

Characterization of Recycled Mushroom Compost Leachate by Chemical Analysis and Thermogravimetry–Mass Spectrometry

GARY LYONS,^{*,†} MAIREAD KILPATRICK,[‡] H. S. SHEKHAR SHARMA,^{†,§}
RALPH NOBLE,^{||} ANDREJA DOBROVIN-PENNINGTON,^{||} PHIL HOBBS,[⊥]
FIONA ANDREWS,[†] AND EUGENE CARMICHAEL[†]

Applied Plant Science Division, Agri-Food and Biosciences Institute, Newforge Lane, Belfast BT9 5PX, United Kingdom, Horticulture and Plant Breeding Station, Loughgall, Co. Armagh BT60 8JB, United Kingdom, School of Biological Sciences, Queens University Belfast, Belfast, United Kingdom, Warwick HRI, University of Warwick, Wellesbourne, Warwick CV35 9EF, United Kingdom, and Institute of Grassland and Environmental Research, North Wyke, Okehampton, Devon EX20 2SB, United Kingdom

Recycled compost leachate (RCL or euphemistically named “goody water”) can be a potent source of foul odor on mushroom substrate production sites and contributes to composting smells. A complex mixture of sulfur compounds, fatty acids, and nitrogen containing compounds is responsible for odor production. Fifty samples, collected from 14 compost production sites in Ireland and the U.K. over a 2 year period, were analyzed for chemical properties and by thermogravimetry–mass spectrometry (TG–MS) for compositional differences. Results indicated that aerated samples had lower values of electrical conductivity, redox potential, and dry matter content than nonaerated samples and that the higher thermal stability of aerated samples measured by TGA could be attributed to greater mineralization of the substrate due to aerobic processes. The lower temperatures noted for peak evolution of methane, water, and carbon dioxide from TG–MS analysis suggested that a more energetic process had occurred in aerated RCL storage facilities, producing greater decomposition of macromolecules that volatilized at lower temperatures. Chemical composition, thermal stability of the freeze-dried leachate, pyrolysis profiles, and relative amounts of pyrolysis products were all markers of as to how effective control measures could influence RCL quality.

KEYWORDS: Recycled compost leachate; thermogravimetry; mass spectrometry; odors

INTRODUCTION

The commercial production of compost for cultivation of mushrooms (*Agaricus bisporus*) relies on the bioconversion of a mixture of animal manures (horse and/or poultry), wheat straw, and gypsum to produce a nutritionally balanced substrate (1, 2). Composting produces odorous compounds associated with foul smells and environmental pollution due to the production of sulfur containing gases, amines, volatile fatty acids, ketones, and aromatic compounds (3–5). Attempts have been made to reduce odor emissions from compost production by improving aeration in compost piles (6) and adjusting raw material formulations (7), with some success. Poultry manure, the main

nitrogen source used in the U.K. and Ireland, has a pungent odor as a raw material, contributing organic sulfur in the form of amino acids cysteine and methionine (8). Substitution of 50% or more of the poultry manure with other N sources causes significant reduction in odor emissions but also a negative effect on yield. However, the use of some urea during the prewetting stage of composting has been adopted by a number of compost yards, leading to a reduction in the amount of poultry manure used and reduced odor problems, without any yield penalty (7). Recycled compost leachate (RCL) is made up of water soluble organic and inorganic fractions from compost raw materials, insoluble yard washings (particularly poultry manure and gypsum), and bacterial cells. It is applied to wheat straw to increase moisture content and add nutrients and microorganisms to help initiate composting and during the phase I stage (bioconversion of raw materials into compost) keep substrate moisture levels above 70% to stop excessive drying out by heat and aeration (9). Further, reuse of RCL on the site reduces the need for excess storage facilities and treatment plants. Production facilities with good RCL management strategies employ

* Author to whom correspondence should be addressed. Tel.: +44 28 9025 5245; fax: +44 28 9025 5007; e-mail: gary.lyons@afbini.gov.uk.

[†] Agri-Food and Biosciences Institute.

[‡] Horticulture and Plant Breeding Station.

[§] Queens University Belfast.

^{||} University of Warwick.

[⊥] Institute of Grassland and Environmental Research.

Table 1. Details of RCL Pits Displaying as to Whether Aeration and Screening Were Used, Nitrogen Source (Either Poultry Manure (P), Urea (U), Horse Manure (H)), or a Combination of These and Associated Chemical Data (pH, Electrical Conductivity, Redox Potential, and Dry Matter) from 14 Mushroom Composting Sites^a

site	aeration	screened	vol (m ³)	depth (m)	N source	pH	E _c (mS/cm)	redox (mV)	D _m (g/L)
1	yes	yes	150	2	P,U	7.33	6.57	-284	7.22
2	yes	no	80	2	P	7.19	5.96	-317	6.58
3	yes	yes	450	4	P,H,U	7.12	5.92	-342	5.72
5	yes	yes	450	4	P	7.50	3.99	-320	3.55
6	yes	yes	450	4	P,H,U	7.31	4.55	-220	4.71
7	yes	no	200	4	P,U	7.22	10.16	-294	12.31
8	yes	yes	10	2	P,H	6.89	1.22	-203	2.53
9	yes	yes	517	1.3	P,U	7.42	6.79	-311	8.25
					mean	7.25	5.65	-287	6.36
4	no	no	50	1.5	P,U	7.65	6.70	-329	6.88
10	no	no	450	4	P,H	7.08	13.93	-342	13.69
11	no	yes	240	2	P	7.19	7.38	-315	8.41
12	no	no	450	4	P	7.36	8.39	-337	9.55
13	no	yes	450	4	P	7.34	14.79	-366	17.64
14	no	no	450	4	P	7.61	3.39	-269	3.23
					mean	7.37	9.10	-326	9.90
					overall mean	7.31	7.38	-306	8.13
					SEM	0.05 ^{ns}	0.71*	9.40*	0.78*

^a Mean chemical measurements for aerated and nonaerated sites and overall parameter means and standard error of means (SEM) for all sites with ANOVA significance level are displayed. ANOVA results: ns (not significant); **p* < 0.05.

effective cleaning and aeration of storage pits along with screening of solids to reduce odor problems.

