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Development of odour-free mushroom compost by modifying the

organic and inorganic nitrogen sources and process technology

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#### PRACTICAL SECTION FOR GROWERS

This report covers progress during the second year of the project and is divided into three parts, with the overall objective of developing a quantifiable method of producing odour-free mushroom composts.

The three sections involve developing:

- alternatives to broiler poultry manure as a nitrogen source in mushroom compost
- methods for quantifying mushroom composting odours
- microbial inocula which metabolise the odorants produced during composting

## Part 1: Alternative Nitrogen Sources

Mushroom substrates were prepared in aerated bulk composting tunnels using two types of straw (wheat or oil seed rape) and different organic and inorganic nitrogen sources. All the compost ingredient treatments were compared at two nitrogen rates: 1.8 and 2.2% of dry matter at filling of Phase O. All the composts were prepared using the same composting regime: a seven-day mixing and blending stage, two aerated, high temperature tunnel stages, Phases O and I of five and six days respectively and a conventional Phase II pasteurisation.

Wheat straw could be replaced by rape straw and poultry manure could be replaced by spent hop powder without significantly affecting mushroom yield, and in both cases, with an increase in compost bulk density. Yields using cocoa meal waste or inorganic nitrogen sources (ammonium sulphate or urea) were lower than those from straw and poultry manure composts. It may be possible to use these latter nitrogen sources with an extended period of pre-mixing. Ammonium sulphate reduced compost pH whereas spent hop powder increased compost pH; a mixture of ammonium sulphate and spent hop powder may produce a suitable compost pH.

There was no significant difference in mushroom yield between composts with initial nitrogen rates of 1.8 or 2.2% of dry matter, for poultry manure, urea or cocoa meal waste. With ammonium sulphate, and spent hop powder composts, mushroom yields were significantly reduced by increasing the initial nitrogen content, probably due to adverse effects on compost pH.

Odour concentrations and air sulphide levels were higher in composts which included poultry manure or high levels of spent hop powder, than in composts incorporating inorganic nitrogen sources or cocoa meal waste.

## Part 2: Odour Quantification Techniques

The aims of the experiments in Year 2 of the project were:

- 1. to obtain further odour samples from each of the composts yards sampled in Year 1, together with samples from a new entrant to the consortium.
- 2. to analyse the odour samples using the following methods and determine any relationships between the methods
  - (i) odour panel serial dilution (olfactometry)
  - (ii) chemical analysis using gas chromatography-mass spectrometry (GC-MS)
  - (iii) gas detector tubes for specific odorants
  - (iv) electronic sulphide detectors.
- 3. to determine the effects of aeration during pre-wet and Phase I composting and compost analysis on odour and gaseous emissions.

Sulphur containing compounds in compost odour samples were found to be important in exceeding detection thresholds, but volatile fatty acids and triethylamine were also found in odour samples at concentrations exceeding their detection thresholds.

There was a close correlation between the compost odour concentration of the pre-wet and Phase I composts sampled and the combined hydrogen sulphide + dimethyl sulphide concentrations from gas detector tubes. Concentrations of ammonia were above the detection threshold in most of the odour samples, but were not correlated with odour concentration.

Two electronic instruments (a pulsed fluorescence sulphur dioxide analyser produced by Thermo Environmental Instruments Ltd and a 'chemcassette' produced by Zellweger Analytics Ltd) were found to be sensitive to sulphur containing compounds at concentrations less than 60ppb. Their use in detecting low odour concentrations should be investigated further.

Odour concentrations and sulphide levels from aerated composting systems were generally lower than those from non-aerated systems. Higher total compost nitrogen resulted in greater ammonia emissions but there were no correlations between the analysis of composts and the resulting odour concentrations.

# Part 3: Microbial Degradation of Hydrogen Sulphide and Dimethyl Sulphide in Compost

The aim of this part of the project is to remove or break down odorous sulphur containing compounds produced during composting. A strain of *Hyphomicrobium* has been identified which removes hydrogen sulphide from compost samples in a bench-scale composting system. A larger-scale system is being developed to examine the introduction of suitable strains on the removal of odorous sulphur-containing compounds.

# **Actions Points for Growers**

- 1. Replacement of broiler poultry manure with spent hop powder should result in reduced odour emissions without affecting compost quality. The compost nitrogen content at the end of Phase I should not exceed 1.8% of dry matter, otherwise the pH of the compost with spent hop powder may be too high.
- 2. Replacing wheat straw with rape straw reduces the poultry manure requirement by about 10%, since the rape straw has a higher nitrogen content. This should reduce odour emissions.
- 3. Using ammonium sulphate, urea or cocoa meal waste requires a longer period of composting than broiler poultry manure, to achieve an equivalent amount of compost breakdown and/or availability of nitrogen.
- 4. Compost nitrogen levels above 1.8% of dry matter at filling of pasteurisation tunnels did not increase mushroom yields but resulted in greater odour emissions in the experiments.
- 5. Aeration of pre-wet and Phase I areas results in a significant reduction in compost odours.
- An indication of likely odour levels from a pre-wet or Phase I compost can be obtained by using hydrogen sulphide and dimethyl sulphide detector tubes. Any detectable levels, one metre from the compost, are likely to produce an odour problem at a greater distance; levels exceeding 1ppm are likely to produce a significant odour off-site.

# **Project Milestones**

Task	Target Date	Milestones
1/1	12 months	Methodology to monitor and sample odours developed: Relationship between laboratory-based odour quantification techniques and subjective methods established (HRI, IGER, Aromascan plc)
1/2 1/3	12 months	Organic waste N sources analysed and processed into odour- free forms (HRI, Bulrush, Holdsworthy Bioplant)
1/4	12 months	Different N sources compared in laboratory-based composting processes; N balance in substrate and its biomass and mushrooms determined (HRI)
	12 months	Consortium to decide whether odour quantification techniques are sufficiently reliable to use in intermediate and large scale composting experiments or whether further laboratory development is needed. Decision on which N sources should be taken into intermediate scale facilities.
2/1 .	18 months	If Task 1/1 completed on time, odour quantified in intermediate-scale facilities and bulk chamber composts using GC-MS, olfactometry and electronic nose (HRI-W, Aromascan, IGER)
2/2	24 months	Composting temperature and aeration regimes developed for bulk chambers (HRI)
2/3	24 months	If Tasks 1/1 and 1/2 were completed on time, quantitative methods for measuring smell at commercial sites will have been developed (Industrial partners a - f, HRI, IGER, Aromascan)
2/4	24 months	If Task $2/3$ was completed on time, odour of conventional composting will have been quantified (Industrial partners $a-f$ , IGER, Aromascan)
2/5	24 months	Evaluation of N sources in bulk chamber experiments completed (HRI)
	24 months	Consortium to decide on which temperature/aeration regime(s) and composting system(s) to be used for larger scale experiments, or whether further intermediate scale experiments are needed to develop the regimes. Decision on which N sources are suitable for larger scale experiments.

	24 months	Decision on whether odour quantification of conventional composting sites is reliable or whether further assessments or development of quantification techniques are needed.
3/1	30 months	Influence of microbial inoculation on odour emissions and degradation and additives to enhance water retention determined in laboratory conditions. (HRI)
3/2	30 months	Compost odours synthesised in the laboratory to test the parameters of the electronic nose (IGER).
	30 months	Consortium to assess the performance of microbial inocula in reducing odour levels. Decision on whether larger scale experiments with microbial inocula can commence.
3/3	36 months	If Task $2/2$ was completed on time, temperature and aeration regimes will have been evaluated at commercial sites (Industrial Partners $a-f$ , HRI).
3/4	36 months	Evaluation of N sources in commercial scale experiments completed (HRI, Bulrush, Holdsworthy Bioplant, Industrial Partners $a-f$ ).
	36 months	Consortium to compare conventional and experimental composting odour levels and to decide what levels of improvement are necessary in the experimental and commercial systems. Consortium to decide which further developments in N sources are required.
4/1	42 months	If Tasks 3/1 was completed on time, the effect of microbial additives and methods for enhancing compost water retention in bulk chamber experiments will have been determined (HRI).
4/2	42 months	Modified N sources further examined in laboratory experiments; methods for reducing N losses from compost determined (HRI).
	46 months	Consortium to decide on the format of the manual and preparation of remaining publications.
4/3	47 months	Combined effect of new composting regimes, N sources, microbial additives and methods of enhancing water retention determined at commercial sites (Ind. Partners a-f; HRI)
4/4	48 months	Production of a manual on odour assessment, compost preparation and N sources in compost (HRI, IGER and Industrial Partners)

All the milestones to the end of Year 2 have been achieved. The remaining milestones should be achieved within the timescales specified.

