

This is not a peer-reviewed article.

Pp. 026-033 in Air Pollution from Agricultural Operations III, Proceedings of the 12-15 October 2003 Conference (Research Triangle Park, North Carolina USA), Publication Date 12 October 2003. ASAE Publication Number 701P1403, ed. H. Keener.

CHARACTERIZATION OF ODORANTS FROM PRODUCTS OF 14 DIFFERENT COMMERCIAL COMPOSTS USING SOLID PHASE MICROEXTRACTION

H. Kim¹, L. L. McConnell², P. Millner³

ABSTRACT

In this study, headspace odorants from market-ready, commercial composts supplied by 14 different producers were characterized with a recently developed analytical method using solid phase microextraction (SPME). The products analyzed were derived from a cross-section of the wide array of compost feedstock ingredients used in the U.S., e.g., biosolids, yard trimmings, animal manure, and industrial by-products. A variety of quality assessment tests were performed using test procedures specified in a national certification program offered through the U.S. Composting Council. Measurements of odorous chemicals, i.e., trimethylamine, carbon disulfide, dimethylsulfide, dimethyldisulfide, propionic acid, and butyric acid, supplemented other quality aspects in the evaluation of stability. From the results, relatively higher levels of sulfur compounds were detected from marketable composts containing sewage sludge than from composts produced with other feedstocks. The greatest amounts of reduced sulfur compounds were produced from a compost containing an industrial sludge and agricultural byproducts. Pathogen indicator microbes for most composts were within limits for Class A (USEPA 40CFR Part503). Very large numbers of fecal coliforms, *E. coli*, and *Enterococcus* were present in the compost that produced the greatest concentrations of carbon disulfide and dimethylsulfide. Compost containing biosolids and yard wastes produced relatively higher level of propionic and butyric acids than those containing other ingredients. Odorant analysis of final products can be readily evaluated with the SPME method reported here. Results in combination with other compost quality factors may help compost producers and users improve product quality.

KEYWORDS. composting, odor, solid-phase microextraction, trimethylamine, carbon disulfide, dimethylsulfide, dimethyldisulfide, propionic acid, butyric acid, maturity, stability

INTRODUCTION

Composting of agricultural, domestic, and industrial residuals is increasingly employed to reduce weight and volume of the materials, to destroy pathogens, to stabilize nutrients and to produce organic soil amendments for agriculture and horticulture (Lafond et al., 2002). In the U.S., the number of composting facilities processing sludge from municipal or industrial wastewater treatment facilities, yard debris, animal manure, and food residuals also continues to increase.

¹ The University of Seoul Dept. of Environmental Engineering, 90 Jeonnong-dong Dongdaemun-gu, Seoul 130-743, Korea (h_kim@uos.ac.kr)

² US Dept. of Agriculture - Agricultural Research Service, Environmental Quality Laboratory, 10300 Baltimore Ave., Beltsville, MD 20705, USA (mcconnel@ba.ars.usda.gov).

³ US Dept. of Agriculture - Agricultural Research Service, Sustainable Agricultural Systems Laboratory, 10300 Baltimore Ave., Beltsville, MD 20705, USA (millnerp@ba.ars.usda.gov).

As the quantity of the residuals being composted increases, the quality of the final marketable compost products is attracting more interest from the public. The quality of commercial composts is often evaluated by measuring the content of heavy metals, moisture, pathogens and nutrient content (Gagnon et al., 1999) and other factors important to agronomists and horticulturalists (US Composting Council, 2002). However, odors from composts produced with different ingredients have not been assessed systematically. Experience in the U.S. has shown that processing and product odors have a major impact on the success of a facility. When composting facilities consistently create nuisance odors, their neighbors complain and some have even been forced to close (Feinbaum, 2000).

Day et al. (1998) evaluated some volatile compounds using syringe collection followed by GC analysis of emissions from a commercial, outdoor, yard waste compost over 49 days. Several volatile sulfur compounds, for example, methylmercaptan and dimethylsulfide (DMS), are known to be produced through microbial decomposition of sulfur containing organic materials including the amino acids, cysteine, and methionine.

