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Development of odour free mushroom composts by modifying

the organic and inorganic nitrogen sources and process

technology

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### PRACTICAL SECTION FOR GROWERS

This report is divided into two parts, both of which relate to the reduction and eventual elimination of odours from mushroom composting. The first part is on the development of alternatives to broiler poultry manure as a nitrogen source in mushroom compost; the second part deals with the development of methods for quantifying mushroom composting odours.

# **Alternative Nitrogen Sources**

Substrates for mushroom culture were prepared in flasks using two types of straw (wheat or oil seed rape) and different organic and inorganic nitrogen (N) sources. All the composts were prepared using the same controlled temperature regime ie 47°C for 2 days, followed by 72°C for 5 days and 47°C for 7 days or until the air in the flask was clear of ammonia. An oxygen concentration of 11 (± 1.5)% v/v was maintained in the substrate using a controlled airflow.

# **Odour Quantification Techniques**

Techniques for quantifying odour from mushroom composting need to be developed in order to assess the effectiveness of new composting methods and to aid odour control. The method currently used for measuring odour, based on odour panel validation (olfactometry) is costly, time-consuming, subject to error and incurs delays between sampling and measurement. Analysis of all the components of compost odour and its interpretation is impractical on a day-to-day basis due to the large number of compounds involved, cost and the delay between sampling and measurement. Four methods of odour measurement were therefore compared using odour samples obtained from ten different composting yards with pre-wetting and Phase I windrow or tunnel composts:-

- (i) Odour panel serial dilution (olfactometry)
- (ii) Chemical analysis using gas chromatography-mass spectrometry (GC-MS)
- (iii) Gas detector tubes for specific odorants
- (iv) AromaScan 'electronic nose' using an array of conducting polymer sensors, which display reversible changes in electrical resistance when volatile molecules adsorb and desorb from their surface.

# **Summary of Results**

For most of the organic and inorganic nitrogen sources, the optimum nitrogen content for mushroom yield was 1.9% of dry matter at filling and 2.1% of dry matter at spawning. Organic nitrogen (spent hop powder) and inorganic nitrogen (ammonium sulphate or urea) sources were found to produce an equivalent mushroom yield to broiler poultry manure, with significantly less odour during composting.

Rape straw could be used in place of wheat straw, and since it has a higher nitrogen content, required a lower inclusion of poultry manure (or other nitrogen source) to achieve a required compost nitrogen content. A lower inclusion of poultry manure reduced the odour from composting. The nitrogen content of digester wastes is too low for them to be used as a complete replacement for broiler poultry manure. However, they may be suitable as a partial replacement if supplies are readily and locally available. However, composting odour levels were similar to those using broiler poultry manure. Chipboard waste containing urea formaldehyde resin degraded too slowly to act as a significant nitrogen source. At an inclusion rate of 40% (with straw and ammonium sulphate) it resulted in a significantly lower yield than straw and ammonium sulphate alone. However, at a lower inclusion rate it may be useful as a water absorbent during pre-wetting and it does not cause significant odour.

Several other potential alternative nitrogen sources were identified but have yet to be tested in mushroom composting.

Sulphur containing compounds were found to be the major contributors to compost odours. There was a close correlation between the compost odour concentration (OC) of the pre-wet and Phase I composts sampled and the combined hydrogen sulphide (H<sub>2</sub>S) and dimethyl sulphide (DMS) concentrations from gas detector tubes. Using GC-MS, a range of other sulphides and volatile fatty acids were recorded in compost yard odours at concentrations close to their detection thresholds. The AromaScan electronic nose produced positive sensor responses to ammonia (NH<sub>3</sub>) at concentrations of less than 2 ppm and negative responses to hydrogen sulphide and dimethyl sulphide above concentrations of 50 and 20 ppm. Ammonia dominated the sensor response unless the sample gas was passed through a 'Nafion' tube which selectively removed NH<sub>3</sub> but retained sulphides. The AromaScan could distinguish anaerobic odours from composts with odour concentrations of above 50,000 odour units m<sup>-3</sup> (typical of anaerobic zones in windrows) from less odorous composts. The former produced

negative sensor responses whereas the latter produced positive or no sensor responses. The AromaScan can be used for discriminating strong anaerobic odours in flask composting equipment, for example, to examine the effects of different compost ingredients and microfloral inocula on odour, but it is not sufficiently sensitive to sulphides for most on-site measurements, where odour concentrations were generally less than 40,000 odour units m<sup>-3</sup>. For this situation, hydrogen sulphide and dimethyl sulphide detector tubes are more appropriate and relate to odour panel measurements with over 80% accuracy.

Odour concentrations and sulphide concentrations from three out of four aerated Phase I tunnel sites were significantly lower than from six conventional windrow composting sites sampled.

# **Practical and Financial Anticipated Benefits**

The organic and inorganic nitrogen sources identified in the first year of this work may enable mushroom composts to be prepared with significantly less odour than using poultry manure. The small-scale tests showed that equivalent mushroom yields can be obtained but further larger-scale tests are required before the effects of compost nitrogen source on mushroom yield and compost bulk density can be verified.

The relationship between odour concentration and concentration of sulphides in compost odour air may enable rapid and objective measurement of compost odours, without the need for expensive odour panel validation. Further sampling of a range of compost odours is required before this relationship can be confirmed.

The benefits of aerating the composting process in reducing odour levels have been demonstrated, both in terms of odour concentration and sulphide concentration.

### SCIENCE SECTION

# **Alternative Nitrogen Sources**

#### Introduction

The traditional ingredient of mushroom compost, straw bedding horse manure, provided both a source of carbon (C) and nitrogen (N). Due to difficulties in availability and variability in the material, compost formulations with wheat straw and various N sources were developed. These included other animal manures such as poultry, pig and bullock [Ross, 1968; Grabbe, 1974; Dawson, 1978], other organic wastes such as dried blood, cotton seed meal, brewery wastes, horn, whey powder, molasses and sewage-based products [Riethus, 1962; Delmas and Laborde, 1968; Smith and Spencer, 1997; Gerrits, 1988] and inorganic N sources such as ammonium nitrate and sulphate, calcium nitrate, urea and urea formaldehyde [Reithus, 1962; Bech and Rasmussen, 1968; Delmas and Laborde, 1968; MacCanna, 1968]. Due to its low cost, high N content and ease of handling, broiler poultry manure is now an integral part of most mushroom composting in the UK and many other countries [Gerrits, 1988]. However, due to subsidised use as non-fossil fuels in power stations, supplies of broiler chicken manure and turkey manure for mushroom composting have recently declined. In addition, poultry manure has a serious odour problem, both on its own and when incorporated into compost. This is mainly due to the sulphur-containing amino acids which are precursors of volatile, odorous sulphur compounds particularly under anaerobic composting conditions (Miller and Macauley, 1988).

In these experiments, alternatives to poultry manure were therefore examined in an aerated composting system. In the first experiment, the use of a flask composting system for examining the effect of compost N content on mushroom yield was developed. In the second experiment, the effect of compost N from broiler poultry manure and other sources on compost odour and mushroom yield is examined and compared.

### **Materials and Methods**

# Composting procedure

Substrate ingredients were composted in 'Quickfit' multiadapter flasks immersed in thermostatically controlled water baths, each holding three 2-litre flasks (Expt. 1) or two 10-litre flasks (Expt. 2) [Castro de Jimenez *et al*, 1990]. The prepared ingredients (700 g and 3 kg samples in Expts. 1 and 2) were placed on a perforated stainless steel platform within each flask and the flasks immersed in the waterbaths such that the water level was above the level of the enclosed substrate. Each flask was connected to ancillary equipment providing independent aeration and humidification of the compost. The oxygen (O<sub>2</sub>) concentration in the substrate was controlled regularly by adjusting the airflow through the compost in each flask within the range 0-16 litres kg<sup>-1</sup> substrate h<sup>-1</sup> by means of flow meters. The temperature of the substrate in the flasks was monitored with Squirrel multipoint temperature loggers (Grant Instruments Ltd, Cambridge, UK). Ammonia, hydrogen sulphide, carbon dioxide and oxygen levels in the flasks were monitored using a Draeger Gas Detector (Drägerwerk, Lübeck, Germany) with appropriate sample tubes (CH20501, CH31901, CH31401, 8101991 and 6728081 respectively).

For the first 48 h of the composting process, the thermostat of the waterbath was set at  $47^{\circ}$ C to allow a natural succession and gradual build-up of microorganisms. The substrate temperature was then increased to  $72^{\circ}$ C for 5 days, after which the substrate was re-mixed and the temperature reduced to  $47^{\circ}$ C for the remainder of the composting period, which was seven days, or prolonged until the air in the flask was clear of ammonia. An  $O_2$  concentration of  $11(\pm 1.5)\%$  v/v was maintained in the substrate.

Analyses were conducted on freeze-dried, finely milled samples of the compost ingredients and of the substrates before and after processing in the flask composting equipment. Dry matter (DM), N, ammonium (NH<sup>+</sup><sub>4</sub>) and ash contents and pH were determined as described previously [Noble and Gaze, 1994].

# Mushroom yield

At the end of the composting period, the material in each flask was weighed. After samples were taken for analysis, 400 g (Expt 1) or 2 kg (Expt 2) of the residual material was inoculated with mushroom spawn (spawned) at two percent of the fresh weight of compost with *Agaricus bisporus* spawn (Hauser A12) and filled into plastic pots: 115 mm diameter x 145 mm depth in Expt 1 and 230 mm diameter x 220 mm depth in Expt 2. The pots were placed in polythene bags in an incubator at 25°C and when the substrate was fully colonised with mushroom mycelium, about 15 days after spawning, the containers were covered (cased) with a moist mixture of peat and sugar beet lime; 400 g in Expt 1 and 900 g in Expt 2. When mushroom mycelium was visible on the surface of the casing, the containers were transferred to a controlled environment chamber with an air temperature of 18°C, relative humidity of 90% and a CO<sub>2</sub> concentration of 0.1% to induce fruiting. Mushrooms were harvested daily over a 30 day period (cap diameter 25-30 mm).