#### SCIENCE SECTION

## Part 1: Alternative Nitrogen Sources

The main nitrogen (N) source used in mushroom compost is broiler poultry manure. This material has a serious odour problem, both on its own and when incorporated into compost. In the first year of the project, a number of alternative organic and inorganic N sources were examined using a flask composting system. Several of these materials were found to produce an equivalent mushroom yield to broiler poultry manure but with significantly less odour. The aim of the experiments in Year 2 of the project was to examine the most promising nitrogen sources using 4-tonne batches of compost in a bulk tunnel facility.

#### Materials and Methods

# Composting tunnels

Six aerated bulk composting tunnels at HRI Wellesbourne were used for the experiments. Compost was filled on to a slatted base in the tunnels, mounted above an air plenum through which a controlled flow of fresh and/or recirculated air could be blown. Two of the tunnels consisted of modified insulated cargo containers. Both of these tunnels had a vertical partition, which did not extend into the air plenum below, to enable two different composts to be filled into each tunnel (Type A). The other four tunnels consisted of insulated polythene tunnels, inside which were two parallel walls, joined by a wall at one end (Type B). The compost was enclosed by a removable end wall, which fitted across the sidewalls. Details of the tunnels, temperature, oxygen and air flow measurement and control, methods for filling and emptying the tunnel and methods for measuring ammonia concentrations are given in Noble & Gaze (1994 & 1998).

## Preparation of materials

The substrates were prepared from wheat (*Triticum aestivum*) or oilseed rape (*Brassica napus*) straw as the main carbon (C) source and different organic and inorganic nitrogen sources (Table 1). Rape straw was only used with broiler poultry manure. The proportions of carbon and nitrogen sources in the formulation were calculated on the basis of their N and dry matter (DM) contents using the formula in Noble & Gaze (1994) to achieve blended ingredients with nitrogen contents of 1.8 or 2.2% w/w dry matter (Table 1).

Bales of 6-7 month old straw were wetted and formed into stacks using a compost turning machine. Further water was added to the straw in a separate turn to achieve a moisture content of 70%. After 4 days, 50% of the required N source was mixed into the stack; the remaining nitrogen source and gypsum at 30 kg tonne<sup>-1</sup> fresh compost ingredients were mixed into the stack after a further 2 days. Water was added in a further three turns after day 4, to achieve a moisture content of 78%. Water applications were 2.3 - 2.7 and 3.1 - 3.5 m<sup>3</sup>/t dry compost ingredients for organic and inorganic nitrogen source treatments respectively.

Stack temperatures were monitored with platinum resistance sensors and data logger. The preparation time for the blended compost ingredients, before filling into the tunnels was seven days.

## Tunnel composting regime

The tunnels were filled with 4 t batches of blended compost ingredients to heights of 1.4 and 1.6 m for organic and inorganic N-source treatments. The Type A tunnels were each filled with two 4 t batches of blended compost ingredients separated by a central partition. In the Type B tunnels the airflow was set at 9 m<sup>3</sup>h<sup>-1</sup>, unless the oxygen concentration in the compost fell below 6%, in which case the airflow was increased to 13 m<sup>3</sup>h<sup>-1</sup> until the oxygen concentration was above 6%. The respective airflows in the Type A tunnels were 12 and 26 m<sup>3</sup>h<sup>-1</sup>. After five days (Phase 0), the compost was emptied from the tunnels, mixed and if necessary re-wetted to achieve a moisture content of 77%, and then re-filled. The subsequent 6 day Phase I was similar to the Phase 0 regime.

For the Phase II pasteurisation regime, the tunnels were filled with 2.5 t of material from the Phase I stage to a height of 0.9 – 1.1 depending on the ingredients. Following a 20 h equalisation of compost temperature at 45 - 48°C, the composts were pasteurised at 58 - 60°C for 6 h. Compost temperatures were then reduced to 46 - 49°C (conditioning). A minimum oxygen concentration of 13% was maintained during Phase II. Composting was completed when the compost temperature had fallen to within 1°C of the air temperature and ammonia could no longer be detected in the compost. Details of temperature and airflow control during Phase II are given in Noble & Gaze (1998).

#### Experimental design

The experiment was replicated with time, with two replicates of each of the 6 straw type/nitrogen source combinations x 2 nitrogen rates prepared in three incomplete replicate runs. During each run, four of the six straw type/nitrogen source combinations were examined at the two nitrogen rates in the eight tunnel compartments. A split-plot design was used, with nitrogen-rate treatments arranged as sub-lots in pairs of tunnels (or front and back of Type B tunnels). The straw/nitrogen source treatments were paired as follows:

- (i) treatments containing poultry manure (with wheat or rape straw)
- (ii) treatments containing other organic nitrogen sources (spent hop powder or cocoa meal waste)
- (iii) treatments containing inorganic nitrogen sources (ammonium sulphate or urea).

The pairs of treatments were arranged as an incomplete Trojan square so that straw/nitrogen source treatments within pairs occurred twice with each other, and

straw/nitrogen source treatments in different pairs occurred once with each other. Each treatment was prepared once in a Type A tunnel and once in a Type B tunnel.

## Odour analysis

Odour samples were collected in 20 L Teflon bags, 0.2 m downwind of the compost during the emptying of the Phase 0 tunnel stage. The odour samples were then transported to IGER North Wyke and analysed within 24 h. Odour concentration (OC) was determined by an odour panel using dilution olfactometry and volatile organic compounds detected by gas chromatography – mass spectrometry (GC – MS) (Noble et al., 1999). A Dräger Accuro bellows pump with appropriate detector tubes (Drägerwerk, Lübeck, Germany) was used for on-site measurement of ammonia and specific sulphides, in the same way as sampling odours for collection in Teflon bags. Two replicate measurements were made for each sampling.

# Mushroom cropping procedure

The cropping procedure is outlined in Noble & Gaze (1998). The composts were inoculated with mushroom spawn ("spawned") using the Hauser A15 (Sylvan Spawn Ltd, Peterborough, UK) and 2100 (Amycel-UK Ltd, Burton-on-Tent, UK) strains. Half the compost spawned with each strain was supplemented with the soya meal-based "Betamyl 1000" (Sylvan Spawn Ltd) at a rate of 1% of compost fresh weight. Spawned trays were stacked four high in cropping sheds, with four replicate trays of each spawn and supplement sub-treatment from each of eight compost treatments (128 trays per shed with 16 trays from each of the compost treatments). A split-plot design was used with compost treatments allocated to main plots, which were arranged in a Latin square design, and spawn/supplement treatments allocated to sub-plots within each main plot. Mushrooms were picked as large buttons (diameter 30-40mm) over a 24 day period (three flushes of mushrooms). The yields of each run were analysed separately and the means of each treatment were incorporated into the analysis structure of the tunnel composting stage of the experiment.

Percentage dry matter content of each batch (treatment and run) of mushrooms from the first and second flushes was calculated from the fresh weight of 20 mushrooms, and the dry weight after oven drying (Burton & Noble, 1993). The nitrogen and ammonium (NH<sub>4</sub><sup>+</sup>) contents of mushrooms from the first and second flush were determined on freeze-dried samples of 20 mushrooms from each batch (Noble & Gaze, 1994).

Composts were sampled and analysed at each filling of the bulk tunnels, at the end of each composting period and at the end of mushroom cropping for compressed bulk density, pH and dry matter, nitrogen, ammonium and ash contents (Noble & Gaze, 1994). Total sulphur was measured using the method in Anon. (1981) since the main odorants are sulphur-containing compounds.

#### Results

# Analysis of compost ingredients

Dry matter, nitrogen, ammonium and ash contents of the compost ingredients are shown in Table 1. Rape straw had a significantly higher nitrogen (N) content than wheat straw, and required less poultry manure than wheat straw to achieve the same compost nitrogen rate. Spent hop powder and cocoa meal waste had lower nitrogen contents than poultry manure, but higher dry matter contents.

# Mushroom yields and analysis of composts

Mushroom yields from composts prepared using poultry manure (with wheat or rape straw) or spent hop powder, at 1.8%N, were not significantly different (Table 2). Yields from composts prepared from wheat straw with ammonium sulphate, urea or cocoa waste were significantly lower than those from poultry manure and straw composts. Using poultry manure, urea or cocoa waste, there was no significant difference in yield between composts with initial N rates of 1.8 or 2.2% of dry matter. With ammonium sulphate and spent hop powder composts, mushroom yields were significantly reduced by increasing the initial nitrogen content from 1.8 to 2.2% of dry matter (Table 2). There was no overall significant difference in yield between the strains A15 and 2100 and the effects of supplementation with Betamyl 1000 were variable (Appendix 1).

