Environment Agency

# Odour Assessment of an Intensive Livestock Facility

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Miranda Kavanagh

Director of Evidence

# Foreword

This report presents the results of a study to measure the quantities and types of odorous substances at an intensive poultry farm at Lower Farm, Eastmoor, Derbyshire, where there have been odour complaints from local residents. The farm rears broiler chickens in four identical sheds; the study focussed on one shed - as a representative unit. The study measured the overall odour concentration inside the shed, and estimated the rate of odour emission from the shed. It also investigated if the odour was mainly due to one substance – because, if it was, then the relevant substance might conveniently have been targeted for odour control.

The farm was slightly unusual because its sheds had under-floor heating for part of the time while the broilers were growing. However, the under-floor heating was not used during the main period of odours, which occurred when broilers were nearing their final weights. It is therefore possible that the Lower Farm measurements may be representative of odours at most broiler farms - which do not have under-floor heating.

It was found from detailed chemical analysis of the substances in the air of the shed, that the broiler poultry odour was not dominated by one species that could be conveniently targeted. Instead, the odour was found to be made up from a wide and variable range of chemical species, whose overall odour strength and emissions could be best determined using Dynamic Dilution Olfactometry (DDO).

It was found that the total concentration in the air of the shed, as measured by DDO, was about 3,000 odour units per cubic metre - where 1 odour unit per cubic metre represents the point of odour detection. This result was based on measurements on two days during the main period of odours. Based on the same two days, the rate of odour emission from the shed was determined to be about 100,000 odour units per second. The other three identical sheds on the farm are likely to have similar emissions. These emission results are useful for inputting to an atmospheric dispersion model in order to estimate the impact of broiler poultry odours on local people.

The study has confirmed that DDO is an effective technique for estimating the odour strength and emissions of complex substance mixtures, like those in a broiler shed. It has also confirmed that there is no single chemical substance that can simply represent broiler poultry odour in general. A technique like DDO, that measures the combined effect of mixed substances, is therefore more appropriate for regulatory purposes.

In order to understand and manage poultry odours, it is desirable to consider making further DDO measurements covering a wider range of farming conditions, such as different bird ages and different conditions of feeding, littering, housing and ventilation. These measurements may be used to assess how representative the Lower Farm measurements are, and to estimate emissions for use in dispersion modelling of local odour impacts. For regulatory purposes it will also be useful to consider different options for discharging odorous air from poultry houses, in order to help the adequate dispersion and control of odours.

# Executive summary

RPS was commissioned by the Environment Agency to carry out a study of emissions of odour from Lower Farm in Eastmoor, Derbyshire. Lower Farm is a broiler chicken intensive poultry installation operated by Brackenmore Ltd., trading as Applied Poultry. The chickens are reared within four sheds, which are ventilated by side inlets coupled with gable-end extraction units. Each shed stocks 44,700 birds and the total number of birds on site at any one time is 178,800. The birds arrive at the farm at one-day old and remain until they are between 33 and 42 days old. The birds are 'thinned,' a process by which some birds are removed, when they reach between 33 and 35 days old; the remaining birds are removed when aged between 38 and 42 days old. Complaints about odour are said to begin, typically, when the chicks are around 20 days old and reach a peak just before thinning.

A number of complaints have been received alleging odours from the farm. The aims of the study were to identify the compounds likely to be causing the odours and to calculate emission rates of odours and dusts from the sheds where poultry are kept. This information is to be used:

- to inform modelling studies that will be undertaken by the Air Quality Modelling and Assessment Unit (AQMAU); and
- to further understanding of the issues.

The first sampling campaign was carried out on 29th October 2009. On the basis of their concentration-to-ODT ratios, the VOCs most likely to be contributing to the odour from the poultry shed were:

- Carboxylic acids, specifically acetic acid, butanoic acid, and 2-methyl butanoic acid and 3-methyl butanoic acid;
- Branched ketones, specifically 2,3-butanedione;
- High molecular weight aldehydes, specifically 2-methyl butanal and 3-methyl butanal; and
- Amines, specifically trimethylamine.

These are all compounds that, according to the literature, are commonly associated with poultry farm odour. The mass emission rates of these compounds from the poultry shed have been calculated.

The semi-quantitative measurements of ammonia concentrations in and around the poultry shed indicated that the ODT was not exceeded, and ammonia is not therefore expected to be a significant contributor to the total odour (although it could interact synergistically with other compounds). The mass emission rate of ammonia from the poultry shed has been calculated.

Total odour concentration in the poultry shed air was measured by dilution dynamic olfactometry (DDO) and the total odour emission rate from the shed has been calculated.

Some literature studies have suggested particulate matter plays a role as a carrier of odorous compounds in air from livestock facilities. The particulate matter concentration

in the air in the poultry shed was measured and the mass emission rate has been calculated.

Having obtained knowledge of the identity of the odorous compounds in the first study, a second sampling campaign was carried out on 12th May 2010, using a refined sampling approach targeting each chemical group with a sorbent that was tailored to its characteristics (polarity, boiling point, etc). The second study also included repeating the triplicate measurements of total odour by lung sampling/DDO, so as to better understand the variability in total odour emission rates between bird batches; and measurement of $H_2S$ concentrations by Jerome® gold-film analyser.

The VOCs from the second study that were most likely to be contributing to the odour from the poultry shed were:

- Carboxylic acids, specifically acetic acid;
- Branched ketones, specifically 2,3-butanedione and cyclohexanone;
- High molecular weight aldehydes, specifically benzaldehyde, octanal, nonanal and decanal;
- Reduced sulphides, specifically methyl mercaptan, carbon disulphide and dimethy disulphide;
- Aliphatic and aromatic hydrocarbons, specifically xylenes, toluene, methyl cyclohexane, n-Pentane, n-heptane, 1-butene; and
- 1-methyl butanol and phthalate anhydride.

The mass emission rates of these compounds from the poultry shed have been calculated. It should be noted that the birds were fed on a different mixture at the second sampling campaign compared to the first study.

Hydrogen sulphide was present in the shed above its ODT and the mass emission rate has been calculated.

The total odour emission rate (as measured by DDO) was 81,848 $ou_E\ s^{-1}$ in the second study compared to 117,326 $ou_E\ s^{-1}$ in the first study.

# Contents

# 1 Introduction

RPS was commissioned by the Environment Agency in September 2009 to carry out a study of emissions of odours and dusts from Lower Farm in Eastmoor, Derbyshire. In May 2010, informed by the results of the first study, the Environment Agency expanded the scope to include a further sampling survey.

A number of complaints have been received alleging odours from the farm. The aim of the study was to identify the compounds likely to be causing the odours and to calculate emission rates of odours and dusts from the sheds where poultry are kept. This information is to be used to:

- inform modelling studies that will be undertaken by the Air Quality Modelling and Assessment Unit (AQMAU); and
- to further the Agency's understanding of the issues.

Lower Farm is a broiler chicken intensive poultry installation operated by Brackenmore Ltd., trading as Applied Poultry. The chickens are reared within four sheds, which are ventilated by side inlets coupled with gable-end extraction units. Each shed uses underfloor heating until the birds are around 21 days old at which point the body heat from the birds triggers the underfloor heating to switch off. Each shed stocks 44,700 birds and the total number of birds on site before thinning is 178,800. The birds arrive at the farm at one-day old and remain until they are between 33 and 42 days old. The birds are 'thinned,' a process by which some birds are removed, when they reach between 33 and 35 days old; the remaining birds are removed when aged between 38 and 42 days old. Complaints about odour are said to begin, typically, when the chicks are around 20 days old and reach a peak just before thinning (Environment Agency 2009a).

Sampling for the identification and quantification of odours and particulate matter was carried out on 29th October 2009, when the chicks were 29 days old to coincide with the expected period of maximum emissions before thinning. Sampling was repeated on 12th May 2010, again when the chicks were 29 days old. This report describes the methodology used in this study and presents the results of the monitoring.

# 2 Literature Review

Wright et al. (2005) used headspace solid-phase microextraction (SPME) for field air sampling of odorous air near and downwind of a beef cattle feedyard and swine finisher barn. Analysis by multidimensional chromatography-mass spectrometry-olfactometry (GC-MS-O) was used to try and define and prioritise the compounds that constitute the primary odour impact from the large field of potential odorants. Only a few compounds constitute the main cause of odours in complaints from these facilities and this appeared to be especially true for the case of increasing distance from both cattle feedyard and swine barn facilities, with *p*-cresol consistently taking on the dominant odour impact role with ever increasing distance. The other top odorants at distant locations were isovaleric acid and *p*-ethyphenol. In contrast, at or near-site odour profiles were shown to be much more complex, with many of the well known lower-tier odour compounds rising in relative significance: for cattle feedyards the top odorants were triethylamine, *p*-cresol and butyric acid; triethylamine was shown to represent a significant odour impact relative to more often cited livestock odorants such as hydrogen sulphide ($H_2S$), organic sulphides and volatile fatty acids.

The objective of the study by Bulliner et al. (2006) was to develop a novel method for long-term (e.g. one week duration) sampling of odours in air in swine houses. Odorous gases were adsorbed onto carbon steel plates, which were then transferred to clean storage jars. Headspace SPME was used to extract the compounds and analysis was carried out using a gas chromatography-mass spectrometry-olfactometry (GC-MS-O) system, where the human nose is used as detector simultaneously with chemical analysis by a mass spectrometer. It was concluded that the steel plate technique was best used for qualitative rather than quantitative analysis. Butyric acid, isovaleric acid, *p*-cresol and skatole were found to play a large role in the odour from particulate matter (PM) in ambient air at swine facilities. Dimethytrisulphide (DMTS) was found to play a significant role in the odour in ambient air at swine facilities regardless of the presence of PM. *p*-Cresol was present in all samples, even those at distant locations with no PM present, underlining the potential for this compound to remain in environments exposed to air from livestock facilities for extended periods of time after exposure. The authors chose to ignore several compounds because they were deemed to be background interferences, including pentanol, toluene, 3-heptanone, 2-ethyl hexanol, benzaldehyde, benzene methanol and phenol.

As part of a study to evaluate the effectiveness of Zeolite for control of odour emissions from poultry manure storage, Cai et al. collected headspace samples from the storage vessels with SPME and carried out analysis by GC-MS-O. They noted the volatile components identified by earlier workers, which included: butyric acid, ethanol and acetone in stored poultry manure; mercaptans, sulphides and diketones in the headspace of liquid poultry manure; volatile fatty acids (VFAs), indole and skatole in the liquid; volatile sulphur compounds such as hydrogen sulphide, methyl mercaptan (MM), dimethyl suphide (DMS) and dimethyl disulphide (DMDS) from poultry manure under anaerobic conditions; various alcohols, ketones, esters and carboxylic acids together with DMS and DMDS from poultry incubated in an argon atmosphere; branched aliphatic alcohols, many esters, dimethyl trisulphide (DMTS) and alkanamides from poultry manure; and butyric acid, isovaleric acid, DMTS, indole and skatole were identified as the most important odorous components based on the ratio of concentration to odour detection threshold value.

Cai et al. (2007) also reviewed sampling methods, noting that caution should be used when using standard volatile organic compounds (VOCs) whole-air (evacuated bag or canister) procedures, which can be associated with poor sample recoveries for typical livestock malodorous gases because livestock gases are often polar, reactive and can interact with each other, moisture in the air and the sampling container materials. Regarding active

sampling onto sorbent tubes, the authors noted that the EPA TO-17 method was not specifically developed for the compounds of interest, namely carboxylic acids, sulphides, amides, indolics, phenolics, branched ketones and high molecular weight aldehydes. Cai et al. (2007) therefore used SPME as an alternative to the conventional sampling techniques, as the long sampling duration allowed a SPME to be used quantitatively to collect a time weighted sample. More than 90 volatile compounds were identified in the headspace air; from this, six characteristic odours in the poultry manure were selected on the basis of the odour intensity (%) and odour duration (min) for each odour recorded in the aromagram. The six characteristic odours were correlated with their corresponding compounds:

- Onion/garlic – DMTS
- Fatty acid/body odour – butanoic acid
- Body odour – isovaleric acid
- Phenolic – phenol
- Barnyard – indole
- Naphthalenic – skatole.
- A seventh, the vinegar smell associated with acetic acid, was less intense and less offensive than the others

Koziel et al. (2006) noted that that SPME was capable of recovering an average of 98% of odorous analytes from a standard gas mixture, compared to 88% for Tenax® TA/thermal desorption. The standard gas contained volatile fatty acids (C2-C7), *p*-cresol, 4-ethyl phenol, 2-aminoacetophenone and indole.

SPME is a research sampling technique, with no standard protocols or equipment available. On the basis that Tenax® TA with thermal desorption has been shown to offer reasonable recoveries, the latter has been chosen for this current Environment Agency study.

# 3 Methodology

## Methodology for First Study

### General Approach

The general approach to the assessment was informed by a meeting between representatives from the Environment Agency and RPS on 14th August 2009. From this meeting it was understood that the Agency required monitoring to further its understanding of the issues. The results of this study would be used in a modelling exercise to be undertaken by the AQMAU. The Agency advised RPS that indicative operator measurements suggested that the odour levels were not likely to be due to high ammonia ($NH_3$) emissions, and consequently the study was to focus on identifying and quantifying other sources of odour; nevertheless, for completeness, indicative measurements of ammonia concentration were also made.

The following issues were identified that required consideration in the sampling strategy:

- The emissions profile of the poultry crop means the part of the cycle with the highest potential for odour is expected to be just before thinning; and
- Air extracted from the four identical poultry sheds is exhausted by fans through the gable walls at waist-to-head height, there being no external flue, duct or vent.

The aim of the study was:

- to identify those compounds emitted from the poultry sheds that were likely to be responsible for odours perceived beyond the site boundary;
- to measure the concentration of odours and dusts in the sheds; and
- to calculate emission rates of odours and dusts from the sheds.

The compounds causing significant odour were identified by measuring the concentrations of VOCs in the poultry sheds and comparing the results with published Odour Detection Thresholds. The Odour Detection Threshold (ODT) is the concentration at which fifty percent of a panel of test subjects were able to detect that an odour is present.

Five techniques were used to measure odour and dust (particulate matter, $PM_{10}$), within the poultry sheds. These techniques are summarised in Table 3.1 below.

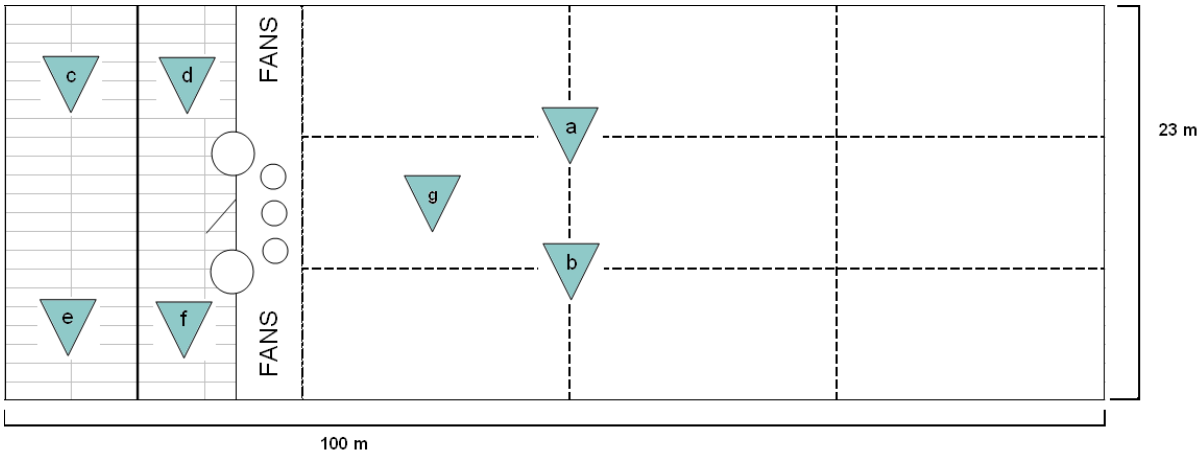
**Table 3.1: Techniques used to Measure Odour and Dust within the Poultry Sheds.**

| Measurement | Sample Media/Monitor | Analysis | Laboratory used for Analysis |
|---|---|---|---|
| Identification of odorous VOCs | Active pumped sampling onto Tenax® TA adsorption tubes | GC-MS scan *(semi-quantitative)* | M-Scan |
| Quantification of odorous VOCs | Active pumped sampling onto Tenax® TA adsorption tubes | Targeted GC-MS *(fully-quantitative)* | M-Scan |
| Total Odour Concentration | Collected using the 'lung' sampling technique into a 40 litre Nalophane sample bag | Dynamic Dilution Olfactometry (DDO) analysis to BS EN 13725 | Silsoe Odours Ltd. |
| Ammonia | Colour-change gas detection tubes (Gastec – Type 3L) | Ammonia neutralises sulfuric acid to change the colour of pH indicator to yellow. | N/A |
| Particulate matter ($PM_{10}$) | Direct-reading light-scattering monitor (TSI DustTrak™) | | N/A |

## Sampling Locations

The sampling locations within Shed 1 and in the space behind the ventilation fans are illustrated in Figure 1.