# Experiment 1: Effect of substrate N from poultry manure on mushroom yield

Compost N content was varied by altering the ratio of broiler poultry manure to wheat (*Triticum aestivum*) straw, taking into account the N and moisture contents of the poultry manure and straw [Noble and Gaze, 1994]. Water was first added to the straw to achieve a moisture content of 70% before the addition of poultry manure. Gypsum was added at 30 g kg<sup>-1</sup> fresh compost ingredients to reduce the physical greasiness and to reduce the pH and dissociation of ammonium [Gerrits, 1988]. Further water was added over a period of 4 days to achieve a moisture content of 78% (±1.5%), before the substrate ingredients were filled into the flasks.

Compost ingredients with calculated or 'target' N contents varying between 1.1 and 2.6% of DM were produced with the range in target N content divided into six subdivisions, each covering a range of c. 0.25% N. Six composts with calculated N contents within each subdivision were produced. Composts within each target N content subdivision were randomly paired with other target N content treatments, such that each treatment was produced once in each of six waterbaths. A total of 36 substrates were prepared. Quantities of poultry manure and wheat straw used in the treatments are shown in Table 1.1.

Compost ingredients were prepared from wheat straw and the following N sources:

- i. Broiler poultry manure
- ii. Anaerobic digester waste based on deep litter poultry manure
- iii. Anaerobic digester waste based on 55% liquid pig manure, 25% liquid cattle manure and 20% food processing waste
- iv. Spent hop powder
- v. Ammonium sulphate + chipboard waste, consisting of sawdust with urea formaldehyde resin
- vi. Ammonium sulphate
- vii. Urea
- viii. Composted wood waste with animal manure (Forest N-rich, supplied by Bulrush Peat Company)(not replicated)

Compost ingredients were also prepared from oilseed rape (*Brassica napus*) straw and broiler poultry manure (treatment ix.). Nitrogen sources i-iv, viii and ix were regarded as organic, and the other N sources as inorganic.

Target compost N contents were calculated in the same way as per broiler poultry manure and straw in Experiment 1. For each N source, composts ingredients with target N contents varying between 1.3 and 2.9% of DM were produced with the range in target N content divided into eight subdivisions, each covering a range of c. 0.2% N. Eight waterbaths were used on four occasions for the experiment. On each occasion, the eight N sources were allocated to the eight waterbaths and paired with other N sources. On any one occasion (16 flasks), there were two flasks of each target of N content.

A total of 64 substrates were prepared. Quantities of N source and wheat straw or oilseed rape straw used in the treatments are shown in Table 1.1.

#### Results

Analysis of compost ingredients

Dry matter, nitrogen, ammonium and ash contents of the compost ingredients are shown in Table 1.1. The digester wastes and Forest N-rich had significantly lower dry matter contents than the other materials. Broiler poultry manure had a significantly higher nitrogen content than the other organic materials, although the digester wastes had higher ammonium contents. Rape straw had a significantly higher nitrogen content than wheat straw. Digester waste based on deep litter poultry manure had a significantly higher ash content than the other materials due to the grit added to the poultry feed.

# Experiment 1: Effect of substrate N from poultry manure on mushroom yield

Increasing the N content of the compost ingredients from 1.1 to 2.6% of DM increased the duration to clear NH<sub>3</sub> from the compost from 71 hours to 343 hours and increased the maximum NH<sub>3</sub> concentration in the flasks from 200 to 840 ppm. This resulted in an increase in compost N losses from 352 to 3142 mg/kg. There were also significant linear correlations between the N content of the compost ingredients and the N and ash contents of the processed substrates (Table 1.2). About 16% of the initial N in the composts was in the ammonium form. There were no significant correlations between the initial N content and final ammonium and dry matter content or pH of the composts, for which the mean values were  $0.09 (\pm 0.03)\%$  of DM,  $27(\pm 2.3)\%$  and  $7.4 (\pm 0.31)\%$ .

There was considerable variation in the mushroom yields obtained from the small pots. A weak correlation between the compost N content at spawning and mushroom yield was observed, with an optimum N content of 2-2.5% of DM (Fig. 1). This was equivalent to an initial compost N content of 1.5 to 1.8% of DM. No other significant correlations between mushroom yield and compost analysis factors were observed.

# Experiment 2: Effect of substrate N from different N sources on mushroom yield

Fig. 1.2 shows the NH<sub>3</sub> concentration in the flask air during the composting of different materials with a range of initial N contents. The NH<sub>3</sub> concentration increased as the initial compost N content increased from 1.4% of DM (Fig. 1.2a) to 2.4% of DM (Fig. 1.2b). With an initial compost N content of 1.4% of DM, urea produced the highest NH<sub>3</sub> concentration (Fig. 1.2a). Poultry manure (with wheat or rape straw) and spent hop waste produced similar NH<sub>3</sub> concentrations. Ammonium sulphate and digester waste produced the lowest NH<sub>3</sub>

concentrations. With initial compost N contents of 2.4% of dm, poultry manure and urea produced similar concentrations of NH<sub>3</sub>, rape straw and poultry manure produced significantly more NH<sub>3</sub> whereas ammonium sulphate, with or without chipboard waste, produced lower concentrations. Little NH<sub>3</sub> was evolved from chipboard waste (Fig. 1.2b).

The relationship between the initial and final N contents of the composts differed between the organic and inorganic N sources. For the same initial compost N content, organic N sources resulted in a higher total N content at spawning but a lower NH<sub>4</sub><sup>+</sup> content (Fig. 1.3 and 1.4). The regression equations for the relationships between N at filling and at spawning using different N sources are shown in Table 1.3. For organic N sources, there was a weaker correlation between the initial N and NH<sub>4</sub><sup>+</sup> contents of the substrates than for inorganic N sources.

For all the N sources except chipboard waste, there was an optimum compost N content at spawning of about 2.1% of DM or 1.9% of DM at filling of flasks (Figs. 1.5 and 1.6). The yields obtained at the optimum substrate N content at spawning were similar for broiler poultry manure (with wheat or rape straw), spent hop waste, ammonium sulphate and urea, ie 600-700 g mushrooms/kg spawned substrate. Yields obtained with digester wastes (poultry manure or animal manure based) and chipboard waste + ammonium sulphate were significantly lower. In the case of digester wastes, this may have been due to the higher inclusion rates needed to achieve sufficiently high compost N contents (Table 1.1). At inclusion rates of 70% w/w, the physical properties of the compost may have been adversely affected. The optimum N content at spawning for chipboard wastes + ammonium sulphate composts was higher (2.8% of DM) due to the undergraded urea formaldehyde.

Odour levels of broiler poultry manure (with wheat or rape straw) and digester waste composts were similar ( $H_2S$  concentration in flask air up to 3 ppm) and generally increased with the quantity of N source used. Odour levels from chipboard waste, spent hop waste, ammonium sulphate and urea were lower and no  $H_2S$  was detected in the flask air.

### Discussion

The optimum initial N content in these experiments of 1.9% of DM is similar to that reported previously for a similar composting system using broiler poultry manure (Gerrits, 1992).

Noble and Gaze (1994) found no difference in yield between composts of equivalent N content using poultry manure or poultry manure and Sporavite (a molassed fibrous meal with an N content of 7.4% of DM). However, composts based on barley straw as the main carbon source produced significantly lower yields than wheat straw-based composts, at equivalent N contents. The results found here show that wheat straw can be replaced with rape straw, and since the latter has a higher N content it requires less poultry manure to achieve a required compost N content. This may reduce the odour of the compost but further odour measurements from wheat and rape straw composts with equivalent N contents are needed. Several other potential alternative N sources were identified but have yet to be tested in mushroom composting (Table 1.4).

#### **Conclusions Part 1**

- Several alternative N sources have been found to produce an equivalent mushroom yield
  to broiler poultry manure when used in an aerated flask composting system. These
  include organic (spent hop powder waste) and inorganic (ammonium sulphate and urea)
  sources. Odour from these N sources in composting was significantly less than from
  poultry manure.
- 2. Rape straw can be used in place of wheat straw, and since it has a higher N content, requires a lower inclusion of poultry manure (or other N source) to achieve a required compost N content.
- 3. The N content of digester wastes is too low for them to be used as a complete replacement for broiler manure. However, they may be suitable as a partial replacement if supplies are readily and locally available.
- 4. Chipboard waste containing urea formaldehyde resin degraded too slowly to act as a significant N source. At an inclusion rate of 40% (with straw and ammonium sulphate) it resulted in a significantly lower yield than straw and ammonium sulphate alone. However, at a lower inclusion rate it may be useful as a water absorbent during prewetting.
- 5. For most of the organic and inorganic N sources, the optimum compost N content for mushroom yield was 1.9% of DM at filling and 2.1% of DM at spawning.

Table 1.1 Analysis of compost ingredients and quantities used (± S.D.)

| Ingredient/                                | % w/w <sup>a</sup> | DM %             | % of DM             |                              |                |  |
|--|--------------------|------------------|---------------------|------------------------------|----------------|--|
| Treatment                                  |                    |                  | N                   | NH <sup>+</sup> <sub>4</sub> | Ash            |  |
| Wheat straw <sup>b</sup> (1)               | (100-              | 88 (±2.7)        | $0.5 (\pm 0.15)$    | $0.05 (\pm 0.004)$           | 5 (±1.3)       |  |
| (2)  | N source)          | $88 (\pm 1.0)$   | $0.8 (\pm 0.02)$    | $0.04 (\pm 0.010)$           | 8 (±1.3)       |  |
| i. Broiler poultry (1)                     | 17-55              | $70 (\pm 6.3)$   | $6.0 (\pm 0.55)$    | $0.97 (\pm 0.346)$           | $15 (\pm 1.2)$ |  |
| manure <sup>b</sup> (2)                    | 3-44               | 69 (±7.3)        | $5.7 (\pm 0.63)$    | $1.00 \ (\pm 0.376)$         | 15 (±0.4)      |  |
| ii. Poultry manure digester waste          | 40-64              | 31 (±0.7)        | 3.5 (±0.47)         | 1.12 (±0.110)                | 33 (±4.1)      |  |
| iii. Animal manure/<br>food digester waste | 62-73              | 22 (±2.5)        | 2.8 (±0.11)         | 1.19 (±0.094)                | 11(±1.3)       |  |
| iv. Spent hop powder                       | 29-48              | 90 (±2.0)        | 3.3 (±0.52)         | $0.05(\pm0.007)$             | 8 (±0.5)       |  |
| v. Rape straw                              | 57-100             | 85 (±2.6)        | 1.2 (±0.09)         | 0.04 (±0.008)                | 6 (±1.8)       |  |
| vi. Chipboard waste + ammonium sulphate    | 40-38<br>0-5       | 87 (±4.5)<br>100 | 4.2 (±1.25)<br>21.2 | 0.26 (±0.149)<br>27.27       | 1 (±0.2)       |  |
| vii. Ammonium sulphate                     | 5-10               | 100              | 21.2                | 27.27                        | -              |  |
| viii. Urea                                 | 2-5                | 100              | 46.7                | 0                            | -              |  |
| ix. Forest N-rich                          | 50                 | 31               | 3.4                 | 0.43                         | 3              |  |

<sup>&</sup>lt;sup>a</sup> Original fresh weight in compost excluding added water and gypsum. The remainder in treatments i. to viii. was wheat straw, and in treatment ix. was broiler poultry manure.