The moisture content of composts at spawning was 70.9 – 73.2%. Nitrogen at spawning was significantly lower in urea composts and significantly higher in cocoa meal waste or spent hop powder composts than that in poultry manure composts with the same initial nitrogen content (Table 3). Bulk density of rape straw composts was slightly higher than of wheat straw composts (Table 3). Spent hop powder composts had significantly higher bulk density than poultry manure composts, whereas the bulk density of inorganic nitrogen composts was very low. Compared with poultry manure composts, the pH of ammonium sulphate composts was significantly lower whereas the pH of spent hop powder composts was significantly higher (Table 4).

# Compost odours and temperatures

Odour concentration during the emptying of Phase 0 tunnels was highest in the wheat straw and poultry manure compost at 2.2%N. The inorganic nitrogen sources and cocoa meal waste generally produced the lowest odour concentrations (Table 5). Total sulphide (hydrogen sulphide + dimethyl sulphide) concentrations in the air were 0.2 - 0.2 ppm for the poultry manure composts and spent hop powder composts at 2.2%N. Sulphides were not detected in the air during the Phase 0 emptying of the other treatments.

Losses in total sulphur during composting were calculated from the initial and final compost sulphur and dry matter contents and the weight loss during composting. Calculated sulphur losses from the wheat straw and poultry manure and ammonium sulphate composts were significantly higher than those from the other treatments (Table 4).

Maximum compost temperatures during the mixing period on the compost yard and during Phase I were significantly lower in the ammonium sulphate composts than in the other treatments (Table 5). Temperatures during Phases 0 and I in the other treatments generally exceeded 70°C.

Mushroom dry matter and nitrogen contents

Mushroom dry matter content was slightly higher from the urea, cocoa waste and spent hop powder composts than from the poultry manure composts (Table 6). There was no significant difference in mushroom dry matter content between the 1.8 and 2.2% compost nitrogen rates.

Mushroom nitrogen content was significantly increased by increasing the compost nitrogen at filling from 1.8 to 2.2% of dry matter (Table 6). Mushrooms grown on rape straw had a lower nitrogen content than those grown on wheat straw.

#### Discussion

In agreement with results from flask-scale experiments (Project Report Year 1), the results from bulk tunnels experiments have shown that wheat straw can be replaced with rape straw with no effect on yield and a slight improvement in compost bulk density. Since the latter has a higher nitrogen content, it requires less poultry manure to achieve a required compost nitrogen content. Compost odours were only reduced to very low levels in these experiments when poultry manure was replaced by inorganic nitrogen sources, cocoa meal waste or spent hop powder (at 1.8%N). However, only the latter treatment produced a compost with an equivalent mushroom yield potential to poultry manure composts. The other treatments were either undercomposted, or in the case of cocoa waste, continued to produce ammonia for an extended period during Phase I. It is possible that the inorganic sources or cocoa waste could produce suitable mushroom composts with very low odour if the yard preparation stage was extended from seven days to up to 10 days.

Sulphur losses during composting may have been done to the emission of volatile sulphides and the leaching of sulphates during mixing. The sulphur losses measured here were smaller than those measured by Derikx *et al* (1990) (8.3mg sulphur per kg fresh weight of compost during conventional windrow Phase I composting). However, the high levels of sulphides emitted during conventional composting may explain the higher losses recorded by these workers.

The reduction in yield caused by increasing the inclusion rate of spent hop powder may have been due to the high pH of the compost at spawning, causing a release of ammonia. A mixture of spent hop powder and ammonium sulphate, which reduced compost pH, may produce a suitable compost formulation.

The best yields obtained in these experiments (248 kg t<sup>-1</sup> in three flushes) compare with commercial yields in the UK, but are about 10% lower than those obtained from HRI Formula 3 compost (Noble *et al*, 1998). The bulk density of the rape straw and poultry manure treatment was only 3% lower than the average bulk density of Formula 3 compost.

#### Conclusions - Part 1

- 1. Rape straw can be used in place of wheat straw, and since it has a higher nitrogen content, requires a lower inclusion of poultry manure (or other nitrogen source) to achieve the same compost nitrogen content.
- 2. Spent hop powder, added to produce a compost with 1.8% of dry matter nitrogen, resulted in similar mushroom yield and higher compost density than a straw and poultry manure compost.
- 3. Cocoa meal waste and high rates of spent hop powder resulted in either slow clearance of ammonia or high compost pH at spawning, with subsequently reduced mushroom yields.
- 4. Inorganic nitrogen sources (ammonium sulphate or urea) produced undercomposted substrates with low bulk density and lower mushroom yields than poultry manure composts.
- 5. Odour concentration and air sulphide levels were higher in composts which included poultry manure or high levels of spent hop powder, than in composts incorporating inorganic nitrogen sources or cocoa meal waste.
- 6. Ammonium sulphate reduced compost pH; a mixture of ammonium sulphate and spent hop powder may produce a suitable compost pH.
- 7. It may be possible to produce very low odour composts by using inorganic nitrogen sources, cocoa meal waste or spent hop powder by extending the period of pre-mixing from seven days.
- 8. There was no significant difference in mushroom yield between composts with initial nitrogen rates of 1.8 or 2.2% of dry matter, for poultry manure, urea or cocoa waste. With ammonium sulphate and spent hop powder composts, mushroom yields were significantly reduced by increasing the initial nitrogen content, probably due to the adverse effects of compost pH.
- 9. Mushroom dry matter content was higher from the urea, cocoa waste and spent hop powder treatments than from the poultry manure and ammonium sulphate composts.
- 10. Mushroom nitrogen content was significantly increased by increasing the nitrogen content of the compost. Mushrooms grown on rape straw had a lower nitrogen content than those grown on wheat straw.

Fig. 1a Ammonia emissions during Phases 0 and I; poultry manure composts, N = 2.2% of DM at filling

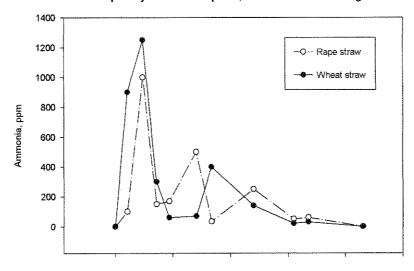


Fig. 1b Ammonia emissions during Phases 0 and I;

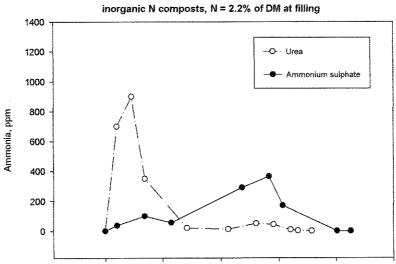


Fig. 1c Ammonium emissions during Phases 0 and I;

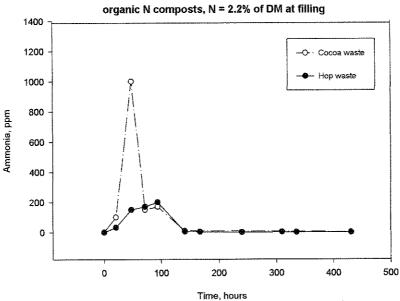


Table 1. Analysis of straw and N sources and quantities used. Analyses are means of three replicate samples.

	% w		DM%	% of DM		
Ingredient	N-13	2.2	DIV178	N	NH4 <sup>+</sup>	Ash
Wheat straw	100-N	source	87	0.7	0.04	5.2
Rape straw	100-poultry	y manure <sup>b</sup>	84	1.2	0.04	5.0
Poultry manure <sup>a</sup>	34.5	40.4	71	4.9	0.93	12.8
Poultry manure <sup>b</sup>	31.0	39.1	-	-	-	<u>-</u>
Spent hop powder	36.6	52.7	89	3.8	0.05	8.0
Shell extracted cocoa meal	35.9	44.1	90	4.3	0.07	6,5
Ammonium sulphate	3.2	6.7	100	21.2	27.24	••
Urea	2.1	3.6	100	46.7	0	

a rate with wheat straw

b rate with rape straw

<sup>°</sup> original fresh weight in compost excluding added water and gypsum, at compost N-rates of 1.8 and 2.1%

Table 2. Mushroom yields (kg t<sup>-1</sup> spawned compost) from composts with different straw types and N sources at two N rates (flushes of mushrooms)

	N rate	(% of DM)
Treatment	1.8	2.2
Wheat straw + poultry manure (control)	247	238
Rape straw + poultry manure	248	244
Ammonium sulphate	120	60
Urea	126	. 126
Cocoa waste	129	132
Spent hop powder	229	141

