Volatile Organic Acids In Compost: Production and Odorant Aspects

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■ Samples of active and cured compost from across the U.S. are examined for volatile organic acids (VOA) in relation to other microbiological and chemical properties. VOA are considered important because they reflect temporal microbiological properties of active and cured compost that influence the potential for compost to become odorous and phytotoxic. Data collected from 712 compost samples reveals a wide range of concentration for VOA between 75 and 51,474 ppm (dry basis) with a mean concentration of 4,385 ppm. To understand the variability of VOA, technology and site-specific testing data are needed. The results underscore concern for phytotoxicity and odor release potential, as 15 percent of samples exceeded 10,000 ppm and 2.5 percent exceeded 25,000 ppm VOA. Data and methodologies presented are viewed as useful to better understand relationships between compost biological activities and production of malodorous and phytotoxic VOA.

The production of volatile organic acids (VOA) prior to and during composting imparts an objectionable "garbage" or spoiled food like odor which frequently results in nuisance complaints. VOA can be responsible for phytotoxicity (plant growth suppression) when the compost is used for growing plants. This twofold aspect of VOA makes them a very interesting group to be studied in compost products.

The volatile acids which occur in composts range from very short-chain compounds such as formic acid to longer-chain compounds such as butyric and iso-valeric acids, usually in the C2-C9 carbon range. In this paper, various methods are employed such as total distillation and fractional liquid chromatography to quantity and isolate these compounds and determine their relation to the composting process and also to plant performance.

VOA are readily apparent olfactorily in the air stream at sub-ppm levels and their release from compost is pH dependent. In plant growing media, VOA levels as low as 300-500 ppm can exert a phytotoxic influence on plant seedlings, largely through root suppression and nutrient-ion leakage (Lynch 1977; Lee 1977). Therefore, for obvious reasons, specific methods are needed to reduce VOA production in composts to levels that are not objectionable. This requirement must be viewed realistically, however, in view of the costs of aeration and other treatments weighed against the actual impact of VOA and the fact that organic acids in general are excellent microbial food.

The author's laboratory has shown previously that VOA correlate negatively with age and are highest in the first 20 days, declining exponentially in the zero to 40 day period somewhat independently of compost treatment (NYC-DOS 1993). Other studies have shown that, in sample groups comprised of different compost technologies, respiration rates of compost reveal characteristic slopes that are indicative of the process and unique time constraints (Seekins 1997). Microbial communities vary widely during composting (Brinton and Droffner 1994). Therefore, it becomes interesting to investigate relationships of compost biology and VOA production. VOA levels are controlled by a dynamic relationship between substrate biodegradability, moisture and porosity. Additionally, microbial dynamics are involved which are as yet poorly understood.

Chemical and olfactory analyses reveal a sharp relationship between molecular composition of VOA to odor intensity decreasing in the order of iso-valeric > isobutyric > valeric > propionic > butyric > acetic (Pino *et al.* 1986). Therefore, a basis should exist to compute a true odor index based on quantitative separation of VOA in compost materials. This paper explores the general background and principles of production and odorant aspects. A future paper will describe phytotoxicity traits and analysis for compost products.

Materials and Methods

For this project, 712 compost samples were collected for analysis from compost sites around the U.S. during the second half of 1994 and the beginning of 1995. Samples were shipped next day service to the laboratory in iced coolers.

The samples represent a cross section of source ingredients including biosolids, yard trimmings, manures, MSW and food scraps from compost producers who routinely furnish materials for laboratory analysis during and after active composting. The age of composts ranged from 10 days to 1,100 days. Additionally, we sampled in replicate a low-tech food composting project for the first 75 days of the process to determine VOA and respiration levels in relation to age and microbial inoculation.

VOA were determined by two methods including total distillation and chromatographic separation. For distillation, samples were water extracted and distilled in H_2SO_4 at pH 1.8 and the resulting distillate titrated to a standard endpoint (SWMM 1994). For testing individual volatile organic acids in the C2-C9 range, we extracted composts with weak alkaline solution, filtered and diluted prior to injection into a liquid-ion chromatograph with a PRP-X300 base-anion exchange column equipped with macroporous copoly (styrene-divinylbenzene) and single gradient eluent (Lee 1984; Bevilacqua and Califano 1989).