<sup>&</sup>lt;sup>b</sup> Experiments 1 and 2

Table 1.2 Linear correlations between compost N content<sup>a</sup> at filling of flasks (x) and N losses during composting or compost analysis factors at emptying of flasks (y). The regressions are for y or x; Experiment 1

| Dependent variate y                         | Regression equation <sup>b</sup>     |
|---|--------------------------------------|
| Duration to clear NH <sub>3</sub> (h)       | $y = -120.0 + 182.9 x, r^2 = 0.44$   |
| NH <sub>3</sub> losses from compost (mg/kg) | $y = -581.4 + 1278.0 x, r^2 = 0.28$  |
| N losses from compost (mg/kg)               | $y = -1694.9 + 1860.4 x, r^2 = 0.30$ |
| N content <sup>a</sup>                      | $y = 0.14 + 1.29 x, r^2 = 0.35$      |
| Ash content <sup>a</sup>                    | $y = 7.05 + 3.38 x, r^2 = 0.25$      |

<sup>&</sup>lt;sup>a</sup> N, NH<sup>+</sup><sub>4</sub> and ash contents were expressed as percentage of dry matter

<sup>&</sup>lt;sup>b</sup> All the regression coefficients were significantly different from zero

Table 1.3 Linear correlations between compost N content<sup>a</sup> at filling (x) and at emptying of flasks (y). The regressions are for y on x; Expt. 2.

| N source                            | Regression equation <sup>b</sup>    |
|-------------------------------------|-------------------------------------|
|                                     |                                     |
| ORGANIC SOURCES                     |                                     |
| Broiler poultry manure              | $y = 0.43 + 1.06 x$ , $r^2 = 0.69$  |
| Digester wastes                     | $y = -0.71 + 2.85 x$ , $r^2 = 0.61$ |
| Spent hop powder                    | $y = 1.33 + 0.46 x$ , $r^2 = 0.28$  |
| Rape straw + broiler poultry manure | $y = 0.49 + 0.77 x, r^2 = 0.70$     |
| INORGANIC SOURCES                   |                                     |
| Chipboard waste + ammonium sulphate | $y = 0.96 + 0.68 x,  r^2 = 0.65$    |
| Ammonium sulphate                   | $y = 1.04 + 0.53 x$ , $r^2 = 0.66$  |
| Urea                                | $y = 0.67 + 0.55 x,  r^2 = 0.67$    |

<sup>&</sup>lt;sup>a</sup> N expressed as percentage of dry matter

<sup>&</sup>lt;sup>b</sup> All the regression coefficients were significantly different from zero.

Table 1.4 Alternative nitrogen sources which have not yet been tested in the flask composting experiments

| N source                    | DM%   | % of DM |                              |     |
|-----------------------------|-------|---------|------------------------------|-----|
|                             |       | N       | NH <sup>+</sup> <sub>4</sub> | Ash |
|                             |       |         |                              | _   |
| Shell extracted cocoa meal  | 88    | 2.65    | 0.03                         | 5   |
| Cocoa shell waste           | 90    | 3.1     | 0.02                         | na  |
| Spent coffee grounds        | 27    | 1.87    | 0.02                         | 1   |
| Brewery waste               | 30    | 2.0     | na                           | na  |
| Cotton seed meal            | 85    | 7.0     | na                           | na  |
| Caster seed meal            | 90    | 5.5     | na                           | na  |
| Rape meal                   | 90    | 5.8     | na                           | na  |
| Milk (whey) products wastes | 70-95 | 1.8-4.3 | na                           | 21  |
| Whisky distillery wastes    | 70    | 4.2-5.6 | na                           | na  |

na = not analysed

Fig. 1.1 Relationship between substrate N content at spawning and mushroom yield, Expt 1

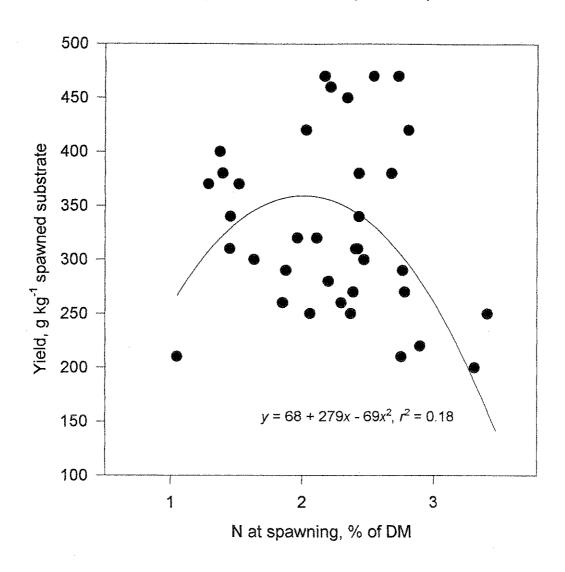
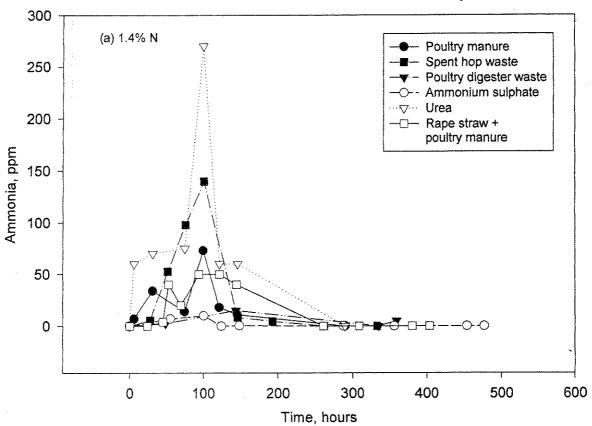


Fig.1.2. Flask ammonia concentration during composting of different N sources with wheat or rape straw



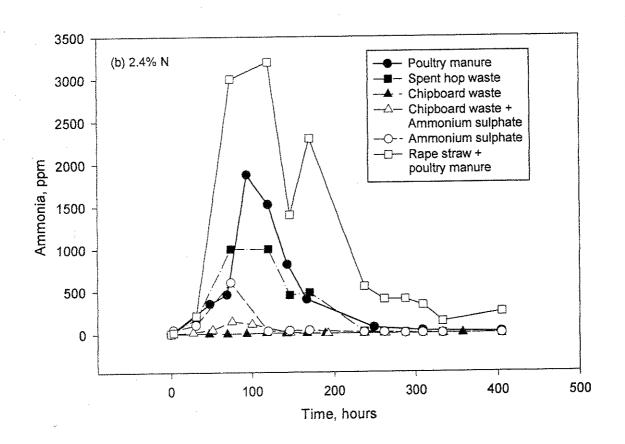


Fig. 1.3 Relationships between N contents at filling and at spawning for organic and inorganic N sources

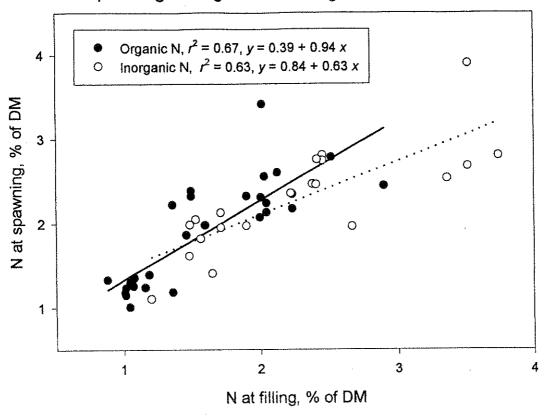


Fig. 1.4 Relationships between compost N content at filling and ammonium content at spawning for organic and inorganic N sources

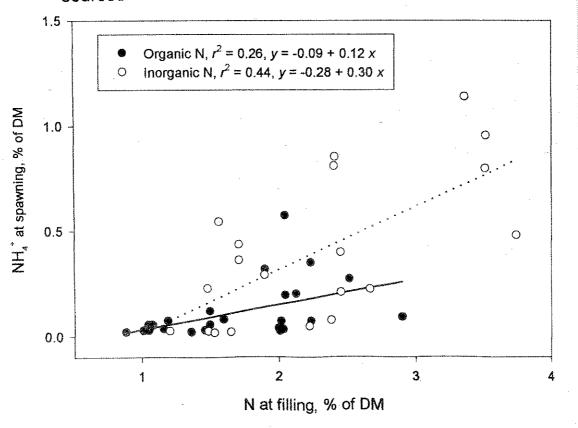


Fig. 1.5 Relationship between substrate N at spawning and mushroom yield using organic N sources