L.S.D. (P = 0.05) Between compost treatments and N rates = 39.1

Table 3. Analysis of composts at spawning

Treatment	N rate at fill,	Total N	Ash	Bulk density
	% of DM	% of I	DM	kg m <sup>-3</sup>
Wheat straw + poultry manure	1.8	2.38	17	438
	2.2	2.63	23	450
Rape straw + poultry manure	1.8	2.09	20	488
	2.2	2.32	18	500
Ammonium sulphate	1.8	2.37	14	350
	2.2	2.56	15	350
Urea	1.8	1.82	14	400
	2.2	2.09	11	400
Cocoa waste	1.8	2.68	17	450
	2.2	3.34	13	475
Spent hop powder	1.8	2.58	18	525
	2.2	3.18	12	525
L.S.D.		1.10	4.2	37.5

L.S.D. (P = 0.05) Between compost treatments and N rates

Table 4. Sulphur losses during composting, sulphur content and pH of composts at filling and spawning

Treatment	N rate at	Sulphur	Sulphur % of DM pH		pH	
	fill, % of DM	losses, mg kg <sup>-1</sup> FW	Filling	Spawning	Filling	Spawning
Wheat straw +	1.8	114	1.06	1.44	8.0	7.7
Poultry manure	2.2	101	1.09	1.45	8.2	7.7
Rape straw +	1.8	68	1.13	2.04	8.2	7.6
Poultry manure	2.2	44	0.97	1.93	8.1	7.6
Ammonium sulphate	1.8	208	1.58	1.95	7.8	6.7
	2.2	183	1.91	2.60	7.8	6.4
Urea	1.8	30	0.79	1.34	8.7	7.8
	2.2	30	0.76	1.66	8.7	7.6
Cocoa waste	1.8	17	0.68	1.46	7.9	7.6
	2.2	18	0.99	1.40	8.3	7.6
Spent hop powder	1.8	33	0.90	1.65	8.2	8.0
	2.2	28	0.95	1.65	8.3	8.1
L.S.D.		35	0.23	0.21	0.34	0.20

L.S.D. (P=0.05) Between compost treatments and N rates

FW = fresh weight

DM = dry matter

Table 5. Odour concentration (OC) during emptying of Phase 0 tunnels and maximum temperatures during yard blending, Phase 0 and Phase I

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Treatment	N rate at Fill, % of DM	OC, OUm <sup>-3</sup>	Yard	Phase 0	Phase I
Wheat straw +	1.8	1790	62	78	69
poultry manure	2.2	5157	62	78	71
Rape straw +	1.8	3142	49	70	75
poultry manure	2.2	2377	48	71	79
Ammonium	1.8	. 1187	16	72	65
sulphate	2.2	1094	32	69	58
Urea	1.8	1213	37	67	69
	2.2	890	51	73	72
Cocoa waste	1.8	1265	65	70	80
	2.2	570	67	74	71
Spent hop powder	1.8	1000	36	72	71
-r	2.2	3627	63	80	78
L.S.D.		1057	19.1	5.2	5.4

L.S.D (P = 0.05) Between compost treatments and N rates

Table 6. Mushroom dry matter and nitrogen contents, strain A15, mean of flushes 1 and 2.

Treatment	N rate at	Mushroom DM	Mushroom N
	Fill, % of DM	%	% of DM
Wheat straw + poultry manure	1.8	7.82	6.08
	2.2	7.89	6.25
Rape straw + poultry manure	1.8	7.68	4.76
	2.2	7.44	4.82
Ammonium sulphate	1.8	7.48	6.10
	2.2	7.72	7.08
Urea	1.8	8.72	6.25
	2.2	8.46	6.35
Cocoa waste	1.8	7.89	6.90
	2.2	8.03	6.91
Spent hop powder	1.8 2.2	8.40 7.96	6.32 6.31

L.S.D. (P = 0.05) Between compost treatments and N rates = 0.29 (%DM) and 0.19 (N)

# Part 2: Odour Quantification Techniques

In the first year of the project (1997/98), four methods of odour measurement were 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 absorb and desorb from their surface.

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 samples 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" with polypyrrole sensors was insufficiently sensitive to sulphides to discriminate compost odour levels.

The aims of the experiments in Year 2 of the project were:

- (i) to obtain further odour samples from each of the compost yards sampled in Year 1, together with samples from a new entrant to the consortium (Gateforth Park Ltd)
- (ii) to analyse the odour samples using the methods previously outlined, and to confirm the relationship between odour and sulphide concentrations
- (iii) to determine the effects of aeration during pre-wet and Phase 1 composting and compost analysis on odour levels
- (iv) to assess the suitability of electronic sulphide detectors for compost odour samples.

# **Compost Yard Odour Measurements**

#### 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.

Replicate samples were collected simultaneously. Background samples were collected 200 m upwind of the composting sites. Samples were transported 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 eleven sites: Blue Prince, Chesswoods (Sussex), Gateforth Park, 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; four 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 and at Gateforth Park and Pond Chase, prewetting was conducted on an aerated pad. Pre-wetting was conducted in flat heaps on the remaining sites. 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 prewet and Phase I windrows at HRI was 16 days. Phase I tunnel composts at HRI were pre-wetted for 7 days. The pre-wet areas were sampled 3-6 days after setting up of the heaps and the Phase I windrows or tunnels were samples 3-7 days after the start. The combined pre-wet and Phase I windrows at HRI were sampled after 12 days.

All the composts were analysed for moisture, nitrogen and ammonium contents and pH according the methods in Noble and Gaze (1994).

### **Olfactometry**

A dynamic dilution olfactometer (Project Research, Amsterdam) was used according to recommendations in van den Berg (1992), i.e. 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. Odour concentration was calculated according to the Dravneiks and Prokov (1975) method. Measurements of the sensitivity of the odour panellists for each set of odour concentration measurements was performed with 198.2 mg m<sup>-3</sup> (60 ppm) butan-1-ol in nitrogen.

## GC-MS analysis

Volatile compounds were preconcentrated from 600 ml odour samples 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 µl 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 of 0.2 mm and a 0.34 µm film with a 1m deactivated fused silica guard column (0.25mm internal diameter) were used. The flow rate of 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 spectrometer were identified using a probability based matching algorithm and a NIST mass spectral library, ie a reference list of known compounds which was used for matching the peaks of unknown compounds in the samples. 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 (Drägerwerek, Lübeck, Germany) was used in conjunction with appropriate detector tubes: acetic acid (6722101), amines (8101061), ammonia (CH2051 and CH31901), carbon disulphide (8101891), dimethyl sulphide (6728451), hydrogen sulphide (8101991 and 8101831), mercaptan (thiols) (6728981) and phenol (8101641). Detector tubes were used on-site in the same way as sampling odours for collection in Teflon bags, 24h after on-site sampling. Two replicate measurements were made for each sampling.

#### Results

### Olfactometric analysis

The odour concentration of the pre-wet and Phase I compost areas of the eleven composting yards in Years 1 and 2 are shown in Table 7. On Yard C the pre-wet area had a higher odour concentration than the Phase I compost area; the reverse situation was found on Yards F, H and I. Composts produced in aerated systems (sites D, E, G and K) generally had lower odour concentrations than non-aerated composts. However, the Phase I of site D in Year 1 and the pre-wet of site E in Year 2 produced significant odour levels.

# GC-MS analysis

Odorants detected in the pre-wet and Phase I air samples are shown in Table 8. The odorants exceeding the threshold levels were mainly sulphur containing compounds,

but volatile fatty acids (acetic, butanoic and propanoic) and triethylamine also were found in samples at concentrations exceeding their threshold values.

#### Gas detector tubes

On-site measurement of hydrogen sulphide, dimethyl sulphide and ammonia with gas detector tubes in Year 2 are shown in Table 9. Pre-wet on sites C and I had significantly higher hydrogen sulphide and dimethyl sulphide levels than the other sites. Phase I composts on sites B and I had significantly higher hydrogen sulphide and dimethyl sulphide levels than the other sites. Ammonia levels were highest on sites A, B and D.

There was a close correlation between the olfactometric odour concentration and the combined concentration of hydrogen sulphide + dimethyl sulphide in pre-wet or Phase I odour samples (Figs. 2 and 3). Ammonia concentrations were above the detection threshold in most of the odour samples, but were not correlated with odour concentration.

# Compost analyses

Compost moisture, N and NH<sub>4</sub><sup>+</sup> contents and pH are shown in Table 10. There was a weak positive correlation between the total compost N content and the emission of ammonia. No other correlations between odour or gas concentrations and the different compost analysis factors were found.