**Figure 1: Plan of Shed 1 with Sample Locations**




Not to Scale

**Table 3.2: Key to accompany Figure 1.**

| Sample Position | Measurements Undertaken |
|---|---|
| Sample Location a | 4 x Tenax® TA, 3 x Ammonia, $PM_{10}$ |
| Sample Location b | 4 x Tenax® TA, 3 x Ammonia, $PM_{10}$ |
| Sample Location c | 1 x Ammonia, $PM_{10}$ |
| Sample Location d | 1 x Ammonia, $PM_{10}$ |
| Sample Location e | 1 x Ammonia, $PM_{10}$ |
| Sample Location f | 1 x Ammonia, $PM_{10}$ |
| Sample Location g | 3 x Total Odour Concentration (triplicate sample) |

## VOCs Measurement

### *VOCs Sampling Approach*

A review of relevant literature was undertaken to establish the compounds likely to cause odour from poultry farming and the available methods for their identification and quantification. This indicated that the following compounds were likely to cause odour from poultry farming:

- Sulphides, such as dimethytrisulphide (DMTS);
- Carboxylic acids, such as butanoic acid, butyric acid, isovaleric acid, acetic acid;
- Phenolics, such as *p*-cresol, *p*-ethylphenol;
- Indole and skatole;
- Triethylamine;
- Amides;
- Branched ketones; and
- High molecular-weight aldehydes.

The following two methods were identified as being suitable for measuring the compounds listed above:

- solid-phase microextraction (SPME) followed by analysis by multidimensional chromatography-mass spectrometry-olfactometry (GC-MS-O); and
- sampling onto Tenax® TA adsorption tubes, followed by thermal desorption (TD) and analysis by gas chromatography-mass spectrometry (GC-MS).

The first method can be used for headspace / GC-MS analysis in the laboratory, although there are known issues with quantitation. This method is still largely a research tool and a search could identify no laboratory in the UK able to carry out this analysis on a commercial basis. Export of samples to laboratories outside the UK was considered unsuitable as the sample could deteriorate during transit.

The second method is available commercially in the UK and TD / GC-MS is the standard technique for the analysis of VOCs in air. Therefore, in consultation with the Agency, this method was used.

M-Scan, an accredited lab specialising in odour analysis, was selected to supply the sampling media (Tenax® TA adsorption tubes) and perform the analysis. M-Scan's standard TD/GC-MS method was reported to offer sufficient sensitivity, with limits of detection below one part per billion (ppb), and the Tenax® TA adsorbent offers good sensitivity over a wide range of volatile organic compounds. M-Scan confirmed that Tenax® TA is suitable for the semi-quantitative and quantitative analysis of all the compounds that were likely to cause odour from poultry farming.

Air samples were collected onto pre-conditioned Tenax® TA adsorption tubes, at a height of approximately 1 m above the floor, towards the gable-wall ventilation end of the chosen operational poultry shed. A calibrated low-flow sample pump was used to draw a known volume of air (approximately 1 litre for primary samples and 0.5 litre for back-ups) through each sample tube. The collected samples were stored and transported to the laboratory in cool boxes to minimise desorption or deterioration.

Eight samples were taken in total as shown in Figure 1: four samples were taken at two sample locations a and b – two primary samples, plus two back-ups at half volume (in case the first tubes were overloaded). Two samples of each were taken to allow two forms of analysis to be undertaken: a semi-quantitative scan and a fully quantitative targeted GC-MS analysis.

### *Identification of Odorous VOCs*

Semi-quantitative GC-MS analysis of the compounds on the tube was carried out to identify the compounds present in the shed that were likely to be responsible for the odour. Compounds were considered as potential contributors to the poultry odour if:

- they were present at concentrations at or above their odour detection threshold (ODTs); or
- for compounds on the likely candidate list as described in the VOCs Sampling Approach on page 12, they were present at concentrations above 50% of their ODTs,

Compounds meeting these criteria were selected for fully quantitative GC-MS analysis.

### *Analysis - Quantification of Odorous VOCs*

Targeted TD/GC-MS analysis provides a fully quantitative measure of the concentration of selected VOC compounds on the sample media. Whereas the semi-quantitative analysis uses one reference standard compound and relates the concentration of all analysed compounds to the concentration of this compound, the fully quantitative analysis uses specific reference standard compounds for each of the compounds being analysed for. The results of the quantitative analysis are therefore more accurate.

## Determination of Ammonia Concentrations

Ammonia was measured using self-indicating colour-change tubes (Gastec tubes type 3L). These measure ammonia within the range 0.5 ppm to 78 ppm with a precision of approximately ± 30% by means of a chemical reaction between the sample air drawn through the tube and the indicating reagent within the tube. This causes the colour of the tube to change colour and the result is read directly from the tube using the printed scale. Ten samples for ammonia were taken as shown in Figure 1; three samples each at two locations towards the ventilated end of the shed, and four samples behind the ventilation fans. Samples were taken approximately 1 metre above the floor of the poultry shed by drawing air through the tubes using a Gastec hand pump.

## Determination of Total Odour Concentration

Air samples were collected in triplicate (to provide a statistically robust dataset) in accordance with the requirements of BS EN 13725: 2003. In this procedure, a 40 litre Nalophane sample bag housed in a protective sample barrel was connected to a stainless steel sample tube mounted on the outside of the barrel. The barrel was slowly evacuated (at a rate of approximately 2 litres per minute), thus collecting a sample of ambient air within the sample bag. This method, known commonly as the 'lung sampling' technique, minimises any contact between the sample and the sampling equipment and ensures that the sample is obtained at ambient pressure.

The sample inlet was orientated at 90$^{o}$ to the direction of airflow, approximately 1 metre above the floor of the poultry shed. Once the sample bag was inflated (to approximately 90% capacity to allow for expansion), it was capped, given a unique identification number and made ready for transport to the laboratory.

The odour concentration of each sample was determined in accordance with the requirements of BS EN 13725:2003 within 30 hours of collection by Silsoe Odours Ltd in Bedfordshire. Silsoe Odours Ltd holds United Kingdom Accreditation Service (UKAS) accreditation for odour concentration determination. Odour concentration is used to characterise environmental odours in relation to the human sense of smell: in this procedure, the contents of an odour sample bag are presented to a panel of screened human assessors in varying dilutions (with odour-neutral gas) using an olfactometer. The odour concentration of the sample is then determined from the dilution factor at 50% detection threshold ($DT_{50}$) and expressed as multiples of 1 European Odour Unit per cubic metre ($ou_E.m^{-3}$) at standard conditions. One $ou_E.m^{-3}$ is the point of detection.

## Determination of Suspended Particulate Matter Concentrations

Dusts can contain a wide range of particles of different sizes. The size of a particle influences its potential impact, and how long it stays suspended in the air before it settles out onto a surface. The $PM_{10}$ fraction (particles less than 10 µm aerodynamic diameter) were measured in this study as this fraction is small enough to be breathed in. The $PM_{10}$ fraction falls out of the atmosphere very slowly and may travel 1000 metres or more suspended in the air before being deposited out at potentially sensitive receptors located in the vicinity of the farm. There is some evidence that odorous compounds can be adsorbed onto the surface of particles and this can contribute to the transport of odour to receptors.

A direct reading light-scattering nephelometer (TSI DustTrak$^{TM}$) was used to measure $PM_{10}$. The DustTrak$^{TM}$ is a real-time continuous monitor that measures particulates by 90° light-

scattering. A size selective inlet was fitted to the monitor to preclude all but the $PM_{10}$ particulate fraction. The monitor was used to continuously measure for $PM_{10}$ concentrations in six locations for approximately 5-15 minutes at each point: two locations towards the gable-wall ventilation end of the shed, and four locations outside the shed close to the ventilation fan exhausts. The monitor was placed approximately 1 metre above the floor whilst sampling.

### Calculation of Emission Rates from Concentrations

The emission rates of odours and dusts from the sheds were calculated as the product of the concentration of odour ($ou_E.m^{-3}$) and dusts ($mg.m^{-3}$), times the volume flow of air ($m^3.s^{-1}$) exhausted from the shed.

The volume flow of air through the shed was monitored constantly, as part of the computer controlled system, by Brackenmore Ltd. The computer varies the extraction rate depending on the weight of chickens in the shed. Extraction is increased for cooling purposes in the warmer months.

### QA/QC

A number of measures were taken for quality assurance/quality control purposes:

- Samples were collected onto Tenax® TA using a low flow pump with a valid record of calibration;
- The laboratory selected to carry out the analyses worked to Standard Operating Procedures (SOPs) based on Good Laboratory Practice (GLP) principles.
- A Chain of Custody form and two travel blanks accompanied the Tenax® TA adsorption tubes at all times;
- A leakage test was undertaken to check the Gastec sampling pump used for drawing air through the ammonia detector tubes was functioning correctly;
- Triplicate samples for total odour concentration were taken to provide a statistically robust dataset and analysis was undertaken by a laboratory having United Kingdom Accreditation Service (UKAS) accreditation;
- The DustTrak™ $PM_{10}$ monitor had a valid, traceable, record of calibration.

RPS has carried out all work on this project under its ISO9001 – accredited quality management system.

## Methodology for Second Study

### General Approach

The first study was designed to be a purely factual summary of the identity and concentrations of the main odorous VOCs that were measured. It was never the intention of the scope of work to draw any correlation between the odour fingerprint results and the results obtained by DDO for quantification of total odour concentration. It is generally

accepted by workers in this field, and by the Agency in its own publications, that the sum of the speciated compound analyses do not usually add up to the total odour concentration as measured by DDO.

The Tenax® TA sorbent used in the first study is a good general sorbent for trapping a broad spectrum of VOCs where thermal desorption is subsequently to be used. However, having obtained knowledge of the identity of the odorous compounds in the first study, it is possible that improvements in the sample collection efficiencies of individual compounds may be possible by targeting each chemical group with a sorbent that is tailored to its characteristics (polarity, boiling point, etc). The Agency was keen to explore if (notwithstanding the comments in the preceding paragraph) such a refined sampling approach would lead to a sum value of the speciated compounds that more closely matched the total odour concentration as measured by DDO.

The scope of the second study is summarised below:

- Repeating the triplicate measurements of total odour by lung sampling/DDO, so as to better understand the variability in total odour emission rates between bird batches;
- Repeating the measurements of chemical compounds collected on Tenax® TA sorbent tubes with analysis by GC-MS, but additionally using back-up tubes of Carbograph™ 1 TD, which is an appropriate sorbent that is likely to have a good affinity for the types of compounds that might be expected to be less-well collected by Tenax® TA;
- Measurement of a number of volatile/semi-volatile organic reduced sulphur species by collection on a mixture of Tenax® TA and UniCarb™ (Spherocarb™) sorbent, hereon referred to as 'Spherocarb™' sorbent, and analysis by GC-MS; and
- Measurement of $H_2S$ concentrations by Jerome® gold-film analyser.

The compounds causing significant odour were identified by measuring the concentrations of VOCs in the poultry sheds and comparing the results with Odour Detection Thresholds published in a paper by Nagata (2003 cited Environment Agency 2007) and those collated by M-Scan in their ODT library (M-Scan 2010a).

A summary of the four techniques that were used to measure odour and $H_2S$ is shown in Table 3.3.

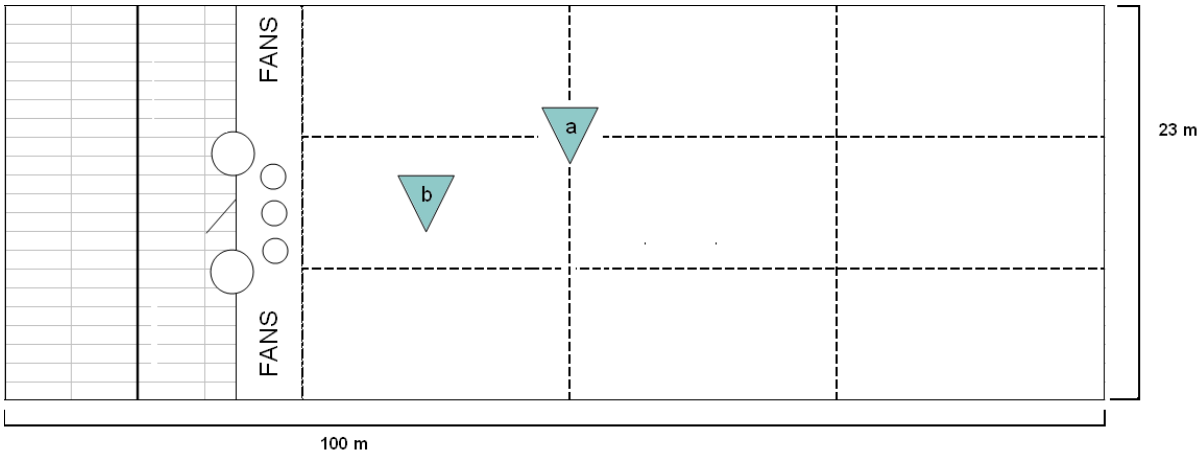
**Table 3.3: Techniques used to Measure Odour and Dust within the Poultry Sheds.**

| Measurement | Sample Media/Monitor | Analysis | Laboratory used for Analysis | Quality Assurance/ Quality Control |
|---|---|---|---|---|
| Identification of odorous VOCs | Active pumped sampling onto Tenax® TA, Carbograph™ 1 TD, and Spherocarb™ adsorption tubes | GC-MS scan (semi-quantitative) | M-Scan | Chain of Custody<br>Record of calibration (sample pump) |
| Quantification of odorous VOCs | Active pumped sampling onto Tenax® TA adsorption tubes | GC-MS (fully-quantitative) | M-Scan | Chain of Custody<br>Record of calibration (sample pump) |
| Total Odour Concentration | 40 litre Nalophane sample bag | Dynamic dilution olfactometry analysis to BS EN 13725 | Silsoe Odours Ltd. | UKAS Accreditation |
| $H_2S$ | Jerome® gold-film analyser | | N/A | Record of calibration |

## *Sampling Locations*

The sampling locations within Shed 1 are illustrated in Figure 2.

**Figure 2: Plan of Shed 1 with Sample Locations**




Not to Scale

**Table 3.4: Key to accompany Figure 2.**

| Sample Position | Measurements Undertaken |
|---|---|
| Sample Location a | 12 x Tenax® TA/Carbograph™ 1 TD tandem, 12 x Spherocarb™, 45 minutes $H_2S$ monitoring |
| Sample Location b | 3 x Total Odour Concentration (triplicate sample) |

## VOCs Measurement

### *Selection of Suitable Sorbents*

From the review of relevant literature carried out as part of the first study, the compounds described previously in the VOCs Sampling Approach on page 12 were considered most likely to cause odour from poultry farming; these compounds, together with the analytical results of the first study, informed the selection of sorbents for this study. The previous study used the Tenax® TA sorbent, which is considered to be a good general purpose sorbent for compounds with a volatility range of n=C7 to n=C30, and is typically used for aromatic compounds, non-polar compounds with boiling points > 100$^{o}$C and polar components > 150$^{o}$C (M-Scan 2010b)(M-Scan 2010c). However, it may have less affinity for non-polar compounds with the volatility range n=C5 to C6 and organic sulphur compounds such as sulphides and mercaptans with lower boiling points.

