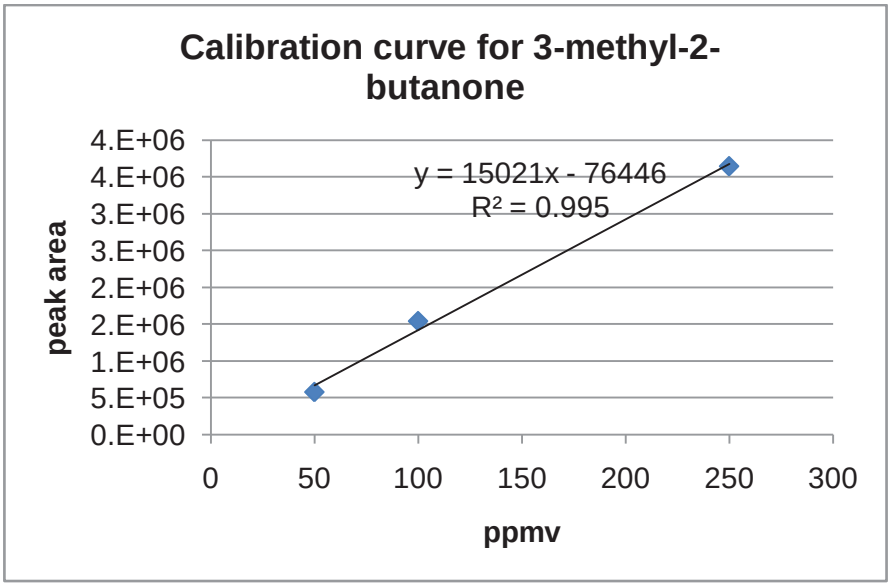


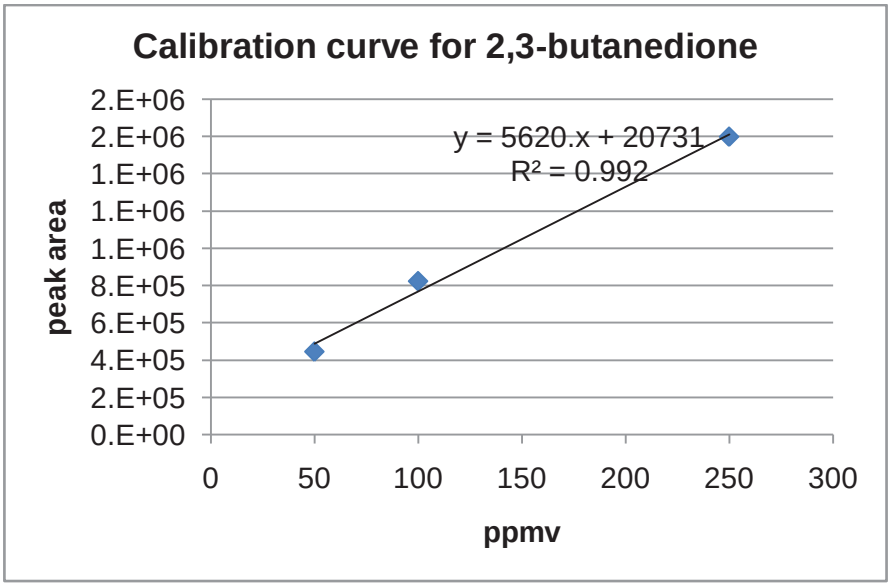
Appendix D

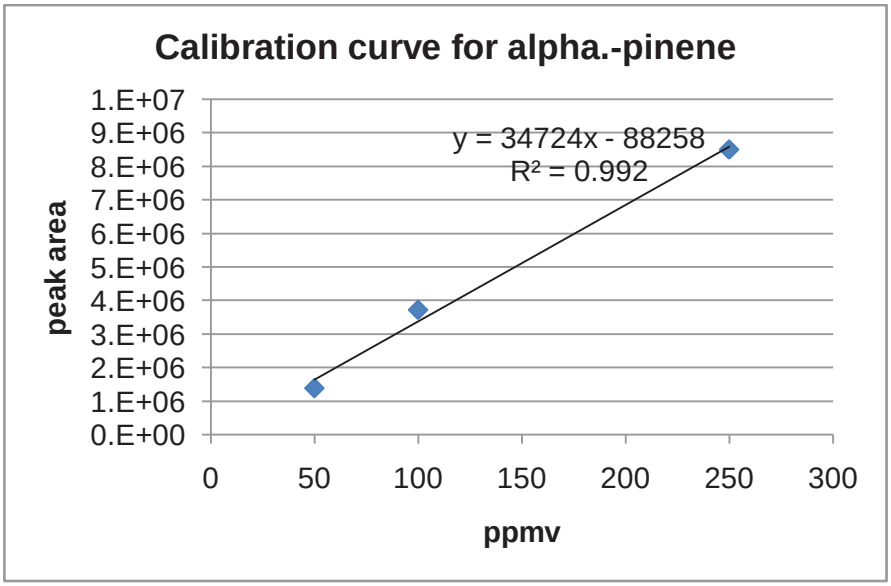
Calibration curves obtained via Tenax TA sorbent tube sampling technique using standard solutions.