Table 7. Odour concentrations by olfactometry for compost yards, Year 1 and Year 2 results

~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Ode	our concentration	n, Odour units m <sup>-3</sup>	air
Compost yard	Pre-	wet	Pha	se I
······	Year 1	Year 2	Year 1	Year 2
A	- -	-	17894	-
В	11796	3849	10316	395533
C	26777	25177	3965	2043
D	6721	1933	20139	921
E	1209	3698	919	885
F	10467	4821	31823	16864
G	6146	538	666	804
Н	10144	3430	19607	20213
I	245100	9553	263758	72319
J	-	1626	13015	1957
K	-	993	-	2919
L.S.D. (P = 0.05)		4	92	

Table 8. Concentrations<sup>a</sup> and odour detection thresholds<sup>b</sup> for odorants identified with GC-MS in compost yard odour samples, µg m<sup>-3</sup> air. Compounds with mean values exceeding the detection threshold are shown in bold.

Odorant	Pre-wet	Phase I	Detection threshold	Characteristic odour
A actic coid	1500/1041	1050(+12(0)	25.000	4
Acetic acid	1588(±941)	1952(±1362)	25,000	vinegar
Acetone	3007(±5644)	2679(±5114)	770,000	ethereal
Ammonia <sup>c</sup>	27976(±28840)	75740(±62750)	260	dry urine
Butanoic acid	481	2603(±3442)	$1 \times 10^{-3}$	rancid
Butanol	3003(±6774)	2715(±6628)	33,000	fusel oil
2-Butanone	697	287(±457)	18,000	
Carbon disulphide	trace	trace	2.6	foul
Dimethyl sulphide	1667(±3290)	3528(±6921)	255	foul
Dimethyl disulphide	$657(\pm 1626)$	$287(\pm 896)$	15.3	foul
Dimethyl trisulphide	83(±170)	130(±292)	$2.6 \times 10^{-2}$	
Ethanol	53460(±103860)	10808(±16281)	93,000	vinous
4-Ethyl phenol	75	$79(\pm 90)$		
Hexane	$150(\pm 276)$	$86(\pm 112)$		ethereal
Hydrogen sulphide	$730(\pm 1310)$	49480(±10595)	1.1	rotten egg
Indole	7	3(±3)	600	faecal
Iso-propyl-alcohol	1837	$195(\pm 245)$		
Methanethiol	211(±246)	$126(\pm 165)$	1.1	rotten cabbage
2-Methyl butanoic acid	238	$165(\pm 350)$		unpleasant
3-Methyl butanoic acid	206	$869(\pm 1531)$	5,000	•
Methyl ethyl ketone	660	5720(±3354)	80,000	acetone-like
Methyl phenol	$101(\pm 50)$	196(±101)	220	
Methyl propanoic acid	26	444(±379)		
Methyl sulphide	156	167		disagreeable
Pentanoic acid	216	$700(\pm 1231)$	800	unpleasant
Phenol	$139(\pm 77)$	189(±170)	12,000	1
Propanoic acid	2004(±2323)	351(±259)	3 ,000	rancid
Propanol	5928(±13171)	678(±879)	80,000	
Toluene	30	18	140,000	
Triethylamine	179(±99)	169(±151)	4	urine/fishy
Trimethylamine	trace	trace	96,000	fishy
p-Xylene	113	25	,	

 $<sup>^{\</sup>circ}$  mean and  $\pm$  standard deviation; compounds without standard deviations were identified in less than five samples

<sup>&</sup>lt;sup>b</sup> after Summer (1971), van Gemert and Nettenbreijer (1977) and Overcash et al (1983)

<sup>°</sup> measured with gas detection tubes

d after Budavari (1989)

Table 9. Gas detector tube measurements at compost yards, Year 2

Compost	H	$_{2}S$	DN	⁄IS	N	NH <sub>3</sub>		
yard	Pre-wet	Phase I	Pre-wet	Phase I	Pre-wet	Phase I		
A	-	2.0	<del>-</del> ·	3.8	ma	120		
В	0.15	160.0	1.0	52.0	55	100		
C	6.5	0.2	10.0	0.6	7.5	26		
D	0.6	0.35	1.1	1.0	400	550		
Е	0.1	0.05	0.5	0.25	60	50		
F	0.3	9.0	1.1	7.0	10	30		
G	0	0	0.15	0	2	20		
Н	0.6	2.0	0.8	3.2	30	45		
I	6.0	41.0	2,0	32.0	3.5	39		
J	0.4	0	1.0	0	5	110		
K	0.1	0	0.1	0.1	75	35		
L.S.D.(P=0.05)	0.	4	0.	4	3.	5		

Table 10. Analysis of pre-wet materials and Phase I composts, Year 2

:22222800000000000000000000000000000000	остичности допосносно поставления	n EEEEnnangagagangken enkeretera feren	rodouhnoooanneessaankeenaakaanaaanne	OTO CONTRACT LANGUAGE CONTRACT	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	0/0	DM	200200000ACCCCCCCCCCCCCCCCCCCCCCCCCCCCC
Compost yard	Moist	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	pH		N	I	NH	$\mathbf{I_4}^+$
yara	pre-wet	Ph I	pre-wet	Ph I	pre-wet	Ph I	pre-wet	Ph I
A	-	76.4	-	8.3	-	1.71	<b></b>	0.40
В	79,0	74.8	8.1	8.1	1.72	2.25	0.45	0.66
С	<u>-</u>	74.8	-	8.5	<b></b>	1.78		0.30
D	<u></u>	77.9	-	8.4	-	1.67	-	0.89
E	74.8	74.3	8.0	8.3	1.71	1.81	0.63	0.66
F	-	75.3	-	8.2	-	1.78	-	0.62
G	76.6	72.6	8.6	8.6	1.75	1.82	0.49	0.47
Н	75.5	73.8	-	7.5	1.97	2.16	0.36	0.55
. <b>I</b>	74.8	75.3	7.4	8.0	2.33	2.28	0.74	0.52
J	80.2	75.5	8.8	8.3	1.49	2.17	0.30	0.40
K	<b></b>	-	-	-	-	-	-	-

Fig.2 Relationship between compost yard odour and combined  $\rm H_2S$  + DMS concentrations

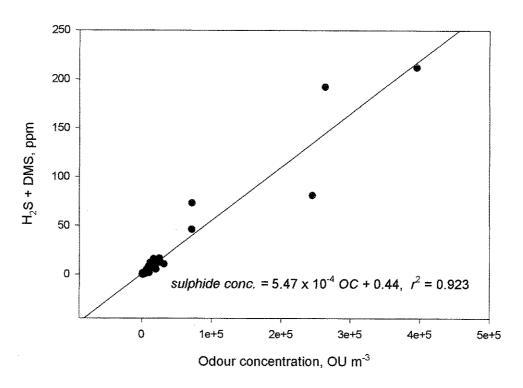
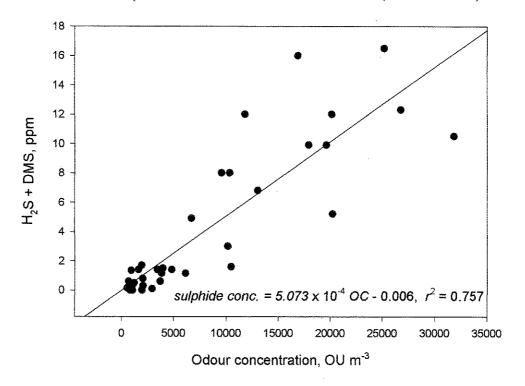


Fig.3 Relationship between compost yard odour and combined  $\rm H_2S + DMS$  concentrations (odour concentrations less than 40,000 OU  $\rm m^{-3}$ )



# Electronic odour compound analysers

#### Materials and Methods

Instruments were tested for measuring sulphides and other compounds in odour samples and their performance assessed in terms of:

- sensitivity to hydrogen sulphide, other sulphides and odorous compounds
- sensitivity to water vapour, ammonia and other interfering gases

Three electrochemical instruments from the following companies were examined:

Analox Sensor Technology Ltd, Stokesley, Cleveland, UK Draeger Ltd, Blyth, Northumberland, UK Gas Measurement Instruments Ltd, Renrew, UK

The remaining five instruments had differing modes of operation:

Aromascan plc, Crewe, UK

'Electronic nose' consisting of an array of 32 conducting polypyrrole sensors Graseby Dynamics Ltd, Watford, UK

'Environmental Vapour Monitor' utilising gas chromatography (GC) and ion mobility spectrometry.