To examine VOA production under controlled compost conditions , we employed thermally insulated 4-liter laboratory bench-scale reactors using a compost mix of 2675g food waste to 400g dried leaves, to achieve a C:N of 28:1 and moisture of 55 percent. To one treatment was added a mixture of eight strains of bacteria comprising the genera of *Bacillus, Pseudomonas* and *Escherichia* to achieve a final concentration of 10^7 cells/g of material to be composted.

Background of VOA in Compost

The presence in composts of volatile organic acids is certainly well established but poorly understood (Manios, *et al.* 1989). VOA represent normal metabolic by-products of anaerobic respiration and are breakdown products of grease and fats present in raw wastes (Henefeld-Fourrier and Rebhun1980). The composting process includes many simultaneous aerobic/anaerobic events which can never be perfectly controlled by any aeration scheme. Episodic oxygen depletion in composts occurs both at macro- and micro-pore levels and results in temporary production of copious amounts of short-chain carbon compounds. While these VOA are odorous they are also rapidly biodegradable, serving as high energy food for aerobic organisms. In a sense, they are "storage energy" which permit the compost to continue biodegradation even though oxygen is depleted, reserving the energy for later combustion when optimal conditions resume. We speculate that the burst of heat observed after turning or aerating following oxygen depletion may result from the rapid microbial proliferation utilizing readily available VOA substrate.

Moist aerosols such as those emitted from compost aeration may contain appreciable levels of volatile organic acids (Ganesan 1988). VOA are frequently associated with wastewater treatment plants (Kawamura *et al.* 1985; Anselme *et al.* 1985) and are contained in large concentrations in digested biosolids (Howgrave *et al.* 1991; Rains *et al.* 1973) and raw manures (Hoshika 1982; Zahn *et al.* 1997). Freshly composted sewage sludge may contain high levels of organic acids, primarily acetic acid, that inhibit plant growth (Devleeschauwer *et al.* 1981). Organic acids are high-fuel compounds that are normally digested during sludge processing, but in some cases VOA degradation is inhibited by metals (Lin 1992). Consequently, we may expect VOA may be high in source ingredients even prior to compost initiation.

Phytotoxicity is frequently associated with immaturity of compost (Ianotti *et al.* 1994) and depletion of organic acids is correlated with improved plant performance (Herrmann *et al.* 1993). Many MSW composts have been associated with high levels of phytotoxicity associated with organic acids (Bertoldi 1992, 1993). Phytotoxicity of immature composts has been positively correlated with organic acid content (Logsdon 1989; Manios *et al.* 1989; Evans and Brinton 1997). A later paper will explore the relationship of VOA and specific aspects of phytotoxicity (Brinton 1996).

Compost odor-causing compounds are frequently cited to include mercaptans and amines as well as aldehydes, alcohol, sulfides and organic acids (Basset *et al.* 1994). Wastewater treatment plants have been found to emit aldehydes, ketones, organic acids, aliphatic amines and NH_3 (Anselme *et al.* 1985; Zahn, *et al.* 1997). VOA odor, as with any other, is not simply a matter of compounds being detectable analytically. A variety of techniques are being developed that incorporate molecular-based structural parameters and analytical behavior for quantitative predictions of odor thresholds (Anker *et al.* 1990; Pino *et al.* 1986). Our laboratory is examining differential behavior of VOA where both undissociated forms and ionized aerosol states exist simultaneously with pH exerting varying influences. A variety of approaches to evaluating odor thresholds for volatile organic acids and other compounds are being explored (Lechner 1993; Hoshika and Walpot 1993; Zahn *et al.* 1997). Several volatile organic acids have been found to have high odor potentials at concentrations as low as 10^{-9} (parts per billion volumes), rivaling some of the more notorious odorants such as H_2S (Leonardos *et al.* 1969; Hoshika 1982). Furthermore, at least some organics acids have been shown to exhibit high transfer efficiencies from liquid-solid to air phase (Zahn *et al.* 1997).