Despite advances in production methods, odor pollution is still a major problem for compost producers throughout the world. Research in Canada has shown that RCL can contribute significantly to site odor levels and increase odors from subsequent composting (10). Anaerobic runoff liquor also can have a deleterious effect on mushroom growth (11). If environmentally unacceptable levels of smell are to be reduced, the use of RCL and watering management need to be improved. Determining the relevant chemical composition of recycled water, and influences of water treatment, could lead to a significant reduction in the odors from mushroom composting and water storage facilities. Examination of the pH, electrical conductivity, dry matter content, and redox potential of RCL could provide some indication as to the chemical composition and oxygenation level and as to how these properties might influence odor production.

Thermogravimetry is a well-established technique to study primary and secondary thermal decomposition of solids and macromolecules from many systems, including municipal solid waste composting (12), wastewater treatment sludge (13), aquatic humic matter (14), and mushroom compost (15). By measuring weight loss and recording peak decomposition temperatures from thermogravimetric (TG) and derivative thermogravimetric (DTG) (rate of weight loss) profiles, it is possible to extract important compositional information. Decomposition can be monitored over a specific temperature range and when comparing similar samples, higher pyrolysis temperatures can be associated with more resistant and structurally ordered organic fractions. Evolved gas analysis using a thermogravimetry-mass spectrometry (TG-MS) system permits examination of volatile products that can be directly related to mass loss associated with specific temperatures on the DTG curve. TG-MS thus provides valuable compositional analysis of the material being examined, and it has been used to study the composition of plant materials (16, 17), contaminated soils (18), and sewage sludge (19). This study involved the detailed analysis of RCL samples from composting sites. The main objectives were to establish as to if chemical and thermal analyses could be used to determine as to how management of

storage systems had a direct influence on the composition and quality of RCL.

MATERIALS AND METHODS

Collection of RCL Samples and Dry Matter Content. RCL was obtained from the storage pits or tanks of 14 mushroom compost production facilities by making a number of visits over a 2 year period. A total of 50 samples was obtained either by immersing a 9 L bucket to the full depth of the storage pit or from a recirculation pipe that drew liquid from the bottom of the pit or tank. Common ingredients for the compost prepared on the sites were wheat straw, poultry manure, and gypsum. Horse manure was used on four of the sites, and urea was used on six of the sites (Table 1). The water was stored in 3 L plastic bottles for up to 2 weeks at 2 °C before analysis of the liquid (after returning to room temperature). Samples (1 L) were freeze-dried in triplicate for 1 week, and the weight of the resulting dry matter was determined. The dried samples were then used for further analysis.

Redox Potential. Redox indicator electrodes measure the ratio of oxidized species to reduced species in a solution, with a less negative value indicating more oxidized species. A WaterWatch System 2600 (EuaxSys Ltd., Camelford, Cornwall, U.K.) probe and data logger were used for measuring redox potential (*R_p*). RCL (1 L) was placed in a beaker at room temperature, the electrode was immersed in the water, and *R_p* was measured after 2 min.

Electrical Conductivity and pH. pH was determined using a Mettler Toledo MP230 pH meter (Mettler Toledo U.K.) with a VWR pHASE combined pH/reference electrode attached (VWR International Ltd. U.K.). The electrical conductivity (*E_c*) was measured by a Mettler Toledo MC226 conductivity meter with an Inlab 730 electrode. pH and conductivity standards were used to calibrate equipment before measurement. All samples were analyzed at room temperature.

Thermal Analysis and Mass Spectrometry. Pyrolysis TGA, DTG, and TG-MS analyses were performed using a Mettler Toledo TGA/SDTA851 thermal analysis system, equipped with an autosampler and TSO801RO sample robot, coupled to a Pfeiffer vacuum thermostat quadrupole mass spectrometer (Pfeiffer Vacuum), equipped with a QME Prisma detector and operated in electron impact ionization mode at 70 eV. Evolved gases passed from the TGA to the mass spectrometer via a heated silica capillary (0.22 mm i.d.) maintained at 180 °C. Three replicates were analyzed for each sample. Freeze-dried material was hand ground in a mortar and pestle, and samples (6 mg) were heated in alumina crucibles (150 μL) from room temperature, with an isothermal hold for 30 min at 100 °C, followed by dynamic heating to 950 °C at a heating rate of 10 °C min⁻¹. Nitrogen was passed through