PE Photovac, Norwalk, CT, USA

'Voyager' portable gas chromatograph, utilising GC and a photoionization detector (PID)

Thermo Environmental Instruments Ltd, Franklin, MA, USA

(instrument supplied by *Unicam Chromatography*, *Cambridge*, *UK*)

Pulsed fluorescence SO<sub>2</sub> analyser, coupled to a H<sub>2</sub>S - to - SO<sub>2</sub> converter

Zellweger Analytics Ltd, Bishop's Stortford, Herts, UK

'Chemcassette' utilising a colorometric gas sensitive paper tape, which is measured with an electronic optical system.

Six of the instruments were portable, although data from the Graseby Dynamics and PE Photovac instruments needed to be downloaded to PC for observation and analysis. The Aromascan and Thermo Environmental Instruments machines were laboratory-based. Specifications of the eight instruments tested are shown in Table 11.

# Results

The three electrochemical sensors tested were found to be cross-sensitive to ammonia and, therefore, unsuitable for measuring sulphide levels in compost odour samples. The Draeger instrument was sensitive to water vapour, and hydrogen sulphide could not be detected in compost odour below 20 ppm. The GMI instrument did not give reliable hydrogen sulphide readings below 2 ppm; the Analox analyser could detect less than 1 ppm hydrogen sulphide, but only in the absence of ammonia.

The Aromascan instrument was only sensitive to hydrogen sulphide and dimethyl sulphide concentrations greater than 20 ppm and was sensitive to ammonia in the compost odour samples. The PE Photovac instrument did not respond to control samples of hydrogen sulphide. No relationship between the output of the Graseby Dynamics instrument and the concentration of sulphides in compost odour samples could be established.

The Thermo Environmental Instruments analyser was found to give readings which corresponded with the total sulphur concentration of samples to less than 10 ppb. The instrument was not influenced by the water vapour or ammonia concentration in compost odour samples.

The Zellweger Analytics instrument was sensitive to hydrogen sulphide and methanethiol to levels of 50 ppb but was not sensitive to dimethyl sulphide. No tests were conducted with the 2 ppb instrument.

Of the eight instruments examined, only the Thermo Environmental Instruments and Zellweger Analytics analysers were sensitive to sulphides at concentrations less 1 ppm, without interference from water vapour and/or ammonia in compost odour samples. Further tests are needed with these two analysers to determine how the readings correspond with odour panel measurements on compost odour samples.

#### **Conclusions – Part 2**

- 1. Sulphur containing compounds in compost odour samples were found to be important in exceeding detection thresholds, but volatile fatty acids and thiethylamine were also found in odour samples at concentrations exceeding their detection thresholds.
- 2. There was a close correlation between the compost odour concentration of the prewet and Phase I composts samples and the combined hydrogen sulphide + dimethyl sulphide concentration from gas detector tubes. Concentrations of ammonia were above the detection threshold in most of the odour samples, but were not correlated with odour concentration.
- 3. Out of eight electronic instruments examined, two were found to be sensitive to sulphide levels less than 60 ppb (and in one case to less than 10 ppb). The use of these instruments in detecting low odour levels should be examined further.
- 4. Odour concentrations and sulphide concentrations from aerated composting systems were generally lower than those from non-aerated systems.
- 5. Higher total compost nitrogen resulted in greater ammonia emissions but there were no correlations between the analysis of composts and the resulting odour concentrations.

Table 11. Electronic odour compound analysers

Company	Analyser	Mode of Operation	Compounds Measured	Specified L.D.L.*	Cross Sensitivity	Portable	Cost £K
Analox	101DZ	electrochemical	$_{2}$	0.1 ppm	ammonia other sulphides	Yes	8
Aromascan	A8S	conducting polypyrroles	polar compounds	The contraction of the contracti	ammonia alcohols	°N	32
Draeger	PacIII	electrochemical	H <sub>2</sub> S	2 ppm	ammonia other sulphides	Yes	7
GMI	Personal surveyor	electrochemical	H <sub>2</sub> S	l ppm	ammonia other sulphides	Yes	7
Graseby Dynamics	EVM	GC+ion mobility spectrometry	ionized molecules	The state of the s	ı	Yes	6
PE Photovac	Voyager	GC+ photoionization	volatile organic		t	Yes	18
T.E.I. **	43C+45C	pulsed fluorescence	sulphur containing	0.5 ppb	l	No	18
Zellweger	7100	colorometric paper	H <sub>2</sub> S	2 ppb	other sulphides	Yes	5
***************************************		A LL -	***************************************			***************************************	The state of the s

# Part 3: Microbial Degradation of Hydrogen sulphide and Dimethyl Sulphide in Compost.

#### Introduction

Both hydrogen sulphide and dimethyl sulphide have been shown to correlate with the production of odour during the composting process. Because of this and the fact that they are known odour pollutants they have both been targeted as major compounds for removal from the air above the compost stack. The overall aim for this part of the project is to try and remove or break down these chemicals by microbial activity, in a way that is suitable to their application within the UK mushroom industry. It is already known that total enclosure of a composting unit and extraction of the air through a bio-filter can lead to the microbial breakdown of these compounds. However, this process is extremely expensive and alternative solutions may be found. By taking the microbial breakdown process to the compost stack it is hoped that a reduction in the release of odour compounds can be achieved, which could offer a low-tech solution to this problem.

Since the composting process is inherently variable, conducted using different ingredients, formulations and processes, it was decided that a model system should be used to control some of the experimental parameters, and offer reliability and reproducibility within and between experiments. Once established these systems would be used and microbial inocula introduced and tested for their ability to remove hydrogen sulphide and dimethyl sulphide. The most effective systems would then be tested for their ability to remove these compounds from the air released above large composting stacks.

#### Materials and Methods

Strains. Hyphomicrobium species (obtained from Dr H. Op den Camp, Netherlands). This strain removes hydrogen sulphide and it is easily grown since it does not require specialised conditions (generalist). Ten additional isolates were obtained from the surface of 5-day-old compost at HRI. They were isolated on R2A agar after growth at 37°C for 7 days and purified by two rounds of sub-culture on R2A media.

**Compost.** 'Formula 3' compost was obtained from HRI (Noble *et al*, 1998). It was thoroughly mixed and smaller samples used to set up microcosms.

**Temperature measurements.** Compost temperature measurements around and within the stack were taken using a Grant logger.

Measurement of Hydrogen sulphide, dimethyl sulphide, and ammonia. All three chemicals were measured using the Drager system fitted with an appropriate detection tube. The air just above the compost was sampled using a hand held pump.

Microcosms design. The basic microcosm design can be seen in figure 4. 1L of compost was placed in a 2L flask; the temperature of this system was maintained using an external water bath (55°C). Air was pumped to the bottom of the compost and flowed upwards, the flow rate controlled (5-0L min<sup>-1</sup>). Measurements of

hydrogen sulphide, dimethyl sulphide and ammonia were taken from the upper airspace, and a temperature profile down the compost within the microcosm measured. Microcosm temperature and air flow rate were altered during replicate experiments

#### Results

Isolates. Hyphomicrobium species (when incubated in odorous mushroom composting air samples collected from above the stack) was found to significantly remove hydrogen sulphide (Figure 5). At the start of the experiment the air contained 34ppm hydrogen sulphide, 3ppm dimethyl sulphide and 0ppm ammonia. After 8h at 30°C the control had been reduced to 22ppm hydrogen sulphide while only 2ppm hydrogen sulphide was detected in the presence of the bacterial strain. This experiment was repeated using activated charcoal as the support for the bacterial strain. Activated charcoal alone, and activated charcoal with Hyphomicrobium cells, both reduced the levels of hydrogen sulphide to below the detection level (1ppm). Dimethyl sulphide was undetectable in the control and all test samples after 8h incubation, and ammonia was not detected in samples during this experiment. In conclusion the bacterium used was able to remove hydrogen sulphide from a sample of compost odour.

Compost stack. The following temperatures were measured in and around the compost stack at HRI:

16°C,
15.7°C,
16.6°C
variable-19.3°C; 43°C; 39°C; 50°C
50-60°C
55°C

The temperatures recorded just within the stack and on the stack surface were high; a temperature above 42°C is too high for any isolates tested (optimal growth at 37°C). Therefore, it is difficult to see this approach working within the compost itself with the isolates available to HRI. In conclusion the isolates will have to be used above the compost surface itself, using a matrix or support of some form. Attempts to obtain isolates that function at 55°C and above have not been successful but will continue.