Odor evaluation by olfactometry with human subjects typically involves collecting volatiles into Tedlar bags and transporting them back to a laboratory for analysis. It is an expensive approach that does not provide specific chemical information. In addition, the method produces large differences in values between laboratories, even with the same sample (Gostelow et al., 2001). This is mainly due to the difficulty in calibration of the olfactometer and sample handling (Duffe and Cha, 1980). Shultz and van Harrelveld (1996) observed 1-3 orders of magnitude difference in odor concentration of a sample between different laboratories.

Recently, we developed a convenient and accurate method to quantify odorous compounds in a gas matrix using solid phase microextraction (SPME) coupled with gas chromatography (GC) (Kim et al., 2002a) and have applied this new method to analysis of odorants from each unit process at a large wastewater treatment plant (Kim et al., 2002b). We have also used the method to study the mechanism of trimethylamine (TMA) generation from biosolids (Kim et al., 2003), and to characterize odorants from heat-dried pellets (Murthy et al., 2002). Since using SPME sample collection and analyte extraction/concentration can be carried out in one step (Pawliszyn, 1997), Tedlar bags or Summa Canisters for gas sampling and any extraction procedure are not required. The analysis of the odorous volatile compounds can be performed directly from the fibers without further sample handling.

In this study, headspace odorants from commercial composts from 14 different producers were characterized with the newly developed method with SPME. The products analyzed comprise a cross-section of the wide array of compost feedstock ingredients used throughout the U.S., e.g., biosolids, yard trimmings, animal manure, and industrial by-products. We investigated the relationship between odorant characteristics, feedstocks, and stability of the products.

MATERIAL AND METHODS

Gas Analysis

Calibration of SPME Fibers

The preparation of gas standards that are used for SPME calibration is an important and challenging component of the method, since the odorous gases are very reactive and unstable. Gas standards were generated using certified Teflon membrane permeation devices (NIST traceable, VICI Metronics, Inc., Santa Clara, California, USA) for each compound (Table 1). The permeation devices were placed together in a thermostated glass chamber of a Model 320 Dynacalibrator (VICI Metronics, Inc.). The high purity (99.99%) nitrogen gas flows through the permeation chamber at 72 ml/min, and the concentration was varied using additional dilution gas. Two SPME fibers were exposed to the gas standard in a temperature-controlled (20 °C), Teflon cylindrical collection chamber (i.d. = 4.1 cm, Savillex, Co., Minnetonka, Minnesota, USA) (Fig. 1). The temperature inside the chamber was measured by inserting a temperature probe (TraceableR-4085, Control Com., Houston, Texas, USA) into the chamber. The chamber was

equipped with two septa ports with Teflon coated septa through which the needle of the SPME device was inserted so that duplicate measurements could be made for all calibration points. A more detailed description of the calibration process is given elsewhere (Kim et al., 2002a).

Table 1. Physical properties, method detection limits, and odorant threshold for human detection of target analyses.

Compounds	Molecular Weight, g/mol	Boiling Point*, °C	MDL**, ppbv	Odor Threshold, Ppbv
Propionic acid	74	141.4	1.80	28 (Hellman and Small, 1974)
Butyric acid	88	163.5	1.32	0.5 (Fazzalari, 1978)
Trimethylamine	59	2.9	2.38	0.44 (O'Neill and Phillips, 1992)
Carbondisulfide	76	46.5	0.19	16 (Verschuere, 1983)
Dimethylsulfide	62	37.3	0.07	0.11 (Amoore and Hautala, 1983)
Dimethyldisulfide	94	109.7	0.06	6.4 (Fors, 1988)

*Obtained from Budavari *et al.* (1996).

**Method detection limit. MDL determined with 8 samples; EPA standard procedure for MDL calculation was followed (Longbottom and Lichtenberg, 1982).