Odor is often viewed as a very subjective matter; however, there is a remarkable similarity in odor threshold values (OTV) determined by panels in different countries and partly as a result, odorant standards that include VOA have been incorporated either into laws or odorant standards in the Netherlands, Germany and Japan (Hoshika and Walpot 1993). Undoubtedly, olfactometry has limitations, and psychophysical scaling shows deviations from linear models (Zahn *et al.* 1997; Pino *et al.* 1986). Nevertheless, it is likely that similar scientific odorant standards will evolve in the U.S. and composters therefore will want to be familiar with these approaches.

Bacteriology of VOA Production

The phenomena of VOA production has long been recognized in farming where large quantities of green crop residues are plowed down with the result that oxygen levels in the soil pores become momentarily limiting. The resultant production of VOA may cause temporary phytotoxicity and has been the subject of considerable study (Patrick and Koch 1958; Lynch 1977). In composting similar factors are involved but VOA is produced at even greater rates resulting in significant concentrations with great odorant and phytotoxicity potential (Liao *et al.* 1994, Van Durme *et al.* 1992; Lechner 1993).

Phytotoxic and odorant compounds like volatile organic acids are regularly produced in normal composts. The basis for production is fermentative respiration which occurs where oxygen levels are low but not necessarily absent in such a manner as to induce microbes to utilize compounds other than oxygen as terminal electron acceptors for respiration (Brock and Madigan 1991). A wide variety of otherwise beneficial organisms are involved in production of organic acids and in fact, once produced, organic acids are readily consumed by aerobes (Brock and Madigan 1991).

Generally, anaerobic organisms produce VOA in response to low oxygen levels, but the levels of O_2 which favor production are not known and are clearly much lower than the frequently cited oxygen optima in composting. The issue is complicated because facultative anaerobes will grow aerobically during optimal composting but switch to VOA production after a certain amount of oxygen stress. Not only this, but several aerotolerant anaerobes such as lactobacillus will grow in the presence of oxygen and also produce VOA. These aerotolerant anaerobes are of course agriculturally significant as they are exploited for silage production and food preservation processes.

The presence in compost of fluctuating oxygen conditions and various organisms which can grow where O_2 supply is episodic or limited is very significant. In this sense it is fundamentally incorrect to characterize VOA production as resulting simply from "bad, anaerobic conditions." The shifting of microbial populations during composting (Droffner *et al.* 1995) and the shunting of metabolic by-products between aerobes and facultative anaerobes in composts — and the resulting influence on system temperature and pH — we conjecture, constitutes a dynamic self-regulatory mechanism (see Figure 1). VOA belong to this cycle and the reason to study them is to understand where the line is drawn.

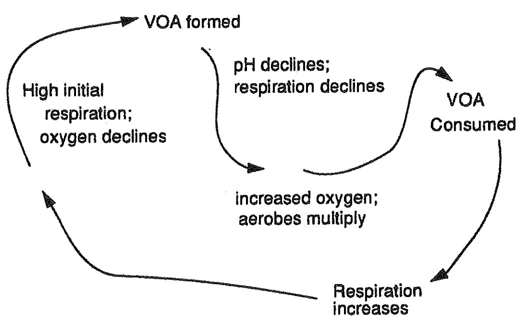

Figure 1. Hypothesized respiration - VOA cycle

To examine the relationship of microbiological properties of compost VOA level we added bacteria by inoculating a laboratory in-vessel food-scrap compost in the presence of oxygen and observed a significant increase in VOA production (see Figure 2). We observed a moderate correlation (r = 0.61) between substrate respiration rate and VOA levels in composts across all sample types (see Figure 3). This constitutes indirect evidence for the oxygen transfer-rate limitation hypothesis.

