Odor characteristics of commercial composts from 14 different producers using solid phase microextraction

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Ⅰ. 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[1].

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[2] and other factors important to agronomists and horticulturalists[3]. However, odors from composts produced with different ingredients have not been assessed systematically.

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[4]. This is mainly due to the difficulty in calibration of the olfactometor and sample handling[5]. Shultz and van Harrelveld[6] 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)[7]. Using SPME, sample collection and analyte extraction/concentration can be carried out in one step[8]. Therefore, 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 throughout the US were characterized with the newly developed method with SPME. We investigated the relationship between odorant characteristics and feedstocks of the products.

Ⅱ. Material and Methods

Gas Analysis

A 75 mm Carboxen-Polydimethylsiloxane (Car-PDMS) coating was used to capture trimethylamine (TMA), carbon disulfide (CS_2), dimethyl sulfide (DMS) and dimethyldisulfide (DMDS), and an 85 mm Polyacrylate coating was used for propionic acid (PA) and butyric acid (BA) (Supelco, Bellefonte, Pennsylvania, USA). 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.

Sample collection and analysis

Fourteen different producers sent samples of their final stage (marketable) compost products to a laboratory in Beltsville, Maryland, USA. 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. 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. 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.

Ⅲ. 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.

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 3. 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 CS_2, 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.[9] and Europe[10]. Reduced sulfur compounds have also been found in association with livestock operations and composted manure[11].

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

site number	Feedstock	Annual volume, m^3	pathogen/metal 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 byproducts;

AB: agricultural byproducts; CG: coffee grounds; TL: tea leaves; FS: food processing sludge; FT: feathers; CB: coconut byproducts

Table 3. Concentration (ppbv) of odorous gases from final products of different composting faciliti

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

BS: biosolids; YW: yard waste; WC: wood chips; PH: peanut hulls; FD: food; MN: manure; IB: industrial byproducts;

AB: agricultural byproducts; CG: coffee grounds; TL: tea leaves; FS: food processing sludge; FT: feathers; CB: coconut byproducts

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 $10^7 \sim 10^8$ 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.

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.

Ⅳ. 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.[12)] 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* (> 103 MPN/g).

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