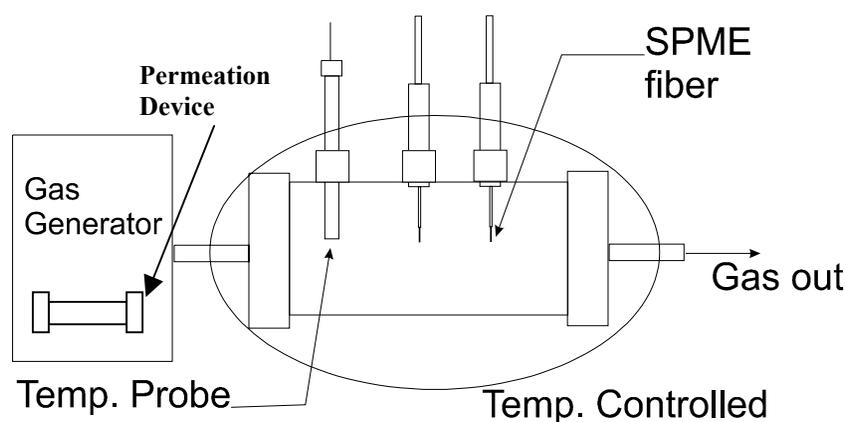


Figure 1. Schematic diagram of experimental set up for SPME calibration

SPME and Gas Chromatography Conditions

A 75 μm Carboxen-Polydimethylsiloxane (Car-PDMS) coating was used to capture TMA, carbon disulfide (CS_2), DMS and dimethyldisulfide (DMDS), and an 85 μm Polyacrylate coating was used for propionic acid (PA) and butyric acid (BA) (Supelco, Bellefonte, Pennsylvania, USA). Car-PDMS has been used for the analysis of reduced sulfurs (Abalos et al., 1999; Hill and Smith, 2000). Polyacrylate fibers are often used for polar compounds (Pan et al., 1995). Analysis of propionic and butyric acids was performed using capillary gas chromatography with flame ionization detector using a Hewlett Packard 5890 gas chromatograph. A Hewlett Packard 5890 gas chromatograph coupled to an HP 5970 mass spectrometer was used in selected ion monitoring mode for TMA and the reduced sulfur compounds. Both GC systems were equipped with a Merlin microseal septum (Supelco, Bellefonte, Pennsylvania, USA) designed for SPME to insure reproducibility between injections. Detailed chromatographic conditions are given elsewhere (Kim et al., 2002a).

Sample Collection and Analysis

Fourteen different producers sent samples of their final stage (marketable) compost products to our laboratory in Beltsville, Maryland. Once each sample was delivered, it was assigned a code number and stored at 4 °C until its odorous compounds were analyzed.

Sub-samples (200 mg) of the final products were transferred into a 1.0 L Teflon jar (Fig. 2). The headspace was flushed with pure N_2 gas at a constant rate (72 mL/min) at room temperature which was controlled at 20 ± 2 °C. Odorous compounds in the headspace were sampled by exposing SPME fibers to the off gas for 1 hr in the collection chamber portion of the sample assembly (Fig. 2). After sampling, the fibers were withdrawn (self-sealed from the atmosphere) and immediately

stored in a freezer (-20 °C) until directly injected into the GC for analysis. The GC analysis was performed on the same day to minimize losses.

Compost Quality Analyses

The pH, moisture and microbial analyses (fecal coliforms, *E. coli*, and *Enterococcus*) were conducted according to the protocols described in the Test Methods for Compost and Composting (U.S. Composting Council, 2002).