Development of model systems. Microcosms were used as model systems to provide hydrogen sulphide, dimethyl sulphide and ammonia concentrations equivalent to that found above a compost stack under conditions relevant to the normal composting process. With a flow rate of 5L/h at 55 C, the hydrogen sulphide levels were below detection, 1ppm. With lower flow rates of 0.5L/h and intermittent flow rates 5L/h for 1h, 0L/h for 1h again no hydrogen sulphide or dimethyl sulphide was detected. When the flow rate was reduced to OL/H, variable results were obtained (summary figure 6). In the four replicates for each experiment, either the compost samples produced significant levels of hydrogen sulphide or dimethyl sulphide or they didn't produce any. When replicated on a smaller level (Experiment 6), 18/24 samples were positive for both these compounds and off scale for detection, while 6 were negative. These

again indicating that the production of odour in the flasks is either very strong or not at all. To try and determine the reason for this variability a comparison of the different microcosms was made.

No significant difference in bacterial population numbers growing on Nutrient Agar at 30, 42 and 55°C for 4 days was detected. When a sub sample of a positive pot was used to inoculate a negative pot, no hydrogen sulphide or dimethyl sulphide was detected in the new system. A small difference in pH was noted between positive and negative pots. In the odorous pots a pH of 7.9 was recorded (n=18) while in the negative pots a pH of 8.28 was recorded (n=6). This difference was significant (p<0.05). To overcome the problems of variability in results a larger design is being tested. Model systems comprising 50kg of compost are being used. Once stable results for the production of hydrogen sulphide and dimethyl sulphide have been achieved, microbial inoculants from the first part of this work will be applied to the upper surface of the compost on a variety of matrices. These applications will include single strain inoculum on a straw mat, a blanket and an activated carbon support. In addition, mixed microbial inoculants from the compost outer layer and from biofilters that are enriched in degraders will be applied to the compost surface.

#### Conclusions - Part 3

- 1. A *Hyphomicrobium* species was found to significantly remove hydrogen sulphide from odorous mushroom composting air samples.
- 2. A small-scale flask composting system resulted in either very strong or no odours under apparently similar conditions. A larger scale laboratory composting system is therefore being developed for examining the effects of introducing microbes on the reduction of odours.

Figure 4. Design of the compost model system.

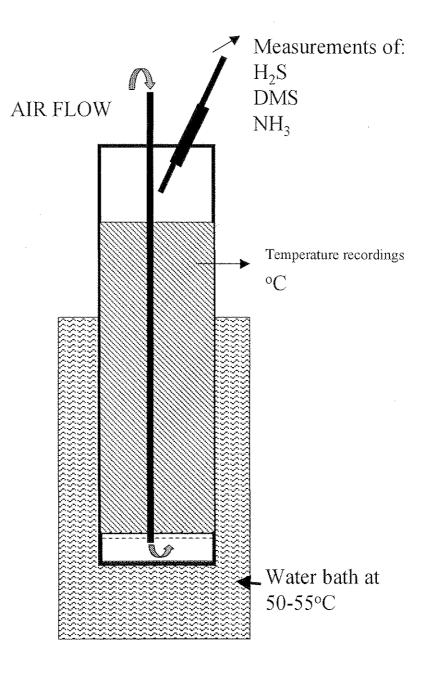


Figure 5. Removal of H<sub>2</sub>S by *Hyphomicrobium* species (VS) after 8h at 30°C.

Levels at the start of the experiment.

H<sub>2</sub>S: 34ppm

DMS: 3ppm

NH<sub>3</sub>: 0

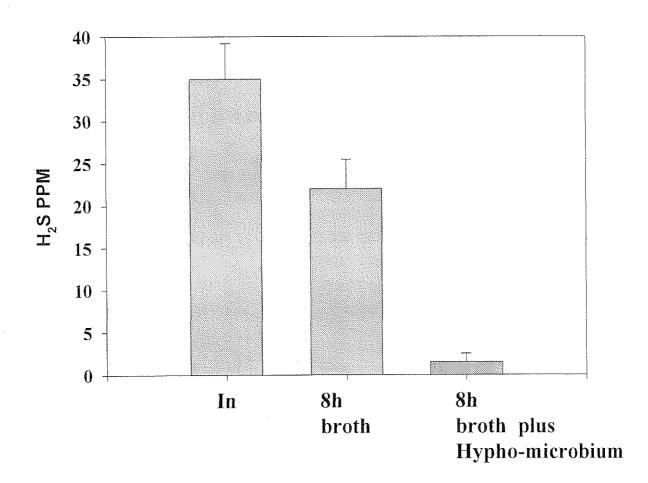


Figure 6. Levels of H<sub>2</sub>S, DMS and NH<sub>3</sub> (ppm) detected within individual microcosms over 6 experiments. Air flow was set at 0L/h and the water bath temperature at 55°C.

# Experiment 1.

# Experiment 2.

$NH_3$	$H_2S$	DMS	$NH_3$	$H_2S$	DMS
0	10	5	0	140	120
0	0	3	0.5	0	8
0	10	7	1	.1	8
0	0	0	.5	0.2	20

# Experiment 3.

# Experiment 4.

$H_2S$	$H_2S$	DMS
100	200+	300+
100	200+	300+
1	200+	300+
1	200+	300+

# Experiment 5.

# **Experiment 6.**

$H_2S$	DMS	24 pots:	
200+	300+	18 200+	$H_2S$
200+	300+	6 0	$H_2S$
200+	300+		
200+	300+		

#### **OVERALL CONCLUSIONS**

- 1. Rape straw can be used in place of wheat straw, and since it has a higher nitrogen content, requires a lower inclusion of poultry manure (or other nitrogen source) to achieve the same compost nitrogen content.
- 2. Spent hop powder, added to produce a compost with 1.8% of dry matter nitrogen, resulted in similar mushroom yield and higher compost density than a straw and poultry manure compost, with significantly less odour.
- 3. Odour concentration and air sulphide levels were higher in composts which included poultry manure or high levels of spent hop powder, than in composts incorporating inorganic nitrogen sources or cocoa meal waste.
- 4. Ammonium sulphate reduced compost pH; a mixture of ammonium sulphate and spent hop powder may produce a suitable compost pH.
- 5. Mushroom dry matter content was higher from the urea, cocoa waste and spent hop powder treatments than from the poultry manure and ammonium sulphate composts.
- 6. Sulphur containing compounds in compost odour samples were found to be important in exceeding detection thresholds, but volatile fatty acids and thiethylamine were also found in odour samples at concentrations exceeding their detection thresholds.
- 7. There was a close correlation between the compost odour concentration of the prewet and Phase I composts samples and the combined hydrogen sulphide + dimethyl sulphide concentration from gas detector tubes. Concentrations of ammonia were above the detection threshold in most of the odour samples, but were not correlated with odour concentration
- 8. Out of eight electronic instruments examined, two were found to be sensitive to sulphide levels less than 60 ppb (and in one case to less than 10 ppb). The use of these instruments in detecting low odour levels should be examined further.
- 9. Odour concentrations and sulphide concentrations from aerated composting systems were generally lower than those from non-aerated systems.
- 10. A *Hyphomicrobium* species was found to significantly remove hydrogen sulphide from odorous mushroom composting air samples.

#### References

Anon (1981) Analysis of Agricultural Materials. ADAS Reference Book 427, London :HMSO

Anon 1997 Dräger-Tube Handbook, 11<sup>th</sup> Edition. Drägerwerk Aktiengesellschaft, Lübeck, Germany, 367 pp.

Anon 1998 Gastec Gas Detection System Detector Tubes List, 5<sup>th</sup> Edition. Gastec Corporation, Kanagawa, Japan, 31 pp.

Budavari S (1989) The Merck Index 11th edn. Merck & Co. Inc, Rahway, NJ, USA.

Burton KS, Noble R (1993) The influence of flush number, bruising and storage temperature on mushroom quality. *Post harvest Biology and Technology* **3**, 39 – 47.

Derikx P J L, Op den Camp H J M, Van der Drift C, Van Griensven L J L D, Vogels G D 1990. Identification and quantification of odorous compounds emitted during the production of mushroom compost. *Appl Environ Microbiol* **56** 563-567.

Dravneiks A, Prokop, W H 1975 Source emission odour measurement by a dynamic forced-choice triangle olfactometer. J Air Pollut Cont Assn 25 1.

Hobbs PJ, Misselbrook TM, Pain BF (1995) Characterisation of odorous compounds and emissions from slurries produced from weaner pigs fed dry feed and liquid diets. J. Sci. Food Agric. 73, 437 – 445.

Noble R, Gaze R H 1994 Controlled environment composting for mushroom cultivation: substrates based on wheat and barley straw and deep litter poultry manure. *J agric Sci, Camb* 123 71-79.

Noble R, Gaze RH (1998) Composting in aerated tunnels for mushroom cultivation: influences of process temperature and substrate formulation on compost bulk density and productivity. *Acta Horticulturae* **469**, 417 – 426.