Table 2. Mean Thermal Analysis Data (TGA and DTG) for Eight Aerated and Six Nonaerated Sites Showing Number of Pyrolysis Processes, Main Weight Losses (% Wt Loss 1–4), Decomposition Temperatures (Wt Loss 2 and 3 Temp), and TGA Residue Values^a

site	no. of pyrolysis processes	wt loss 2 temp (°C)	wt loss 3 temp (°C)	% wt loss (100–200 °C)	% wt loss (200–350 °C)	% wt loss (350–600 °C)	% wt loss (600–900 °C)	TGA residue (%)
Aerated								
1	5	272	542	2.4	15.9	21.2	13.2	46.9
2	5	257	529	2.8	14.0	18.2	18.3	46.3
3	4	281	502	1.3	16.6	20.4	9.6	51.7
5	6	278	550	3.1	14.9	21.8	14.1	45.9
6	4	280	489	1.4	15.5	20.9	9.2	52.7
7	5	267	549	3.1	17.6	20.2	17.9	40.4
8	3	301	525	1.9	18.1	26.8	6.0	46.6
9	4	278	509	1.1	16.7	21.5	10.3	50.0
mean	4.5	277	524	2.2	16.1	21.4	12.3	47.6
Nonaerated								
4	4	276	505	1.4	17.3	23.7	16.8	40.9
10	6	265	570	3.0	15.9	19.5	18.4	42.7
11	7	262	582	1.7	16.3	17.8	20.8	43.1
12	5	256	549	2.1	14.3	17.8	20.0	45.6
13	5	267	573	2.0	15.7	18.9	16.5	46.3
14	5	277	515	3.0	13.4	17.5	11.8	42.7
mean	5	268	549	2.2	15.5	19.2	17.40	41.15
overall mean				2.2	15.8	20.3	14.9	44.4
SEM				0.19 ^{ns}	0.37 ^{ns}	0.69*	1.23*	1.11*

^a Mean measurements for aerated and nonaerated sites and overall parameter means and SEM for all sites with ANOVA significance level are displayed. ANOVA results: ns (not significant); * $p < 0.05$.

the furnace at a flow rate of 40 mL min⁻¹. The furnace was calibrated using the manufacturer's indium/aluminum calibration protocol (measuring the Curie transition temperatures at 156.6 and 660.4 °C, respectively, using the SDTA signal).

TG weight losses and decomposition temperatures were measured for each sample, and the evolved gases from the samples were monitored for 10 specific ion currents, normalized to sample mass. Intensity values and peak evolution temperature for each particular ion current were compared between samples. Reference compounds representing materials likely to be found in RCL dry matter also were analyzed using the same protocol. These included mono- and polysaccharides, humic acids, amino acids, peptides, and bacterial cell wall fractions. Freeze-dried mushroom compost and poultry manure also were assessed for decomposition characteristics when heated to 950 °C.

Data Analysis. All chemical, thermal, and mass spectrometry data were submitted to spreadsheets and analyzed using the Microsoft Excel Descriptive Statistics and ANOVA tools to calculate statistical properties. This facilitated assessment of variation from all sites studied. SEM with significance levels (p value) were calculated to evaluate differences between sites. Continuous TGA data (i.e., exported raw data) of freeze-dried samples (**Table 2**) also were analyzed by principal components analysis (PCA) using the Unscrambler (Camo, Norway) multivariate statistical software package to examine possible relationships between sample sets. Data were transposed and then transformed using Savitzky and Golay smoothing and derivative treatments (1, 4, 4, 1).

RESULTS AND DISCUSSION

Chemical Analyses. Dimensions and other details of RCL pits are shown in **Table 1**. Some form of screening of solid matter from the recycled water was conducted on eight of the 14 sites, and nine of the storage pits had some type of aeration. This usually consisted of submerged pipes, submerged propeller with pipes, or recirculation of liquor from the bottom of the pit or storage tank but on site 13 consisted of a surface aerator (site 13 was considered as nonaerated due to the ineffectiveness of surface aeration).

There were wide ranges in pH, E_c , R_p , and D_m content of RCL samples from different sites (**Table 1**). The pH exhibited least variation, ranging from 6.89 to 7.65 with no significant difference between means. Mean aerated (7.25) and nonaerated (7.37) pH values were similar (**Table 1**). E_c varied significantly

($p < 0.05$) across all sites ranging from 1.22 to 14.79 mS/cm, and mean E_c was lower for aerated sites (5.65 mS/cm) than nonaerated sites (9.10 mS/cm). R_p levels were significantly ($p < 0.05$) different across the 14 compost sites, varying between -203 and -366 mV, and aerated sites had a less negative mean R_p (-287 mV) than nonaerated (-326 mV). Mean D_m content differed significantly ($p < 0.05$) for all sites studied with a minimum of 2.53 g/L and maximum of 17.64 g/L observed (**Table 1**). Sites with aeration had a lower mean D_m (6.36 g/L) than sites without aeration (9.90 g/L). This may also have had a major effect on the quality of the RCL along with oxygenation caused by aeration. D_m content and E_c of samples were highly correlated ($R^2 = 0.93$).

Increased aeration of RCL has been shown to significantly reduce foul odor emissions from production sites (20). Chemical data (**Table 1**) indicated that pH levels could not discriminate between aerated and nonaerated RCL, and the pH was therefore a poor indicator of quality. E_c , R_p , and D_m levels for aerated sites were on average lower than nonaerated sites (**Table 1**). These three properties appear to be useful indicators of RCL quality, suggesting that measurement of these on-site would enable managers to assess the quality status of recycled water and thus make changes to screening of solids and aeration levels as required. From the chemical data produced, it is evident that some sites were managed less efficiently than others. Sites 1, 2, 7, and 9 produced higher levels of E_c , R_p , and D_m than the means for all aerated samples. Site 7 did not screen RCL, and this may help to explain very high E_c and D_m , but when compared to site 2 which had no screening either, it appears that aeration and cleaning also were poor. Site 8 used fresh water to initially wet the compost (as opposed to recycled water used by all others), and this is the likely reason that it had the lowest values of measured chemical data.

