

# Amelioration of Odorous Components in Spent Mushroom Compost

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Volatile sulfur compounds, as well as other volatiles found in the headspace above spent mushroom compost (SMC), were analyzed by gas chromatography and mass spectrometry. Data from these techniques as well as organoleptic evaluation of both the SMC and the chromatographic eluant indicated that the volatile sulfur compounds and cresol were important odorous components in SMC; cresol was reported as a musty, cattle-feces aroma. Samples consisted of headspaces from untreated SMC as well as SMC stirred with 1% (by weight) powdered activated carbon (PAC). SMC stirred with and without PAC reduced headspace volatile concentrations, but the stirred with added PAC further decreased concentrations of important malodorants such as volatile sulfur compounds and cresol.

**Keywords:** *Odor; powdered activated carbon; volatile sulfur compounds; gas chromatography/olfactometry; malodors*

## INTRODUCTION

The 1998 crop of *Agaricus* mushrooms (conventional, white, button variety and the majority of mushroom sales in the United States) grown in the State of Pennsylvania was estimated to be 172 million kg and was valued at 280 million dollars. Pennsylvania's crop accounted for 47% of the total *Agaricus* mushroom sales in the United States (Stout, 1998). Soil utilized for mushroom farming is produced in a three-phase composting process. In phase one, straw from horse stables (including horse manure), hay, crushed corn cobs, cotton seed hulls, gypsum, coco shells, chicken manure, and water are blended together to form large stacks or ricks (Arell, 1999; Derikx et al., 1990; Duns et al., 1997). Ricks are periodically turned and mixed using special machinery to increase compost aeration. This process requires 2–3 weeks to produce a soil-like growing medium. In phase two, the compost is placed in growing rooms and heated with steam to arrest undesirable microbial activity. Mushroom growth and harvest occur in phase three, after the compost is inoculated with spores.

During phase one, considerable volatile materials are typically released into the environment, some of which can cause complaints of malodors. Some of the volatiles identified during the creation of phase one compost have been examined (Derikx et al., 1990; Duns et al., 1997; Miller and Mcauley, 1988). These analyses demonstrated the presence of several volatile sulfur compounds (VSC) and further suggested these compounds as major contributors to malodorous off-gassing. Wheat straw and gypsum have been suggested as important

sources of inorganic sulfur, which is used by anaerobic bacteria to create VSC (Heinemann and Wahanik, 1998).

Following mushroom cultivation, spent mushroom compost (SMC) may be treated in one of two ways. It may be spread onto fields with no additional treatment (no induced aeration) and allowed to remain for approximately 2 years, or it may be placed in ricks to be turned approximately once per week, which significantly increases the rate of microbial decomposition. Subsequently, this spent compost can be utilized for top soil, or it can be bagged and sold as garden soil.

Aeration of spent compost, as in composting phase one, may decrease offensive odors by preventing anaerobic fermentation. The addition of an adsorbing material, such as active carbon, may also lessen the environmental impact of malodorous volatiles produced during spent mushroom composting. Active carbon has been utilized to collect organic volatiles from the atmosphere (Dravnieks et al., 1970), to extract volatiles from headspace (Sakaki et al., 1984), and for ingredient purification in the brewing industry (Ragan and Bayati, 1993).

Carbon is treated with either excessive heat (typically 1000 °C) or acids (such as phosphoric), or both, to increase molecular pore structure. "Activated" carbon traps molecules by processes that include van der Waals forces and chemisorption. Increased porosity also may selectively trap molecules according to size (Smith, 1999). Our study was conducted to identify the volatile odorous components of SMC and to evaluate the potential use of active carbon to reduce the emission of odor-causing molecules from SMC.