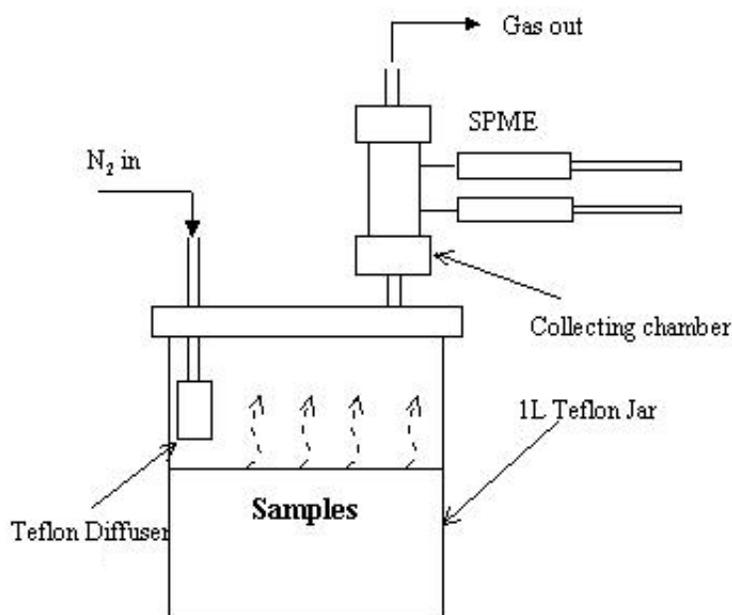


Figure 2. Schematic diagram for experimental set up for sample analysis

RESULTS AND DISCUSSION

Ingredients and Biological Properties of Composts under Study

Each producer provided a list of feedstocks used to prepare their compost and annual volume of materials composted; data are summarized in Table 2. All facilities mix their feedstocks together prior to composting to meet porosity, moisture, and carbon:nitrogen criteria needed to support aerobic microbial decomposition. Six out of 14 facilities were composting biosolids from their local wastewater treatment plants. Eight facilities were composting yard wastes. Two facilities were using industrial byproducts as a feedstock for their composting. Three facilities compost animal manures or byproducts.

The composting facilities participating in this research were asked if they were doing pathogen and metal tests for their composts. All the facilities composting biosolids were performing pathogen and metal testing on their composts. However, regulatory requirements for testing yard debris compost differ by jurisdiction. So, not all those products were routinely tested.

Table 3 shows pH, moisture content and biological properties of the composts provided by the 14 different commercial producers. The high microbial count of some composts (site # 6, # 8, and # 9) suggest that thermophilic heating throughout the composting mass was not high enough or long enough to disinfect the material to meet Class A criteria (EPA, 1993). Some of the composts were highly variable in microbial counts, indicating that the composts were not well homogenized.

Table 2. General information on composts and their producers under study

Site number	Feedstock	Annual Vol m ³ .	Pathogen/Metals Testing
1	BS, YW	134,000	Yes/yes
2	BS, YW	N/A*	Yes/yes
3	BS, WC	53,000	Yes/yes
4	BS, PH	57,000	Yes/yes
5	YW, FD, MN	15,000	No/yes
6	YW, MN, IB, WC	N/A	Yes/yes
7	BS, YW	54,000	Yes/yes
8	IB, AB	35,000	No/yes
9	BS, WC	38,000	Yes/yes
10	YW	67,000 tons	No/no
11	YW	N/A	No/no
12	YW, WC	38,000	No/yes
13	YW, FT	46,000	Yes/yes
14	CG, TL, YW, CB, FS	42,000	No/yes

*N/A: not available

BS: biosolids; YW: yard waste; WC: wood chips; PH: peanut hulls; FD: food; MN: manure; IB: industrial by-products; AB: agricultural by-product; CG: coffee grounds; TL: tea leaves; FS: food processing sludge; FT: feathers; CB: coconut by-product

For most of the samples, pH was in a typically moderate range, with the exception of sites # 8 and # 14. The latter two used feedstock ingredients that promoted this lowered pH. However, microbial decomposition should not be inhibited in either of these situations.