M-Scan was selected to supply the sampling media and conduct the analysis, so as to be consistent with the previous study. M-Scan was consulted (M-Scan 2010b)(M-Scan 2010c) to establish: a sorbent that could be used in Tandem with Tenax® TA that would be likely to have a good affinity for the types of compounds that might be expected to be less well collected by Tenax® TA; and a sorbent that would be appropriate to measure a number of volatile/semi-volatile organic reduced sulphur species. The outcome of this discussion was that:

- For ketones , aldehydes and non-polar compounds within the volatility range of n=C5 or C6 to n=C14, and a volatility from 50$^{o}$C, M-Scan recommended a carbon-based sorbent such as Carbograph™ 1 TD (Mesh 40/60); and
- For organic sulphur compounds such as the sulphides and mercaptans with lower boiling points, M-Scan advised that the Spherocarb™ sorbent is recommended by the suppliers as a suitable sorbent.

Therefore the second study used Tenax® TA sorbent in tandem with Carbograph™ 1 TD and Spherocarb™. All three sorbent tubes were analysed using M-Scan's standard TD/GC-MS method. This was reported to offer sufficient sensitivity with limits of detection below one part per billion (ppb).

### *VOCs Sampling*

Sampling Procedure

Air samples were collected onto pre-conditioned Tenax® TA, Carbograph™ 1 TD and Spherocarb™ adsorption tubes. Two sampling train arrangements were used, each designed to be optimised for different groups of compounds as described in the preceding section. The two sampling trains were:

i. Sampling in triplicate of gas-phase organic compounds onto a Tenax® TA sorbent tube backed-up with a Carbograph™ 1 TD sorbent tube, and analysis of each tube separately by TD-GC-MS. In total, two sets of triplicate samples were collected in one location within the shed (Location a) and the same number of back-up samples at half volume (in case the first set were overloaded), as per the following sampling scheme:

- The first set of triplicate samples were to be used for the semi-quantitative screening analysis to identify what the main odorous compounds were (on the basis of their ratios of concentrations to ODT values held by M-Scan and published ODTs in Negata (2003 cited Environment Agency 2009b) and H4 (Environment Agency 2009b) and approximately how much was present there. In the event that these samples were overloaded, the back-up samples (with half the sample volumes) would be analysed.
- The second set of triplicate sample were to be used for the fully quantitative targeted analysis of selected compounds that were identified above as being most likely to be responsible for the odour. In the event that these samples were overloaded the back-up samples (with half the sample volumes) would be analysed.
- Information (where available) from the Operator on the ventilation flows from the shed over the sampling period was noted.

ii. Sampling in triplicate of gas-phase organic reduced sulphur compounds onto single Spherocarb™ sorbent tubes and analysis of each tube separately by TD-GC-MS. In total, two sets of triplicate samples were collected in one location (Location a) within the shed together with the same number of back-ups at half volume (in case the first set are overloaded), as per the following sampling scheme:

- The first triplicate sample set was to be used for the semi-quantitative screening analysis to identify what the main odorous compounds were and approximately how much was present. In the event that these samples were overloaded the back-up samples (with half the sample volumes) would be analysed.
- The second triplicate sample set was to be used for the quantitative targeted analysis of selected compounds that were identified as being most likely to be responsible for the odour. In the event that these samples were overloaded, the back-up samples (with half the sample volumes) would be analysed.
- Information (where available) from the Operator on the ventilation flows from the shed over the sampling period was noted.

Air Samples were taken at approximately 1 m above the floor towards the gable-wall ventilation end of the chosen operational poultry shed. A calibrated low-flow sample pump was used to draw a known volume of air through each sample tube. Three pumps were used to take the samples, numbered 196, 197 and 198 respectively. Sample pumps 196 and 197 were calibrated to take the tandem samples, and 196 was calibrated for use with the single Spherocarb™ sorbent tubes. Air samples were collected by drawing air over a period of sixteen minutes for the tandem samples, and over a period of four minutes for the single Spherocarb™ samples. The collected samples were stored and transported to the laboratory in cool boxes to minimise desorption or deterioration.

Twelve samples were taken in total: six full volume samples, and six at half volume (back-ups in case the first tubes were overloaded). Six samples were taken to allow a triplicate to be analysed using two forms of analysis: semi-quantitative and quantitative GC-MS.

The samples were allocated codes, so that each could be readily identified and traced. The code was formed so that the sorbent, triplicate and sample number could be identified, as follows:

- The sorbent was denoted by a T, C or U, to represent Tenax® TA, Carbograph™ 1 TD or Spherocarb™ respectively;
- The Triplicate was denoted by a T1, T2, T3, T4, to represent triplicates 1, 2, 3 and 4. Triplicate 1 samples were full volume samples for semi-quantitative analysis, Triplicate 2 samples were full volume samples for quantitative analysis, Triplicate 3 samples were half volume back-ups intended for the semi-quantitative samples and Triplicate 4 samples were half volume back-ups intended for the quantitative samples.
- The sample number - The three full volume samples within a triplicate were denoted by S1, S2 and S3; the three half volume back-ups in a triplicate were denoted BU1, BU2 and BU3, respectively.

## Analysis – Identification of Odorous VOCs

Semi-quantitative GC-MS analysis of the compounds on the tube was carried out to identify the compounds present in the shed that were likely to be responsible for the odour. Compounds were considered as potential contributors to the poultry odour if:

- they were present at concentrations at or above their ODTs; or
- for compounds on the likely candidate list as described in the VOCs Sampling Approach on page 12, they were present at concentrations above 50% of their ODTs as published in the M-Scan database, Nagata and H4.

## Analysis – Quantification of Odorous VOCs

Compounds meeting these criteria were selected for targeted quantitative GC-MS analysis, as described previously in the section entitled: Analysis – Quantification of Odorous VOCs on page 13.

## Determination of Hydrogen Sulphide Concentrations

The TD-GC-MS method used to analyse the sorbent tubes is not appropriate for measuring $H_2S$, therefore $H_2S$ was measured using a suitable portable automatic continuous analyser.

$H_2S$ was measured using a Jerome® gold-film analyser. This instrument measures $H_2S$ within the range 0.001 ppm to 50 ppm with a precision of approximately 5% relative standard deviation, and response time of 30 seconds for concentrations between 0.001 to 0.099 ppm (in sample mode). The instrumental technique uses a thin gold film, which undergoes an increase in electrical resistance proportional to the mass of $H_2S$ in the sample. The monitor measures $H_2S$ concentrations every minute and the total duration of the sampling run was 45 minutes. Samples were taken approximately 1 m above the floor of the poultry shed in the location marked on Figure 2 (Location a).

## Determination of Total Odour Concentration

Total odour concentration was measured as per the first study and using the methodology detailed previously in the section entitled: Determination of Total Odour Concentration on page 14. Samples were collected at Location b as shown in Figure 2.

## Calculation of Emission Rates from Concentrations

Emission rates were calculated as per the first study and detailed previously in the section entitled: Calculation of Emission Rates from Concentrations on page 15.

## QA/QC

A number of measures were taken for quality assurance/quality control purposes:

- A Chain of Custody form and two travel blanks accompanied the Tenax® TA, Carbograph™ 1 TD and Spherocarb™ adsorption tubes at all times;
- Triplicate samples were taken to provide a statistically robust dataset using calibrated low flow pumps;
- The laboratory selected to carry out the analyses worked to Standard Operating Procedures (SOPs) based on Good Laboratory Practice (GLP) principles.
- Triplicate samples for total odour concentration were taken to provide a statistically robust dataset and analysis was undertaken by a laboratory having United Kingdom Accreditation Service (UKAS) accreditation;
- The Jerome® $H_2S$ Analyser had a valid, traceable, record of calibration.

RPS has carried out all work on this project under it's ISO9001 – accredited quality management system.

# 4 Results

## First Study

### Results of Odour Monitoring

#### *Identifcation of Odorous VOCs*

The results of the semi-quantitative analysis of samples taken on 29th October 2009 at locations a and b (as depicted in Figure 1) are shown in Table 4.1 and Table 4.2.

The concentrations of the following compounds exceeded their respective Odour Detection Thresholds (ODTs):

- acetic acid;
- 2,3-butanedione;
- 2-methyl butanal;
- butanoic acid; and
- 3-methyl butanoic acid.

These compounds were selected for further quantitative analysis. Additionally 3-methyl butanal and 2-methyl butanoic acid were selected for quantitative analysis because these compounds are known to be implicated in livestock odours and their concentrations were greater than 50% of the odour threshold (this allows for some uncertainty in the published ODTs).

Trimethylamine was also at a concentration of greater than 50% of the ODT; however, under normal environmental conditions this compound exists as a very flammable gas and thus a reference material cannot be used in a safe manner to fully quantify it within the parameters and scope of analytical approach used by the laboratory in this current study. Therefore the results of the semi-quantitative scan were used to calculate the emission rate of this compound.

## Table 4.1: Results – Semi-Quantitative VOCs Analysis, Sampling 29th October 2009 on Tenax® TA, Location a

| Retention Time (Min) | Assignment [a] | Measured Concentration (ng / litre) [b] | | ODT (ng / litre) [c] | Ratio (Sample less blank : ODT) |
|---|---|---|---|---|---|
| | | Sample | Blank [d] | (M-Scan 2010a) | |
| 2.27 | Isobutane [e] | 4.1 | nd | 24000 | <0.05 |
| 2.42 | Methanol [e] | 43 | 6.9 | 190000 | <0.05 |
| 2.49 | Acetaldehyde [e] | 1.4 | 0.65 | 340 | <0.05 |
| 2.65 | n-Butane [e] | 3 | nd | 490000 | <0.05 |
| 3.12 | Trimethylamine [e] | 3.2 | nd | 5.9 | 0.5 |
| 3.39 | Ethanol [e] | 18 | nd | 55000 | <0.05 |
| 4.27 | Acetonitrile [e] | 2.4 | 0.73 | 170000 | <0.05 |
| 4.31 | Acetone [e] | 45 | 0.2 | 35000 | <0.05 |
| 4.37 | Isopropanol [e] | 2.6 | 0.15 | 26000 | <0.05 |
| 4.47 | n-Pentane [e] | 10 | 3.9 | 95000 | <0.05 |
| 5.62 | Methanesulphonyl chloride | 1.7 | nd | - | - |
| 6.01 | 1-Propanol | 5.6 | nd | 6000 | <0.05 |
| 6.05 | 2-Methyl propanal | 0.87 | nd | 120 | <0.05 |
| 6.29 | 2-Methyl pentane | 5.7 | nd | - | - |
| 6.74 | 3-Methyl pentane | 5.1 | nd | - | - |
| **6.81** | **Acetic acid [e]** | **530** | **nd** | **360** | **1.5** |
| **6.89** | **2,3-Butanedione** | **81** | **nd** | **16** | **5.1** |
| 7.14 | 2-Butanone | 12 | nd | 23000 | <0.05 |
| 7.20 | n-Hexane | 14 | nd | 79000 | <0.05 |
| 7.24 | 2-Butanol | 0.7 | nd | 5200 | <0.05 |
| 8.17 | Methyl cyclopentane | 2 | nd | - | - |
| 8.88 | 3-Methyl butanal | 5.6 | nd | 8.1 | 0.7 |
| 9.08 | 1-Butanol | 2.8 | nd | 1500 | <0.05 |
| **9.20** | **2-Methyl butanal** | **3** | **nd** | **0.54** | **5.6** |
| 9.25 | Benzene | 0.71 | nd | 12000 | <0.05 |
| 9.45 | Propanoic acid | 6.3 | nd | 110 | 0.1 |
| 9.80 | 2-Pentanone | 4 | nd | 5500 | <0.05 |
| 10.42 | 3-Hydroxy 2-butanone | 650 | nd | - | - |
| 11.09 | 3-Methyl-1-butanol | 13 | nd | 160 | 0.1 |
| 11.21 | 2-Methyl propanoic acid | 8.7 | nd | 72 | 0.1 |
| 11.72 | Dimethyl disulphide | 21 | nd | 48 | 0.4 |
| **11.83** | **Butanoic acid** | 78 | nd | 14 | 5.6 |
| 12.27 | Toluene | 4.9 | nd | 5900 | <0.05 |
| **13.46** | **3-Methyl butanoic acid** | **14** | **nd** | **10** | **1.4** |
| 13.74 | 2-Methyl Butanoic acid | 4.6 | nd | 7.9 | 0.6 |
| 14.18 | 4-Hydroxy 2-butanone ? | 3 | nd | - | - |
| 14.51 | Pentanoic acid | nd | nd | 20 | <0.05 |
| 15.03 | m- / p- Xylenes | nd | nd | 1750 | <0.05 |
| 17.33 | Phenol | 0.6 | nd | 430 | <0.05 |
| 17.34 | Benzaldehyde | 2.7 | nd | 190 | <0.05 |
| 17.70 | 4-Isothiocyanato-1-butene | 4.8 | nd | - | - |
| 20.16 | Nonanal | nd | nd | 13 | - |

Notes: Concentration results are for a 1.0 litre sample : Tube ref JAP5547/3A.

nd = below detect limit. Compounds in **bold** are at concentrations above the ODT

a. Assignments by computer library matching and manual inspection of individual mass spectra and mass chromatograms. No confirmatory analyses have been carried out.

b. Approximate quantification by direct reference to the external standard (o-xylene-$d_{10}$). No allowance has been made for trapping efficiency, desorption efficiency or relative GC-MS response. Concentrations are at the prevailing temperature (approx 297K) and pressure at the time of measurement

c. Reported ODTs are from the M-Scan database – This has been compiled over a number of years from published literature. It has been assumed that a significant part of the data has been obtained by olfactometry and on this basis all ODTs are assumed to have been measured at normal room temperature (assumed to be 293 K).

d. Equivalent concentration for a volume of 1.0 litre.

e. The volume sampled exceeded the breakthrough volume for this component and its concentration may be underestimated.

## Table 4.2: Results – Semi-Quantitative VOCs Analysis, Sampling 29th October 2009 on Tenax® TA, Location b

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) [b] | | ODT (ng / litre) [c] | Ratio (Sample less blank : ODT) |
|---|---|---|---|---|---|
| | | Sample | Blank [d] | (M-Scan 2010a) | |
| 2.27 | Isobutane [e] | nd | nd | 24000 | <0.05 |
| 2.42 | Methanol [e] | 20 | 6.9 | 190000 | <0.05 |
| 2.49 | Acetaldehyde [e] | 4.8 | 0.65 | 340 | <0.05 |
| 2.65 | n-Butane [e] | 4.2 | nd | 490000 | <0.05 |
| 3.12 | Trimethylamine [e] | 5.5 | nd | 5.9 | 0.9 |
| 3.39 | Ethanol [e] | 16 | nd | 55000 | <0.05 |
| 4.27 | Acetonitrile [e] | 2.4 | 0.73 | 170000 | <0.05 |
| 4.31 | Acetone [e] | 45 | 0.2 | 35000 | <0.05 |
| 4.37 | Isopropanol [e] | 2.3 | 0.15 | 26000 | <0.05 |
| 4.47 | n-Pentane [e] | 11 | 3.9 | 95000 | <0.05 |
| 5.62 | Methanesulphonyl chloride | 2.7 | nd | - | - |
| 6.01 | 1-Propanol | 4.7 | nd | 6000 | <0.05 |
| 6.05 | 2-Methyl propanal | 1.1 | nd | 120 | <0.05 |
| 6.29 | 2-Methyl pentane | 5.5 | nd | - | - |
| 6.74 | 3-Methyl pentane | 6.5 | nd | - | - |
| 6.81 | Acetic acid [e] | 590 | nd | 360 | 1.6 |
| 6.89 | 2,3-Butanedione | 64 | nd | 16 | 4.0 |
| 7.14 | 2-Butanone | 11 | nd | 23000 | <0.05 |
| 7.2 | n-Hexane | 23 | nd | 79000 | <0.05 |
| 7.24 | 2-Butanol | 0.68 | nd | 5200 | <0.05 |
| 8.17 | Methyl cyclopentane | 2.4 | nd | - | - |
| 8.88 | 3-Methyl butanal | 5.8 | nd | 8.1 | 0.7 |
| 9.08 | 1-Butanol | 3.8 | nd | 1500 | <0.05 |
| 9.2 | 2-Methyl butanal | 2.9 | nd | 0.54 | 5.4 |
| 9.25 | Benzene | 0.97 | nd | 12000 | <0.05 |
| 9.45 | Propanoic acid | 7.4 | nd | 110 | 0.1 |
| 9.8 | 2-Pentanone | 4.4 | nd | 5500 | <0.05 |
| 10.42 | 3-Hydroxy 2-butanone | 640 | nd | - | - |
| 11.09 | 3-Methyl-1-butanol | 16 | nd | 160 | 0.1 |
| 11.21 | 2-Methyl propanoic acid | 10 | nd | 72 | 0.1 |
| 11.72 | Dimethyl disulphide | 21 | nd | 48 | 0.4 |
| 11.83 | Butanoic acid | 95 | nd | 14 | 6.8 |
| 12.27 | Toluene | 5.3 | nd | 5900 | <0.05 |
| 13.46 | 3-Methyl butanoic acid | 18 | nd | 10 | 1.8 |
| 13.74 | 2-Methyl Butanoic acid | 5.1 | nd | 7.9 | 0.6 |
| 14.18 | 4-Hydroxy 2-butanone ? | 3.6 | nd | - | - |
| 14.51 | Pentanoic acid | 2.2 | nd | 20 | 0.1 |
| 15.03 | m- / p- Xylenes | 1.5 | nd | 1750 | <0.05 |
| 17.33 | Phenol | 0.45 | nd | 430 | <0.05 |
| 17.34 | Benzaldehyde | 3.1 | nd | 190 | <0.05 |
| 17.7 | 4-Isothiocyanato-1-butene | 4.7 | nd | - | - |
| 20.16 | Nonanal | 2.4 | nd | 13 | 0.2 |

Notes: Concentration results are for a 1.0 litre sample : Tube ref JAP5547/3B.

nd = below detect limit. Compounds in **bold** are at concentrations above the ODT

a. Assignments by computer library matching and manual inspection of individual mass spectra and mass chromatograms. No confirmatory analyses have been carried out.

b. Approximate quantification by direct reference to the external standard (o-xylene-$d_{10}$). No allowance has been made for trapping efficiency, desorption efficiency or relative GC-MS response. Concentrations are at the prevailing temperature (approx 297K) and pressure at the time of measurement

c. Reported ODTs are from the M-Scan database – This has been compiled over a number of years from published literature. It has been assumed that a significant part of the data has been obtained by olfactometry and on this basis all ODTs are assumed to have been measured at normal room temperature (assumed to be 293 K).

d. Equivalent concentration for a volume of 1.0 litre.

e. The volume sampled exceeded the breakthrough volume for this component and its concentration may be underestimated.