## MATERIALS AND METHODS

Two separate batches of SMC from Chester County, PA, were collected 5 months apart (February 1999 [batch 1] and July 1999 [batch 2]), packaged in 5-gal plastic buckets, and sealed with air-tight lids. Each batch had been spread on a neighboring farm field for approximately 2 weeks prior to

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packaging for our studies. Approximately 25 g of compost was removed from the buckets, placed in each of four, 122-mL glass jars, and sealed with screw-top caps. The volatile materials in the headspace of each jar were analyzed in duplicate for volatile sulfur compounds (VSC) by gas chromatography with flame photometric detection (GC/FPD). The VSC were monitored for carbonyl sulfide (COS), hydrogen sulfide ( $\text{H}_2\text{S}$ ), methyl mercaptan ( $\text{CH}_3\text{SH}$ ), dimethyl sulfide [ $(\text{CH}_3)_2\text{S}$ ], and carbon disulfide ( $\text{CS}_2$ ), as described below. Additionally, the volatiles in the headspace above SMC were collected using solid phase microextraction (SPME). Analyses of volatiles collected by SPME were subsequently performed with gas chromatography (GC), GC/mass spectrometry (GC/MS), and GC/olfactometry (GC/O), described in detail below. Duplicate, identical analyses were conducted on each of the two SMC samples.

#### Treatment with Powdered Activated Charcoal (PAC).

Following initial analyses by GC/FPD, SPME/GC, GC/MS, and GC/O, two of the four jars were treated with 1% (by weight) PAC (Nuchar SA-20, Westvaco Corp, Covington, VA), stirred vigorously for 7 s with a stainless steel spatula with the sample exposed to the atmosphere (stirred/aerated), and then resealed with a screw lid. No carbon was added to the remaining two jars, but they were stirred and treated in the exact manner. The last step was included to determine whether simply exposing compost to air during stirring affected quantities of headspace volatiles in a manner similar to that caused by adding carbon and stirring. Analyses were again conducted with the techniques listed above.

**Gas Chromatography with Flame Photometric Detection (GC/FPD).** VSC were measured by analyzing 5-mL aliquots of headspace from each jar using a gas chromatograph (Finnigan model 9001) equipped with a flame photometric detector (FPD, Finnigan Corp, Austin, TX) and a 6-port air sampling valve (Valco Corp., Houston, TX). Separation and analysis of VSC were accomplished using a 36 ft  $\times$  1/8 in. Teflon sulfur gas column. Analysis conditions were as follows: initial oven temperature 90 °C held for 4 min, followed by 16 °C/min ramp to 140 °C which was held for 10 min; injector and detector temperatures were 100 and 125 °C, respectively; column flow rate was 30 mL/min. An analogous system has been described previously for analysis of VSC from human mouth air (Tonzetich, 1971; Kostelc et al., 1984).

**SPME/Gas Chromatography with Flame Ionization Detection (SPME/GC).** Headspace volatiles were also collected/extracted by SPME. A 2 cm, three-component fiber was used for extraction of volatiles (30  $\mu\text{m}$  carboxen, 50  $\mu\text{m}$  divinyl benzene, polydimethyl siloxane, Supelco Corp, Bellefonte, PA). Analysis was conducted with a Hewlett-Packard 5890 GC (Hewlett-Packard, Palo Alto, CA) equipped with a flame ionization detector (FID) and a 30 m  $\times$  0.32 mm (i.d.) column with a 1.0  $\mu\text{m}$  coating of STABILWAX (Restek Corp. Bellefonte, PA). Equilibration (extraction of volatiles above SMC) was conducted for 5 and 30 min. GC operating conditions were as follows: 60 °C for 4 min followed by 6 °C/min to 220 °C, then held at 220 °C for 10 min. Injector and detector temperatures were 230 and 240 °C, respectively; column flow rate was 100 cm/s. Analyses were repeated four times for each sample.

**Gas Chromatography/Mass Spectrometry (GC/MS).** Volatiles in the headspace above SMC collected by SPME (30 min extraction) were further analyzed with a Finnigan 4510 GC/MS equipped with a 30 m  $\times$  0.32 mm i.d. column with a 1.0  $\mu\text{m}$  coating of STABILWAX. Operating parameters were as follows: ion source temperature 150 °C, ionizing energy at 70 eV; the chromatographic analysis was 60 °C for 4 min followed by 6 °C/min to 220 °C for 10 min; injector and detector temperatures were 230 and 240 °C, respectively; column flow rate was 35 cm/s.