Among the nonaerated samples (**Table 1**), sites 10 and 13 had much higher E_c , R_p , and D_m levels than overall means. Sites 11 and 13 were the only nonaerated yards employing screening, and site 11 produced lower levels of all three quality characteristics when compared to site 13. Site 13 appeared to have the poorest RCL storage strategy of all of those tested. In sharp contrast, data from site 14, which despite having neither screened

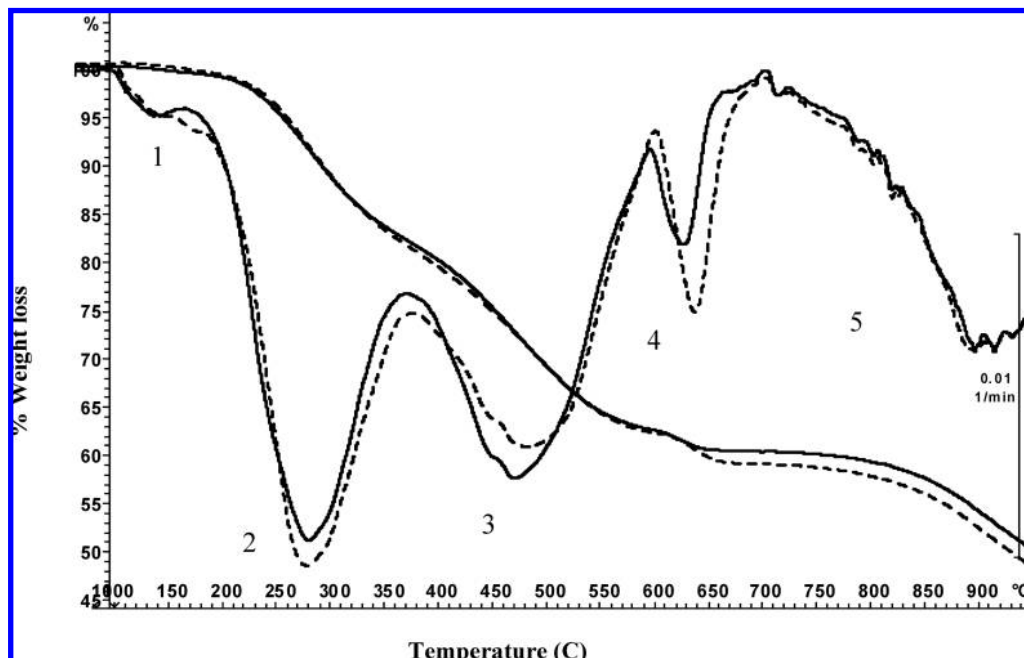


Figure 1. TG and DTG decomposition profiles for an aerated site (6) illustrating a sample taken at the beginning of the trial (—) and a corresponding sample (---) taken 18–20 months later. Major pyrolysis processes (numbered 1–5) are noted as areas of significant weight loss with increasing temperature on the DTG thermograms.

nor aerated RCL, managed to produce results that were comparable to the best managed aerated yards (i.e., 5 and 6). Information from **Table 1** suggests that the quality of RCL used at sites was not influenced by the N source, pit volume, or depth but rather by the introduction of effective screening and aeration practices to reduce E_c , R_p , and D_m levels. From the data collected, tentative thresholds could be assigned as target values for composters to use. E_c below 6 mS/cm, R_p below -300 mV, and D_m below 6 g/L indicate that effective management of storage pits was evident.

TGA and DTG. Weight losses below 140 °C are associated with the loss of hygroscopic water by dehydration, and below 200 °C, decarboxylation and further dehydration takes place (12). Above 200 °C, elimination and decomposition of aliphatic compounds due to further decarboxylation and breakage of C–C bonds occur (13, 14). At higher temperatures (above 400 °C), weight losses can be attributed to the thermal decomposition of aromatic structures (21), although aliphatic macromolecules in the form of long chain hydrocarbons and nitrogen compounds also contribute to thermal reactions above 400 °C (14).

Upon heating from 100 to 950 °C, between three and seven pyrolysis events were observed for samples from each site (**Table 2**), and these were clearly visible on the TG and DTG weight loss curves (**Figures 1–3**). The mean number of pyrolysis events was lower for aerated sites. Important weight losses were observed from 140 to 180, 200 to 350, 360 to 440, 460 to 580, 610 to 690, and 710 to 750 °C. By examining the weight loss thermograms for reference compounds, it was possible to study as to how RCL fractions decomposed over a wide temperature range. Partial decomposition of peptides, amino acids, humic acids, and galacturonic acids occurred between 150 and 190 °C. Monosaccharides, polysaccharides, cellulose, peptides, and bacterial cell wall fractions (including acetyl-glucosamine and lipopolysaccharides) decomposed between 200 and 350 °C. Poultry manure fractions demonstrated partial weight loss between 150 and 190 °C, and both poultry manure and mushroom compost exhibited major weight losses in the

200–350 °C range. Pyrolysis char formation was noted above 360 °C for all reference compounds and for mushroom compost, although this was higher for poultry manure at 420 °C and for peptides at ~ 440 °C. Components formed by secondary endothermic rearrangement reactions, which did not exist in the original samples, were decomposed during further thermal degradation stages before and after charring.

Table 2 shows the peak temperature for maximum rate of weight loss due to organic material decomposition (wt loss 2 temp) and char decomposition (wt loss 3 temp). Mean decomposition temperature for the organic fraction was higher for aerated sites (277 °C) than nonaerated sites (268 °C). A higher thermal stability of the aerated samples could be attributed to greater mineralization of the substrate due to aerobic processes (13). The peak char decomposition temperature was higher for nonaerated sites (549 °C) as compared to aerated sites (524 °C), and this was probably due to the presence of greater amounts of less degraded polysaccharides, peptides, humic acid residues, compost, and poultry manure fractions in the nonaerated samples. Char formation and burnout occurred at lower temperatures for aerated samples (400 and 640 °C, respectively) than nonaerated samples (500 and 660 °C, respectively).