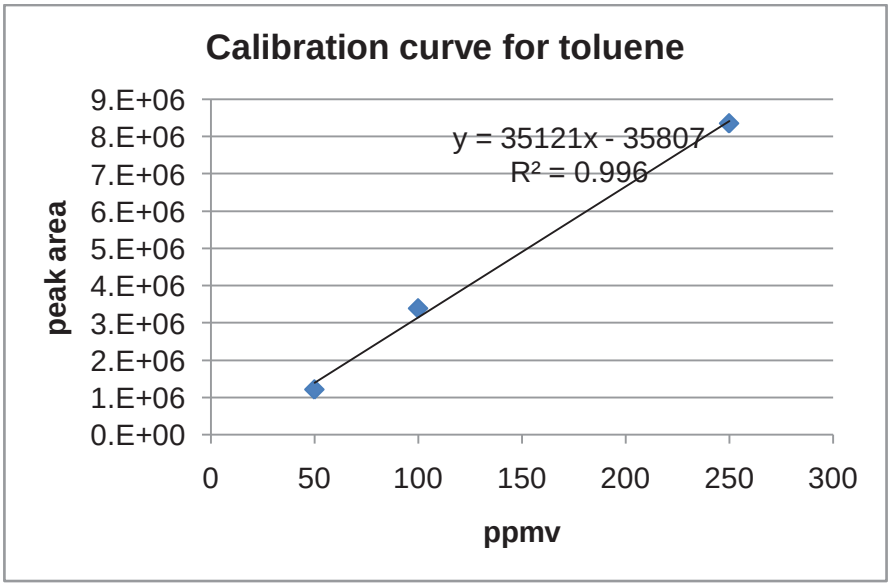

Calibration curve for acetone
y = 2421.x + 12771
R² = 0.986
peak area
7.E+05
6.E+05
5.E+05
4.E+05
3.E+05
2.E+05
1.E+05
0.E+00
0
50
100
150
200
250
300
ppmv

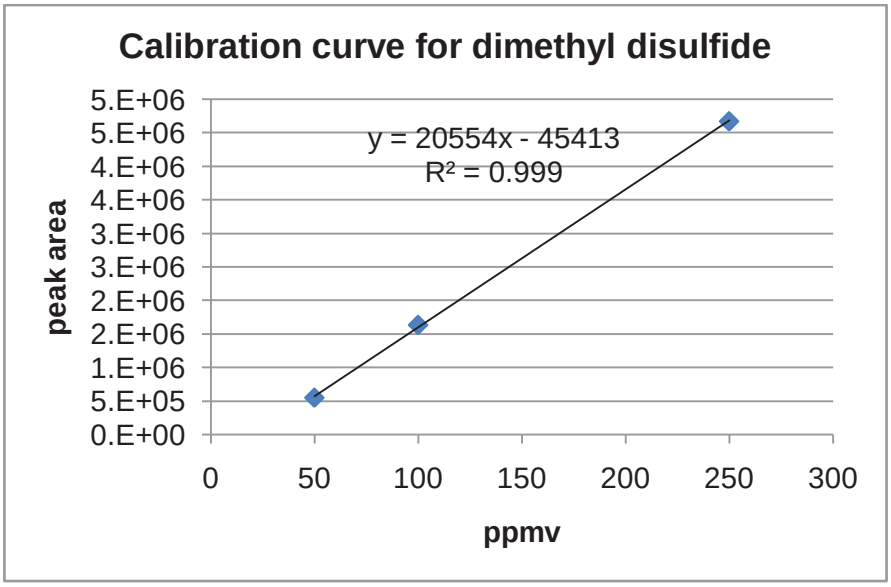

Calibration curve for 2-Butanone
y = 11981x + 13009
R² = 0.992
peak area
4.E+06
3.E+06
3.E+06
2.E+06
2.E+06
1.E+06
5.E+05
0.E+00
0
50
100
150
200
250
300
ppmv

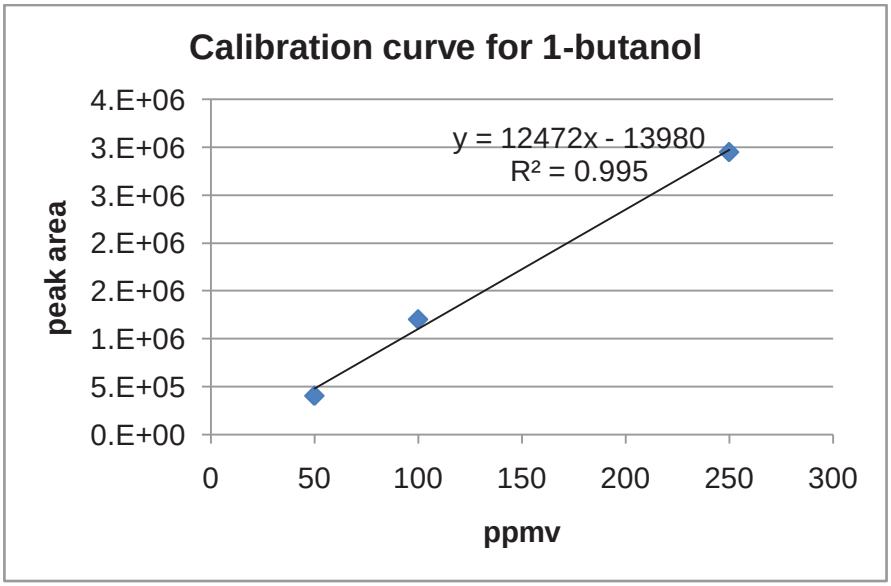

Calibration curve for 3-methyl-2-butanone
y = 15021x - 76446
R² = 0.995
peak area
4.E+06
4.E+06
3.E+06
3.E+06
2.E+06
2.E+06
1.E+06
5.E+05
0.E+00
0
50
100
150
200
250
300
ppmv

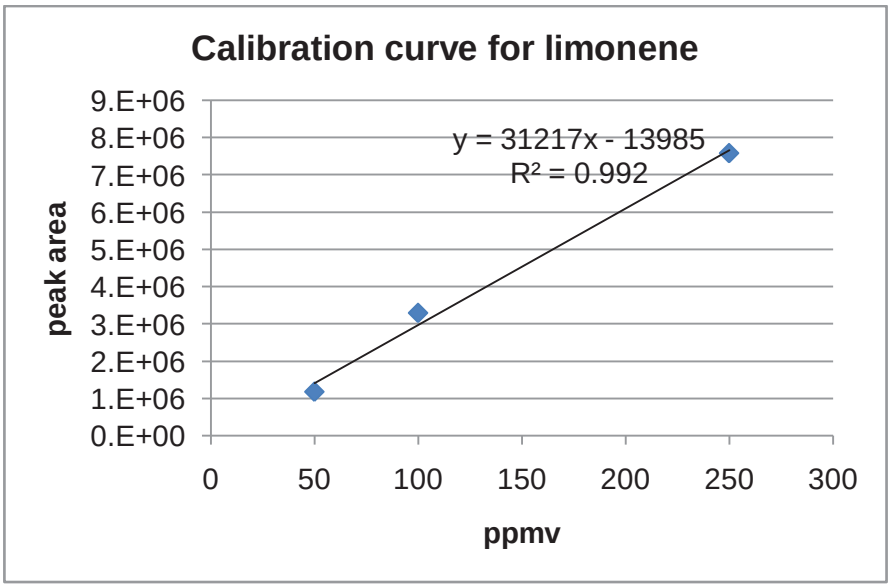

Calibration curve for 2,3-butanedione
peak area
2.E+06
2.E+06
1.E+06
1.E+06
1.E+06
8.E+05
6.E+05
4.E+05
2.E+05
0.E+00
y = 5620.x + 20731
R² = 0.992
0
50
100
150
200
250
300
ppmv