**Gas Chromatography/Olfactometry (GC/O).** Sensory screening of chromatographic eluants was conducted to determine whether odorants in the headspace above spent compost and PAC-treated SMC compost differed in odor quality and intensity. GC/O analysis was conducted with a model 9001 Finnigan GC equipped with a 15 m, 0.53 mm i.d. STABILWAX column (2.0  $\mu\text{m}$  coating). This GC was modified

so that 90% of the eluate flowed to a "sniff port" and the remaining 10% of eluate was directed to the FID. Our sniff port consisted of a 7.5 cm, 2.1 mm i.d. Silcosteel (Restek Corp, Bellefonte, PA) line coupled to a 10 cm, 4 mm i.d. glass line that is adjoined by a glass brace to the glass tube that carried GC effluent was an identical glass tube that carried humidified air. Both tubes were attached to a single glass funnel so that effluent was mixed with humidified air at the point where effluent was sniffed by panelists.

Purified, humidified air was obtained by directing compressed air through activated carbon then sequentially through Drierite molecular sieve 5A (Alltech, Deerfield, IL) and a temperature controlled, water-filled, round-bottomed flask fitted with input and output glass fittings. This humidified, purified airstream was adjusted to a flow rate of 1 L/min and directed orthogonally to the sniff-port effluent so as to sweep the eluting chromatographic components to the nose. Panelists verbally described the aroma to an experimenter, recording both the retention times and verbal descriptions. This allowed aroma descriptors to be coupled with the FID response and retention time. A series of C2–C18 ethyl esters was employed to obtain relative retention times for all analyses. This allowed us to assign a relative retention time index (ethyl ester index; EEI; van den Dool and Kratz, 1963; relative to ethyl esters) to important odors and further link these to mass spectra.

## RESULTS

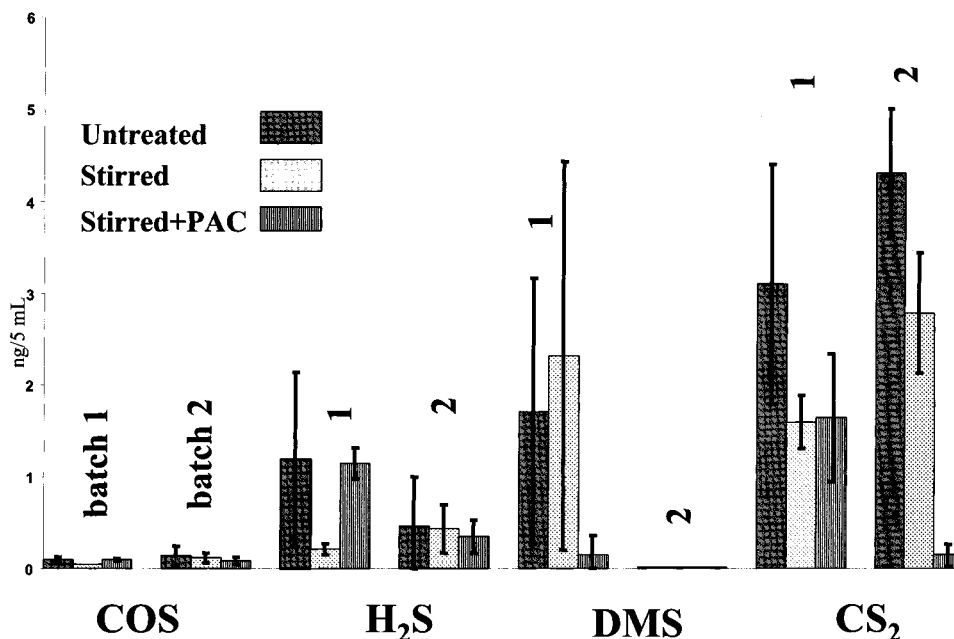
Analysis for VSC by GC/FPD revealed the presence of four compounds: COS,  $\text{H}_2\text{S}$ ,  $(\text{CH}_3)_2\text{S}$ , and  $\text{CS}_2$ . Figure 1 shows the levels of VSCs before and after. The two VSCs present in highest amounts in SMC are  $(\text{CH}_3)_2\text{S}$  and  $\text{CS}_2$ . VSCs were decreased by each treatment with PAC. Reductions in COS and  $\text{H}_2\text{S}$  were not apparent. No methyl mercaptan was found during our analyses. The VSC analyses also suggest differences in the amounts of DMS between two batches of SMC as seen in Table 1.