TG weight loss was measured over four temperature ranges (**Table 2**). There was no significant difference in weight loss in the first two temperature ranges. The % wt loss 3 data suggested that there was a significantly ($p < 0.05$) higher loss of organic material for aerated sites. This could be a consequence of greater substrate breakdown in the aerated samples and is supported by the much higher char decomposition temperature reported for nonaerated samples due to less degraded macromolecules (**Table 2**). The % wt loss 4 results indicated that the nonaerated sites had significantly ($p < 0.05$) higher weight loss than aerated. It is evident that nonaerated samples contained higher levels of organic material in this fraction, highlighting that greater mineralization was achieved in the aerobic process (19). TGA residue levels were significantly ($p < 0.05$) higher for aerated sites, indicating a higher inorganic ash level and therefore lower organic matter content for aerated samples.

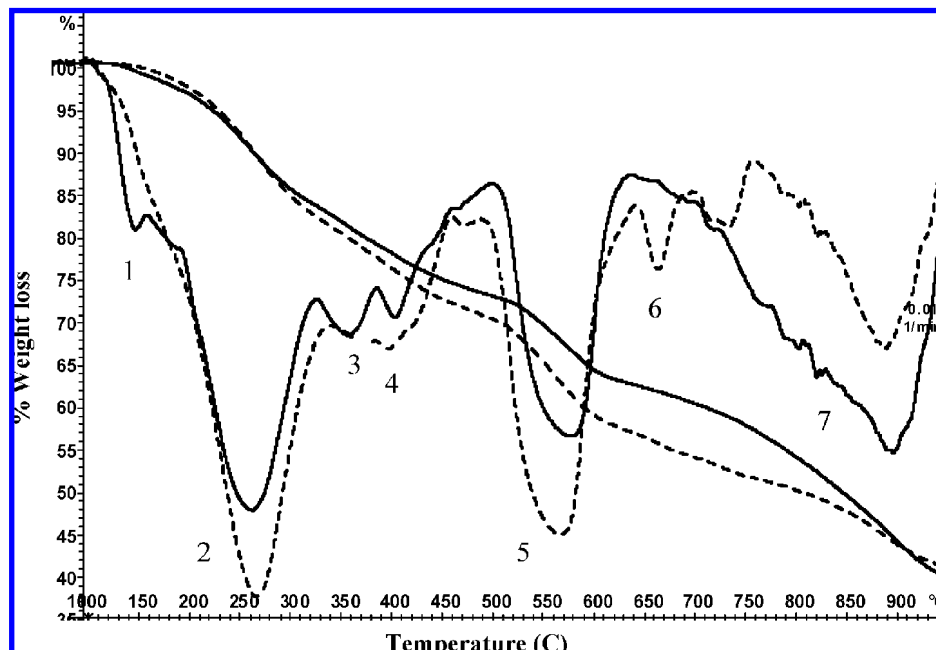


Figure 2. TG and DTG decomposition profiles for a nonaerated site (10) illustrating a sample taken at the beginning of the trial (—) and a corresponding sample (---) taken 18–20 months later. Major pyrolysis processes (numbered 1–7) are noted as areas of significant weight loss with increasing temperature on the DTG thermograms.

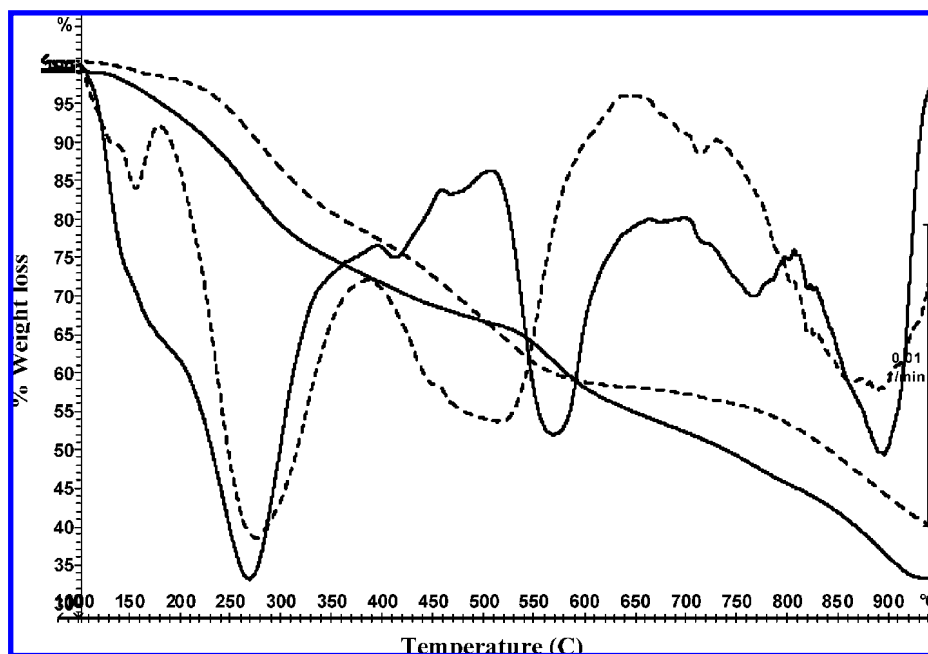


Figure 3. TG and DTG decomposition profiles for an aerated site (7) illustrating a sample taken at the beginning of the trial (—) and a corresponding sample (---) taken 18–20 months later. The early sample has decomposition characteristics that look like those of nonaerated RCL, and the later sample has the profile of aerated RCL.