### *Quantitative Determination of Targeted Odorous VOCs*

The results of the quantitative analysis of samples taken in locations a and b are detailed in Table 4.3 and Table 4.4 below. The compounds targeted for quantitative analysis were selected on the basis of the criteria listed in the section entitled: Identification of Odorous VOCs on page 13.

**Table 4.3: Results – Quantitative VOCs Analysis, Sampling 29th October 2009, Location a, on Tenax® TA tube reference JAP 5547/4A, 0.5 litre sample[d]**

| Retention Time (Min) | Assignment [a] | Concentration (ng / litre) [b*] | | Published ODT (ng / litre) (M-Scan 2010a) | | | Calculated $ou_E.m^{-3}$ equivalent using different published ODTs (Sample less blank/ODT) | | | Calculated Mass Emission Rate using different published ODTs ($ou_E.s^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Sample | Travelling Blank [c] | M-Scan Library | Nagata | H4 | M-Scan | Nagata | H4 | M-Scan | Nagata | H4 |
| **6.49** | **Acetic acid** | 2000 [e] | nd | 360 | 16 | 39 | 5.6 | 125 | 51.3 | 197 | 4442 | 1823 |
| **6.69** | **2,3-Butanedione** | 150 | nd | 16 | 0.18 | - | 9.4 | 833 | - | 333 | 29616 | - |
| **8.68** | **2-Methyl butanal** | 9.2 | nd | 8.1 | - | - | 1.1 | - | - | 40.4 | - | - |
| **8.96** | **3-Methyl butanal** | 7.4 | nd | 0.54 | - | 1.5 | 13.7 | - | 4.9 | 487 | - | 175 |
| **11.8** | **Butanoic acid** | 180 | nd | 14 | 5.4<br>0.69 | -<br>- | 12.9 | 33.3<br>12.9 | -<br>- | 457 | 1185<br>457 | - |
| **13.29** | **2-Methyl butanoic acid** | 21 | nd | 10 | 0.16 | - | 2.1 | 131 | - | 74.6 | 4664 | - |
| **13.58** | **3-Methyl butanoic acid** | 8.3 | nd | 7.9 | 0.33 | - | 1.1 | 25.2 | - | 37.3 | 894 | - |

Notes: nd = below detect limit

Sampling Period = 13:45 – 13:50;

a. Assignments by computer library matching and manual inspection of individual mass spectra and mass chromatograms. No confirmatory analyses have been carried out.

b. Quantification by direct reference to the prepared methanoic solution containing reference standard. Concentrations are at the prevailing temperature (approx 297K) and pressure at the time of measurement

c. Equivalent concentration for a volume of 1.0 Litre.

d. Results for tube ref JAP5547/4A are quoted here as these were analysed using the full set of reference standards

e. Determination based on comparison of mass ion m/z 60 of acetic acid.

**Table 4.4: Results – Quantitative VOCs Analysis, Sampling 29th October 2009, Location b, on Tenax® TA tube reference JAP 5547/4B, 0.5 litre sample[d]**

| Retention Time (Min) | Assignment [a] | Concentration (ng / litre) [b*] | | Published ODT (ng / litre) (M-Scan 2010a) | | | Calculated $ou_E.m^{-3}$ equivalent using different published ODTs (Sample less blank/ODT) | | | Calculated Mass Emission Rate using different published ODTs ($ou_E.s^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Sample | Travelling Blank [c] | M-Scan | Nagata | H4 | M-Scan | Nagata | H4 | M-Scan | Nagata | H4 |
| **6.49** | **Acetic acid** | 900 [e] | nd | 360 | 16 | 39 | 2.5 | 56.3 | 23.1 | 85.0 | 1913 | 785 |
| **6.69** | **2,3-Butanedione** | 120 | nd | 16 | 0.18 | - | 7.5 | 667 | - | 255 | 22676 | - |
| **8.68** | **2-Methyl butanal** | 11 | nd | 8.1 | - | - | 1.4 | - | - | 46.2 | - | - |
| **8.96** | **3-Methyl butanal** | 6.9 | nd | 0.54 | - | 1.5 | 12.8 | - | 4.6 | 435 | - | 157 |
| **11.8** | **Butanoic acid** | 108 | nd | 14 | 5.4<br>0.69 | -<br>- | 7.7<br>- | 20.0<br>157 | -<br>- | 262<br>- | 680<br>5324 | -<br>- |
| **13.29** | **2-Methyl butanoic acid** | 15 | nd | 10 | 0.16 | - | 1.5 | 93.8 | - | 51.0 | 3189 | - |
| **13.58** | **3-Methyl butanoic acid** | 5.9 | nd | 7.9 | 0.33 | - | 0.7 | 17.9 | - | 25.4 | 608 | - |

Notes: nd = below detect limit

Sampling Period = 14:35 – 14:40;

a. Assignments by computer library matching and manual inspection of individual mass spectra and mass chromatograms. No confirmatory analyses have been carried out.

b. Quantification by direct reference to the prepared methanoic solution containing reference standard. Concentrations are at the prevailing temperature (approx 297K) and pressure at the time of measurement

c. Equivalent concentration for a volume of 1.0 Litre.

d. Results for tube ref JAP5547/4B are quoted here as these were analysed using the full set of reference standards.

e. Determination based on comparison of mass ion m/z 60 of acetic acid.

The mass emission rates for odorous compounds (ammonia, and particulate matter in subsequent sections) were calculated using the average measured shed volumetric flow-rates over the relevant sampling periods.

### *Results of Ammonia Monitoring*

The results of ammonia measurements are detailed in Table 4.5.

## Table 4.5: Results of Ammonia Measurements, Sampling 29th October 2009

| Sample Location and Code Number | Time Start | Time Finish | No. of Pump Strokes | Result (ppm) | Published ODT | | Calculated $ou_E.m^{-3}$ Equivalent Using Different Published ODTs (Sample less blank/ODT) | | Calculated Mass Emission Rate Using Different Published ODTs ($ou_E.s^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Smeets et al. (2007) * (ppm) | Nagata (ppm v/v) | Smeets et al. (2007) * (ppm) | Nagata | Smeets et al. (2007) * (ppm) | Nagata |
| Ammonia a1 | 13:52 | 13:54 | 2 | 1.5 | 2.6 | 1.5 | 0.6 | 1.0 | 19 | 32 |
| Ammonia a2 | 13:57 | 13:59 | 2 | 2 | 2.6 | 1.5 | 0.8 | 1.3 | 26. | 45 |
| Ammonia a3 | 14:00 | 14:02 | 2 | 2 | 2.6 | 1.5 | 0.8 | 1.3 | 28 | 48 |
| Ammonia b1 | 14:37 | 14:40 | 2 | 1.5 | 2.6 | 1.5 | 0.6 | 1.0 | 20 | 35 |
| Ammonia b2 | 14:41 | 14:42 | 2 | 1 | 2.6 | 1.5 | 0.4 | 0.7 | 14 | 24 |
| Ammonia b3 | 14:43 | 14:45 | 2 | 1 | 2.6 | 1.5 | 0.4 | 0.7 | 13 | 22 |
| Ammonia c1 | 14:54 | 14:56 | 2 | 0.5 | 2.6 | 1.5 | 0.2 | 0.3 | N/A | 11 |
| Ammonia d1 | 14:57 | 14:59 | 2 | 0.5 | 2.6 | 1.5 | 0.2 | 0.3 | N/A | 11 |
| Ammonia e1 | 15:00 | 15:02 | 2 | 0.5 | 2.6 | 1.5 | 0.2 | 0.3 | N/A | 11 |
| Ammonia f1 | 15:03 | 15:05 | 2 | 0.5 | 2.6 | 1.5 | 0.2 | 0.3 | N/A | 11 |

Notes : *ODT measured using static and dynamic olfactometry and on this basis the ODT is assumed to have been measured at normal room temperature (assumed to be 293 K).

*Results of Total Odour Concentration by Dilution Dynamic Olfactometry*

The measured total odour concentrations and the derived mass emission rates of odour are shown in Table 4.6.

For the total odour concentrations, the mass emission rates were calculated using the mean volumetric flow rates (referenced at 293K, 101.3 kPa) shown in Table 4.7.

Three repeat samples were taken and analysed; the analytical total odour concentrations ranged from 2981 to 4179 $ou_E.m^{-3}$. The mean odour emission concentration in the shed was 3629 $ou_E.m^{-3}$ and the mean mass emission rate was 117,326 $ou_E.s^{-1}$.

**Table 4.6: Results of Total Odour Measurements, Sampling 29th October 2009**

| Parameter | Sample Ref | Date Sample Taken | Time Sample Taken | Date of Analysis | Ambient Conc. $ou_E.m^{-3}$ | Standardised Conc. $ou_E.m^{-3}$ § | Measurement Uncertainty ($ou_E.m^{-3}$) # | Mass Emission Rate ($ou_E.s^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| Odour Conc. | T116571 | 29/10/09 | 13:30 – 13:47 | 30/10/09 | 2981 | 2994 | 1355 to 6614 | 98,832 |
| Odour Conc. | T116572 | 29/10/09 | 13:57 – 14:14 | 30/10/09 | 3681 | 3697 | 1674 to 8167 | 126,326 |
| Odour Conc. | T116573 | 29/10/09 | 14:17 – 14:34 | 30/10/09 | 4179 | 4197 | 1900 to 9271 | 135,689 |
| Mean Result ¥ | - | - | - | - | - | 3629 | 2296 to 5735 | 117,326 |

Samples were collected directly (without dilution) and analysed by dynamic dilution olfactometry according to the requirements of BSEN 13725:2003

# The uncertainty associated with the quoted result is at the 95% confidence interval

§ Concentrations referenced to 293K, 101.3kPa on a wet basis

¥ Geometric mean of the samples taken

**Table 4.7: Shed Data, 29th October 2009**

| Parameter | Units | Sample ref: T116571 | Sample ref: T116572 | Sample ref: T116573 |
|---|---|---|---|---|
| Date | - | 29/10/09 | | |
| Age of Chickens | Days | 29 | | |
| Time Sample Taken | | 13:30 – 13:47 | 13:57 – 14:14 | 14:17 – 14:34 |
| Barometric pressure | kPa | 102.1 | 102.2 | 102.2 |
| Mean Ambient Temperature in Poultry Shed | °C | 24.47 | 24.38 | 24.36 |

## Results of Particulate Matter Monitoring

The results of measurements of $PM_{10}$ are detailed in Table 4.8. The concentrations of $PM_{10}$ measured inside the poultry shed (samples a and b) were greater than in the space behind the ventilation fans (samples c-f).

**Table 4.8: Results of $PM_{10}$ Measurements, Sampling 29th October 2009**

| Sample Location | Time Start | Time Finish | Concentration* ($mg.m^{-3}$) | Mass Emission Rate ($mg.s^{-1}$) |
|---|---|---|---|---|
| | | | Average | |
| a1 | 13:09 | 13:24 | 2.2 | 73.7 |
| b1 | 14:05 | 14:20 | 2.1 | 70.8 |
| c1 | 14:29 | 14:49 | 1.4 | N/A |
| d1 | 14:50 | 14:55 | 1.7 | N/A |
| e1 | 14:57 | 15:11 | 1.4 | N/A |
| f1 | 15:12 | 15:16 | 1.7 | N/A |

Notes : *Concentrations are at the prevailing temperature and pressure at the time of measurement

# Second Study

## Results of Odour Monitoring

### *Identification of Odorous VOCs*

The scope of the second study has been described in section 3, Methodology. The sampling was undertaken on 12th May 2010 and the samples were dispatched in cool boxes by courier to the M-Scan laboratory, arriving on 14th May 2010.

The first set of analyses were to be semi-quantitative scans to identify which compounds were likely to be above their ODTs. M-Scan reported to us on 21st May 2010 that there had been an instrument problem, which meant a delay in analysing the samples. When the first set of full-volume tubes were eventually run through the GC-MS for the semi-quantitative scan there was another problem with M-Scan`s instrument and the results were invalid. M-Scan then went ahead and analysed semi-quantitatively two of our triplicate fall-back (half-volume) samples; these were reported to us on 14th June 2010, four weeks after the sampling took place, and the results are shown in Table 4.9, Table 4.10 Table 4.11 and Table 4.12.

We then (having been advised by M-Scan that the sampled tubes would be stable for at least 2-3 months under the conditions of storage) instructed M-Scan to carry out the semi-quantitative scan on the third of our triplicate fall-back samples for each sample train: M-Scan reported the results of these final semi-quantitative scans to RPS on 5th July 2010 and these are shown in Table 4.13 and Table 4.14.