Table 3. pH, moisture content and microbial count of composts under study

Site number	Feedstock	pH	Moisture %	<i>Fecal Coliforms</i> , (Log ₁₀ MPN [*])/g	<i>E. coli</i> , (Log ₁₀ MPN)/g	<i>Enterococci</i> , (Log ₁₀ MPN)/g
1	BS, YW	7.53 (0.10)**	63 (8)	ND***	ND	ND
2	BS, YW	7.18 (0.08)	29 (2)	< 0.7	< 0.7	< 0.7
3	BS, WC	8.06 (0.10)	39 (4)	2.9 (3)	1.9 (1.9)	5.9 (5.6)
4	BS, PH	6.99 (0.05)	17 (1)	ND	ND	ND
5	YW, FD, MN	7.25 (0.00)	37 (1)	1.4 (1.6)	1.2 (1.3)	2.5 (2.6)
6	YW, MN, IB, WC	6.90 (0.03)	16 (1)	3.1 (3.1)	1.5 (1.6)	6.3 (5.9)
7	BS, YW	8.77 (0.04)	33 (0)	ND	ND	ND
8	IB, AB	6.44 (0.46)	49 (3)	7.1 (7.0)	3.3 (2.1)	7.1 (5.8)
9	BS, WC	7.25 (0.02)	48 (0)	2.4 (0.6)	1.3 (0.8)	6.7 (6.1)
10	YW	6.98 (0.03)	54 (0)	2.1 (2.0)	2.0 (2.0)	2.8 (2.5)
11	YW	7.91 (0.00)	47 (2)	ND	ND	ND
12	YW, WC	6.52 (0.60)	29 (7)	ND	ND	ND
13	YW, FT	6.92 (0.06)	18 (2)	2.7 (2.5)	2.7 (1.5)	4.4 (4.6)
14	CG, TL, YW, CB, FS	6.29 (0.13)	56 (4)	2.6 (2.8)	2.1 (2.3)	4.4 (4.6)

*MPN: most probable number

** () : standard deviation of triplicates

***ND: not detected.

BS: biosolids; YW: yard waste; WC: wood chips; PH: peanut hulls; FD: food; MN: manure; IB: industrial by-products; AB: agricultural by-product; CG: coffee grounds; TL: tea leaves; FS: food processing sludge; FT: feathers; CB: coconut by-product

Odorant Characteristics of Composts under Study

The mean concentration of selected odorants in the 200 mg sub-samples of each compost characterized by headspace analysis using SPME are shown in Table 4. No TMA, which is noticeable by its “fishy” odor, was detected in any of the compost products, either by chemical analysis or technical staff conducting the analyses. Reduced sulfur compounds, especially CS₂, were found in all composts, but the amounts and types vary. Generally, composts containing biosolids had greater concentration and types of reduced sulfur compounds than non-biosolids

composts. The presence of reduced sulfur compounds in biosolids compost is consistent with previous reports from the U.S. (Hentz et al., 1992) and Europe (Van Durme et al., 1992). Reduced sulfur compounds have also been found in association with livestock operations and composted manure (O'Neill and Phillips, 1992).

Relatively high (PA + BA > 10 ppb) concentrations of PA and BA were found in headspace of the composts containing biosolids and yard waste (sites #2 and #7). These volatile fatty acids are the products of anaerobic fermentative decomposition, such as occurs in production of silage and in the bovine rumen. Composts from yard wastes can also develop these fatty acid byproducts when anaerobic fermentative conditions occur, even in localized places within a pile. The presence of large numbers of heterotrophic microbes, typically $10^7 - 10^8$ MPN per gram dry weight of compost solids (data not shown), combined with microsites of anaerobiosis in a compost feedstock mix containing yard waste, would support production of PA and BA until the carbon sources supporting such a microbial transformation are depleted. The presence of high amounts of volatile fatty acids, e.g. PA + BA > 10 ppb, in marketable composts would indicate that compost is still unstable and that additional rapid decomposition could still take place given proper condition.

Table 4. Concentration (ppbv) of odorous gases from final products of different composting facilities