Based on these considerations, it may be readily apparent that approaching the

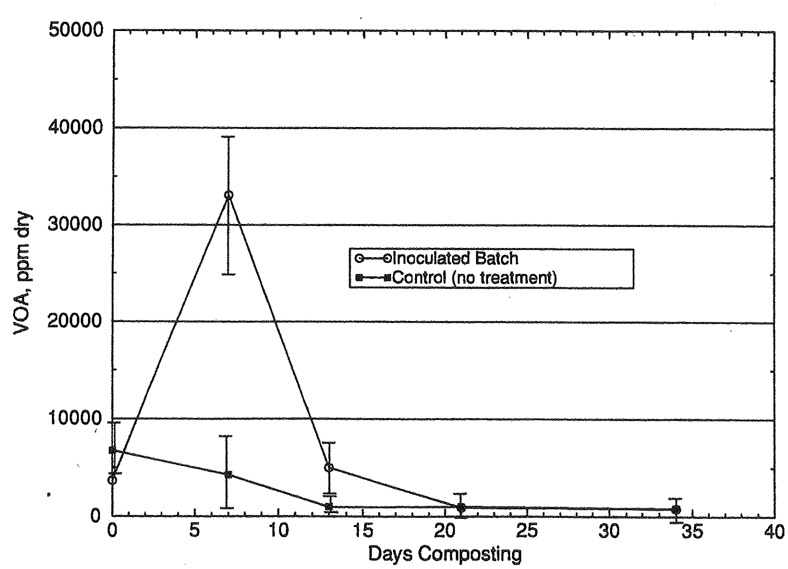

Figure 2. Effects of bacterial inocula on volatile organic acid (VOA) content of food scrap compost in laboratory vessel trials

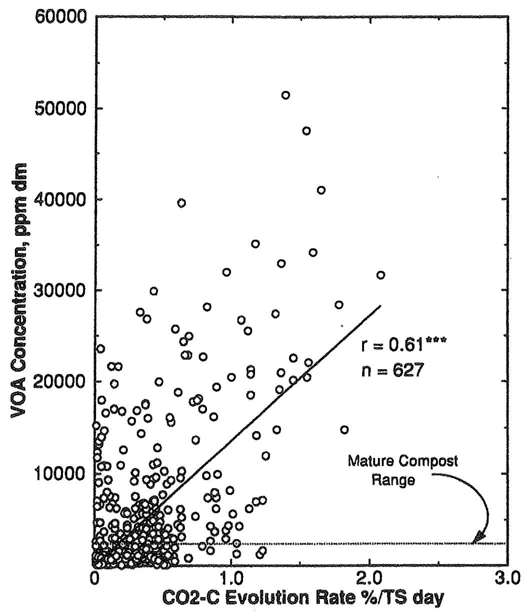

Figure 3. Compost volatile organic acids in relation to CO_2-evolution rate

problem of VOA strictly from an engineering model of supplemental forced aeration is not a guarantee of eliminating VOA (Lechner 1993); in fact, it may lead to over-supply of air (Lechner 1994).

Odorant detection and phytotoxicity of VOA is complicated by volatility factors that are dependent on the system pH which means more VOA is released as the pH drops. Furthermore, the relative proportions of VOA production changes as the pH is altered. For example, at pH 5.0 *Streptococcus fecalis* makes 174 μmoles lactic and 15.4 μmoles formic acid per 100 μmoles glucose, respectively, but at pH 9.0 makes 122 and 53 μmoles of lactic and formic acids, respectively. With these factors, it is apparent that VOA may be present but not be a problem under certain compost conditions.

Results and Discussion

We analyzed several compost samples from across the U.S. Table 1 presents summary data for VOA from 626 individual samplings taken from 340 compost sites.

VOA in Compost vs Biological Activity

To identify traits in the compost that may be useful for predicting VOA levels

TABLE 1. Concentration of volatile organic acids in 626 USA compost samples

	VOA (ppm)
Mean	4,385
Min	75
Max	51,474
SD	7,298
Geom. mean	1,510

TABLE 2. Distribution of volatile organic acids by number of USA compost samples

VOA (ppm)	Number of Samples
>25,000	18
>10,000	87
>5,000	149
>1,500	264
>500	160

we examined the relation to other measured attributes. The most significant correlation which emerged was that between VOA and CO_2 evolution (see Figure 3). The higher the respiration rate the more VOA is evident. High CO_2 evolution rates may be viewed as an indicator of young or immature composts, hence increased oxygen deprivation with potential oxygen diffusion limitations. In Figure 3, each doubling in respiration rate is associated with about a 150 percent increase in VOA levels. VOA tend to reduce compost solution pH values, and for this set of samples a negative correlation was observed ($r = -.45, p=0.001$). The pH effect is tempered by presence of alkaline compounds which form buffered salts such as ammonium acetate with VOA.