Figures 1 and 2 show typical TG and DTG decomposition profiles for an aerated (site 6) and a nonaerated facility (site 10), respectively. Each thermogram illustrates a sample taken at the beginning and one near the end of the trial, and differences in the major pyrolysis events between aerated and nonaerated samples are obvious. It was possible to distinguish eight sites (aerated from nonaerated), by examining DTG curves, and all samples produced consistent decomposition profiles similar to those depicted in **Figures 1 and 2**. However, the other six sites produced mixed decomposition profiles depending on when samples were taken, exhibiting both aerated and nonaerated characteristics. This is illustrated in **Figure 3**, showing TG and

DTG profiles for two samples from site 7, taken at the beginning and end of the trial. The early sample has decomposition characteristics similar to those of nonaerated RCL (**Figure 2**), with high values for E_c (26.4 mS/cm), R_p (−325 mV), and D_m (31.5 g/L). The later sample has the profile of aerated RCL (**Figure 1**), with lower E_c (3.4 mS/cm), R_p (−280 mV), and D_m (4.2 g/L) values. The clear variation in thermal analysis data supports the differences noted in the chemical characteristics (**Table 1**).

PCA of TGA Data. Continuous TGA weight loss data, representing organic material decomposition, was submitted for PCA analysis. **Figure 4** shows how the 50 samples were

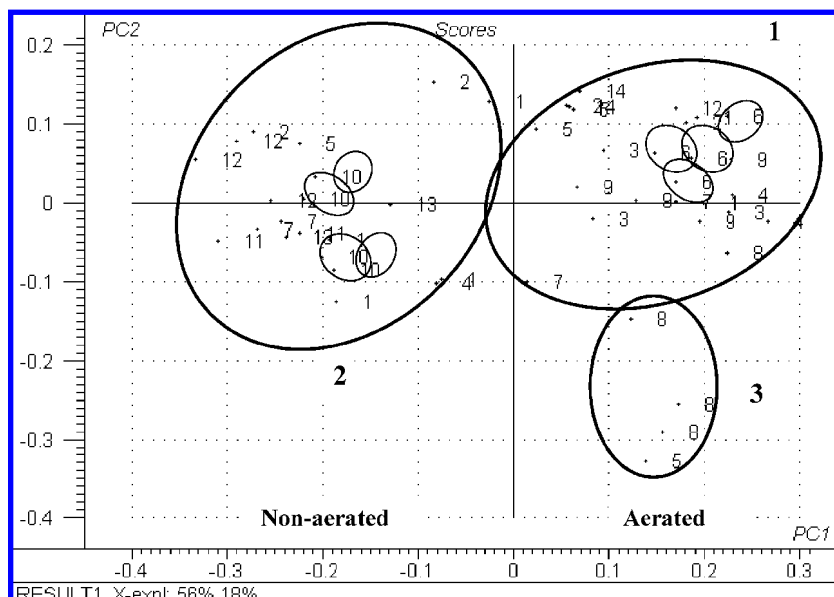


Figure 4. PCA of continuous TGA weight loss data. Three clusters were formed along the first two PC (PC 1 and 2), which explained 74% of the variation within the population of 50 samples. Eight principle components explained 95% of the variation within the sample set. Aerated and nonaerated samples are divided by the vertical axis.

Table 3. Key Ion Currents (m/z) Monitored with Their Associated Mass Number and Parent Molecule

(m/z)	ion	parent molecule
15	CH_3^+	methane
18	H_2O	water
44	CO_2	carbon dioxide
47	CH_3SH^+	methanethiol
60	CH_3COOH^+	acetic acid
62	$\text{C}_2\text{H}_6\text{S}^+$	dimethyl sulfide
64	SO_2^+	sulfur dioxide
74	$\text{C}_2\text{H}_5\text{COOH}^+$	propionic acid
76	CS_2^+	carbon disulphide
94	$(\text{CH}_3\text{S})_2^+/\text{C}_6\text{H}_6\text{O}^+$	dimethyl disulphide/phenol

Table 4. Mass Spectral Peak Temperature Evolution Data ($^\circ\text{C}$) for the Ten Ion Currents (m/z) Monitored^a

site	m/z									
	15	18	44	47	60	62	64	74	76	94
	Aerated									
mean	432	309	535	294	270	299	325	296	312	301
min	295	270	348	274	234	274	297	271	239	271
max	490	379	757	314	319	324	348	337	475	321
SD	67.4	25.8	58.8	10.1	21.9	12.8	13.0	18.2	94.4	12.6
	Nonaerated									
mean	451	341	564	289	266	302	321	275	280	301
min	303	277	501	269	234	269	298	189	228	274
max	474	387	741	312	303	443	338	316	460	330
SD	40.0	34.1	54.8	13.1	19.6	40.0	10.8	18.2	94.4	12.6
overall mean	437	320	545	293	269	300	324	289	301	301
SEM	8.4 ^{ns}	4.6 ^{**}	8.3 ^{ns}	1.6 ^{ns}	3.0 ^{ns}	3.6 ^{ns}	1.8 ^{ns}	3.2 [*]	12.1 ^{ns}	1.9 ^{ns}

^a Mean, minimum, maximum, and SD are shown for aerated and nonaerated sites. Overall means and SEM for all sites with ANOVA significance level are displayed. ANOVA results: ns (not significant); * $p < 0.05$; ** $p < 0.01$.

separated along the first two principle components (PC 1 and 2) with 74% of the sample variation explained. Two large sample clusters were formed along with a smaller one. Cluster 1 contained 25 samples of which 20 were from aerated sites and five from nonaerated. Cluster 2 consisted of 21 samples of which nine were from aerated sites and 12 from nonaerated. Cluster 3 was made up of four samples from aerated sites only.