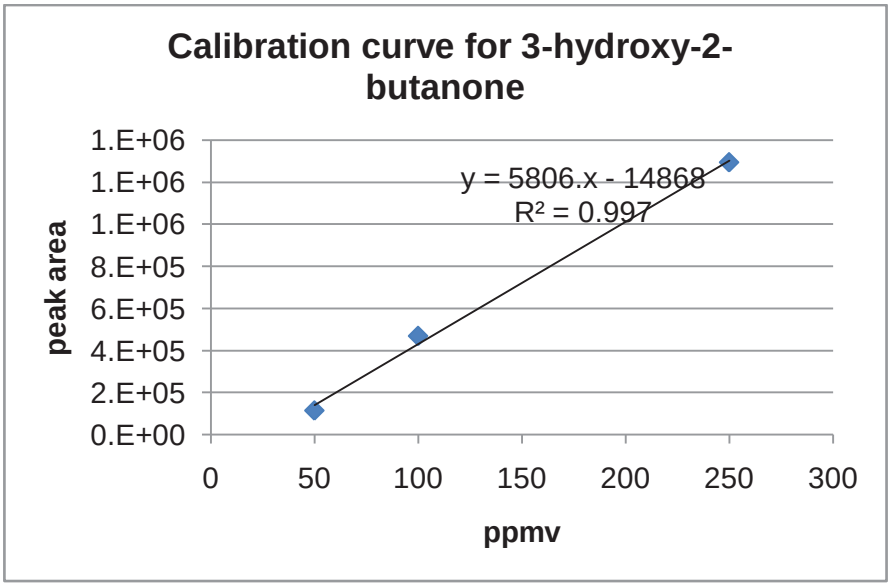

Calibration curve for alpha.-pinene
peak area
1.E+07
9.E+06
8.E+06
7.E+06
6.E+06
5.E+06
4.E+06
3.E+06
2.E+06
1.E+06
0.E+00
y = 34724x - 88258
R² = 0.992
0
50
100
150
200
250
300
ppmv

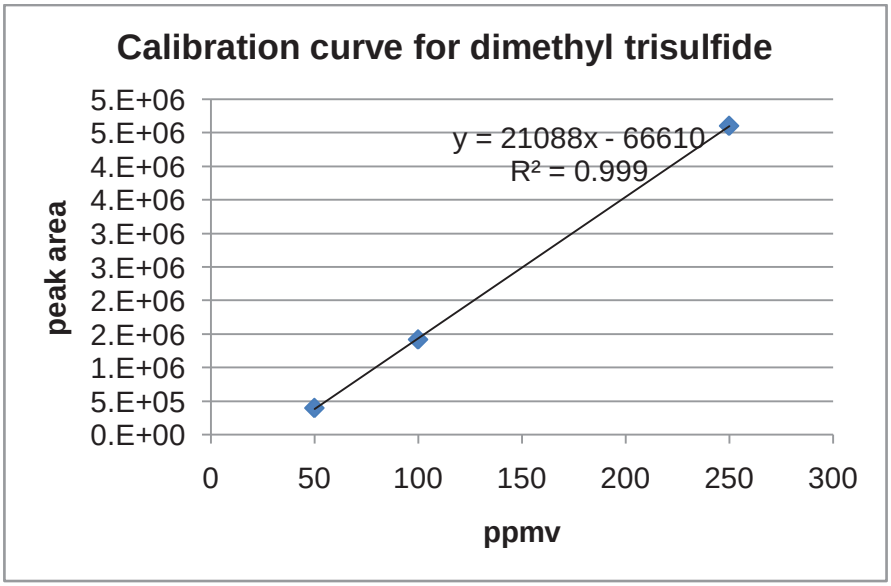

Calibration curve for toluene
peak area
9.E+06
8.E+06
7.E+06
6.E+06
5.E+06
4.E+06
3.E+06
2.E+06
1.E+06
0.E+00
y = 35121x - 35807
R² = 0.996
0
50
100
150
200
250
300
ppmv

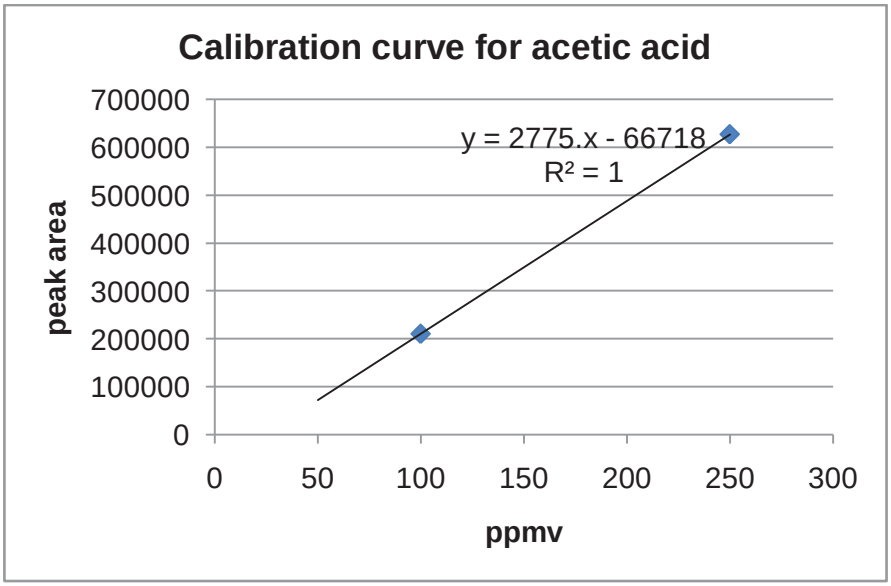

Calibration curve for dimethyl disulfide
y = 20554x - 45413
R² = 0.999
peak area
5.E+06
5.E+06
4.E+06
4.E+06
3.E+06
3.E+06
2.E+06
2.E+06
1.E+06
5.E+05
0.E+00
0
50
100
150
200
250
300
ppmv