**Table 4.9: Results – Semi-Quantitative VOCs Determination, Sampling 12th May 2010 onto Tandem Tubes T/T3/BU1 and C/T3/BU1 (Tenax® TA followed by Carbograph™ 1 TD), Analysis 14th June 2010**

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Measured Concentration (ng / litre) | | Ratio (Sample less blank : Published ODT) | | |
|---|---|---|---|---|---|---|---|---|
| | | Sample T/T3/BU1 | Blank | Sample C/T3/BU1 | Blank | M-Scan | Nagata | H4 |
| 1.75 | Sulphur dioxide[e] | 340 | 520 | 420 | 470 | - | - | - |
| 2.01 | Formic acid[e] | nd | nd | nd | nd | - | - | - |
| 2.17 | Isobutane | 110 | nd | 430 | 110 | 0.02 | - | - |
| 2.19 | Methanol[e] | 770 | 260 | nd | nd | <0.01 | 0.01 | - |
| 2.41 | 1-Butene[e] | nd | nd | | | - | - | - |
| 2.54 | n-Butane[e] | 320 | nd | 600 | nd | <0.01 | <0.01 | - |
| 2.68 | Methyl mercaptan | nd | nd | 22 | 37 | <0.01 | - | - |
| 2.85 | 2-Butene[e] | nd | nd | nd | nd | - | - | - |
| 3.13 | Ethanol[e] | 340 | nd | 65 | nd | <0.01 | 0.41 | - |
| 3.40 | Dimethyl ketene | nd | nd | 170 | nd | - | <0.01 | - |
| 3.41 | Acetonitrile | 2200 | nd | nd | 54 | 0.01 | 0.10 | - |
| 3.73 | Acetone | 200 | nd | 93 | 87 | 0.06 | <0.01 | 0.02 |

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Measured Concentration (ng / litre) | | Ratio (Sample less blank : Published ODT) | | |
|---|---|---|---|---|---|---|---|---|
| | | Sample T/T3/BU1 | Blank | Sample C/T3/BU1 | Blank | M-Scan | Nagata | H4 |
| 3.80 | 2-Methyl butane | 1100 | nd | 1700 | nd | - | - | - |
| 3.98 | Isopropanol | 2400 | nd | 91 | 16 | 0.10 | - | - |
| 4.11 | $C_5H_{10}$ Alkene | nd | nd | 65 | nd | <0.01 | - | - |
| 4.11 | Pentene | nd | nd | 32 | nd | - | - | - |
| 4.27 | $C_5H_{10}$ Alkene | 52 | nd | nd | nd | <0.01 | <0.01 | - |
| 4.27 | 2-Pentene | nd | nd | 74 | nd | - | <0.01 | - |
| 4.39 | n-Pentane | 410 | nd | 360 | nd | 0.01 | 0.18 | - |
| 4.56 | 2-Methyl-1-butene | nd | nd | 36 | nd | - | - | - |
| 4.84 | Dichloromethane | 680 | nd | 120 | nd | 0.01 | <0.01 | - |
| 5.32 | 2,2-Dimethylbutane | 110 | nd | 120 | nd | - | <0.01 | - |
| 6.16 | Cyclopentane | 140 | nd | 270 | nd | - | - | - |
| 6.18 | 2,3-Butanedione | 160 | nd | 240 | nd | 25.00 | - | - |
| 6.28 | 2-Methyl pentane | 250 | nd | 260 | nd | - | 0.02 | - |
| 6.31 | Acetic acid | 260 | nd | 43 | nd | <0.01 | 20.24 | 7.59 |
| 6.47 | 2-Butanone | 42 | nd | 14 | nd | <0.01 | - | 0.07 |
| 6.69 | 3-Methyl pentane | 210 | 37 | 190 | nd | - | 0.01 | - |
| 6.82 | Unknown | 39 | nd | nd | nd | - | - | - |
| 7.20 | n-Hexane | 260 | nd | 100 | 24 | <0.01 | 0.06 | - |
| 8.07 | Methyl cyclopentane | 110 | 34 | 58 | nd | <0.01 | 0.02 | - |
| 8.36 | Unknown | 64 | nd | nd | nd | - | - | - |
| 8.63 | 1-Butanol | 32 | nd | nd | nd | 0.02 | - | 0.35 |
| 8.80 | Benzene | 34 | nd | nd | 21 | <0.01 | <0.01 | <0.01 |
| 9.08 | Cyclohexane | 75 | nd | 40 | nd | <0.01 | 0.01 | - |
| 9.23 | $C_7$ Alkane | 89 | nd | nd | nd | - | - | - |
| 9.23 | C7 Alkane (2-Methyl hexane ?) | nd | nd | 59 | nd | - | - | - |
| 9.33 | $C_7H_{16}$ Branched alkane | 570 | 570 | 22 | nd | - | - | - |
| 9.51 | $C_7$ Alkane (ethylpentane ?) | 82 | nd | nd | nd | <0.01 | - | - |
| 9.51 | C7 Alkane (3-Methylhexane ?) | nd | nd | 68 | nd | - | - | - |
| 9.58 | 3-Hydroxy-2-butanone | 110 | nd | nd | nd | - | - | - |
| 9.77 | 1,3-Dimethyl cyclopentane | 360 | 360 | 11 | nd | <0.01 | - | - |
| 9.85 | Alkene | 100 | 100 | 16 | nd | - | - | - |
| 9.93 | Branched alkane (a trimethyl hexane) | 63 | nd | 47 | nd | - | - | - |
| 10.19 | n-Heptane | 140 | nd | 120 | 35 | 0.01 | 0.08 | - |
| 10.73 | 1-Methyl butanol | nd | nd | nd | nd | - | - | - |
| 10.81 | Methyl isobutyl ketone (MiBK) | 130 | 15 | 36 | 19 | - | 0.19 | - |
| 10.94 | Methyl cyclohexane | 59 | nd | 43 | nd | - | 0.16 | - |

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Measured Concentration (ng / litre) | | Ratio (Sample less blank : Published ODT) | | |
|---|---|---|---|---|---|---|---|---|
| | | Sample T/T3/BU1 | Blank | Sample C/T3/BU1 | Blank | M-Scan | Nagata | H4 |
| 11.09 | Dimethy disulphide | 26 | nd | 1.2 | 5.5 | 0.45 | 2.37 | - |
| 11.72 | Oxygenated hydrocarbon | 10 | nd | nd | nd | <0.01 | - | - |
| 11.90 | Toluene | 180 | 9 | 20 | nd | 0.03 | 0.15 | 0.31 |
| 12.42 | Oxygenated hydrocarbon ? | 7.9 | nd | nd | nd | <0.01 | - | - |
| 13.00 | Branched alkane | 12 | nd | nd | nd | <0.01 | - | - |
| 13.46 | Hexamethyl cyclotrisiloxane | nd | nd | 67 | 89 | - | - | - |
| 13.64 | Branched alkane | 44 | nd | nd | nd | - | - | - |
| 14.01 | Chlorobenzene | nd | nd | 16 | nd | <0.01 | - | - |
| 14.47 | Ethyl benzene | 110 | nd | nd | nd | 0.04 | 0.15 | - |
| 14.68 | m- /p- Xylenes | 500 | 10 | 18 | nd | 0.29 | 2.81 | 7.20 |
| 14.88 | Cyclohexanone | 75 | 24 | 71 | nd | 0.04 | - | 1.58 |
| 15.30 | o-Xylene | 52 | 9.4 | 16 | nd | 0.02 | 0.03 | 0.83 |
| 15.56 | Branched alkane | 24 | nd | nd | nd | - | - | - |
| 16.56 | Benzaldehyde | 29 | nd | 13 | 23 | 0.10 | - | - |
| 16.84 | Phenol | nd | nd | 20 | nd | <0.01 | <0.01 | - |
| 17.55 | Octanal | nd | nd | nd | nd | - | - | - |
| 17.75 | 1,3,5-Trimethylbenzene | 150 | nd | nd | nd | 0.14 | 0.18 | - |
| 17.91 | n-Decane | 45 | nd | nd | nd | <0.01 | 0.01 | - |
| 18.44 | 1,2,4-Trimethylbenzene | nd | nd | nd | nd | <0.01 | <0.01 | - |
| 18.66 | A dichlorobenzene isomer | nd | nd | 3.7 | nd | 0.01 | - | - |
| 18.68 | d-Limonene | 22 | nd | 9.6 | nd | - | - | - |
| 19.01 | Acetophenone | 57 | nd | nd | 20 | - | - | - |
| 19.29 | n-Undecane | 54 | nd | nd | nd | 0.01 | 0.01 | - |
| 19.80 | Nonanal | 54 | nd | 16 | nd | 5.38 | - | - |
| 21.89 | Decanal | 86 | 100 | 11 | nd | - | - | - |
| 22.08 | n-Dodecane | 32 | 47 | nd | nd | - | - | - |
| 22.56 | Unknown | 52 | nd | nd | nd | - | - | - |
| 23.75 | Unknown | 54 | nd | nd | nd | - | - | - |
| 27.39 | Squalene | 2800 | nd | nd | nd | - | - | - |

**Table 4.10: Results – Semi-Quantitative VOCs Determination, Sampling 12th May 2010 onto Tandem Tubes T/T3/BU3 and C/T3/BU3 (Tenax® TA followed by Carbograph™ 1 TD), Analysis, 14th June 2010**

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Measured Concentration (ng / litre) | | Ratio (Sample less blank : Published ODT) | | |
|---|---|---|---|---|---|---|---|---|
| | | Sample T/T3/BU3 | Blank | Sample C/T3/BU3 | Blank | M-Scan | Nagata | H4 |
| 1.75 | Sulphur dioxide[e] | 380 | 520 | 620 | 470 | 0.01 | <0.01 | - |
| 2.01 | Formic acid[e] | 150 | nd | | | <0.01 | - | - |
| 2.17 | Isobutane | 630 | nd | 800 | 110 | 0.06 | - | - |
| 2.19 | Methanol[e] | 1000 | 260 | nd | nd | <0.01 | 0.02 | - |
| 2.41 | 1-Butene[e] | 63 | nd | | | 0.05 | 0.08 | - |
| 2.54 | n-Butane[e] | 1700 | nd | 1200 | nd | 0.01 | <0.01 | - |
| 2.68 | Methyl mercaptan | | | 28 | 37 | <0.01 | - | - |
| 2.85 | 2-Butene[e] | 52 | nd | | | <0.01 | - | - |
| 3.13 | Ethanol[e] | 380 | nd | 75 | nd | <0.01 | 0.46 | - |
| 3.40 | Dimethyl ketene | | | 180 | nd | - | <0.01 | - |
| 3.41 | Acetonitrile | 1100 | nd | nd | 54 | 0.01 | 0.05 | - |
| 3.73 | Acetone | 210 | nd | 76 | 87 | 0.06 | <0.01 | 0.02 |
| 3.80 | 2-Methyl butane | 6400 | nd | 3400 | nd | - | - | - |
| 3.98 | Isopropanol | 190 | nd | 46 | 16 | 0.01 | - | - |
| 4.11 | $C_5H_{10}$ Alkene | 170 | nd | 130 | nd | <0.01 | - | - |
| 4.11 | Pentene | | | 37 | nd | - | - | - |
| 4.27 | $C_5H_{10}$ Alkene | 410 | nd | | | <0.01 | <0.01 | - |
| 4.27 | 2-Pentene | | | 71 | nd | - | <0.01 | - |
| 4.39 | n-Pentane | 2400 | nd | 660 | nd | 0.03 | 0.73 | - |
| 4.56 | 2-Methyl-1-butene | 210 | nd | 56 | nd | - | - | - |
| 4.84 | Dichloromethane | 1500 | nd | 200 | nd | 0.02 | <0.01 | - |
| 5.32 | 2,2-Dimethylbutane | 520 | nd | 240 | nd | - | 0.01 | - |
| 6.16 | Cyclopentane | 1200 | nd | 540 | nd | - | - | - |
| 6.18 | 2,3-Butanedione | 390 | nd | 490 | nd | 55.00 | - | - |
| 6.28 | 2-Methyl pentane | 1700 | nd | 550 | nd | - | 0.11 | - |
| 6.31 | Acetic acid | 270 | nd | 34 | nd | <0.01 | 20.31 | 7.62 |
| 6.47 | 2-Butanone | 120 | nd | 29 | nd | 0.01 | - | 0.18 |
| 6.69 | 3-Methyl pentane | 890 | 37 | nd | nd | - | 0.03 | - |
| 6.82 | Unknown | 5.2 | nd | | | <0.01 | - | - |
| 7.20 | n-Hexane | 500 | nd | 610 | 24 | 0.01 | 0.20 | - |
| 8.07 | Methyl cyclopentane | 450 | 34 | 120 | nd | - | 0.09 | - |
| 8.36 | Unknown | 77 | nd | | | - | - | - |
| 8.63 | 1-Butanol | nd | nd | | | <0.01 | - | <0.01 |
| 8.80 | Benzene | nd | nd | 35 | 21 | <0.01 | <0.01 | <0.01 |
| 9.08 | Cyclohexane | 240 | nd | 70 | nd | <0.01 | 0.04 | - |
| 9.23 | $C_7$ Alkane | 570 | nd | | | - | - | - |
| 9.23 | C7 Alkane (2-Methyl hexane ?) | | | 140 | nd | - | - | - |
| 9.33 | $C_7H_{16}$ Branched | 570 | 570 | 54 | nd | - | - | - |

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Measured Concentration (ng / litre) | | Ratio (Sample less blank : Published ODT) | | |
|---|---|---|---|---|---|---|---|---|
| | | Sample T/T3/BU3 | Blank | Sample C/T3/BU3 | Blank | M-Scan | Nagata | H4 |
| | alkane | | | | | | | |
| 9.51 | $C_7$ Alkane (ethylpentane ?) | 650 | nd | | | - | - | - |
| 9.51 | C7 Alkane (3-Methylhexane ?) | | | 170 | nd | - | - | - |
| 9.58 | 3-Hydroxy-2-butanone | 360 | nd | | | - | - | - |
| 9.77 | 1,3-Dimethyl cyclopentane | 360 | 360 | 27 | nd | <0.01 | - | - |
| 9.85 | Alkene | 100 | 100 | 49 | nd | - | - | - |
| 9.93 | Branched alkane (a trimethyl hexane) | 420 | nd | 120 | nd | - | - | - |
| 10.19 | n-Heptane | 1200 | nd | 360 | 35 | 0.04 | 0.55 | - |
| 10.73 | 1-Methyl butanol | 34 | nd | | | - | - | - |
| 10.81 | Methyl isobutyl ketone (MiBK) | 150 | 15 | 89 | 19 | - | 0.29 | - |
| 10.94 | Methyl cyclohexane | 530 | nd | 120 | nd | - | 1.04 | - |
| 11.09 | Dimethy disulphide | 52 | nd | 3.1 | 5.5 | 1.03 | 5.42 | - |
| 11.72 | Oxygenated hydrocarbon | 91 | nd | | | - | - | - |
| 11.90 | Toluene | 170 | 9 | 63 | nd | 0.04 | 0.18 | 0.37 |
| 12.42 | Oxygenated hydrocarbon ? | 16 | nd | | | - | - | - |
| 13.00 | Branched alkane | 25 | nd | | | - | - | - |
| 13.46 | Hexamethyl cyclotrisiloxane | | | 120 | 89 | - | - | - |
| 13.64 | Branched alkane | 36 | nd | | | - | - | - |
| 14.01 | Chlorobenzene | 51 | nd | nd | nd | 0.01 | - | - |
| 14.47 | Ethyl benzene | 77 | nd | | | 0.03 | 0.10 | - |
| 14.68 | m- /p- Xylenes | 430 | 10 | 100 | nd | 0.30 | 2.88 | 7.37 |
| 14.88 | Cyclohexanone | 240 | 24 | 97 | nd | 0.11 | - | 4.04 |
| 15.30 | o-Xylene | 120 | 9.4 | 76 | nd | 0.05 | 0.11 | 2.65 |
| 15.56 | Branched alkane | 41 | nd | 36 | nd | - | - | - |
| 16.56 | Benzaldehyde | 61 | nd | 38 | 23 | 0.40 | - | - |
| 16.84 | Phenol | | | 37 | nd | <0.01 | - | - |
| 17.55 | Octanal | 44 | nd | | | 6.11 | - | - |
| 17.75 | 1,3,5-Trimethylbenzene | 100 | nd | | | 0.09 | 0.12 | - |
| 17.91 | n-Decane | 21 | nd | | | <0.01 | 0.01 | - |
| 18.44 | 1,2,4-Trimethylbenzene | nd | nd | | | <0.01 | <0.01 | - |
| 18.66 | A dichlorobenzene isomer | 22 | nd | 10 | nd | 0.09 | - | - |
| 18.68 | d-Limonene | 36 | nd | 38 | nd | - | - | - |
| 19.01 | Acetophenone | 87 | nd | 17 | 20 | - | - | - |
| 19.29 | n-Undecane | 18 | nd | | | <0.01 | <0.01 | - |

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Measured Concentration (ng / litre) | | Ratio (Sample less blank : Published ODT) | | |
|---|---|---|---|---|---|---|---|---|
| | | Sample T/T3/BU3 | Blank | Sample C/T3/BU3 | Blank | M-Scan | Nagata | H4 |
| 19.80 | Nonanal | 160 | nd | 45 | nd | 15.77 | - | - |
| 21.89 | Decanal | 260 | 100 | 58 | nd | - | - | - |
| 22.08 | n-Dodecane | 27 | 47 | | | - | - | - |
| 22.56 | Unknown | 29 | nd | | | - | - | - |
| 23.75 | Unknown | 74 | nd | | | - | - | - |
| 27.39 | Squalene | nd | nd | | | - | - | - |

**Table 4.11: Results – Semi-Quantitative VOCs Determination, Sampling 12th May 2010 onto Single Tube U/T3/BU1 (Spherocarb™), Analysis, 14th June 2010**