VOA vs. Age in Food Scrap Compost

We followed the concentration of VOA at two compost sites. One was a static nonaerated bin food scrap compost where we measured VOA from day three until day 75. The second was a municipal food scrap composting pro-

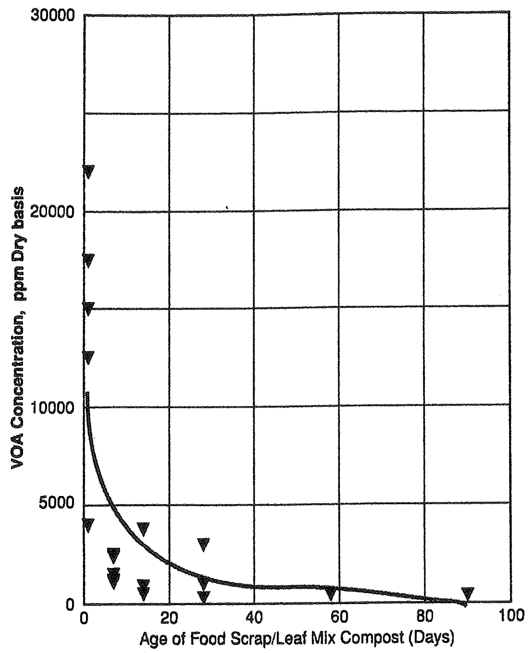

Figure 4. Volatile organic acid content in relation to age of municipal food scrap compost

TABLE 3. Proposed odor index for lower fatty acids encountered in compost samples[a]

Fatty Acids	Odor Index Value
Acetic	15
Butyric	50
Propionic	112
Valeric	255
Isobutyric	340
Isovaleric	365

[a]Source: Lechner (1993)

ject where we measured VOA from day one to day 90. At both locations, VOA declined rapidly in relation to age. For the static bins the rate of decline was approximately 1,000 ppm each 10 days. The relationship for the municipal project is seen in Figure 4. For both sites, VOA attained acceptable levels between 65 and 45 days, respectively. Thus, as respiration declines and stability increases, VOA levels will tend of their own accord to be decomposed. It appears that the key to proper management of VOA levels in composts is understanding these relationships and not "overreacting" when levels are elevated.

Odor Indices for Lower Fatty Acids in Composts

The use of VOA odor indices for calculating odorant potential in composts has been recently proposed (Lechner 1994). Using VOA analysis data from compost and weighting it with published odor indices for VOA (see Table 3) an accurate estimate of odorant potential can be formulated.

Increased understanding and investigation of VOA in composts will improve our understanding of the impact of management on the potential to control levels without undue over engineering.

Conclusion

Results presented here represent an attempt to develop testing and interpretation techniques in connection with production of volatile organic acids in composting materials. The VOA are important in so far as they indicate temporal biochemical properties of active and cured compost, as well as the potential for compost to become odorous and phytotoxic. However, the variability of compost microbiology and the differing rates of production of VOA are as yet poorly understood.

Unlike other organic or inorganic compounds that are regulated for their content in compost under EPA-503 rules, or airborne pollutants regulated under the Clean Air and Water Act, no guidelines exist for VOA, despite their immediate and obvious effect on soil and air. The wide range of concentration for VOA we observed in compost samples taken from around the U.S. indicate the need for more site and compost-specific testing data. While the geometric mean we calculated for VOA concentration is 1,510 ppm VOA, and is reassuring with regard to concerns for phytotoxicity or odor release, nearly 15 percent of samples exceed 10,000 ppm and 2.5 percent were extremely high and odorous at 25,000 ppm. The failure of the compost industry to adopt emission or concentration guidelines for VOA or other microbial based compounds is clearly reflected in a great diversity of processing technologies. The data and methodologies presented herein may be useful to help establish relationships between compost biological activities and production of malodorous and phytotoxic VOA.

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