Table 5. Mean Mass Normalized Integrated MS Intensities from Aerated and Nonaerated Sites for the Ten Ions (m/z) Showing Peak Area Measured in Arbitrary Units (nsA)

site	m/z									
	15	18	44	47	60	62	64	74	76	94
aerated	131	8604	13 857	2.8	4.0	1.3	8.8	0.8	1.3	0.1
nonaerated	151	8626	14 016	2.8	4.6	1.4	10.7	1.3	1.1	0.1

The five samples from nonaerated sites present in cluster 1 had thermal characteristics (weight loss and DTG profiles) and chemical properties (Table 1) that resembled those of aerated RCL. The nine samples from aerated sites found in cluster 2 (Figure 4) displayed thermal characteristics (weight loss and DTG profiles) and chemical properties that resembled those of nonaerated sites. Cluster 3 contained three samples from site 8 and one from site 5. Site 8 used fresh water with each new batch of compost, and this is the most likely reason that a separate cluster was formed, although one sample from this site was found in cluster 1 (this is also confirmed by chemical data). The presence in cluster 3 of the first sample taken from site 7 suggested that a high proportion of fresh water was present in RCL from this compost yard at the beginning of the study.

Within cluster 1, all samples taken from site 6 were grouped very closely, indicating that RCL at this site was well-managed (Figure 4), with little change in quality characteristics. The same is true for site 14 and to a lesser extent for sites 3 and 9, where more sample spread was evident. Examination of cluster 2 showed that samples from site 10 were closely grouped (Figure 4) as were samples from sites 11–13. With the exception of site 12, RCL quality from the other three highlighted sites did not significantly improve during the study.

TG–MS. The ten ion currents (m/z) monitored by TG–MS are listed in Table 3, and their identification was based on data from the NIST website. By using TG–MS to monitor the production of compounds listed in Table 3, significant information on the composition of the organic fraction of the RCL dry matter could be obtained. Evolved gas analysis by TG–MS is a thermal decomposition process as opposed to production of VOC by microbiological activity.

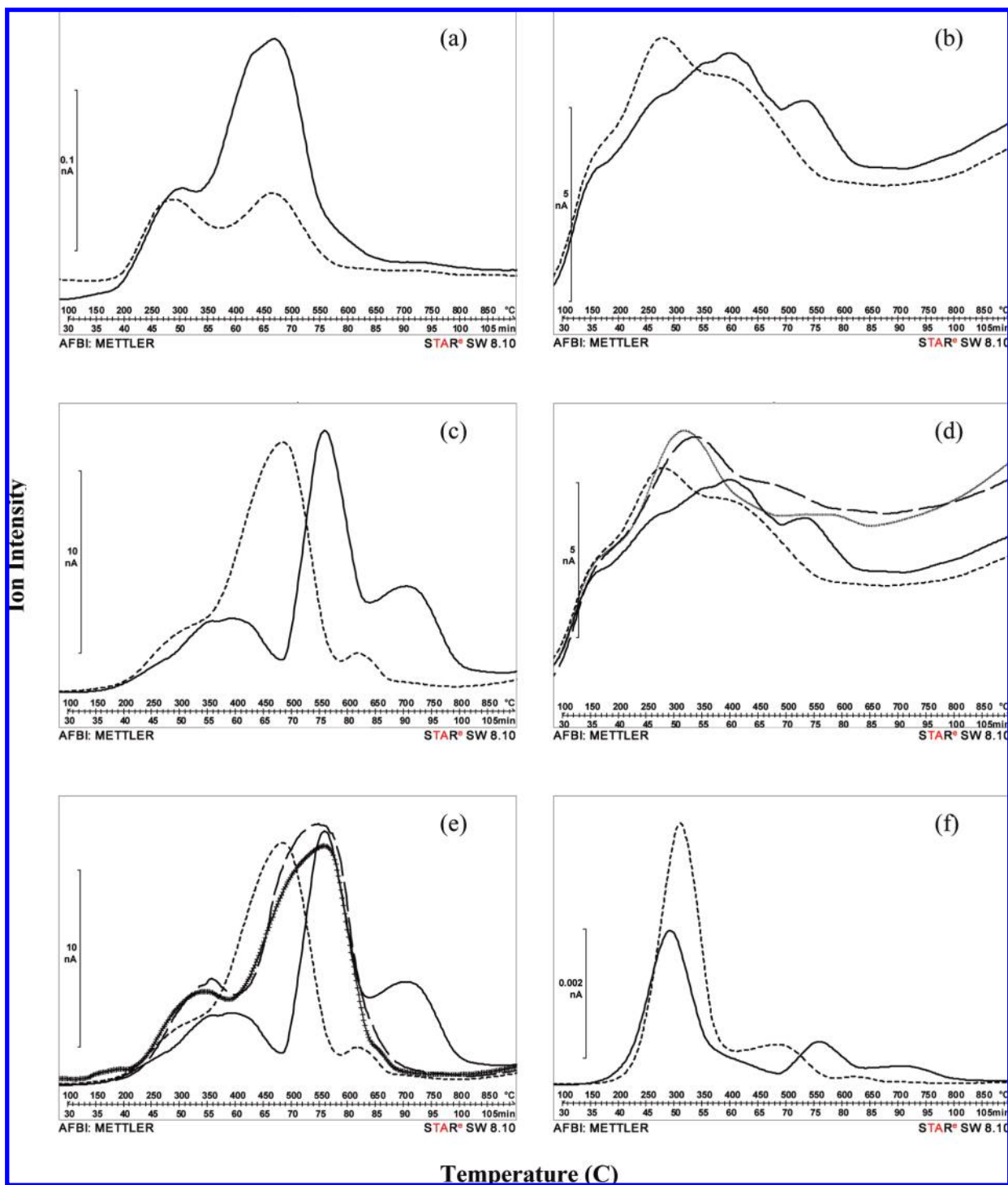


Figure 5. Typical mass spectral evolution profiles for aerated (---) and nonaerated (—) samples from sites 6 and 10, respectively: (a) m/z 15, (b) m/z 18, and (c) m/z 44. Profiles from sites 6 and 10 (— and ---) with two samples from PCA cluster 3 (+++ and ---): (d) m/z 18, (e) m/z 44, and (f) m/z 47.