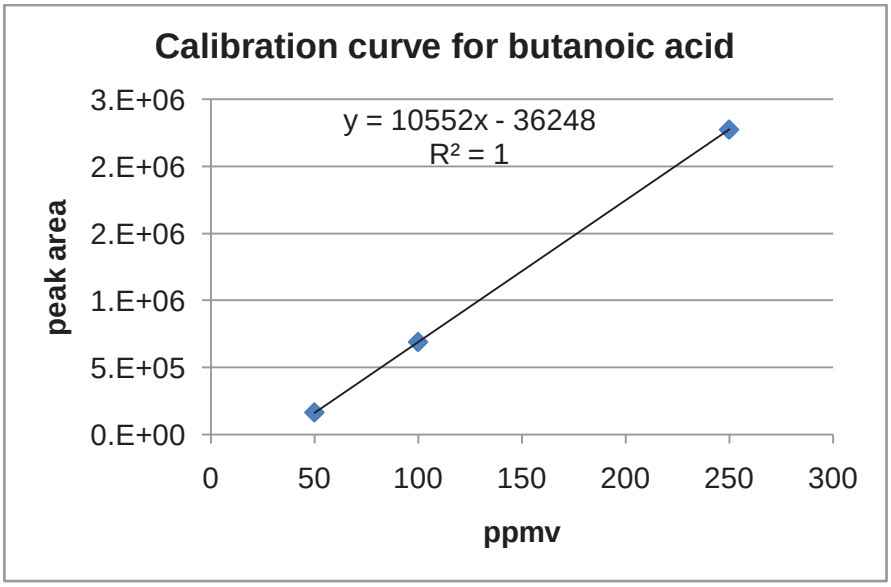

Calibration curve for 1-butanol
y = 12472x - 13980
R² = 0.995
peak area
4.E+06
3.E+06
3.E+06
2.E+06
2.E+06
1.E+06
5.E+05
0.E+00
0
50
100
150
200
250
300
ppmv


Calibration curve for limonene
y = 31217x - 13985
R² = 0.992
peak area
9.E+06
8.E+06
7.E+06
6.E+06
5.E+06
4.E+06
3.E+06
2.E+06
1.E+06
0.E+00
0
50
100
150
200
250
300
ppmv


Calibration curve for 3-hydroxy-2-butanone
peak area
1.E+06
1.E+06
1.E+06
8.E+05
6.E+05
4.E+05
2.E+05
0.E+00
y = 5806.x - 14868
R² = 0.997
0
50
100
150
200
250
300
ppmv

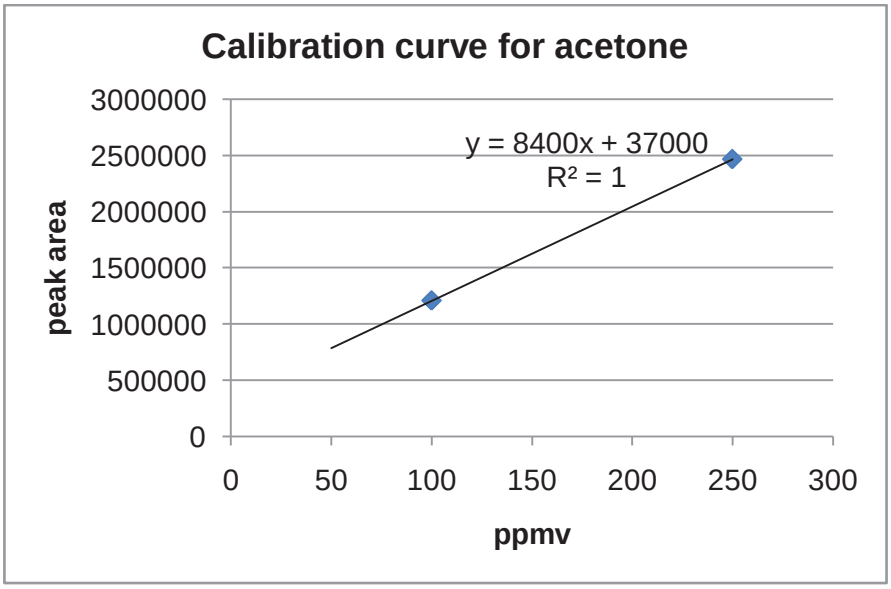

Calibration curve for dimethyl trisulfide
peak area
5.E+06
5.E+06
4.E+06
4.E+06
3.E+06
3.E+06
2.E+06
2.E+06
1.E+06
5.E+05
0.E+00
y = 21088x - 66610
R² = 0.999
0
50
100
150
200
250
300
ppmv