Addition of 1% PAC to SMC also resulted in reductions of most headspace volatile components measured by SPME/GC, GC/MS, and GC/O. This reduction is most apparent in the results of the GC/O and SPME/GC experiment as seen in Table 2.

**SPME/GC.** Collection and analysis of volatiles in the headspace above SMC by SPME/GC revealed a complex mixture of compounds. A large number of compounds collected by the SPME technique elute early in the chromatogram. In addition to the VSC displayed in Figure 1, a variety of other compounds in this complex mixture appear to contribute to SMC aroma. Their times of elution in the chromatogram were identified by the GC/O technique. GC/MS data combined with the EEI were used to identify a number of the constituents. Table 2 also demonstrates the percent reduction in constituents listed by retention times and identity.

**GC/O.** A considerable number of compounds with sulfurous notes elute within the first 10–15 min of the GC analysis (EEI < 9) including dimethyl disulfide and dimethyl trisulfide. Those that elute within the first 3 min include  $(\text{CH}_3)_2\text{S}$  and  $\text{CS}_2$ , which were described as dull earthy and oniony. The odor description given to cresol was musty cow feces. This compound was judged as being intense and characteristic of the non-sulfurous odor from SMC.

Except for the VSC listed in Figure 1, no quantitation of the volatile constituents above SMC was performed. Table 2 provides all identifications, both tentative and certain, where possible. Furthermore, we have paired the mass spectral data with the organoleptic evalua-



**Figure 1.** VSC in 5 mL of SMC headspace with standard deviations indicated by error bars.

**Table 1.** Mean Values for VSC in SMC Headspace Shown as ng/10 mL Headspace

SMC collection date	COS			H <sub>2</sub> S			DMS			CS <sub>2</sub>		
	ng/10 mL headspace	SD	% reduction	ng/10 mL headspace	SD	% reduction	ng/10 mL headspace	SD	% reduction	ng/10 mL headspace	SD	% reduction
February 28, 1999												
no treatment	0.09	0.03	***	1.19	0.95	***	1.71	1.45	***	3.1	1.31	***
stirred only (aerated)	0.04	0	55.56	0.21	0.06	82.35	2.32	2.2	0	1.6	0.29	48.39
carbon + aeration	0.09	0.02	0	1.15	0.17	3.36	0.15	0.21	91.23	1.65	0.7	46.77
July 13, 1999												
no treatment	0.13	0.11	***	0.46	0.54	***	0.01	0.02	***	4.3	0.7	***
stirred only (aerated)	0.12	0.05	7.69	0.43	0.26	6.52	0	0	100	2.79	0.65	35.12
carbon + aeration	0.08	0.04	38.46	0.35	0.18	23.91	0	0	100	0.14	0.12	96.74

**Table 2.** Identity of SMC Odors: Untreated and Following PAC Addition/Stir

identity	EEI	retention time (min)	% FID peak area reduction after PAC + stir	aroma descriptors (GCO) untreated	aroma descriptors (GCO) after PAC + stir <sup>e</sup>
dimethyl sulfide/carbon disulfide	2.00–4.00	1.13	94	soft fruity onion	none
butyl cyclohexane <sup>a</sup> /dimethyl disulfide	4.28	1.87	0 <sup>c</sup>	dull earthy, oniony	none
unsaturated hydrocarbon <sup>b</sup>	4.65	2.83	95	coal tar, phenolic	woody, soft
pentyl cyclohexane <sup>b</sup>	5.33	4.52	0 <sup>c</sup>	tar	oily tar
cyclic terpene	5.9	5.92	97	onion	weak sulfurous
C-6 cyclohexane/ <i>n</i> -hexyl cyclohexane <sup>b</sup>	6.68	7.76	98	earthy, sulfur	none
dimethyl trisulfide/isoctanol	7.54	9.7	100	pungent sulfur, bad eggs	dirty sulfurous
acetic acid	8.21	11.19	0 <sup>c</sup>	smoked fish, coal tar	none
unknown	8.44	11.68	100	sulfury	soft sulfury
3-keto compound <sup>b</sup>	9.24	13.4	0 <sup>c</sup>	blips of sulfur	blips of sulfur
unknown	9.79	14.54	0 <sup>c</sup>	earthy, strong, humenol	none
isovaleric acid	10.42	15.83	0 <sup>c</sup>	cooked egg whites	none
unknown	11.21	17.4	0 <sup>c</sup>	cigar-like	none
unknown	11.43	17.83	0 <sup>c</sup>	fresh air solvent	none
unknown	12.03	19	0 <sup>c</sup>	metallic, burnt	none
phenol	13.14	21.1	100	burnt plastic	none
cresol	13.89	23.83	100	musty cow feces	none
4-hydroxybenzaldehyde <sup>b</sup>	16.86	27	0 <sup>c</sup>	almonds, benzaldehyde	honey, green
indole <sup>b</sup>	18.1	34.21	0 <sup>d</sup>		