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Ratio (Sample less blank : ODT) U/T3/BU1 | | |
|---|---|---|---|---|---|---|
| | | Sample U/T3/BU1 | Blank | M-Scan | Nagata | H4 |
| 1.58 | Norfluranee | 2500 | nd | - | - | - |
| 1.75 | Sulphur dioxide | nd | nd | - | - | - |
| 2.18 | Isobutanee | 5900 | 220 | 0.24 | - | - |
| 2.19 | Methanole | nd | nd | - | - | - |
| 2.39 | 1-Butenee | 780 | nd | 0.65 | - | - |
| 2.54 | n-Butanee | 5200 | nd | 0.01 | - | - |
| 2.83 | 2-Butenee | 180 | nd | <0.01 | - | - |
| 3.13 | Ethanole | 400 | nd | 0.01 | 0.40 | - |
| 3.38 | Dimethyl ketenee | 610 | nd | - | - | - |
| 3.46 | Acetonitrile | nd | nd | - | - | - |
| 3.75 | Acetone | nd | nd | - | - | - |
| 3.77 | Dimethyl butene | 16000 | nd | - | - | - |
| 4.09 | C5H10 Alkene | 380 | nd | - | - | - |
| 4.25 | C5H10 Alkene | 670 | nd | - | - | - |
| 4.36 | C5H10 Alkene | 4200 | nd | - | - | - |
| 4.53 | C5H10 Alkene | 350 | nd | - | - | - |
| 4.84 | Dichloromethane | 1100 | nd | 0.01 | <0.01 | - |
| 4.86 | C5H10 Alkene | 570 | nd | - | - | - |
| 5.21 | Carbon disulphide | nd | nd | - | - | - |
| 5.41 | 2,2-Dimethylbutane | 590 | nd | - | - | - |
| 5.80 | C5H8 A dialkene | 75 | nd | - | - | - |
| 6.16 | Cyclopentane | 2400 | nd | - | - | - |
| 6.18 | 2,3-Butanedione | 750 | nd | 46.88 | - | - |
| 6.28 | 2-Methyl pentane | 1400 | nd | - | - | - |
| 6.31 | Acetic acid | 62 | nd | 0.17 | 4.14 | 1.55 |
| 6.47 | 2-Butanone | 120 | nd | 0.01 | - | 0.15 |
| 6.69 | 3-Methyl pentane | 970 | nd | - | - | - |

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Ratio (Sample less blank : ODT) U/T3/BU1 | | |
|---|---|---|---|---|---|---|
| | | Sample U/T3/BU 1 | Blank | M-Scan | Nagata | H4 |
| 6.81 | Unknown | 180 | nd | - | - | - |
| 7.2 | n-Hexane | 380 | nd | <0.01 | 0.07 | - |
| 8.07 | Methyl cyclopentane | 340 | nd | 0.01 | 0.06 | - |
| 8.8 | Benzene | 130 | nd | 0.01 | 0.01 | <0.01 |
| 9.08 | Cyclohexane | 210 | nd | <0.01 | 0.02 | <0.01 |
| 9.23 | C7 Alkane | 250 | nd | - | - | - |
| 9.51 | C7 Alkane (ethylpentane ?) | 370 | nd | - | - | - |
| 9.58 | 3-Hydroxy-2-butanone | 220 | nd | - | - | - |
| 9.85 | Alkene | 2600 | nd | - | - | - |
| 9.93 | Branched alkane (a trimethyl hexane) | 260 | nd | - | - | - |
| 10.19 | n-Heptane | 420 | 71 | 0.01 | 0.13 | - |
| 10.73 | 1-Methyl butanol | 88 | nd | 0.20 | - | - |
| 10.94 | Methyl cyclohexane | 320 | nd | <0.01 | - | - |
| 11.09 | Dimethy disulphide | 230 | nd | 4.79 | 26.75 | - |
| 11.9 | Toluene | 63 | nd | 0.01 | 0.05 | 0.10 |
| 12.39 | Unknown | 45 | nd | - | - | - |
| 14.01 | Chlorobenzene | nd | nd | - | - | - |
| 14.03 | Alkene substituted benzene [RMM 158] | 220 | nd | - | - | - |
| 14.68 | m- /p- Xylenes | nd | nd | - | - | - |
| 14.88 | Cyclohexanone | 87 | nd | 0.03 | - | 1.12 |
| 15.3 | o-Xylene | nd | nd | - | - | - |
| 16.56 | Benzaldehyde | 140 | 51 | 0.47 | - | - |
| 16.85 | Phenol | nd | nd | - | - | - |
| 17.41 | C9H18 An alkyl substituted benzene | nd | nd | - | - | - |
| 19.01 | Acetophenone | nd | nd | - | - | - |
| 19.8 | Nonanal | 230 | 42 | 14.46 | - | - |
| 21.89 | Decanal | 550 | 75 | 80.51 | - | - |
| 23.72 | Phthalate anhydride | 440 | 28 | 1.25 | - | - |
| 25.61 | An alkanal | 210 | nd | - | - | - |

**Table 4.12: Results – Semi-Quantitative VOCs Determination, Sampling 12th May 2010 onto Single Tube U/T3/BU3 (Spherocarb™), Semi-Quantitative Analysis, 14th June 2010**

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Ratio (Sample less blank : Published ODT) U/T3/BU3 | | |
|---|---|---|---|---|---|---|
| | | Sample U/T3/BU3 | Blank | M-Scan | Nagata | H4 |
| 1.58 | Norfluranee | nd | nd | - | - | - |
| 1.75 | Sulphur dioxide | 11000 | nd | 5.79 | 4.75 | - |
| 2.18 | Isobutanee | 2400 | 220 | 0.09 | - | - |
| 2.19 | Methanole | 1700 | nd | 0.09 | 0.04 | - |
| 2.39 | 1-Butenee | nd | nd | - | - | - |
| 2.54 | n-Butanee | 3400 | nd | 0.01 | - | - |
| 2.83 | 2-Butenee | nd | nd | - | - | - |
| 3.13 | Ethanole | nd | nd | - | - | - |
| 3.38 | Dimethyl ketenee | nd | nd | - | - | - |
| 3.46 | Acetonitrile | 380 | nd | <0.01 | 0.02 | - |
| 3.75 | Acetone | 340 | nd | 0.01 | <0.01 | 0.03 |
| 3.77 | Dimethyl butene | 12000 | nd | - | - | - |
| 4.09 | C5H10 Alkene | 170 | nd | - | - | - |
| 4.25 | C5H10 Alkene | 310 | nd | - | - | - |
| 4.36 | C5H10 Alkene | 2900 | nd | - | - | - |
| 4.53 | C5H10 Alkene | 94 | nd | - | - | - |
| 4.84 | Dichloromethane | 1100 | nd | 0.01 | <0.01 | - |
| 4.86 | C5H10 Alkene | nd | nd | - | - | - |
| 5.21 | Carbon disulphide | 240 | nd | 0.80 | 0.36 | - |
| 5.41 | 2,2-Dimethylbutane | 390 | nd | - | - | - |
| 5.8 | C5H8 A dialkene | nd | nd | - | - | - |
| 6.16 | Cyclopentane | 1700 | nd | - | - | - |
| 6.18 | 2,3-Butanedione | 51 | nd | 3.19 | - | - |
| 6.28 | 2-Methyl pentane | 820 | nd | - | - | - |
| 6.31 | Acetic acid | 300 | nd | 0.83 | 20.04 | 7.52 |
| 6.47 | 2-Butanone | nd | nd | - | - | - |
| 6.69 | 3-Methyl pentane | 430 | nd | - | - | - |
| 6.81 | Unknown | nd | nd | - | - | - |
| 7.2 | n-Hexane | 250 | nd | <0.01 | 0.05 | - |
| 8.07 | Methyl cyclopentane | nd | nd | - | - | - |
| 8.8 | Benzene | 200 | nd | 0.02 | 0.02 | 0.01 |
| 9.08 | Cyclohexane | 190 | nd | <0.01 | 0.02 | <0.01 |
| 9.23 | C7 Alkane | 340 | nd | - | - | - |
| 9.51 | C7 Alkane (ethylpentane ?) | nd | nd | - | - | - |
| 9.58 | 3-Hydroxy-2-butanone | 390 | nd | - | - | - |
| 9.85 | Alkene | 61 | nd | - | - | - |

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Ratio (Sample less blank : Published ODT) U/T3/BU3 | | |
|---|---|---|---|---|---|---|
| | | Sample U/T3/BU 3 | Blank | M-Scan | Nagata | H4 |
| 9.93 | Branched alkane (a trimethyl hexane) | 68 | nd | - | - | - |
| 10.19 | n-Heptane | 230 | 71 | <0.01 | 0.06 | - |
| 10.73 | 1-Methyl butanol | 320 | nd | 0.74 | - | - |
| 10.94 | Methyl cyclohexane | 220 | nd | <0.01 | - | - |
| 11.09 | Dimethy disulphide | nd | nd | - | - | - |
| 11.9 | Toluene | 400 | nd | 0.07 | 0.32 | 0.65 |
| 12.39 | Unknown | nd | nd | - | - | - |
| 14.01 | Chlorobenzene | 81 | nd | 0.02 | - | - |
| 14.03 | Alkene substituted benzene [RMM 158] | 42 | nd | - | - | - |
| 14.68 | m- /p- Xylenes | 180 | nd | 0.10 | 1.00 | 2.55 |
| 14.88 | Cyclohexanone | 270 | nd | 0.09 | - | 3.49 |
| 15.3 | o-Xylene | 110 | nd | 0.03 | 0.07 | 1.56 |
| 16.56 | Benzaldehyde | 89 | 51 | 0.20 | - | - |
| 16.85 | Phenol | 83 | nd | 0.19 | 3.79 | - |
| 17.41 | C9H18 An alkyl substituted benzene | 390 | nd | - | - | - |
| 19.01 | Acetophenone | 690 | nd | 0.38 | - | - |
| 19.8 | Nonanal | 60 | 42 | 1.38 | - | - |
| 21.89 | Decanal | 53 | 75 | - | - | - |
| 23.72 | Phthalate anhydride | 110 | 28 | 0.25 | - | - |
| 25.61 | An alkanal | nd | nd | - | - | - |

**Table 4.13: Results – Semi-Quantitative VOCs Determination, Sampling 12th May 2010 onto Tandem Tubes T/T1/S2 and C/T1/S2 (Tenax® TA followed by Carbograph™ 1 TD), Analysis 5th July 2010**

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Measured Concentration (ng / litre) | | Ratio (Sample less blank : Published ODT) | | |
|---|---|---|---|---|---|---|---|---|
| | | Sample T/T1/S2 | Blank | Sample C/T1/S2 | Blank | M-Scan | Nagata | H4 |
| 2.25 | Isobutane | 6.1 | 3.1 | 1.9 | 1.4 | <0.01 | - | - |
| 2.28 | Methanol | 74 | 37 | 120 | 230 | <0.01 | <0.01 | - |
| 2.54 | n-Butane | 26 | nd | 5.9 | 1.3 | <0.01 | <0.01 | - |
| 3.13 | Ethanol | 14 | 1.9 | 7.2 | 0.69 | <0.01 | 0.02 | - |
| 3.49 | Acetonitrile | 34 | 2.2 | 16 | 8.2 | <0.01 | <0.01 | - |
| 3.8 | Acetone | 10 | 12 | 8.5 | 3.7 | <0.01 | <0.01 | <0.01 |

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Measured Concentration (ng / litre) | | Ratio (Sample less blank : Published ODT) | | |
|---|---|---|---|---|---|---|---|---|
| | | Sample T/T1/S2 | Blank | Sample C/T1/S2 | Blank | M-Scan | Nagata | H4 |
| 3.89 | 2-Methyl butane | 150 | nd | 8.8 | 2.2 | - | - | - |
| 4.07 | Isopropanol | 8.6 | 0.4 | 3.8 | 1.7 | <0.01 | - | - |
| 4.22 | C5H10 alkene | 3.1 | nd | 0.42 | nd | - | - | - |
| 4.36 | C5H10 alkene | 3.7 | nd | 0 | 0 | - | - | - |
| 4.48 | n-Pentane | 45 | nd | 9.8 | 3.3 | <0.01 | 0.01 | - |
| 4.66 | 2-Methyl-1-butene | 1.7 | nd | 0 | 0 | - | - | - |
| 4.92 | Dichloromethane | 5.2 | nd | 1.6 | 0.5 | <0.01 | <0.01 | <0.01 |
| 4.98 | C5 H10 Alkene | 4.1 | nd | 0 | 0 | - | - | - |
| 5.41 | 2,2-Dimethylbutane | 7.6 | nd | 0 | 0 | - | <0.01 | - |
| 5.47 | Methylsulphonyl chloride | 1.6 | 5.5 | 0 | 0 | - | - | - |
| 6.23 | Cyclopentane | 5.4 | 0.64 | 6.7 | 1.7 | - | - | - |
| 6.27 | 2,3-Butanedione | 11 | 26 | 0.15 | nd | <0.01 | - | - |
| 6.36 | 2-Methyl pentane | 19 | nd | 3.3 | 0.66 | - | <0.01 | - |
| 6.4 | Acetic acid | 7.4 | 2.4 | 0.88 | 0.47 | 0.02 | 0.36 | 0.14 |
| 6.54 | 2-Butanone | 2.2 | nd | 1.3 | 1.1 | <0.01 | - | <0.01 |
| 6.78 | 3-Methyl pentane | 13 | nd | 2.2 | nd | - | <0.01 | - |
| 6.89 | Unknown [RMM 84] | 2.1 | nd | 0 | 0 | - | - | - |
| 7.26 | n-Hexane | 23 | 0.54 | 7.4 | 0.95 | <0.01 | 0.01 | - |
| 8.12 | Methyl cyclopentane | 4.7 | nd | 1.7 | nd | <0.01 | <0.01 | - |
| 8.8 | Benzene | 0.93 | 3.8 | 1.6 | 1.1 | <0.01 | <0.01 | <0.01 |
| 9.08 | Cyclohexane | 1.7 | nd | 0 | 0 | - | <0.01 | <0.01 |
| 9.26 | C7 Alkane (3-methylhexane ?) | 4.5 | nd | 0 | 0 | - | - | - |
| 9.36 | C7H16 Branched alkane | 1.4 | nd | 0 | 0 | - | - | - |
| 9.51 | C7 Alkane (ethylpentane ?) | 5.4 | nd | 0.49 | nd | - | - | - |
| 9.61 | 3-Hydroxy-2-butanone | 10 | 44 | 0 | 0 | - | - | - |
| 9.77 | 1,3-Dimethyl cyclopentane ? | 0.89 | nd | 0 | 0 | - | - | - |
| 9.85 | Alkene | 1.5 | nd | 0.51 | 0.78 | - | - | - |
| 9.93 | Branched alkane (a trimethyl hexane ?) | 4.1 | nd | 0 | 0 | - | - | - |
| 10.19 | n-Heptane | 9.3 | 0.3 | 1.1 | 1 | <0.01 | <0.01 | - |
| 10.73 | 1-Methyl butanol | 0.73 | nd | 0 | 0 | - | - | - |
| 10.81 | Methyl isobutyl ketone (MiBK) | 2.4 | nd | 0 | 0 | - | - | - |
| 10.94 | Methyl cyclohexane | 4.4 | nd | 0 | 0 | - | 0.01 | - |
| 11.09 | Dimethy disulphide | 2.2 | nd | 0.25 | 0.14 | 0.05 | 0.27 | - |
| 11.72 | Butanoic acid | 1.1 | nd | 0 | 0 | - | - | - |
| 11.9 | Toluene | 5.9 | 0.32 | 2.1 | 1.6 | <0.01 | <0.01 | 0.01 |
| 12.12 | Unknown | 0.56 | nd | 0 | 0 | - | - | - |