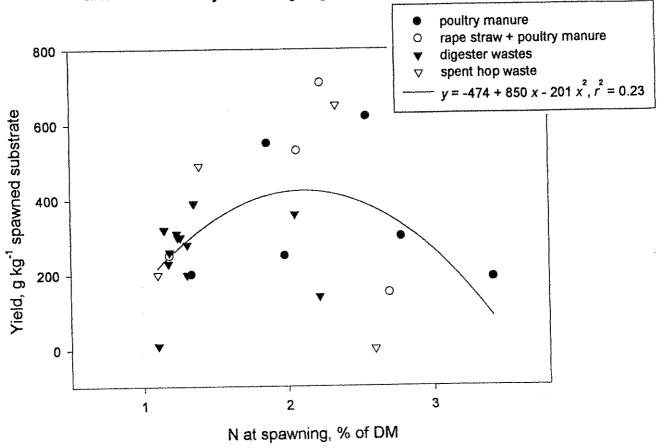
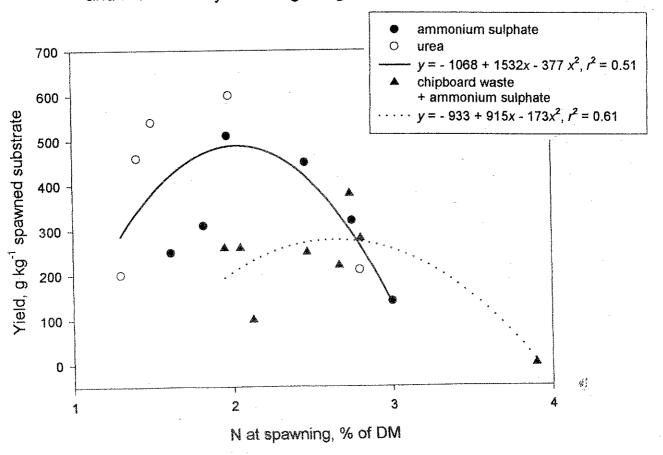


Fig. 1.6 Relationship between substrate N at spawning and mushroom yield using inorganic N sources



# Part 2: Odour Quantification Techniques

# Introduction

Odour pollution is a major problem facing mushroom compost production in the UK and several other countries (Miller and Macauley, 1988; Derikx et al., 1990, Noble and Gaze, 1994). Conventional composting involves wetting and mixing straw and animal manures in heaps (pre-wetting) and then in long stacks (Phase I composting). During these stages fermentation is uncontrolled, resulting in the evolution of gaseous pollutants, causing environmentally unacceptable odour levels. In order to assess the effectiveness of new composting methods in odour reduction, such as forced aeration and changes to the raw ingredients (Perrin and Gaze, 1987; Gerrits, 1989), techniques are needed for quantifying odour levels.

Olfactometry is used to measure the concentration of odour in air through the use of a serial diluter, or an olfactometer, to present odorous air with odourless air dilutions to a panel of people. However, olfactometry is costly, time consuming, subject to error and incurs delays between sampling and measurement (Hobbs *et al.*, 1995).

Several studies have attempted to identify the individual compounds associated with compost odours using gas chromatography-mass spectrometry (GC-MS) (Miller and Macauley, 1988; Derikx *et al.*, 1990; Duns *et al.*, 1997). Compounds shown to be responsible for compost odour include amines, ammonia, organic acids and most importantly, sulphur containing compounds. However, GC-MS analysis and interpretation is impractical on a day-to-day basis due to the large numbers of compounds involved, cost and the delay between sampling and measurement. However, many of the important odorants can be measured quickly and cheaply using gas detection tubes (Anon, 1997, 1998).

There has been research into the development of electronic nose systems for odour detection and measurement. These instruments employ an array of non-specific electronic gas sensors in an attempt to mimic the human olfactory system by utilisation of artificial intelligence (Gardner *et al.*, 1992). Equipment has been developed for a number of applications, mostly in the food industry, but also for agricultural malodour applications (Persaud *et al.*, 1996; Misselbrook *et al.*, 1997).

The AromaScan (AromaScan plc, Crewe, UK) and Odourmapper (UMIST, Manchester) instruments use an array of conducting polymer sensors, which display reversible changes in electrical resistance when volatile molecules adsorb and desorb from their surface. Such instruments have been shown to successfully distinguish between odours from pig and chicken slurry (Hobbs *et al.*, 1995) between odours from slurry from pigs fed with different diets (Byun *et al.*, 1997) and between breath odours from healthy cows and cows with ketosis (Elliott-Martin *et al.*, 1997).

The objective of the present work was to analyse the odours from mushroom composting using the different methods outlined above, and to determine the relationships between these methods.

### **Materials and Methods**

# Odour sample collection

Odour samples were collected in 20 l Teflon bags by placing the bag in a pressure vessel with a PTFE tubing sampling line connected and then evacuating the vessel, thus drawing sample air into the bag over a 4 min period (Hobbs *et al.*, 1995). The open end of the sampling line was held 0.2 m downwind from the compost heap or stack, during turning. Odour samples were also collected in 5 l Duran bottles fitted with 3-way valve PTFE caps by evacuating the air from the bottle with a pump for 2 min. Odour sample air was drawn into the bottle using a PTFE sampling line as above.

Replicate samples were collected simultaneously. Background samples were collected 200 m upwind of the composting sites. Samples were transported to HRI Wellesbourne for electronic nose analysis and to IGER, North Wyke for GC-MS and olfactometry analysis. Two replicate samples were collected for each of the analyses, which were conducted 24 h after sampling.

Windspeed at the point of odour sampling was measured with a vane anemometer (Type 949079, Airflow Developments Ltd, High Wycombe, UK).

### Composting yards and composts

Odour samples were taken from ten sites: Blue Prince, Chesswoods (Sussex), Hensbys, HRI Wellesbourne, Monaghan Middlebrook (Avon and Market Harborough), Pond Chase, Shepherds Grove and Tunnel-Tech (North and South). Six of the sites produced a windrow Phase I compost, turned at two-daily intervals; three sites had an aerated tunnel Phase I and HRI Wellesbourne produced compost using both types of Phase I. With the exception of HRI, all the sites had separate pre-wet and Phase I areas. At Blue Prince, Chesswoods, HRI, Monaghan (Avon), Shepherds Grove and Tunnel-Tech (South), pre-wetting was conducted partially or completely in windrows. On the remaining sites, pre-wetting was conducted in flat heaps. All the sites used proportions of wheat straw, broiler poultry manure and gypsum, although the proportions of these materials and addition of other manures and additives differed between sites. The total durations of pre-wetting and Phase I composting were 7-14 days and 6-7 days. The duration of the combined pre-wet and Phase I windrows at HRI was 16 days. Phase I tunnel composts at HRI were pre-wetted for 4 days. The pre-wet areas were sampled 3-6 days after setting up of the heaps and the Phase I windrows or tunnels were sampled 3-7 days after the start. The combined pre-wet and Phase I windrows at HRI were sampled after 12 days.

Higher concentrations of compost odorants than those sampled on composting yards were obtained by mixing different proportions of odour samples from aerobic and anaerobic composts controlled at 48°C in flask composting equipment (Noble *et al.*, 1997). These were to simulate the conditions found in anaerobic zones in the centre of composting stacks. All the composts were analysed for moisture, nitrogen and ammonium contents and pH according to methods in Noble and Gaze (1994).

# Olfactometry

A dynamic dilution olfactometer (Project Research, Amsterdam) was used according to recommendations in van den Berg (1992), ie. a forced choice type presentation where six panellists were required to choose between two sniffing ports, one containing odourless air, and the other diluted, odorous air. Threshold values, at which 50% of the panel could just detect an odour, were determined and odour concentration (OC) expressed as Odour Units m<sup>-3</sup> (OU m<sup>-3</sup>) air. A range of six dilutions was presented to the panellists in steps of ascending

concentrations, each differing from the next by a factor of two and each range being presented twice. OC was calculated according to the Dravneiks and Prokov (1975) method. Measurements of the sensitivity of the odour panellists for each set of OC measurements was performed with 198.2 mg m<sup>-3</sup> (60 ppmv) butan-1-ol in nitrogen.

# GC-MS analysis

Volatile compounds were preconcentrated from a 600 ml odour sample by adsorbtion onto silica (Orbo 52, Supelco Inc., Supelco Park, Bellefonte, PA, 16823-0048 USA) and carbon (Orbo 32) based adsorbents. The concentrated odorants were then thermally desorbed from the adsorbents into the GC-MS system for identification and quantification. Chromatographic retention time and mass spectral matching were used to confirm odorant identity. Quantification was performed by desorbing 8 1 of a standard odour identified in the preconcentrated headspace, from the adsorbent.

A Hewlett Packard (hp) (hp Ltd, Heathside Park Road, Cheadle Heath, Stockport, Cheshire, UK) GC-MS system consisting of a 5890 II Series gas chromatograph and a 5972A mass selective detector (MSD II) was used for analysis. A 25 m fused silica (cross linked methyl siloxane) hp-1 column with an internal diameter (id) of 0.2 mm and a 0.34 m film with a

1 m deactivated fused silica guard column (0.25 mm id) were used. The flow rate of the helium the eluting gas was 0.75 ml min<sup>-1</sup>. The Optic temperature programmable injector (Ai Cambridge Ltd, Pampisford, Cambridge, UK) was used to desorb headspace samples from the adsorbents and was initially at 30°C and heated to 16°C s<sup>-1</sup> for 1 min. An electronic pressure controller was used to offset peak pressure broadening with increasing GC column temperature. The GC oven conditions were an initial temperature of 40°C, then to 220°C at 15°C min<sup>-1</sup> and remaining at 220°C for 1 min. The GC-MS interface was at 280°C. The mass spectrometer scanned from 35 to 250 mass units every 0.2 s to give responses in the ng range.

Volatile organic compounds (VOCs) detected by the mass spectometer were identified using a probability based matching algorithm and a NIST mass spectral library. Compounds were declared unknown if their matching probability was less than 80 (100 being a perfect match).

#### Gas detector tubes

A Dräger Accuro bellows pump (Drägerwerk, Lübeck, Germany) was used in conjunction with appropriate detector tubes: acetic acid (6722101), amines (8101061), NH<sub>3</sub> (CH2051 and CH31901), carbon disulphide, CS<sub>2</sub> (8101891), DMS (6728451), H<sub>2</sub>S (8101991 and 8101831), mercaptan (6728981) and phenol (8101641). Detector tubes were used on-site in the same way as sampling odours for collection in Teflon bags, and also on the odour samples in the Teflon bags, 24 h after on-site sampling. Two replicate measurements were made for each sampling.