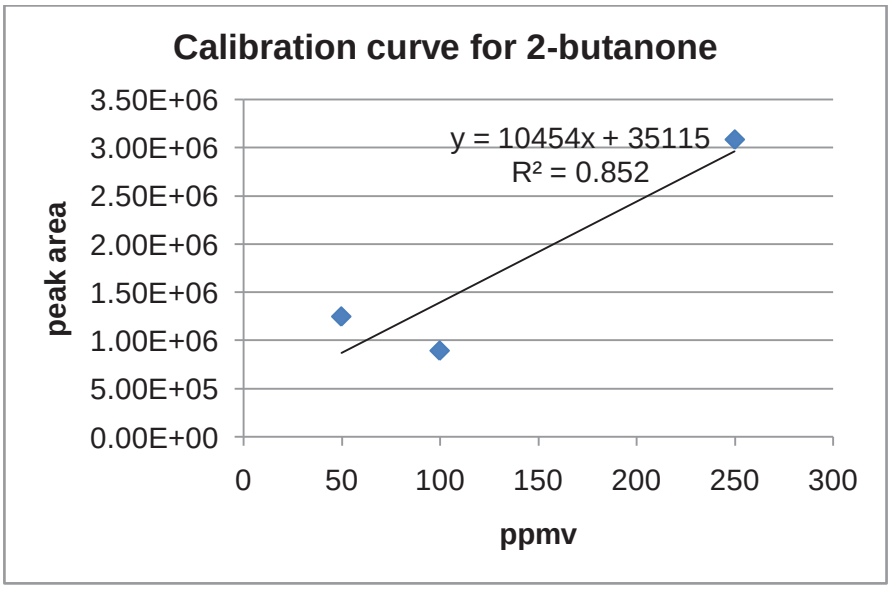

Calibration curve for acetic acid
peak area
700000
600000
500000
400000
300000
200000
100000
0
y = 2775.x - 66718
R² = 1
0
50
100
150
200
250
300
ppmv

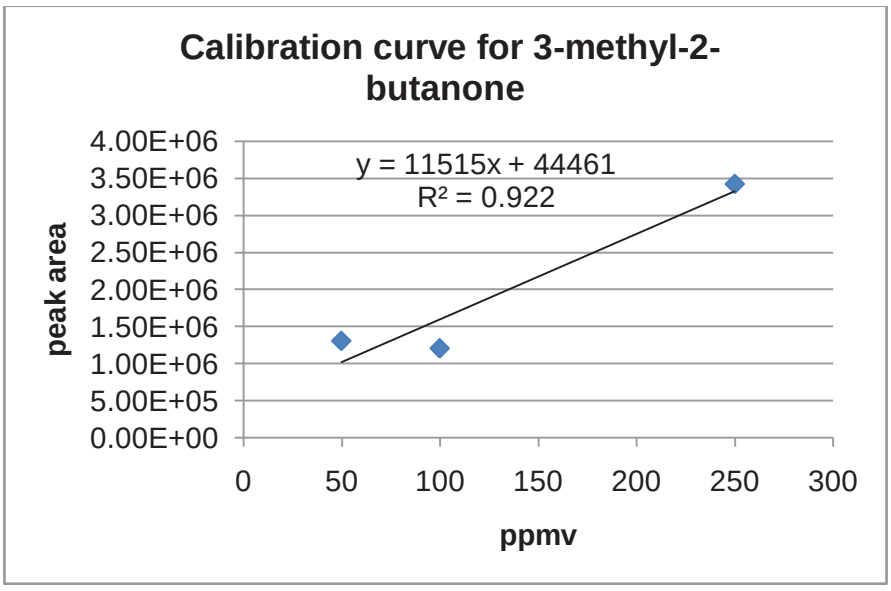

Calibration curve for butanoic acid
y = 10552x - 36248
R² = 1
peak area
3.E+06
2.E+06
2.E+06
1.E+06
5.E+05
0.E+00
0
50
100
150
200
250
300
ppmv

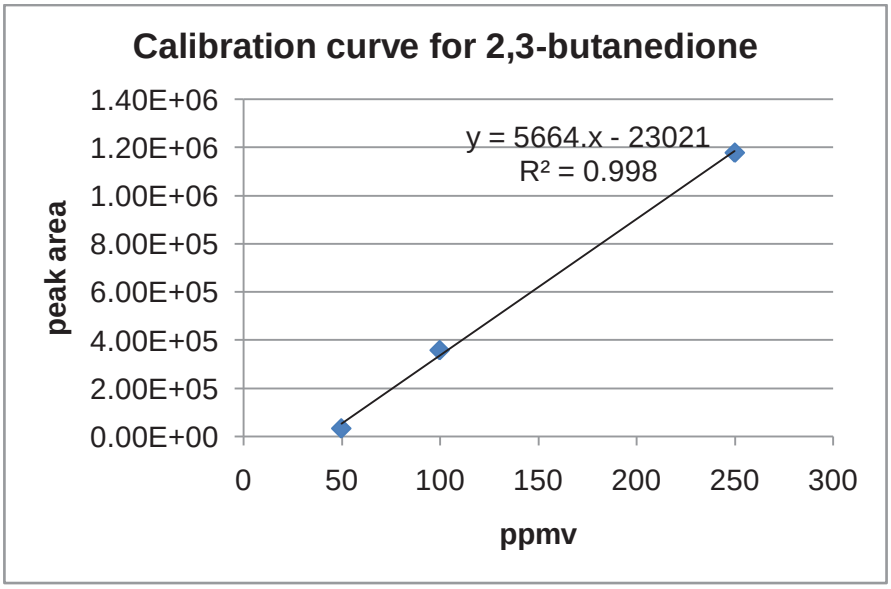
Appendix E

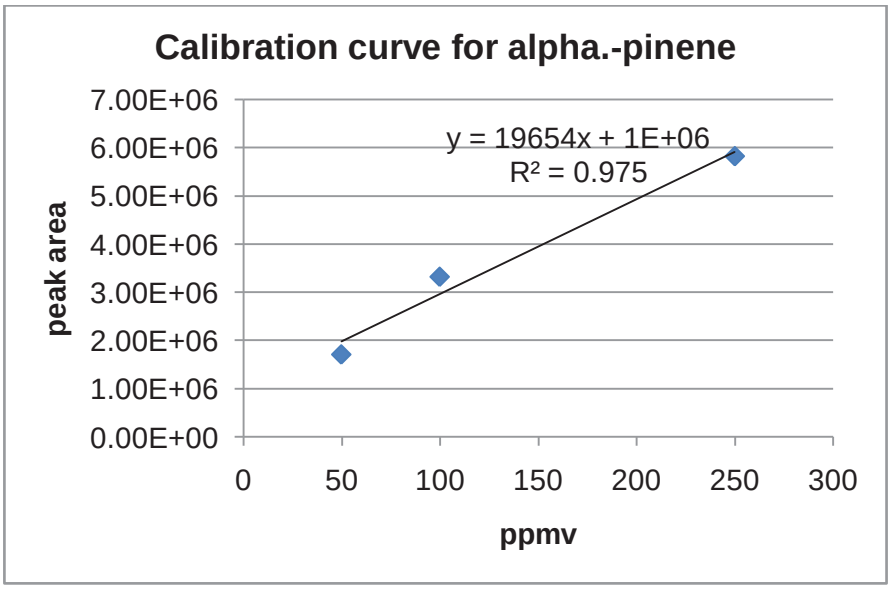
Calibration curves obtained via direct headspace sampling technique using standard solutions.