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Measured Concentration (ng / litre) | | Ratio (Sample less blank : Published ODT) | | |
|---|---|---|---|---|---|---|---|---|
| | | Sample T/T1/S2 | Blank | Sample C/T1/S2 | Blank | M-Scan | Nagata | H4 |
| 12.39 | Hexanal | 0.9 | 0.56 | 0 | 0 | - | - | - |
| 13.5 | Hexamethylcyclotrisiloxane | 2.2 | 7.4 | 5.6 | 0.82 | - | - | - |
| 13.62 | An alkane | 1.9 | nd | 0 | 0 | - | - | - |
| 14.47 | Ethyl benzene | 3.5 | nd | 0 | 0 | - | <0.01 | - |
| 14.68 | m- /p- Xylenes | 16 | nd | 1.5 | 6.5 | 0.01 | 0.06 | 0.16 |
| 14.24 | o-Xylene | 1.9 | nd | 0.71 | 4 | <0.01 | <0.01 | <0.01 |
| 15.5 | n-Nonane | 1 | nd | 0.42 | nd | <0.01 | <0.01 | - |
| 16.56 | Benzaldehyde | 1.7 | 3.1 | 0.88 | 0.6 | <0.01 | - | - |
| 16.87 | Methyl ethyl benzene isomer | 1 | nd | 0 | 0 | - | - | - |
| 17.04 | Methyl ethyl benzene isomer | 0.76 | nd | 0 | 0 | - | - | - |
| 17.48 | Octanal | 0.79 | 0.92 | 0 | 0 | - | - | - |
| 17.67 | 1,3,5-Trimethylbenzene | 4.7 | nd | 0 | 0 | - | 0.01 | - |
| 17.82 | n-Decane | 0.99 | nd | 0 | 0 | - | <0.01 | - |
| 18.15 | A branched alkane | 0.88 | 1.8 | 0 | 0 | - | - | - |
| 18.35 | An alkyl substituted benzene | 0.75 | nd | 0 | 0 | - | - | - |
| 18.68 | d-Limonene | 1.3 | nd | 1.5 | nd | <0.01 | - | - |
| 18.92 | Acetophenone | 2.9 | 2.8 | 0.53 | 0.56 | <0.01 | - | - |
| 19.2 | Branched alkane | 1.1 | nd | 0 | 0 | - | - | - |
| 19.71 | Nonanal | 3.8 | 3.4 | 0 | 0 | - | - | - |
| 19.95 | n-Undecane | 0.6 | nd | 0 | 0 | - | <0.01 | - |
| 20.54 | Benzoic acid | 1.5 | 0.98 | 0 | 0 | - | - | - |
| 21.89 | Decanal | 3.1 | 4.5 | 0 | 0 | - | - | - |
| 22.08 | n-Dodecane | 0.57 | nd | 0 | 0 | - | - | - |
| 22.56 | Unknown | 1.7 | nd | 0 | 0 | - | - | - |
| 23.62 | Phthalic anhydride | 0.88 | nd | 0 | 0 | - | - | - |
| 18.15 | 2-Ethyl hexanol | 0.88 | 1.8 | 0 | 0 | - | - | - |
| 2.49 | A butene | 0 | 0 | 0.72 | 0.51 | <0.01 | - | - |
| 2.73 | Methyl mercaptan | 0 | 0 | 1.8 | 0.75 | 0.50 | 7.68 | - |
| 3.65 | 2-Propenal | 0 | 0 | 0.47 | 0.31 | <0.01 | - | - |
| 5.23 | Carbon disulphide | 0 | 0 | 0.5 | nd | <0.01 | <0.01 | - |
| 8.68 | 1-Butanol | 0 | 0 | 1 | nd | <0.01 | - | 0.01 |
| 13.16 | 3-Methyl heptane ? | 0 | 0 | 0.36 | 1.5 | - | - | - |
| 13.99 | An alkyl substituted benzene [RMM 158] | 0 | 0 | 0.55 | nd | - | - | - |
| 13.61 | A Dimethylheptane ? | 0 | 0 | 0.55 | nd | - | - | - |

**Table 4.14: Results – Semi-Quantitative VOCs Determination, Sampling 12th May 2010 onto Single Tube U/T1/S2 (Spherocarb™), Semi-Quantitative Analysis, 5th July 2010**

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | Ratio (Sample less blank : Published ODT) U/T3/BU3 | | |
|---|---|---|---|---|---|---|
| | | Sample U/T3/BU 3 | Blank | M-Scan | Nagata | H4 |
| 2.25 | Isobutane | 26 | 2 | 0.01 | - | - |
| 2.28 | Methanol | 110 | 42 | <0.01 | <0.01 | - |
| 2.49 | A butene | 7.9 | 7.7 | <0.01 | - | - |
| 2.60 | n-Butane | 29 | nd | <0.01 | <0.01 | - |
| 3.22 | Ethanol | 13 | nd | <0.01 | 0.01 | - |
| 3.49 | Acetonitrile | 41 | 5.4 | <0.01 | <0.01 | - |
| 3.80 | Acetone | 21 | nd | <0.01 | <0.01 | <0.01 |
| 3.89 | 2-Methyl butane | 150 | nd | - | - | - |
| 4.48 | n-Pentane | 31 | 2.8 | <0.01 | 0.01 | - |
| 4.92 | Dichloromethane | 5 | nd | <0.01 | <0.01 | <0.01 |
| 4.98 | C5 H10 Alkene | 3.3 | nd | - | - | - |
| 6.23 | Cyclopentane | 5.2 | nd | - | - | - |
| 6.27 | 2,3-Butanedione | 17 | nd | 1.06 | - | - |
| 6.36 | 2-Methyl pentane | 15 | nd | - | - | - |
| 6.40 | Acetic acid | nd | nd | <0.01 | <0.01 | <0.01 |
| 6.54 | 2-Butanone | 10 | nd | <0.01 | - | 0.01 |
| 6.78 | 3-Methyl pentane | 7.9 | nd | - | <0.01 | - |
| 7.26 | n-Hexane | 6.5 | nd | <0.01 | <0.01 | - |
| 8.12 | Methyl cyclopentane | 3.5 | nd | <0.01 | <0.01 | - |
| 8.80 | Benzene | 5.2 | 4.7 | <0.01 | <0.01 | <0.01 |
| 9.51 | C7 Alkane (ethylpentane ?) | 6.5 | nd | - | - | - |
| 9.61 | 3-Hydroxy-2-butanone | 28 | nd | - | - | - |
| 9.93 | Branched alkane (a trimethyl hexane) | 3.9 | nd | - | - | - |
| 10.19 | n-Heptane | 6.4 | 0.9 | <0.01 | - | - |
| 10.73 | 1-Methyl butanol | 5.3 | nd | 0.01 | - | - |
| 10.94 | Methyl cyclohexane | 2.8 | nd | <0.01 | <0.01 | - |
| 11.09 | Dimethyl disulphide | 7.8 | nd | 0.16 | 0.91 | - |
| 11.72 | Butanoic acid | 2.4 | nd | 0.17 | - | - |
| 11.90 | Toluene | 1.9 | 1.8 | <0.01 | <0.01 | <0.01 |
| 13.99 | An alkyl substituted benzene [RMM 158] | 4.8 | nd | - | - | - |
| 19.71 | Nonanal | 4.5 | nd | 0.35 | - | - |
| 19.95 | n-Undecane | 6.1 | nd | <0.01 | <0.01 | - |
| 21.89 | Decanal | 2.4 | nd | 0.41 | - | - |
| 22.08 | n-Dodecane | 2.7 | nd | <0.01 | - | - |

## *Quantitative Determination of Targeted Odorous VOCs*

On 27th July 2010 (once confirmation had been received that the equipment failure issues resulting in spoiled analyses had been resolved) RPS instructed M-Scan to carry out the fully-quantitative targeted analysis of compounds selected using the criteria listed in the section entitled: Identification of Odorous VOCs on page 13. M-Scan provided the results of the triplicate quantitative analyses of the Spherocarb™ samples on 6th August 2010, and these are shown in Table 4.15; they also informed us that the quantitative analyses of the other samples (Tenax® TA and Carbograph™ 1TD) would be delayed because the instrument had failed again.

**Table 4.15: Results –Quantitative VOCs Determination, Sampling 12th May 2010 onto Single Tubes U/T4/BU1, U/T4/BU2 and U/T2/S2 (Spherocarb™), Quantitative Analysis, 6th August 2010**

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | | |
|---|---|---|---|---|
| | | Sample U/T4/BU1 | Sample U/T2/S2 | Sample U/T4/BU3 |
| 2.24 | 1-Butene | 8.9 | 20 | 16 |
| 5.18 | Carbon disulphide | nd | nd | nd |
| 10.67 | 1-Methyl butanol | nd | nd | nd |
| 11.2 | Dimethyl disulphide | nd | nd | nd |
| 11.79 | Toluene | nd | nd | nd |
| 24.35 | Phthlaic Anhydride | nd | nd | nd |

RPS reviewed the quantitative analysis of the Spherocarb™ tubes and raised concerns about the results: apart from butane, there appeared to be no determinands detected at all, contrasting with the tubes taken at the same time that were analysed semi-quantitatively where these same compounds were present. RPS asked M-Scan on 16th August 2010 to check their results and provide an explanation, particularly on whether they thought the samples had deteriorated due to the time spent before they could be analysed. M-Scan`s initial view was that it would be unlikely that the samples had deteriorated (as information provided by the manufacturer indicates that samples collected on Spherocarb™ tubes should be stable for up to 6 months) and indicated that this may have been due to an analytical problem, specifically a problem with the baseline obscuring peaks. RPS instructed M-Scan to investigate this further.

Two further Spherocarb™ samples were analysed both semi-quantitatively and quantitatively quantitatively to gain further information. Unfortunately, however, M-Scan experienced a further equipment failure and was unable to report the results of their investigation until 13th September 2010, four months after the date of sampling. The results of these analyses were reported to RPS by M-Scan on the 13th September 2010 and are shown in Table 4.16 and Table 4.17. Again, the quantitative Spherocarb™ analysis was inconsistent with the first set of semi-quantitative scans, suggesting that in the lengthy period that M-Scan took to do the quantitative analyses after the first set of semi-quantitative scans were carried out, the quantitative samples had deteriorated.

**Table 4.16: Results –Semi-Quantitative Determination, Sampling 12th May 2010 onto Single Tubes U/T2/S1 and U/T4/BU2 (Spherocarb™), Semi-Quantitative Analysis, 13th September 2010**

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | |
|---|---|---|---|
| | | Sample U/T2/S1 | Sample U/T4/BU2 |
| 2.24 | 1-Butene | 6.5 | 3.3 |
| 5.18 | Carbon disulphide | nd | nd |
| 10.67 | 1-Methyl butanol | 1.7 | 30 |
| 11.2 | Dimethyl disulphide | 0.93 | 8.5 |
| 11.79 | Toluene | 0.38 | 4.6 |
| 24.35 | Phthlaic Anhydride | nd | nd |

**Table 4.17: Results - Quantitative VOCs Determination, Sampling 12th May 2010 onto Single Tubes U/T2/S1 and U/T4/BU2 (Spherocarb™), Quantitative Analysis, 13th September 2010**

| Retention Time (Min) | Assignment | Measured Concentration (ng / litre) | |
|---|---|---|---|
| | | Sample U/T2/S1 | Sample U/T4/BU2 |
| 2.24 | 1-Butene | 5.6 | 2.9 |
| 5.18 | Carbon disulphide | nd | nd |
| 10.67 | 1-Methyl butanol | 2.2 | 38 |
| 11.2 | Dimethyl disulphide | 1.2 | 11 |
| 11.79 | Toluene | 0.33 | 4 |
| 24.35 | Phthlaic Anhydride | nd | nd |

For the above reasons, RPS believes little confidence can be placed on M-Scan`s quantitative results and the decision was taken, in consultation with the Environment Agency, not to proceed with the quantitative analyses of the Carbograph™ and Tenax® TA triplicate samples. For the second study, therefore, mass emission rates for the identified odorous compounds have been based on the results of the semi-quantitative scans. Close examination of the semi-quantitative analyses carried out on 5th July 2010 shows generally lower concentrations than the first two tubes in the triplicate set analysed on 14th June 2010; because deterioration cannot be ruled out for the 5th July 2010 samples (despite manufacturer`s claims), only the results of the semi-quantitative analyses from 14th June 2010 have been used to calculate the mass emission rates for the identified odorous compounds for the second study. These results are shown in Table 4.18, Table 4.19, Table 4.20 and Table 4.21.

**Table 4.18: Calculation of Mass Emission Rates – Sampling 12th May 2010 onto Tandem Tubes T/T3/BU1 and C/T3/BU1 (Tenax® TA followed by Carbograph™ 1 TD), Semi-Quantitative Analysis 14th June 2010**

| Retention Time (Min) | Assignment [a] | T/T3/BU1 Concentration (ng / litre) [b*] | | C/T3/BU1 Concentration (ng / litre) [b*] | | Calculated $ou_E.m^{-3}$ Equivalent Using Different Published ODTs (Sample less blank/ODT) | | | Calculated Mass Emission Rate Using Different Published ODTs ($ou_E.s^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Sample | Blank [c] | Sample | Blank [c] | M-Scan | Nagata | H4 | M-Scan | Nagata | H4 |
| 2.68 | Methyl mercaptan | nd | nd | 22 | 37.0 | - | - | - | - | - | - |
| 4.39 | n-Pentane | 410 | nd | 360 | nd | 0.01 | 0.18 | - | 0.21 | 4.74 | - |
| 6.18 | 2,3-Butanedione | 160 | nd | 240 | nd | 25.00 | - | - | 644.42 | - | - |
| 6.31 | Acetic acid | 260 | nd | 43 | nd | 0.84 | 20.24 | 7.59 | 21.70 | 521.84 | 195.69 |
| 10.19 | n-Heptane | 140 | nd | 120 | 35.0 | 0.01 | 0.08 | - | 0.14 | 2.08 | - |
| 10.94 | Methyl cyclohexane | 59 | nd | 43 | nd | <0.01 | 0.16 | - | <0.01 | 4.22 | - |
| 14.68 | m- /p- Xylenes | 500 | 10 | 18 | nd | 0.29 | 2.81 | 7.20 | 7.48 | 72.47 | 185.71 |
| 14.88 | Cyclohexanone | 75 | 24 | 71 | nd | 0.04 | - | 1.58 | 1.08 | - | 40.62 |
| 15.30 | o-Xylene | 52 | 9 | 16 | nd | 0.02 | 0.03 | 0.83 | 0.40 | 0.90 | 21.42 |
| 16.56 | Benzaldehyde | 29 | nd | 13 | 23.0 | 0.10 | - | - | 2.58 | - | - |
| 17.55 | Octanal | nd | nd | nd | nd | <0.01 | - | - | <0.01 | - | - |
| 19.80 | Nonanal | 54 | nd | 16 | nd | 5.38 | - | - | 138.80 | - | - |
| 21.89 | Decanal | 86 | 100 | 11 | nd | - | - | - | - | - | - |

**Table 4.19: Calculation of Mass Emission Rates Sampling 12th May 2010 onto Tandem Tubes T/T3/BU3 and C/T3/BU3 (Tenax® TA followed by Carbograph™ 1 TD), Semi-Quantitative Analysis 14th June 2010**

| Retention Time (Min) | Assignment [a] | T/T3/BU1 Concentration (ng / litre) [b*] | | C/T3/BU1 Concentration (ng / litre) [b*] | | Calculated $ou_E.m^{-3}$ Equivalent Using Different Published ODTs (Sample less blank/ODT) | | | Calculated Mass Emission Rate Using Different Published ODTs ($ou_E.s^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Sample | Blank [c] | Sample | Blank [c] | M-Scan | Nagata | H4 | M-Scan | Nagata | H4 |
| 2.68 | Methyl mercaptan | nd | nd | 28 | 37.0 | - | - | - | - | - | - |
| 4.39 | n-Pentane | 2400 | nd | 660 | nd | 0.03 | 0.73 | - | 0.83 | 18.82 | - |
| 6.18 | 2,3-Butanedione | 390 | nd | 490 | nd | 55.00 | - | - | 1417.72 | - | - |
| 6.31 | Acetic acid | 270 | nd | 34 | nd | 0.84 | 20.31 | 7.62 | 21.77 | 523.56 | 196.33 |
| 10.19 | n-Heptane | 1200 | nd | 360 | 35.0 | 0.04 | 0.55 | - | 0.96 | 14.11 | - |
| 10.94 | Methyl cyclohexane | 530 | nd | 120 | nd | <0.01 | 1.04 | - | <0.01 | 26.87 | - |
| 14.68 | m- /p- Xylenes | 430 | 10 | 100 | nd | 0.30 | 2.88 | 7.37 | 7.66 | 74.18 | 190.10 |
| 14.88 | Cyclohexanone | 240 | 24 | 97 | nd | 0.11 | - | 4.04 | 2.78 | - | 104.22 |
| 15.30 | o-Xylene | 120 | 9 | 76 | nd | 0.05 | 0.11 | 2.65 | 1.27 | 2.87 | 68.22 |
| 16.56 | Benzaldehyde | 61 | nd | 38 | 23.0 | 0.40 | - | - | 10.31 | - | - |
| 17.55 | Octanal | 44 | nd | nd | nd | 6.11 | - | - | <0.01 | - | - |
| 19.80 | Nonanal | 160 | nd | 45 | nd | 15.77 | - | - | 406.48 | - | - |
| 21.89 | Decanal | 260 | 100 | 58 | nd | 36.95 | - | - | - | - | - |