#### Aromascan electronic nose

A commercially available electronic nose instrument (AromaScan Sample Station, A8S, AromaScan plc, Crewe, UK) was used. The instrument used an array of 32 conducting polypyrrole sensors. A small pump pulled air across the sensor array at approximately 100 ml/min and the change in resistance of individual sensors was recorded as R/R, where R was the change in resistance and R the base resistance of the sensor. The degree of response of each sensor to a given volatile depends upon the type of polymer used, so a pattern of resistance changes across the array was recorded for a particular odour. The instrument incorporated a reference line, which consisted of filtered ambient air of the same relative humidity (rh) as the odour sample, which was used to provide the base resistance for sensors. The odour samples were passed across the sensor array for 8 s.

An initial problem encountered was the high sensitivity of the sensors to ammonia in the odour samples, to the exclusion of a response to other volatiles in the sample. The odour samples were therefore first passed through a Nafion tube gas dryer (Perma Pure Inc., Toms River, New Jersey, USA). Nafion is a copolymer of tetrafluoroethylene (Teflon) and perflouro-3,6-dioxa-4-methyl-7-octane-sulphonic acid. It has selective retention for sulphur compounds, simple hydrocarbons and oxides (CO<sub>2</sub>, SO<sub>X</sub>, NO<sub>X</sub>) but does not retain ammonia, amines, polar organic compounds (alcohols and organic acids) and water vapour. The Nafion tubing (3 mm diameter) was fitted inside a 16 mm diameter PTFE shell tubing. The rh of the air in the shell tubing was controlled to the rh of the odour sample in the Nafion tubing, to avoid changes in the rh of the odour sample. Nafion tube lengths of 0.1, 0.3 and 0.6 m were

used. The odour samples were passed over the sensors for 6 min when the Nafion tubing was used.

The electronic nose was tested with and without the Nafion tubing with known concentrations of the following gases in air: ammonia (NH<sub>3</sub>), dimethyl sulphide (DMS) and hydrogen sulphide (H<sub>2</sub>S). Tests were also conducted on control samples with known concentrations of the above gases with unknown concentrations of other compost odorants, obtained from flask composting equipment.

### Results

# Olfactometric analysis

The OC of the pre-wet and Phase I compost areas of the ten composting yards are shown in Table 2.1. On two yards, C and G, the pre-wet area had a higher OC than the Phase I compost area; the reverse situation was found on three yards, D, F and H, while at sites B, E and I, the OC of the pre-wet and Phase I areas were similar. Pre-wet E had the lowest OC, whereas pre-wet areas C and I had the highest. The lowest Phase I OCs were at yards E and G whereas Phase I area F and I had the highest OC. The background OCs of the sites were lower than the lowest compost OC. Odour samples from flask composting equipment had OCs up to  $7 \times 10^6$  OU m<sup>-3</sup>.

# GC-MS analysis

Odorants detected in the pre-wet and Phase I air samples are shown in Table 2.2. Volatile fatty acids (VFAs) were at higher concentrations in the pre-wet samples than in the Phase I samples, but generally at levels close to or below the lower end of the detection threshold range. Indole was also at a higher concentration in the pre-wet samples than in the Phase I samples, and in both situations, above the detection threshold. Sulphides were the only other group of compounds that were above the detection thresholds. Gas detector tube measurements of  $H_2S$  and mercaptans in Teflon bags, 24 h after sampling, were on average 50% and 59% of those measured with GC-MS ( $r^2 = 0.68$  and 0.49 respectively). In odour samples from flask equipment composts, the following odorants, in addition to sulphides,

were at concentrations above the detection threshold 24 h after sampling: butanoic and pentanoic acids, 4-methyl phenol, indole (Table 2.2).

### Gas detector tubes

On-site measurements of H<sub>2</sub>S, DMS and NH<sub>3</sub> with gas detector tubes are shown in Table 2.3. Pre-wet areas B and I had significantly higher H<sub>2</sub>S concentrations than the other pre-wet areas and the highest Phase I concentrations were at sites A1, D and I. Sites A2, C, E and G had the lowest H<sub>2</sub>S concentrations. Pre-wet areas C and I had the highest DMS and NH<sub>3</sub> concentrations. Phase I areas A1, H and I were highest in DMS and Phase I areas A1, H, I and J were highest in NH<sub>3</sub>. Phase I sites A2, E and G, which produced aerated tunnel composts, had the lowest DMS concentrations.

The concentrations of H<sub>2</sub>S, DMS and NH<sub>3</sub> measured in Teflon bags after 24 h, were on average 52, 59 and 78% of those measured on-site. Thiols could only be detected at site I (0.2 and 0.5 ppm for the pre-wet and Phase I areas) and acetic acid could only be detected in the Phase I area of site I (0.06 ppm). Carbon disulphide and phenol could not be detected with the tubes previously listed on any of the sites. Thiols, acetic acid and phenol could be detected (at up to 28, 0.3 and 0.2 ppm respectively) in odour samples tested immediately from flask composting equipment. Values obtained from the amine test corresponded with the ammonia concentration, ie. additional amines were not detected.

There was a close correlation between the olfactometric OC and the combined concentration of  $H_2S + DMS$  in pre-wet or Phase I odour samples (Fig. 2.1). Data points for site I are not included in Fig. 2.1 since the OUs and  $H_2S + DMS$  concentrations were an order of magnitude greater than the values from the other sites (Table 2.3). Ammonia concentrations were above the detection threshold in most of the odour samples, but were not correlated with OC.

### Electronic nose

The results are presented as the change in resistance of the 32 sensors relative to the base resistance in air of the same rh (R/R). This response is affected both by the chemical species present and their intensity. The relative response of the 32 sensors can also be

presented as a normalised response to produce a 'fingerprint' which is characteristic of the chemical species adsorbed (Persaud *et al.*, 1996). In this situation, the response of the sensors is expressed as a proportion of the response of the entire array of 32 sensors so that the intensity components are nearly eliminated.

The duration that the odour samples pass over the sensors could be varied. Due to strong response of the sensors to the odour samples in the absence of the Nafion tubing, this period was restricted to 8 s so that R/R did not generally exceed 15%. The average response of each sensor over this period was used. In the presence of the Nafion tubing, the response of the sensors to the odour samples was delayed and much weaker, so that the period of sensing could be extended to 6 min without R/R exceeding 15%. The average response of each sensor over the final 10 s of this period was used.

Compared with Teflon bag samples, there was a significant reduction in the sensor response in samples from Duran bottles due to the gradual dilution of the sample with in-blowing air. All tests were therefore conducted with samples collected in Teflon bags.

Ammonia response. All the sensors of the Aromascan responded positively to ammonia at concentrations below 2 ppm. The normalised responses of the sensors to 2 and 50 ppm NH<sub>3</sub> were similar (Fig. 2.2) with sensor numbers 19 and 31 producing the strongest response. There was a positive relationship between the NH<sub>3</sub> concentration in compost odour samples and the average sensor response during the first 8 s of sampling (Fig. 2.3). The effect of passing the sample through different lengths of Nafion tube on the average sensor response is shown in Fig. 2.4. The sensor response was over the final 10 s of a 6 min sampling period. A 0.3 m length tube significantly reduced the sensor response. With a 0.6 m length tube, NH<sub>3</sub> could still be detected at 3 ppm (Fig. 2.2), but there was little effect of NH<sub>3</sub> concentration up to 600 ppm NH<sub>3</sub> on average sensor response (Fig. 2.4). Using a 0.3 m length tube, there was still a positive relationship between the NH<sub>3</sub> concentration in compost odour samples and average sensor response, but no relationship using a 0.6 m length tube (Fig. 2.5).

Hydrogen sulphide and DMS responses. All of the Aromascan sensors responded negatively to both hydrogen sulphide and DMS (Figs. 2.6 and 2.7) although the responses were weak and more delayed than for NH<sub>3</sub>. The normalised responses to 50 and 180 ppm H<sub>2</sub>S or DMS

were similar, as were the normalised responses to 20 and 110 ppm DMS (Figs. 2.6 and 2.7). The strongest (negative) responses to both  $H_2S$  and DMS were generally in sensors 19, 21 and 31. Lower concentrations of  $H_2S$  or DMS resulted in a loss in the normalised response pattern for the particular gas. Passing the samples through a 0.6 m length Nafion tube did not significantly change the sensor response to  $H_2S$  or DMS (Fig. 2.8). The detection thresholds for  $H_2S$  and DMS were about 50 ppm and 20 ppm.

There were negative relationships between average sensor response and the concentrations of H<sub>2</sub>S or DMS in compost odour samples, after passing through a 0.6 m Nafion tubing (Fig. 2.9). These relationships were not present without the use of Nafion tube and all of the odour samples in Fig. 2.9 produced positive sensor responses due to the presence of NH<sub>3</sub>.

Compost odour mixture responses. The effect of passing compost odour samples through Nafion tubing on the Aromascan sensor response to two different mixtures of NH<sub>3</sub>, H<sub>2</sub>S and DMS is shown in Fig. 2.10. Without Nafion tubing, the NH<sub>3</sub> component (50 ppm) dominated, producing strong positive responses in all the sensors (Fig. 2.10a). After the gas mixtures were first passed through a 0.6 m length of Nafion tube, the H<sub>2</sub>S and DMS components dominated (both 60 ppm), producing negative responses in all the sensors (Fig. 2.10b). However, if the H<sub>2</sub>S and DMS components were below their sensor detection thresholds, there was either no significant sensor response or, if NH<sub>3</sub> was present, a positive sensor response (Fig. 2.10c). Site I, which had high NH<sub>3</sub>, H<sub>2</sub>S and DMS concentrations, produced negative sensor responses for both the pre-wet (Fig. 2.10d) and Phase I samples with the Nafion tube, but positive responses without. Compost odour samples with OCs of 30,000 OU m<sup>-3</sup> could not be distinguished from less odorous samples with OCs of less than 10,000 OU m<sup>-3</sup> from either the average sensor response or normalised sensor response pattern. Using compost odour samples from anaerobic composting flasks and very odorous compost yard samples (site I) with OCs of above 50,000 OU m<sup>-3</sup>, there was a negative relationship between average sensor response and OC (Fig. 2.11).

Windspeed at the point of sampling ranged from 0 to 4.5 m s<sup>-1</sup> (mean 2.4 m s<sup>-1</sup>), but there were no relationships between windspeed and any of the odour analyses.