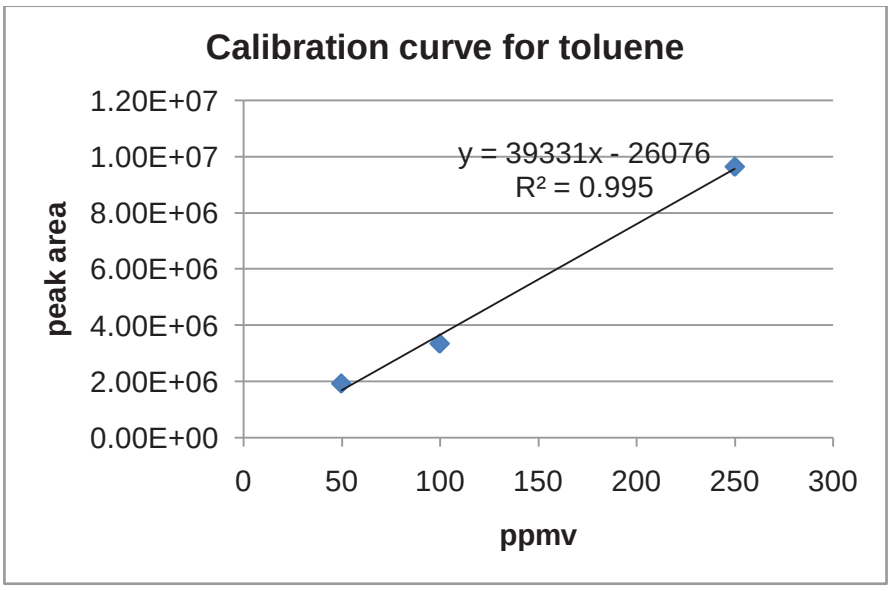

Calibration curve for acetone
peak area
3000000
2500000
2000000
1500000
1000000
500000
0
y = 8400x + 37000
R² = 1
0
50
100
150
200
250
300
ppmv

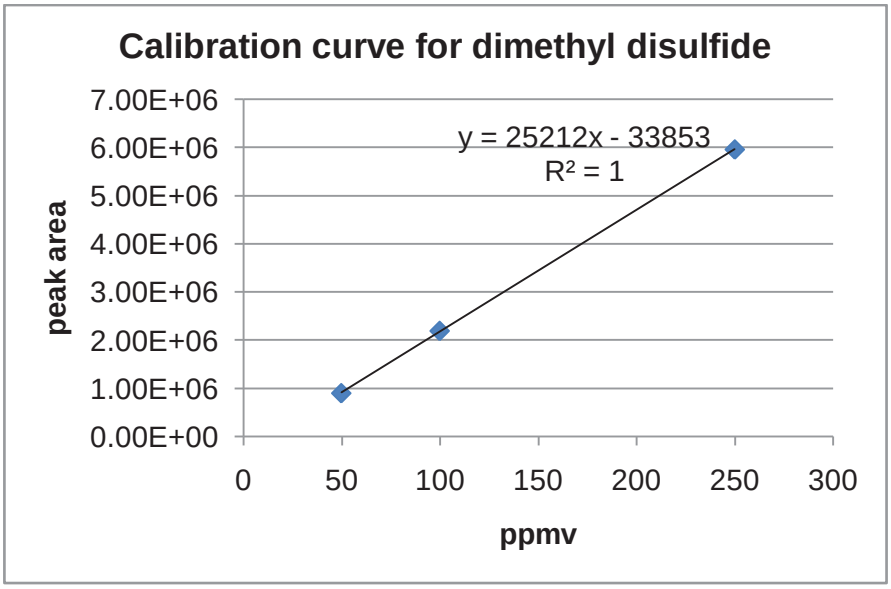

Calibration curve for 2-butanone
peak area
3.50E+06
3.00E+06
2.50E+06
2.00E+06
1.50E+06
1.00E+06
5.00E+05
0.00E+00
y = 10454x + 35115
R² = 0.852
0
50
100
150
200
250
300
ppmv

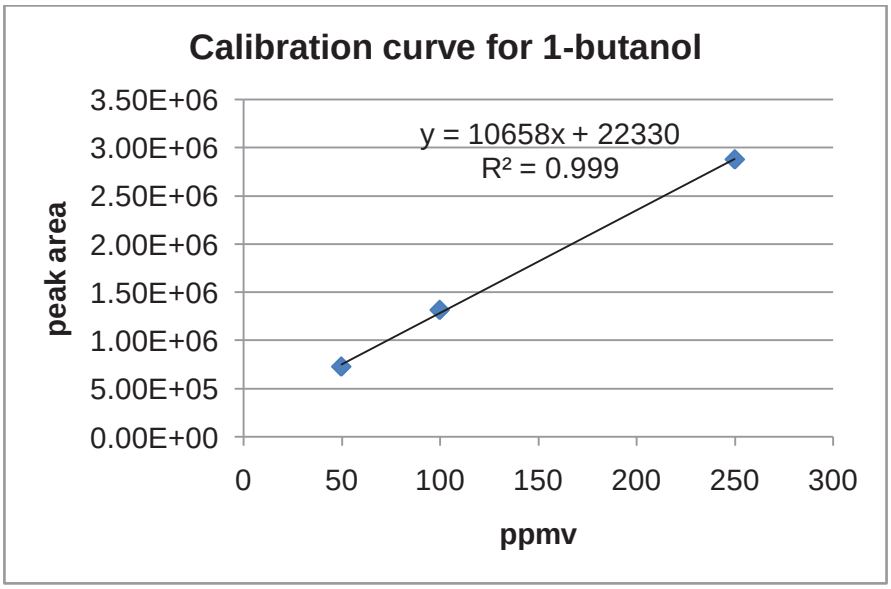

Calibration curve for 3-methyl-2-butanone
peak area
4.00E+06
3.50E+06
3.00E+06
2.50E+06
2.00E+06
1.50E+06
1.00E+06
5.00E+05
0.00E+00
y = 11515x + 44461
R² = 0.922
0
50
100
150
200
250
300
ppmv