Site number	Feedstock	TMA	CS ₂	DMS	DMDS	PA	BA
1	BS, YW	ND*	BQL**	0.2(0.1)***	0.1(0.1)	BQL	BQL
2	BS, YW	ND	11.2(7.6)	0.9(1.0)	5.6(2.4)	7.9(5.7)	16.3(17.9)
3	BS, WC	ND	7.1(1.0)	3.5(0.6)	0.7(0.1)	3.9(1.8)	ND
4	BS, PH	ND	0.6(0.2)	0.7(0.2)	ND	ND	ND
5	YW, FD, MN	ND	ND	0.2(0.3)	ND	BQL	ND
6	YW, MN, IB, WC	ND	0.7(0.3)	0.2(0.1)	0.1(0.1)	ND	ND
7	BS, YW	ND	1.4(0.2)	2.1(0.6)	3.0(0.4)	11.3(10.4)	ND
8	IB, AB	ND	12.9(13.3)	9.8(15.7)	ND	ND	ND
9	BS, WC	ND	3.3(1.1)	9.8(4.2)	ND	3.4(1.2)	ND
10	YW	ND	BQL	0.1(0.0)	ND	BQL	BQL
11	YW	ND	0.2(0.0)	0.1(0.0)	ND	BQL	ND
12	YW, WC	ND	BQL	0.4(0.3)	ND	ND	ND
13	YW, FT	ND	ND	1.5(1.2)	ND	3.0(2.0)	ND
14	CG, TL, YW, CB, FS	ND	0.6(0.1)	0.3(0.2)	0.1(0.1)	BQL	BQL

*ND: not detected.

**BQL: below quantification level.

***(): standard deviation of triplicates

Relatively high concentrations of DMS were detected from compost at sites #8 and #9. These composts also had high counts of pathogen indicator microbes. This suggests that additional thermophilic composting and/or curing are needed to increase the disinfection process and to further decompose the organic constituents to a stable, mature state.

CONCLUSION

This is the first comparative report of odorants from commercially marketed composts in the U.S. A SPME method coupled with GC/FID/MS analysis, as previously reported by Kim et al. (2002b) for use with sewage sludge, was used to characterize selected odorous emissions from compost. Composts containing biosolids continued to emit reduced sulfur compounds in varying amounts (0.1-12.9 ppbv). High concentrations of the volatile fatty acids, PA and BA, in the marketable products were only detected from composts containing both biosolids and yard wastes/woodchips. This suggests that the decomposition of the organic constituents at some places in these materials still remains relatively incomplete, and that some anaerobic biological decomposition is continuing. Volatile fatty acids result from the fermentative decomposition of organic materials such as those found in yard wastes and silage. Because of the potentially phytotoxic effects of some volatile fatty acids, especially acetic acid, additional composting and curing may be helpful to further stabilize such products. This would also benefit those composts in which insufficient

pathogen reduction was achieved as evidenced by relatively high numbers of fecal coliforms, *E. coli*, and *Enterococcus* ($> 10^3$ MPN/g).