# Discussion

Maximum odour concentrations recorded during pre-wetting and turning of Phase I windrows were generally similar to those previously recorded in similar locations on a mushroom composting yard (26,820 and 27,800-33,400 OU m<sup>-3</sup>, NB Gibson, 1996, unpubl.). Bidlingmaier (1992) recorded OCs of up to 17,400 OU m<sup>-3</sup> during the turning of piles of organic waste compost. Two aerated Phase I tunnels produced lower OCs than levels reported by van der Hoek and Oosthoek (1985) for aerated composting piles of organic waste (2400 OU m<sup>-3</sup>) but one aerated Phase I site produced a significantly higher odour level, probably due to inadequate aeration. Perrin and Macauley (1995) reported reductions in OC of 83-96% as a result of aerating Phase I composting, compared with conventional turned windrows.

Sulphur containing compounds in compost odours were found to be most important in exceeding detection thresholds, in agreement with Miller and Macauley (1988), Derikx *et al* (1990) and Duns *et al* (1997). Concentrations of H<sub>2</sub>S and DMS from Phase I stacks during turning were greater than those from static windrows reported by Derikx *et al*, 1990 (maximum concentrations of about 0.5 ppm) and much greater than those reported by Duns *et al* (1997) (0.5-2 ppb and 1-5 ppb DMS for pre-wet and Phase I areas). However, the latter workers did not state the distance at which odour samples were taken from the compost odour source. Derikx *et al* (1990) found that the main sulphide emitted during the earlier part of the Phase I process was DMS; this was followed by a build-up of H<sub>2</sub>S; these gases were exceeded by methanethiol, carbon disulphide and dimethyl disulphide concentrations during the latter stages while dimethyl trisulphide emissions were small and constant. The main sulphides found here during the pre-wet and Phase I stages were H<sub>2</sub>S and DMS; levels of other methyl sulphides and thiols were close to or below their detection thresholds. Carbonyl sulphide and carbon disulphide, which were recorded by Derikx *et al* (1990) were not detected in the compost yard odour samples.

The decay in H<sub>2</sub>S in the Teflon sampling bags of 48% d<sup>-1</sup> was significantly less than 32% h<sup>-1</sup> recorded by Hobbs *et al* (1997) for odour samples from pig slurry. However, they found that under the same conditions, the decay in H<sub>2</sub>S could be as low as 20% d<sup>-1</sup>. They also found that the decay of the OC was similar to the decay of the H<sub>2</sub>S concentration. Due to the

number of compounds contributing to the odour of the pig slurry, no relationship between OC and the concentration of particular compounds was found.

The sensitivity of the electronic nose in detecting OCs greater than 50,000 OU m<sup>-3</sup> is similar to that reported by Hobbs et al (1995) for detecting odours from pig and chicken slurry. Such high OCs may be typical of conditions in anaerobic zones in composting windrows. where Miller et al (1991) recorded H<sub>2</sub>S concentrations up to 50,000 ppm. Misselbrook et al (1997) were able to detect much lower OCs of 50-1000 OU m<sup>-3</sup> from cattle slurry with an AromaScan electronic nose, but the important odorous volatile compounds (VFAs and indole) differed from those in compost odours. However, they found a positive relationship between OC and average electronic nose sensor response, and this may have been due to the presence of NH<sub>3</sub> in the odour samples since VFAs produced a negative sensor response. As in the present work, NH<sub>3</sub> concentrations were not found to be a universally good indicator compound for OC from farm wastes (Misselbrook et al, 1997) or compost odour (Gulliver et al, 1991). The high sensitivity and positive response of conducting polymer sensors to NH<sub>3</sub> reported by Persaud et al (1996) and Misselbrook et al (1997) is similar to that found here. Hobbs (unpubl.) showed that DMS produced positive and negative responses in different AromaScan sensors, whereas all the sensors in a different polypyrrole array responded negatively to DMS in the present work. Miasik et al (1986) showed H<sub>2</sub>S produces a weak negative response in polypyrrole sensors, similar to that found here.

Elliott-Martin *et al* (1997) and Byun *et al* (1997) used principal component analysis and Sammon mapping analysis of the normalised response pattern of electronic nose sensors for distinguishing various agricultural malodours. However, these clustering analysis techniques could not distinguish odorous from non-odorous compost yard odour samples in the present work. This was due to the most important odorous compounds in the compost yard odour samples, H<sub>2</sub>S and DMS, generally being at concentrations below their AromaScan detection thresholds.

### Conclusions - Part 2

Sulphur containing compounds in compost odours were found to be most important in exceeding detection thresholds.

There was a close correlation between the compost odour concentration (OC) of the pre-wet and Phase I composts sampled and the combined H<sub>2</sub>S concentrations from gas detector tubes. Concentrations of NH<sub>3</sub> were above the detection threshold in most of the odour samples, but were not correlated with OC.

Using GC-MS, a range of other sulphides and VFAs were recorded in compost yard odours at concentrations close to their detection thresholds.

An AromaScan electronic nose produced positive sensor responses to NH<sub>3</sub> at concentrations of less than 2 ppm and negative responses to H<sub>2</sub>S and DMS above concentrations of 50 and 20 ppm.

Ammonia dominated the sensor response unless the sample gas was passed through a 'Nafion' tube which selectively removed NH<sub>3</sub> but retained sulphides.

The AromaScan could distinguish anaerobic odours from composts with OCs of above 50,000 OU m<sup>-3</sup> (typical of anaerobic zones in windrows) from less odorous composts. The former produced negative sensor responses whereas the latter produced positive or no sensor responses.

The AromaScan can be used for discriminating strong anaerobic odours in flask composting equipment, for example, to examine the effects of different compost ingredients and microfloral inocula on odour, but is not sufficiently sensitive to sulphides for most on-site measurements. For this situation, H<sub>2</sub>S and DMS detector tubes are more appropriate and relate to odour panel measurements with over 80% accuracy.

OCs and sulphide concentrations from three out of four aerated Phase I tunnel sites were significantly lower than from six conventional Phase I windrow composting sites sampled.

Table 2.1. Odour concentrations by olfactometry for compost yards

|                     | Odoui      | concentration, OU m | ı <sup>-3</sup> air |
|---------------------|------------|---------------------|---------------------|
| Compost yard        | Background | Pre-wet             | Phase I             |
| A                   | 83         | -                   | 17894ª              |
| В                   | -          | 11796               | 10316               |
| C                   | -          | 26777               | 3965                |
| D                   | -          | 6721                | 20139               |
| Е                   | -          | 1209                | 919                 |
| F                   | -          | 10467               | 31823               |
| G                   | 56         | 6146                | 666                 |
| Н                   | 210        | 10144               | 19607               |
| I                   | 608        | 245100              | 263758              |
| J                   | 321        | <b></b>             | 13015               |
| L.S.D. $(P = 0.05)$ |            | 98                  | 38                  |

<sup>&</sup>lt;sup>a</sup> Windrow compost

Table 2.2. Concentrations<sup>a</sup> and odour detection thresholds<sup>b</sup> for odorants identified with GC-MS in compost yard and flask composting odour samples, mg m<sup>-3</sup> air

| Odorant                 | Pre-wet            | Phase I          | Flask      | Detection |
|-------------------------|--------------------|------------------|------------|-----------|
|                         |                    |                  | max. conc. | threshold |
| Acetic acid             | 1.6 (±0.94)        | 0.6 (±0.08)      | 3.9        | 25-10000  |
| Ammonia                 | -                  | -                | <u></u>    | 26        |
| Propanoic acid          | 2.0 (±1.92)        | 0.3 (±0.26)      | 2.0        | 3-890     |
| 2-Methyl propanoic acid | $0.1~(\pm 0.03)$   | 0.1 (±0.04)      | 1.0        | 72        |
| Butanoic acid           | 1.3 (±1.20)        | 0.1 (±0.08)      | 11.3       | 4-3000    |
| 3-Methyl butanoic acid  | 0.3 (±0.28)        | 0.2 (±0.16)      | 6.8        | 5         |
| 2-Methyl butanoic acid  | 2.0 (±0.31)        | 0.1 (±0.07)      | 2.0        | 20        |
| Pentanoic acid          | $0.3 \ (\pm 0.30)$ | 0.2 (±0.20)      | 3.4        | 0.8-70    |
| Phenol                  | $0.1 \ (\pm 0.08)$ | 0.1 (±0.06)      | 0.5        | 22-4000   |
| 4-Methyl phenol         | 0.1 (±0.05)        | 0.1 (±0.06)      | 0.5        | 0.22-35   |
| 4-Ethyl phenol          | $0.1~(\pm 0.08)$   | 0.1 (±0.09)      | 0.4        |           |
| Indole                  | 7.1 (±7.06)        | 3.2 (±3.05)      | 7.1        | 0.6       |
| Ethanol                 | 18.6 (±11.85)      | 7.4 (±7.35)      | 13.3       |           |
| Butanol                 | $1.9~(\pm 0.95)$   | 1.7 (±0.45)      | 31.3       |           |
| Propanol <sup>c</sup>   | -                  | -                | 11.8       |           |
| Acetone                 | 2.8 (±1.92)        | 6.8 (±6.75)      | 5.6        |           |
| Hexane                  | 0.3 (±0.15)        | $0.6 (\pm 0.30)$ | 1.8        |           |
| Iso-propyl-alcohol      | 0.5 (±0.44)        | 0.2 (±0.19)      | 5.5        |           |
| Dimethyl sulphide       | 2.5 (±2.1)         | 2.2 (±1.9)       | 360        | 2-30      |
| Dimethyl disulphide     | 1.3 (±1.26)        | 0.8 (±0.71)      | 107        | 3-14      |
| Dimethyl trisulphide    | 0.5 (±0.24)        | 0.2 (±0.20)      | 11.0       | 7.3       |
| Methanethiol            | 0.6 (±0.45)        | 0.3 (±0.26)      | 60.8       | 0.5       |
| Methyl sulphide         | 0.8 (±0.74)        | 0.3 (±0.24)      | 121        |           |
| Hydrogen sulphide       | 1.6 (±1.44)        | 3.0 (±2.35)      | 400        | 0.1-180   |
| Carbon disulphide       | -                  |                  | -          | 1.6       |

<sup>&</sup>lt;sup>a</sup> Mean and ± standard deviation

<sup>&</sup>lt;sup>b</sup> After van Gemert and Nettenbreijer (1977)