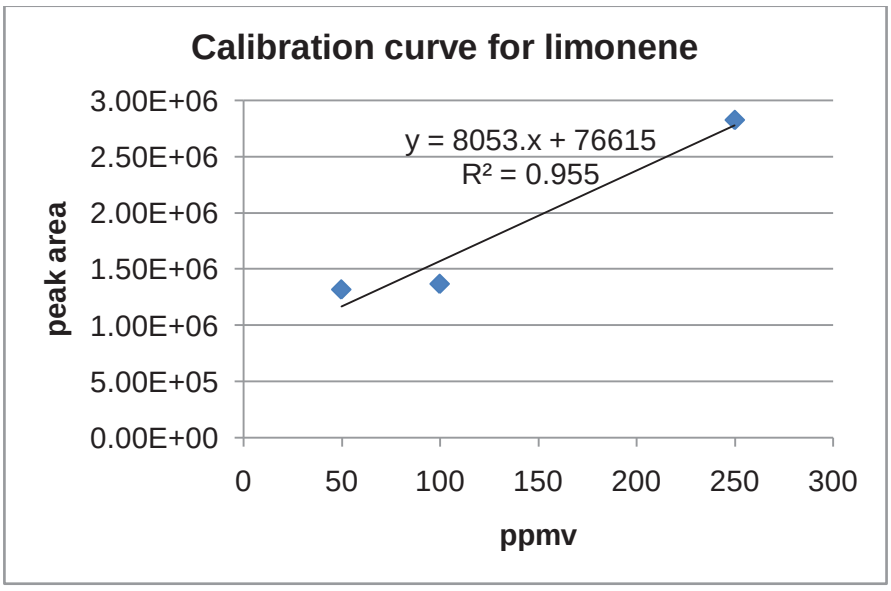

Calibration curve for 2,3-butanedione
peak area
1.40E+06
1.20E+06
1.00E+06
8.00E+05
6.00E+05
4.00E+05
2.00E+05
0.00E+00
y = 5664.x - 23021
R² = 0.998
0
50
100
150
200
250
300
ppmv

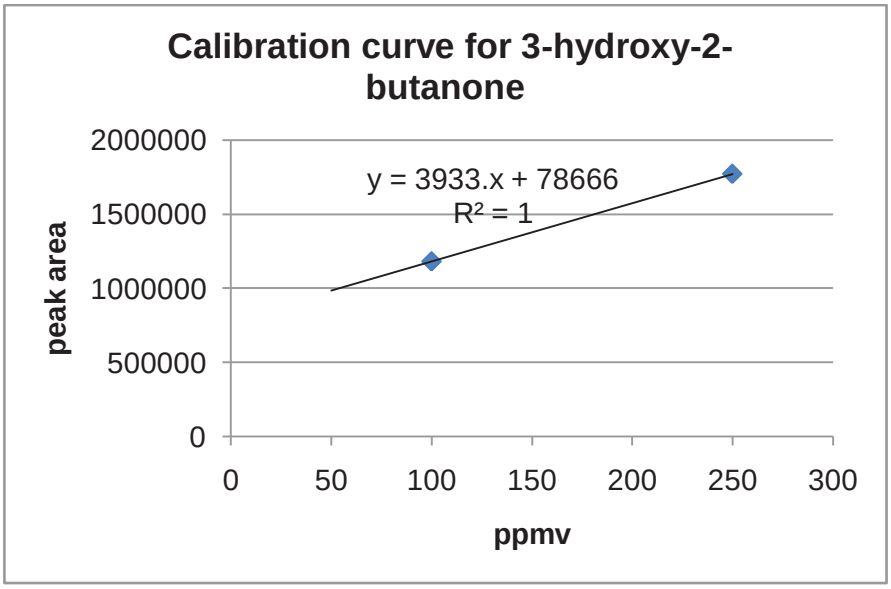

Calibration curve for alpha.-pinene
peak area
7.00E+06
6.00E+06
5.00E+06
4.00E+06
3.00E+06
2.00E+06
1.00E+06
0.00E+00
y = 19654x + 1E+06
R² = 0.975
0
50
100
150
200
250
300
ppmv

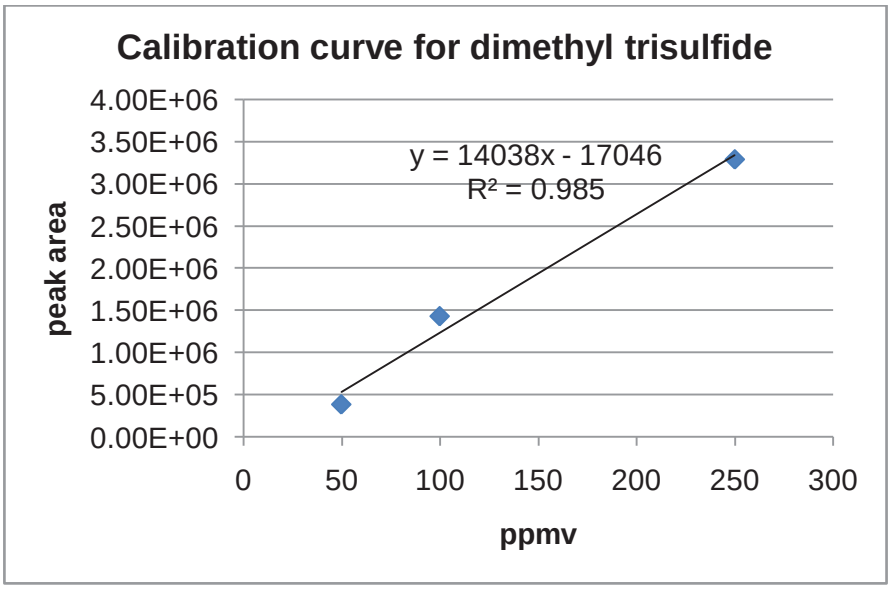

Calibration curve for toluene
peak area
1.20E+07
1.00E+07
8.00E+06
6.00E+06
4.00E+06
2.00E+06
0.00E+00
y = 39331x - 26076
R² = 0.995
0
50
100
150
200
250
300
ppmv