<sup>a</sup> Mass spectrum and retention time identical to commercially available standard; other alkyl cyclohexanes tentatively identified had similar mass spectra. <sup>b</sup> Peak tentatively identified by mass spectrum. <sup>c</sup> Peak found during GC/O only, no corresponding peak seen in SPME/GC analysis; hence, not quantified. <sup>d</sup> Peak found only with MS. <sup>e</sup> Note the numerous absences of odor descriptors relative to untreated samples.

tions. The presence of several cyclohexanes and unsaturated alkenes or alcohols in SMC were tentatively identified from their mass spectra. As noted in Table 2, the identity of butylcyclohexane was confirmed via a commercially available standard. Other homologues listed display similar mass spectra.

## DISCUSSION

Complaints from local property owners of unpleasant odors generated from decomposing compost have grown in recent years due to an increase in land development near areas traditionally utilized in mushroom soil



composting (Arell, 1999). The results presented above strongly suggest that the addition of inexpensive PAC may be a powerful mitigator of odors arising from SMC. Prolonged mixing in air may also yield similar reductions for some VOCs, but adding PAC while mixing appears to be fast, efficacious, and more complete. The reductions seen in Table 1, Table 2, and Figure 1 demonstrate that VSC, cresol, and a variety of other constituents are markedly reduced by treatment with 1% PAC. This suggests an inexpensive, reliable, and safe method for reducing nuisance odors for the mushroom industry, particularly for those farms that wish to convert SMC to a marketable product. We employed and demonstrated the efficacy of 1%, by weight, PAC; it is probable that at 2–5% a greater reduction in odor could be obtained.

The results are the first reported analyses of SMC using multiple analytical techniques. Furthermore, these analyses demonstrate that SMC contained an odor bouquet similar to that reported for phase one compost (Derikx et al., 1990), with respect to sulfur malodorants. Major differences are the lack of methyl mercaptan and lower levels of H<sub>2</sub>S seen in our analyses of SMC. Neither the mixture of alkyl cyclohexyl compounds nor the trace amounts of isovaleric acid have been previously reported in mushroom compost.

One previous study of phase one compost mixes and soil reported VSC levels far in excess of what we noted here (Derikx et al., 1990). In that study, micromolar concentrations of VSC were reported to be emitted from phase one composting activities. The values from that study were based on the amount emitted by kilogram of phase one compost. Assuming a linear increase, the amounts of VSC reported here, in Figure 1, when extrapolated to 1 kg would yield nanomolar levels of materials or 1000 times less that reported for phase one. This suggests far less malodor producing capacity in SMC than phase one compost perhaps due to different bacterial mixes and/or less available sulfate.

The human sense of smell is very sensitive to sulfur-containing compounds. This undoubtedly accounts for organoleptic identification of several sulfurous notes when no mass spectrometry evidence corresponding to sulfur-containing compounds was available. It is possible that our SPME procedure did not capture sufficient amounts of these putative S-containing compounds to yield recognizable mass spectra. Further investigation of SMC utilizing dynamic headspace collection with Tenax may be warranted to determine the nature of these trace sulfurous compounds. However, as seen in Table 1, treatment with PAC reduced or eliminated all the sulfurous odor notes.

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