**Table 4.20: Calculation of Mass Emission Rates – Sampling 12th May 2010 onto Single Tube U/T3/BU1 (Sphersorb), Semi-Quantitative Analysis 14th June 2010**

| Retention Time (Min) | Assignment [a] | Concentration (ng / litre) [b*] | | Calculated $ou_E.m^{-3}$ Equivalent Using Different Published ODTs (Sample less blank/ODT) | | | Calculated Mass Emission Rate Using Different Published ODTs ($ou_E.s^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Sample | Blank [c] | M-Scan | Nagata | H4 | M-Scan | Nagata | H4 |
| 2.41 | 1-Butene | 780 | nd | 0.7 | - | - | 15.3 | - | - |
| 5.21 | Carbon disulphide | nd | nd | - | - | - | - | - | - |
| 10.73 | 1-Methyl butanol | 88 | nd | 0.2 | - | - | 4.8 | - | - |
| 11.09 | Dimethy disulphide | 230 | nd | 4.8 | 26.8 | - | 112.9 | 630.5 | - |
| 11.90 | Toluene | 63 | nd | <0.1 | <0.1 | 0.1 | 0.3 | 1.2 | 2.4 |
| 23.72 | Phthalate anhydride | 440 | 28 | 1.2 | - | - | 29.4 | - | - |

**Table 4.21: Calculation of Mass Emission Rates – Sampling 12th May 2010 onto Single Tube U/T3/BU3 (Sphersorb), Semi-Quantitative Analysis 14th June 2010**

| Retention Time (Min) | Assignment [a] | Concentration (ng / litre) [b*] | | Calculated $ou_E.m^{-3}$ Equivalent Using Different Published ODTs (Sample less blank/ODT) | | | Calculated Mass Emission Rate Using Different Published ODTs ($ou_E.s^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Sample | Blank [c] | M-Scan | Nagata | H4 | M-Scan | Nagata | H4 |
| 2.41 | 1-Butene | nd | nd | - | - | - | - | - | - |
| 5.21 | Carbon disulphide | 240 | nd | 0.8 | 0.4 | - | - | - | - |
| 10.73 | 1-Methyl butanol | 320 | nd | 0.7 | - | - | 20.5 | - | - |
| 11.09 | Dimethy disulphide | nd | nd | - | - | - | - | - | - |
| 11.90 | Toluene | 400 | nd | 0.1 | 0.3 | 0.7 | 1.9 | 8.7 | 18.0 |
| 23.72 | Phthalate anhydride | 110 | 28 | 0.3 | - | - | 9.2 | - | - |

## *Hydrogen Sulphide*

The results of $H_2S$ measurements are detailed in Table 4.22. Of the three sources of ODTs included in this report, only Nagata includes an ODT for $H_2S$ and this has been used to calculate the odour emission rate.

**Table 4.22: Results of Hydrogen Sulphide Measurements 12th May 2010**

| Sample Code | Time | Result (ppm) | Published ODT* (Nagata) (ppm) | $ou_E.m^{-3}$ equivalent (Sample /ODT) | Mass Emission Rate ($ou_E.s^{-1}$) |
|---|---|---|---|---|---|
| H2S 1 | 10:40 | 0.009 | 0.00041 | 14.6 | 319.9 |
| H2S 2 | 10:41 | 0.011 | 0.00041 | 17.1 | 373.3 |
| H2S 3 | 10:42 | 0.014 | 0.00041 | 22.0 | 479.9 |
| H2S 4 | 10:43 | 0.014 | 0.00041 | 22.0 | 479.9 |
| H2S 5 | 10:44 | 0.014 | 0.00041 | 22.0 | 479.9 |
| H2S 6 | 10:45 | 0.014 | 0.00041 | 22.0 | 468.7 |
| H2S 7 | 10:46 | 0.014 | 0.00041 | 22.0 | 468.7 |
| H2S 8 | 10:47 | 0.015 | 0.00041 | 24.4 | 520.8 |
| H2S 9 | 10:48 | 0.014 | 0.00041 | 22.0 | 468.7 |
| H2S 10 | 10:49 | 0.014 | 0.00041 | 22.0 | 468.7 |
| H2S 11 | 10:50 | 0.012 | 0.00041 | 19.5 | 416.6 |
| H2S 12 | 10:51 | 0.012 | 0.00041 | 19.5 | 416.6 |
| H2S 13 | 10:52 | 0.012 | 0.00041 | 19.5 | 416.6 |
| H2S 14 | 10:53 | 0.014 | 0.00041 | 22.0 | 468.7 |
| H2S 15 | 10:54 | 0.014 | 0.00041 | 22.0 | 468.7 |
| H2S 16 | 10:55 | 0.014 | 0.00041 | 22.0 | 468.7 |
| H2S 17 | 10:56 | 0.011 | 0.00041 | 17.1 | 364.5 |
| H2S 18 | 10:57 | 0.012 | 0.00041 | 19.5 | 416.6 |
| H2S 19 | 10:58 | 0.014 | 0.00041 | 22.0 | 468.7 |
| H2S 20 | 10:59 | 0.015 | 0.00041 | 24.4 | 520.8 |
| H2S 21 | 11:00 | 0.015 | 0.00041 | 24.4 | 606.6 |
| H2S 22 | 11:01 | 0.015 | 0.00041 | 24.4 | 606.6 |
| H2S 23 | 11:02 | 0.012 | 0.00041 | 19.5 | 485.2 |
| H2S 24 | 11:03 | 0.012 | 0.00041 | 19.5 | 485.2 |
| H2S 25 | 11:04 | 0.011 | 0.00041 | 17.1 | 424.6 |
| H2S 26 | 11:05 | 0.014 | 0.00041 | 22.0 | 545.9 |
| H2S 27 | 11:06 | 0.014 | 0.00041 | 22.0 | 545.9 |
| H2S 28 | 11:07 | 0.014 | 0.00041 | 22.0 | 545.9 |
| H2S 29 | 11:08 | 0.012 | 0.00041 | 19.5 | 485.2 |
| H2S 30 | 11:09 | 0.012 | 0.00041 | 19.5 | 485.2 |
| H2S 31 | 11:10 | 0.012 | 0.00041 | 19.5 | 485.2 |
| H2S 32 | 11:11 | 0.012 | 0.00041 | 19.5 | 485.2 |
| H2S 33 | 11:12 | 0.012 | 0.00041 | 19.5 | 485.2 |
| H2S 34 | 11:13 | 0.011 | 0.00041 | 17.1 | 424.6 |
| H2S 35 | 11:14 | 0.012 | 0.00041 | 19.5 | 485.2 |

| Sample Code | Time | Result (ppm) | Published ODT* (Nagata) (ppm) | $ou_E.m^{-3}$ equivalent (Sample /ODT) | Mass Emission Rate ($ou_E.s^{-1}$) |
|---|---|---|---|---|---|
| H2S 36 | 11:15 | 0.012 | 0.00041 | 19.5 | 497.4 |
| H2S 37 | 11:16 | 0.011 | 0.00041 | 17.1 | 435.2 |
| H2S 38 | 11:17 | 0.011 | 0.00041 | 17.1 | 435.2 |
| H2S 39 | 11:18 | 0.011 | 0.00041 | 17.1 | 435.2 |
| H2S 40 | 11:19 | 0.011 | 0.00041 | 17.1 | 435.2 |
| H2S 41 | 11:20 | 0.011 | 0.00041 | 17.1 | 435.2 |
| H2S 42 | 11:21 | 0.011 | 0.00041 | 17.1 | 435.2 |
| H2S 43 | 11:22 | 0.011 | 0.00041 | 17.1 | 435.2 |
| H2S 44 | 11:23 | 0.011 | 0.00041 | 17.1 | 435.2 |
| H2S 45 | 11:24 | 0.011 | 0.00041 | 17.1 | 435.2 |

### *Total Odour Concentration by Dilution Dynamic Olfactometry*

The measured total odour concentrations and the derived mass emission rates of odour are shown in Table 4.6.

Three repeat samples were taken and analysed; the analytical total odour concentrations ranged from 3,025 to 3,641 $ou_E.m^{-3}$. The mean odour emission concentration in the shed was 3,236 $ou_E.m^{-3}$ and the mean mass emission rate was 81,848 $ou_E.s^{-1}$.

**Table 4.23: Results of Total Odour Measurements, Sampling 12th May 2010**

| Parameter | Sample Ref | Date Sample Taken | Time Sample Taken | Date of Analysis | Analytical Conc. $ou_E.m^{-3}$ | Emission Conc. $ou_E.m^{-3}$ § | Measurement Uncertainty ($ou_E.m^{-3}$) # | Mass Emission Rate ($ou_E.s^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| Odour Conc. | T118601 | 12/05/10 | 10:50 – 11:10 | 13/05/10 | 3,020 | 3,041 | 1,376 to 6,717 | 71,991 |
| Odour Conc. | T118602 | 12/05/10 | 11:12 – 11:32 | 13/05/10 | 3,616 | 3,641 | 1,648 to 8,042 | 95,541 |
| Odour Conc. | T118603 | 12/05/10 | 11:58 – 12:18 | 13/05/10 | 3,005 | 3,025 | 1,370 to 6,683 | 78,011 |
| Mean Result ¥ | - | - | - | - | - | 3,236 | 2,048 to 5,114 | 81,848 |

Samples were collected directly (without dilution) and analysed by dynamic dilution olfactometry according to the requirements of BSEN 13725:2003

# The uncertainty associated with the quoted result is at the 95% confidence interval

§ Concentrations referenced to 293K, 101.3kPa on a wet basis

¥ Geometric mean of the samples taken

## Table 4.24: Shed Data, 12th May 2010

| Parameter | Units | Sample ref: T118601 | Sample ref: T118602 | Sample ref: T118603 |
|---|---|---|---|---|
| Date | - | 12/05/10 | | |
| Age of Chickens | Days | 29 | | |
| Time Sample Taken | | 10:50 – 11:10 | 11:12 – 11:32 | 11:58 – 12:18 |
| Barometric pressure | kPa | 101.6 | 101.6 | 101.6 |
| Mean Ambient Temperature in Poultry Shed | °C | 23 | 24 | 23 |

# 5 Conclusion

RPS was commissioned by the Environment Agency to carry out a study of emissions of odours and dusts from Lower Farm in Eastmoor, Derbyshire. A number of complaints have been received alleging odours from the farm. The aims of the study were to identify the compounds likely to be causing the odours and to calculate emission rates of odours and dusts from the sheds where poultry are kept. This information is to be used to:

- inform modelling studies that will be undertaken by the Air Quality Modelling and Assessment Unit (AQMAU); and
- to further understanding of the issues.

From the first sampling campaign, carried out on 29th October 2009, the VOCs that were identified, on the basis of their concentration-to-ODT ratios, as being most likely to be contributing to the odour from the poultry shed were:

- Carboxylic acids, specifically acetic acid, butanoic acid, and 2-methyl butanoic acid and 3-methyl butanoic acid;
- Branched ketones, specifically 2,3-butanedione; and
- High molecular weight aldehydes, specifically 2-methyl butanal and 3-methyl butanal.

Based on the results of the semi-quantitative scan, Trimethylamine is also likely to contribute to the odour from the poultry shed.

These are all compounds that, according to the literature, are commonly associated with poultry farm odour. The mass emission rates of these compounds from the poultry shed have been calculated.

The semi-quantitative measurements of ammonia concentrations in and around the poultry shed indicated that the ODT was not exceeded, and ammonia is not therefore expected to be a significant contributor to the total odour (although it could interact synergistically with other compounds). The mass emission rate of ammonia from the poultry shed has been calculated.

Total odour concentration in the poultry shed air was measured by DDO and the odour emission rate from the shed has been calculated.

Some literature studies have suggested particulate matter plays a role as a carrier of odorous compounds in air from livestock facilities. The particulate matter concentration in the air in the poultry shed was measured and the mass emission rate has been calculated.

Having obtained knowledge of the identity of the odorous compounds in the first study, a second sampling campaign was carried out on 12th May 2010, using a refined sampling approach targeting each chemical group with a sorbent that was tailored to its characteristics (polarity, boiling point, etc). The second study also included repeating the triplicate measurements of total odour by lung sampling/DDO, so as to better understand the variability in total odour emission rates between bird batches; and measurement of $H_2S$ concentrations by Jerome® gold-film analyser.

The VOCs from the second study that were most likely to be contributing to the odour from the poultry shed were:

- Carboxylic acids, specifically acetic acid;

- Branched ketones, specifically 2,3-butanedione and cyclohexanone;
- High molecular weight aldehydes, specifically benzaldehyde, octanal, nonanal and decanal;
- Reduced sulphides, specifically methyl mercaptan, carbon disulphide and dimethy disulphide;
- Aliphatic and aromatic hydrocarbons, specifically xylenes, toluene, methyl cyclohexane, n-Pentane, n-heptane, 1-butene; and 1-methyl butanol and phthalate anhydride.

The mass emission rates of these compounds from the poultry shed have been calculated. It should be noted that the birds were fed on a different mixture at the second sampling campaign compared to the first study.

Hydrogen sulphide was present in the shed above its ODT threshold and the mass emission rate has been calculated.

The total odour emission rate (as measured by DDO) was 81,848 $ou_E\ s^{-1}$ in the second study compared to 117,326 $ou_E\ s^{-1}$ in the first study.

# References


BULLINER, E., KOZIEL, J., CAI, L., AND WRIGHT, D., 2006. Characterisation of Livestock Odours Using Steel Plates, Solid-Phase Microextraction, and Multidimensional Gas Chromatography-Mass Spectrometry-Olfactometry, *Journal of the Air & Waste Management Association*, 56, 1391-1403.

CAI, L., KOZIEL, J., NGUYEN, A., AND XIN, H., 2007. Evaluation of Zeolite for Control of Odourants Emissions from Simulated Poultry Manure Storage, *Journal of Environmental Quality*, 36 (1), 184-193.

Environment Agency, (2007). *Environment Agency Science Report SC030170/SR2 Review of Odour Thresholds*, ISBN:978-1-84432-719-5 p.118.

Environment Agency, (2009a). Request for Technical Support Form issued to RPS, October 2009.

Environment Agency, (2009b). *Environment Agency Technical Guidance Note, H4 – Odour management - Consultation DRAFT*. [online] Available from: http://www.environment-agency.gov.uk/static/documents/Research/H4_Odour_Guidance_consult_v1_2_090626.doc [Accessed 1 October 2009]

Iowa State University, Department of Agricultural and Biosystems Engineering, Personal communication, with Dr Jacek Koziel, 09/06/09

Iowa State University, Department of Agricultural and Biosystems Engineering, Personal communication, with Dr Jacek Koziel, 04/03/10

KOZIEL, J., CAI, L., WRIGHT, D AND HOFF, S., 2006. Solid-Phase Micro-extraction as a Novel Air Sampling Technology for Improved GC-Olfactometry-based Assessment of Livestock Odours, *Journal of Chromatographic Science*, 44 (7), 451-457

M-SCAN, 2010. Library of Odour Detection Thresholds.

M-SCAN, 2010. Personal communication, with Chris Offen at M-Scan, 15/03/10

M-SCAN, 2010. Personal communication, with Chris Offen at M-Scan, 11/03/10

SMEETS M.A.M, BULSING P.J, VAN ROODEN S, STEINMANN R, ALEXANDER DE RU J, OGINK N.W.M., VAN THRIEL C AND DALTON P.H, 2007. Odour and Irritation Thresholds for Ammonia: A Comparison between Static and Dynamic Olfactometry, *Chemical Senses*, 32 (1), 11-20.

University of Minnesota, Department of Bioproducts and Biosystems Engineering, Personal communication, with Professor Larry D. Jacobson, 09/06/2009

WRIGHT, D., EATON, D., NIELSEN, L., KUHRT, F., KOZIEL, J., SPINHIRNE, J. AND PARKER, D., 2005. Multidimensional Gas Chomatography-Olfactometry for the Identification and Prioritisation of Malodours from Confined Animal Feeding Operations, *Journal of Agricultural and Food Chemistry*, 53 (22), 8663-8672.

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