<sup>&</sup>lt;sup>c</sup> Only detected in pre-wet and Phase I samples I (44.5 and 2.4 mg m<sup>-3</sup> air)

Table 2.3. Gas detector tube measurements at compost yards

| Compost          | H <sub>2</sub> S |         | DN      | MS .    | NH <sub>3</sub> |         |  |
|------------------|------------------|---------|---------|---------|-----------------|---------|--|
| yard             | Pre-wet          | Phase I | Pre-wet | Phase I | Pre-wet         | Phase I |  |
| A1 <sup>a</sup>  | <del>-</del>     | 5.3     |         | 4.2     | _               | 135     |  |
| A1               | -                | 39.0    | -       | 7.0     | -               | 71      |  |
| A2               | -                | 0.2     | -       | 0.1     | -               | 35      |  |
| В                | 10.0             | 4.0     | 2.0     | 4.0     | 5               | 40      |  |
| C                | 0.3              | 0.5     | 12.0    | 1.0     | 120             | 30      |  |
| D                | 2.5              | 11.0    | 2.4     | 1.0     | 5               | 30      |  |
| Е                | 0.3              | 0.05    | 0.2     | 0.2     | 8               | 35      |  |
| F                | 1.5              | 6.5     | 0.1     | 4.0     | 19              | 4       |  |
| G                | 0.15             | 0       | 1.0     | 0.6     | 14              | 15      |  |
| Н                | 0.8              | 3.0     | 2.2     | 6.9     | 22              | 110     |  |
| Ι                | 56.7             | 95.0    | 24.3    | 97.1    | 27              | 276     |  |
| J                | -                | 3.2     | -       | 3.6     | -               | 180     |  |
| L.S.D. <i>(P</i> | = 0.05)          | 0.6     | 0       | .5      |                 | 4       |  |

<sup>&</sup>lt;sup>a</sup>A1 – Windrow compost, sampled on two separate occasions; A2 – Tunnel compost

Table 2.4. Analysis of pre-wet materials and Phase I composts

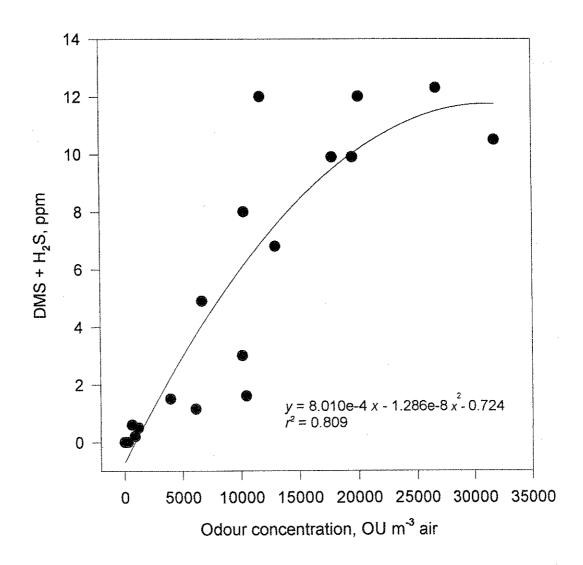
| Compost         | Moisture % |         | рН      |     | % DM     |      |         |      |
|-----------------|------------|---------|---------|-----|----------|------|---------|------|
| yard            |            |         |         |     | N        | N    |         |      |
|                 | pre-wet    | PhI     | pre-wet | PhI | pre-wet  | PhI  | pre-wet | PhI  |
| A1 <sup>a</sup> | -          | 77.2    | - W     | 8.0 | <u>.</u> | 2.19 | -       | 0.58 |
| A1              | <u>-</u>   | 77.9    | -       | 8.2 |          | 2.04 | -       | 0.41 |
| A2              | -          | 76.9    | -       | 7.8 | -        | 3.64 | -       | 0.30 |
| В               | 78.5       | 76.9    | 8.1     | 8.0 | 1.83     | 2.28 | 0.21    | 0.61 |
| С               | 72.3       | 76.2    | <u></u> | 8.4 | -        | 2.35 | -       | 0.41 |
| D               | 79.9       | 75.0    | 8.3     | 7.6 | 1.42     | 1.55 | 0.52    | 0.49 |
| E               | -          | <u></u> | <u></u> | -   | -        | -    | -       | -    |
| F               | 78.1       | 78.4    | 8.2     | 8.2 | 1.47     | 1.72 | -       | 0.35 |
| G               | 77.4       | 75.3    | -       | 7.7 | 1.73     | 1.99 | -       | 0.46 |
| H               | 77.3       | 74.3    | 8.1     | 8.1 | 1.96     | 2.06 | 0.72    | 0.46 |
| I               | -          | 74.5    | -       | 8.3 | -        | 2.20 | -       | 0.70 |
| J               | -          | 75.9    | •••     | 8.5 | No       | 2.52 | -       | 0.63 |

 $<sup>^{\</sup>rm a}$  A1 – Windrow compost, sampled on two separate occasions; A2 – Tunnel compost

Table 2.5. Analysis of aerobic and anaerobic flask composts

| Compost   | Moisture %   | рН          | % DM         |                              |
|-----------|--------------|-------------|--------------|------------------------------|
|           |              | ·····       | N            | NH <sub>4</sub> <sup>+</sup> |
| Aerobic   | 78.0 (±1.92) | 8.4 (±0.20) | 1.72 (±0.28) | 0.46 (±0.03)                 |
| Anaerobic | 79.2 (±2.37) | 8.2 (±0.17) | 1.89 (±0.21) | 0.40 (±0.08)                 |

Fig.2.1 Relationship between odour concentration and the combined H<sub>2</sub>S and DMS concentration of compost yard odour samples



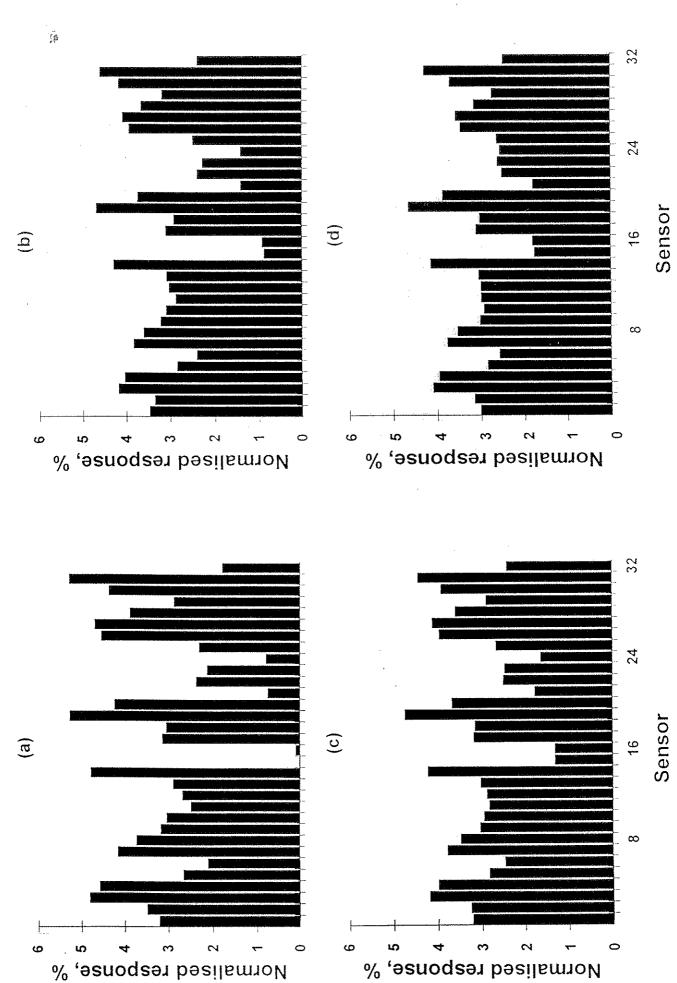


Fig.2.2 Ammonia AromaScan normalised response patterns of each sensor relative to the response of the entire arrav (a) 2 ppm (b) 30 ppm (c) 3 ppm, with Nafion tube (d) 600 nnm with Nafion tube

Fig.2.3 Average AromaScan sensor response to ammonia in compost odour samples, average of first 8 sec of response

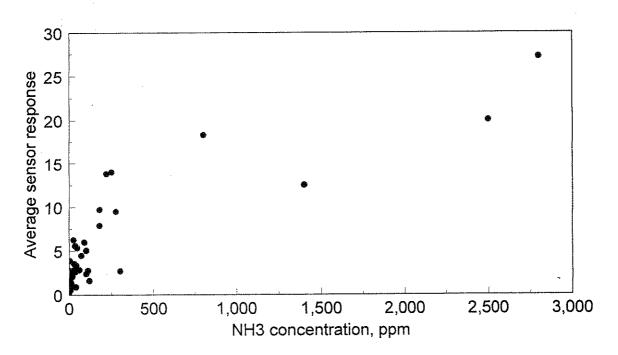


Fig. 2.4 Effect of different Nafion tube lengths on the average sensor response of the Aromascan to ammonia

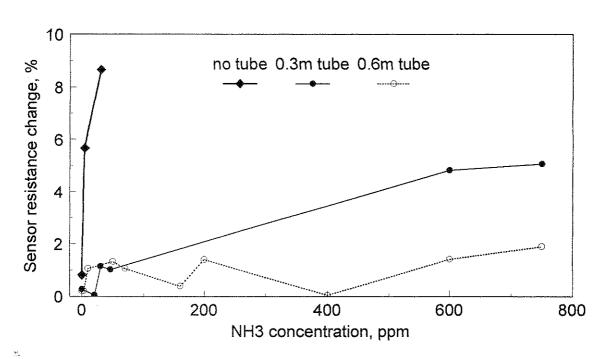
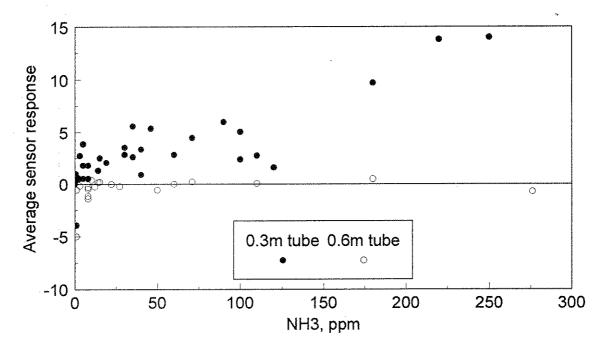