Noble R, Fermor T R, Evered C E, Atkey P T 1997 Bench-scale preparation of mushroom substrates in controlled environments. *Compost Sci Utiliz* 5(3) 32-43.

Overcash MR, Humenik FJ, Miner JR (1983) Livestock Waste Management (Vol II), CRC Press Inc, Boca Raton, Florida, USA, 255pp.

Summer W (1971) Odour Pollution of Air. Leonard Hill, London, 310 pp.

Van den Berg M, 1992 Sensory odour measurements using an olfactometer. Nederlands Normalisatie Instituut, Kalfjeslaan 2, Postbus 5059, 2600 GB Delft, Netherlands.

Van Gemert LJ, Nettenbreijer AH (1977) Compilation of Odour Threshold Values in Air and Water. National Institute for Water Supply and Central Institute for Food and Nutrition Research, Netherlands.

APPENDIX 1. Mushroom yields in each replicate run, kg/t spawned compost

Mushroom strain:	naalamistii Kantoo (1990) (1990) (1990) (1990) (1990) (1990) (1990) (1990) (1990) (1990) (1990) (1990) (1990)	A	.15	2.1	2100	
Betamyl supplem	ent:	**	+	-	+	
RUN 1	(Nat fill, % of DM)					
Poultry manure	(1.8)	200	164	183	236	
	(2.2)	216	258	257	211	
Rape straw + P.manure	1.8)	211	219	206	259	
	(2.2)	192	203	192	183	
Urea	(1.8)	164	203	175	183	
	(2.2)	167	167	156	167	
Amm. Sulphate	(1.8)	122	140 <sup>-</sup>	123	131	
	(2.2)	47	48	36	58	
RUN 2						
Poultry manure	(1.8)	310	328	259	295	
	(2.2)	294	232	235	203	
Rape straw	(1.8)	278	279	277	256	
+ P.manure	(2.2)	293	256	310	223	
Cocoa waste	(1.8)	140	144	104	120	
	(2.2)	148	148	149	147	
Spent hop powder	(1.8)	230	172	241	212	
	(2.2)	180	180	115	117	
RUN 3	(1.8)	56	98	43	89	
Urea	(2.2)	78	105	75	91	
Amm. Sulphate	(1.8)	107	116	106	119	
	(2.2)	43	104	77	76	
Cocoa waste	(1.8)	141	143	104	119	
	(2.2)	114	120	112	117	
Spent hop powder	(1.8)	247	278	205	249	
	(2.2)	128	141	130	137	

APPENDIX 2. Analysis of composts at spawning

Treatment	Total N	NH <sub>4</sub> <sup>+</sup>	Ash	Bulk density
HEALIHEIR		% of DM		kg m <sup>-3</sup>
RUN 1	Nat fill/% of DN	1	~	
Poultry manure	(1.8)	2.65	13	450
	(2.2)	2.81	24	475
Rape straw	(1.8)	1.89	15	475
+ P.manure	(2.2)	2.20	13	500
Ammonium sulphate	(1.8)	2.00	17	300
	(2.2)	2.94	14	300
Urea	(1.8)	1.52	13	400
	(2.2)	2.38	9	375
RUN 2				
Poultry manure	(1.8)	2.11	21	425
	(2.2)	2.44	22	425
Rape straw	(1.8)	2.29	24	500
+ P. manure	(2.2)	2.43	23	500
Cocoa waste	(1.8)	2.03	16	425
	(2.2)	2.72	8	475
Spent hop powder	(1.8)	2.35	19	550
	(2.2)	3.40	10	550
RUN 3				
Ammonium sulphate	(1.8)	2.74	10	400
	(2.2)	2.17	15	400
Urea	(1.8)	2.11	15	400
	(2.2)	1.80	12	425
Cocoa waste	(1.8)	3.32	17	475
	(2.2)	3.96	17	475
Spent hop powder	(1.8)	2.80	17	500
	(2.2)	2.96	14	500

APPENDIX 3. Sulphur content and pH of composts at filling and spawning

		Sulphur,	% of DM	pH	
Treatmen	nt	Filling	Spawning	Filling	Spawning
RUN 1	N at fill, % of DM				
Poultry manure	(1.8)	1.05	1.43	8.1	7.6
	(2.2)	0.92	1.67	8.3	7.7
Rape straw	(1.8)	0.95	1.97	8.3	7.5
+ p.manure	(2.2)	0.96	1.92	8.3	7.2
Ammonium sulph.	(1.8)	1.65	1.93	7.7	6.6
	(2.2)	2.29	2.17	7.7	6.3
Urea	(1.8)	0.77	1.34	8.9	7.7
	(2.2)	0.75	1.63	8.9	7.7
RUN 2					
Poultry manure	(1.8)	1.06	1.44	7.8	7.8
	(2.2)	1.26	1.23	8.0	7.7
Rape straw	(1.8)	1.31	2.11	8.1	7.6
+ p.manure	(2.2)	0.97	1.94	7.8	7.9
Cocoa waste	(1.8)	0.77	1.51	7.2	7.7
	(2.2)	0.98	1.41	8.1	7.4
Spent hop powder	(1.8)	1.21	1.47	8.3	7.9
	(2.2)	0.91	1.68	8.6	8.2
RUN 3					
Ammonium sulph.	(1.8)	1.50	1.96	7.9	6.7
	(2.2)	1.53	3.03	7.9	6.5
Urea	(1.8)	0.80	1.33	8.4	7.8
	(2.2)	0.76	1.68	8.5	7.4
Cocoa waste	(1.8) (2.2)	0.58 1.00	1.40 1.39	8.5 8.5	7.5 7.8
Spent hop powder	(1.8)	0.59	1.82	8.3	8.2
	(2.2)	0.99	1.65	8.6	8.3

APPENDIX 4. Odour concentration (OC) during emptying of Phase 0 tunnels and maximum temperatures during yard blending, Phase 0 and Phase I

		OC	Ma	x. temperature	e, °C
Treatment		Oum <sup>-3</sup>	Yard	Phase 0	Phase I
RUN 1	N at fill, % DM				
Poultry manure	(1.8)	1884	53	77	68
	(2.2)	5801	52	77	69
Rape straw + p.manure	(1.8)	4371	35	64	83
	(2.2)	3465	30	68	83
Amm. Sulph	(1.8)	683	11	76	69
	(2.2)	335	16	71	56
Urea	(1.8)	408	16	73	68
	(2.2)	369	27	76	73
RUN 2					
Poultry manure	(1.8)	1696	71	78	69
	(2.2)	4512	71	78	72
Rape straw	(1.8)	1912	63	75	66
+ p.manure	(2.2)	1288	66	74	75
Cocoa waste	(1.8)	686	54	70	76
	(2.2)	663	61	80	74
Spent hop powder	(1.8)	1180	45	74	65
	(2.2)	4835	66	80	77
RUN 3					
Ammonium. Sulph.	(1.8)	1690	20	67	60
	(2.2)	1852	47	66	59
Urea	(1.8)	2017	58	60	69
	(2.2)	1411	74	70	70
Cocoa waste	(1.8)	1844	76	70	83
	(2.2)	477	73	68	67
Spent hop powder	(1.8)	819	27	69	77
	(2.2)	2418	59	80	78

APPENDIX 5. Mushroom dry matter and nitrogen contents, strain A15, mean of flushes 1 and 2

Treatment	<del>14000000000000000000000000000000000000</del>	Mushroom DM %	Mushroom N % of DM
	<u>Nat fill</u>		
RUN 1	<u>% of DM</u>		
Poultry manure	(1.8)	8.20	6.75
	(2.2)	8.35	6.85
Rape straw +	(1.8)	7.87	5.23
P.manure	(2.2)	7.91	5.51
Ammonium sulphate	(1.8)	7.48	6.09
•	(2.2)	7.03	6.60
Urea	(1.8)	8,52	5.37
	(2.2)	8,20	5.30
RUN 2			
Poultry manure	(1.8)	7.44	5.41
•	(2.2)	7.43	5.65
Rape straw +	(1.8)	7.49	4.28
P.manure	(2.2)	6.96	4.12
Cocoa waste	(1.8)	7.63	6.67
	(2.2)	8.04	6.59
Spent hop powder	(1.8)	8.12	6.69
• • •	(2.2)	7.47	6.68
<u>RUN 3</u>		N.	
Ammonium sulphate	(1.8)		6.11
	(2.2)	8.41	7.56
Urea	(1.8)	8.92	7.13
	(2.2)	8.71	7.39
Cocoa waste	(1.8)	8.14	7.12
	(2.2)	8.02	7.22
Spent hop powder	(1.8)	8.68	5.95
1 F	(2.2)	8.44	5.94