REFERENCES

1. Abalos, M., J. Bayona, and F. Ventura. 1999. Development of a solid phase microextraction GC-NPD procedure for the determination of free volatile amines in wastewater and sewage-polluted water, *Anal. Chem.*, 71, 3531-3537.
2. Amoores, J. E., and E. J. Hautala. 1983. Odor as an aid to chemical safety: odor thresholds compared with threshold limit values and volatilities for 214 industrial chemicals in air and water dilution, *Appl. Toxicol.*, 3, 272-290.
3. Budavari, S., M. J. O'Neil, A. Smith, P. Heckelman, and J. F. Kinnerary. 1996. *The Merck Index*, Merck & Co., Inc., Whitehouse Station, New Jersey, USA.
4. Day, M., M. Krzymien, K. Shaw, L. Zaremba, W. R. Wilson, C. Botden, and B. Thomas. 1998. An investigation of the chemical and physical changes occurring during commercial composting, *Compost Sci. & Util.*, 6(2), 44-66.
5. Duffee R. A. and S. S. Cha. 1980. Consideration of physical factors in dynamic olfactometry. *J. Air Pollut. Control Assoc.*, 30, 1294-1295.
6. EPA. 1993. Federal Register 40 CFR Parts 503: Standards for the Use or Disposal of Sewage Sludge, EPA#: 822/Z-93-001, Washington DC, USA.
7. Fazzalari, F. A. 1978. *Compilation of Odor and Taste Threshold Data*, ASTM Data Series DS 48A.
8. Feinbaum, R. 2000. Compost site pursues odor management goals, *Biocycle*, 41(10), 46-49.
9. Fors, S. 1988. Sensory properties of volatile maillard reaction products and related compounds, In: *The Maillard Reaction in Foods and Nutrition*, 185-286, ACS Symposium Series 215, G. R. Waller and M. S. Feather (ed), ACS, Washington DC, USA.
10. Gagnon, B., R. Robitaille, and R. R. Simard. 1999. Characterization of several on-farm and industrial composted materials. *Can. J. Soil Sci.*, 79(1), 201-210.
11. Gostelow, P., S. A. Parsons, and R. M. Stuetz. 2001. Odour measurements for sewage treatment works. *Water Res.*, 35(3), 579-597.
12. Hellman, T. M., and F. R. Small. 1974. Characterization of the odor properties of 101 petrochemicals using sensory methods, *J. Air Pollut. Control Assoc.*, 24, 979-982.
13. Hentz, L.H. Jr., C. M. Murray, J. L. Thompson, L. L. Gasner, J. B. Dunson, Jr. 1992. Odor control research at the Montgomery County Regional Composting Facility. *Water Env. Res.* 64, 13-18.
14. Hill, P. G., and M. Smith. 2000. Determination of sulfur compounds in beer using headspace solid-phase microextraction and gas chromatographic analysis with pulsed flame photometric detection, *J. Chromatogr. A*, 872, 203-213.
15. Kim, H., C. Nochetto, and L. L. McConnell. 2002a. Gas phase analysis of trimethylamine, propionic and butyric acid, and reduced sulfurs using solid phase microextraction, *Anal. Chem.* 74(5), 1054-1060.
16. Kim, H., S. Murthy, L. L. McConnell, C. Peot, M. Ramirez, and M. Strawn. 2002b. Characterization of wastewater and solids odor using solid phase microextraction at a large wastewater treatment plant. *Water Sci. & Technol.*, 45(10), 9-16.
17. Kim, H., S. Murthy, L. L. McConnell, C. Peot, M. Ramirez, and M. Strawn. 2003. Study on Mechanism for odor production during lime stabilization using solid phase microextraction. *Water Env. Res.* (in press).

18. Lafond, S., T. Pare, H. Dinel, M. Schnitzer, J. R. Chambers, and A. Jaouich. 2002. Composting duck excreta enriched wood shavings: C and N transformations and bacterial pathogen reductions, *J. Environ. Sci. Health Part B-Pestic. Contam. Agric. Wastes*, 37(2), 173-186.
19. Longbottom, J. E., and J. J. Lichtenberg. 1982. *Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*, EPA-600/4-2-057, Washington DC, USA.
20. Murthy, S., H. Kim, C. Peot, L. L. McConnell, M. Strawn, T. Sadick, and I. Dolak. 2003. Characterization of odors from heat-dried pellets. *Water Env. Res.* (accepted).
21. O'Neill, D.H., and V. R. Phillips. 1992. A review of the control of odour nuisance from livestock buildings: properties of the odorous substances which have been identified in livestock wastes or in the around them. Part 3, *J. Agric. Eng. Res.*, 53, 23-50.
22. Pan, L., M. Adams, and J. Pawliszyn. 1995. Determination of fatty acids using solids-phase microextraction, *Anal. Chem.*, 57, 4396-4403.
23. Pawliszyn, J. 1997. *Solid-Phase Microextraction: Theory and Practice*, Wiley-VCH, New York, USA.
24. Schulz T. J. and A. P. van Harreveld. 1996. International moves towards standardisation of odour measurement using olfactometry. *Water Sci. Technol.*, 34, 541-547.
25. US Composting Council, 2002, TMECC CD-ROM
26. Van Durme, G. P., B. f. McNamara, and C. M. McGinley. 1992. Bench-scale removal of odor and volatile organic compounds at a composting facility. *Water Env. Res.*, 64(1), 19-27.
27. Verschueren, K. 1983. Carbon disulfide, In: *Handbook of Environmental Data on Organic Chemicals*, 2nd ed., 1103-1108, Van Nostrand Reinhold Co., New York, New York, USA.