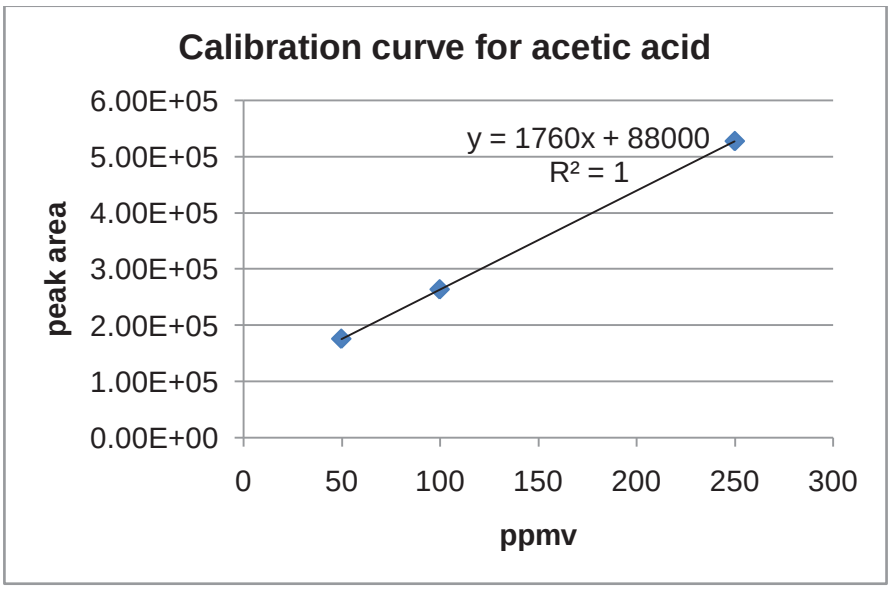

Calibration curve for dimethyl disulfide
y = 25212x - 33853
R² = 1
peak area
7.00E+06
6.00E+06
5.00E+06
4.00E+06
3.00E+06
2.00E+06
1.00E+06
0.00E+00
0
50
100
150
200
250
300
ppmv

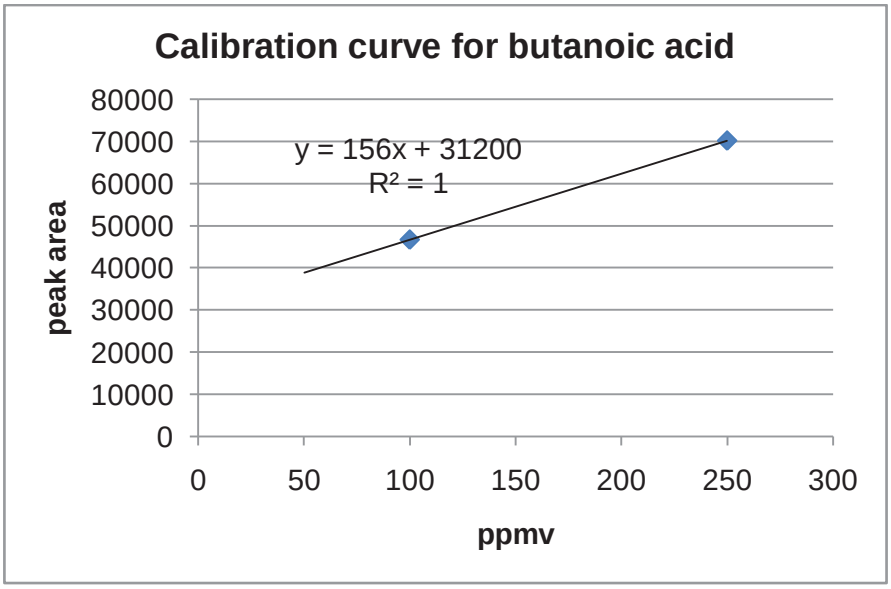

Calibration curve for 1-butanol
y = 10658x + 22330
R² = 0.999
peak area
3.50E+06
3.00E+06
2.50E+06
2.00E+06
1.50E+06
1.00E+06
5.00E+05
0.00E+00
0
50
100
150
200
250
300
ppmv


Calibration curve for limonene
y = 8053.x + 76615
R² = 0.955
peak area
3.00E+06
2.50E+06
2.00E+06
1.50E+06
1.00E+06
5.00E+05
0.00E+00
0
50
100
150
200
250
300
ppmv


Calibration curve for 3-hydroxy-2-butanone
y = 3933.x + 78666
R² = 1
peak area
2000000
1500000
1000000
500000
0
0
50
100
150
200
250
300
ppmv


Calibration curve for dimethyl trisulfide
y = 14038x - 17046
R² = 0.985
peak area
4.00E+06
3.50E+06
3.00E+06
2.50E+06
2.00E+06
1.50E+06
1.00E+06
5.00E+05
0.00E+00
0
50
100
150
200
250
300
ppmv


Calibration curve for acetic acid
y = 1760x + 88000
R² = 1
peak area
6.00E+05
5.00E+05
4.00E+05
3.00E+05
2.00E+05
1.00E+05
0.00E+00
0
50
100
150
200
250
300
ppmv


Calibration curve for butanoic acid
peak area
80000
70000
60000
50000
40000
30000
20000
10000
0
y = 156x + 31200
R² = 1
0
50
100
150
200
250
300
ppmv