Fig.2.5 Effect of different Nafion tube lengths on the average sensor response of the AromaScan to ammonia in compost odour samples



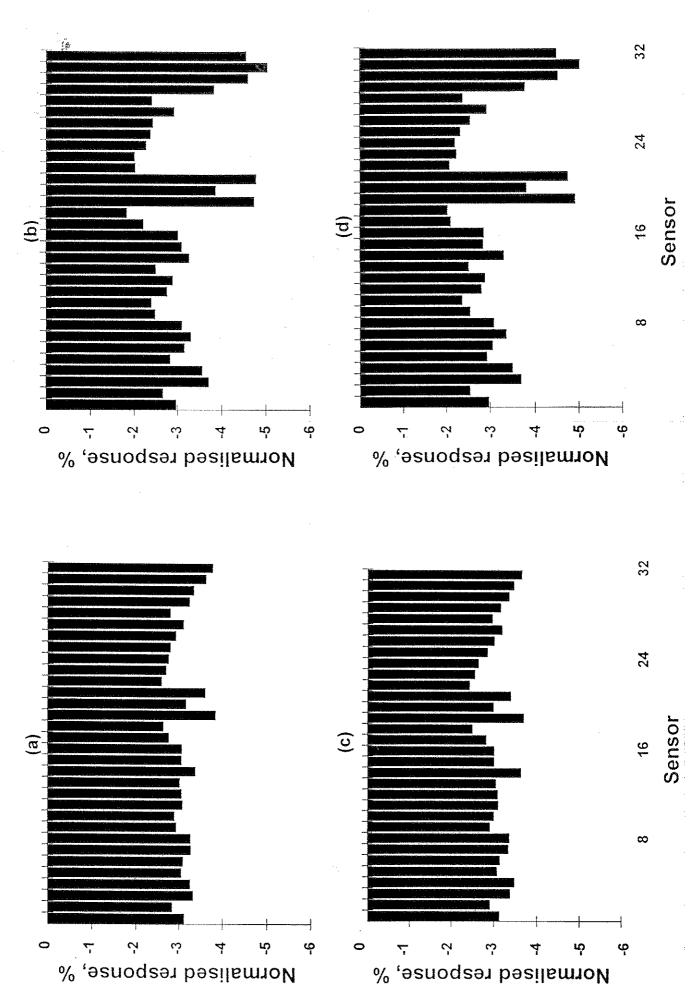


Fig.2.6 Hydrogen sulphide AromaScan normalised response patterns of each sensor relative to the response of the entire array (a) 60 ppm (b) 180 ppm (c) 60 ppm, with Nafion tube (d) 200 ppm with Nafion tube

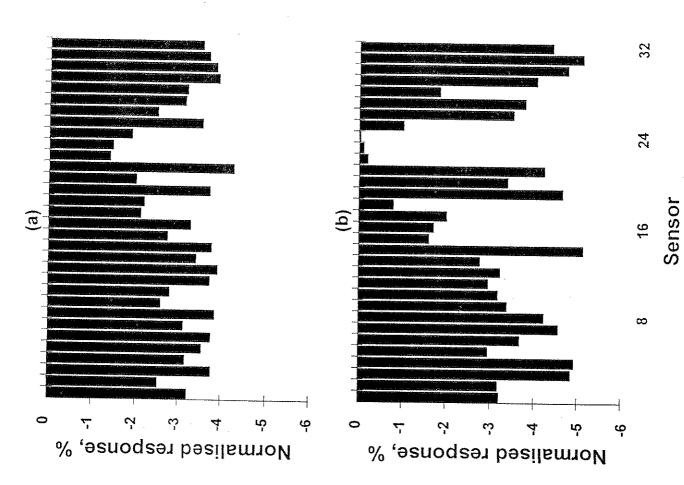
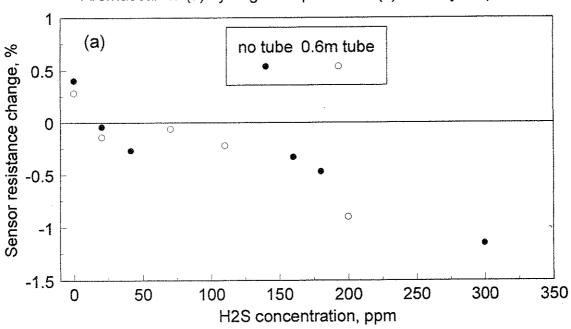


Fig.2.7 Dimethyl sulphide AromaScan normalised response patterns of each sensor relative to the response of the entire array (a) 26 ppm, with Nafion tube (b) 110 ppm with Nafion tube

Fig. 2.8 Effect of Nafion tube on the average sensor response of the Aromascan to (a) hydrogen sulphide and (b) dimethyl sulphide



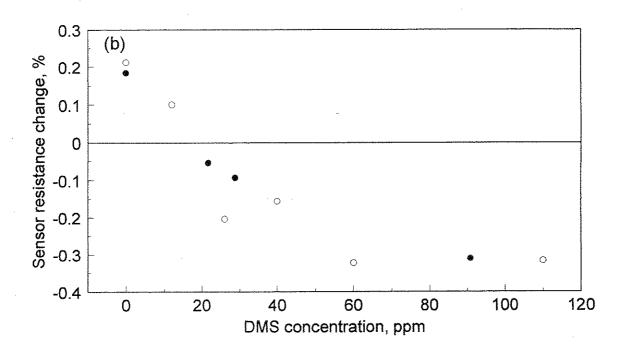
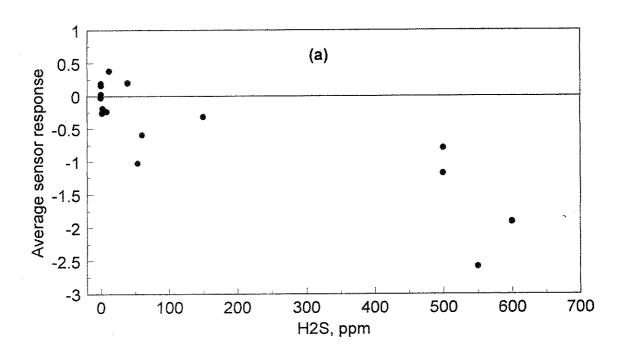
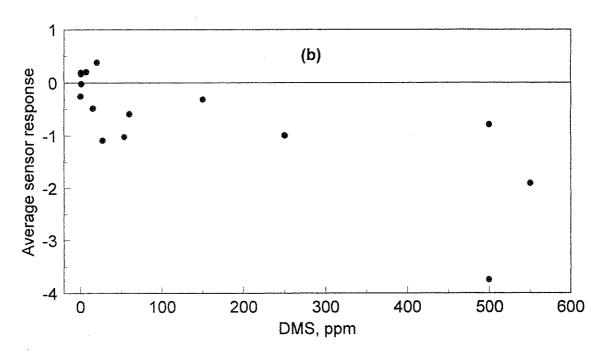


Fig. 2.9 Relationship between (a) H2S and (b) DMS in compost odour samples and AromaScan average sensor response with Nafion tube





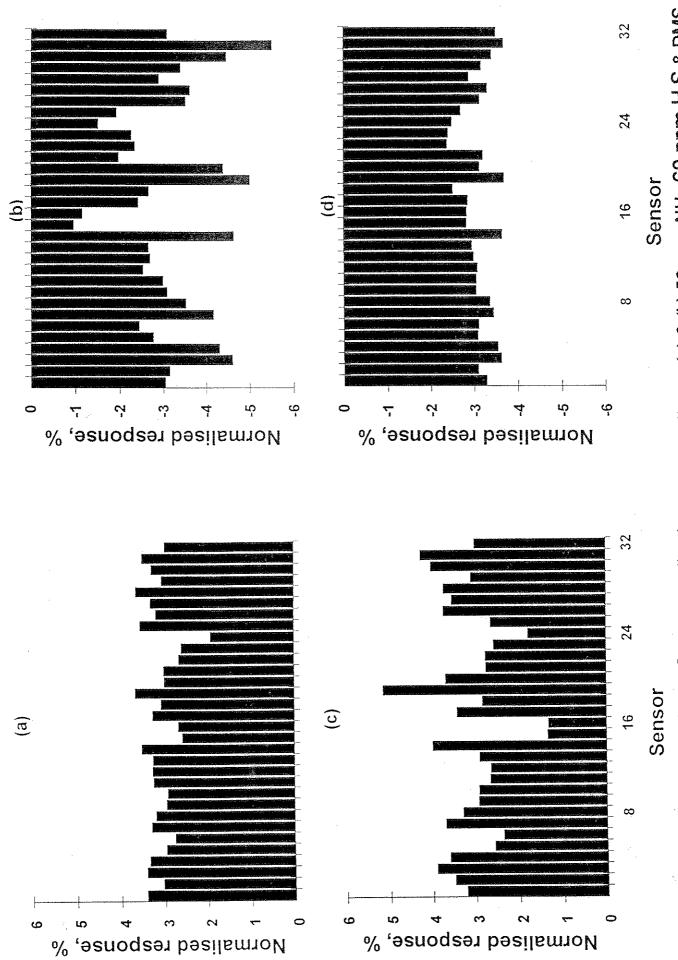
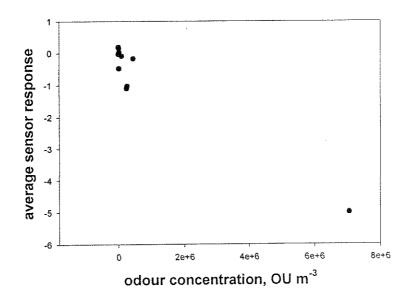


Fig.2.10 Compost odour AromaScan normalised response patterns. (a) & (b) 50 ppm NH<sub>3</sub>, 60 ppm H<sub>2</sub>S & DMS (c) 71 ppm NH<sub>3</sub>, 39 ppm H<sub>2</sub>S, 7 ppm DMS (d) site I pre-wet. (b) (c) & (d) with Nafion tube.

Fig.2.11 Relationship between odour concentration and AromaScan average sensor response



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