Peak temperatures of pyrolysis products were examined for samples from all sites (Table 4). Relative amounts of each ion current produced were assessed using mass normalized integrated intensity values (Table 5) to compare aerated with nonaerated sites. The lower temperatures noted for peak evolution of methane (m/z 15), water (m/z 18), and carbon dioxide (m/z 44) (Table 4) suggested that a more energetic process had occurred in aerated RCL storage facilities, producing greater decomposition of macromolecules that volatilized at lower temperatures than samples from nonaerated facilities. A similar observation was made for sewage sludge digested both

aerobically and anaerobically (19). Methane evolved as two processes (Figure 5a), which could be linked to the decomposition of organic polymers, and at higher temperatures, to the charring process (17).

Peak water production was at a lower temperature for aerated sites (Table 4), and a higher temperature process was noted in nonaerated sites at ~ 530 °C (Figure 5b) associated with char decomposition. Carbon dioxide evolution involved three processes; however, these occurred at lower temperatures for aerated sites (Figure 5c). Mean peak production was noted for char decomposition at 535 °C for aerated sites as compared to

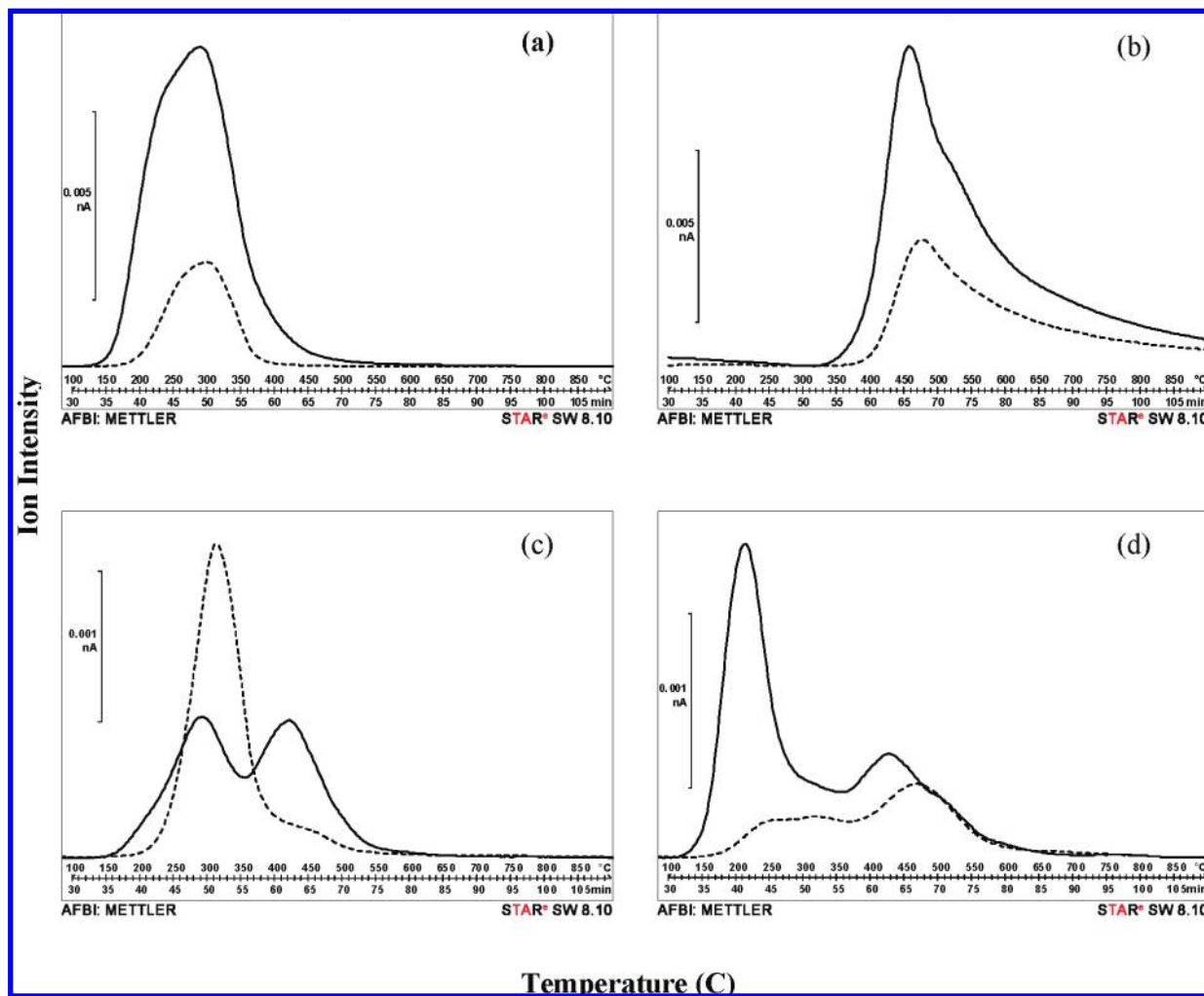


Figure 6. Typical mass spectral evolution profiles for aerated (---) and nonaerated (—) samples from sites 6 and 10, respectively: (a) m/z 60, (b) m/z 64, (c) m/z 62, and (d) m/z 76.

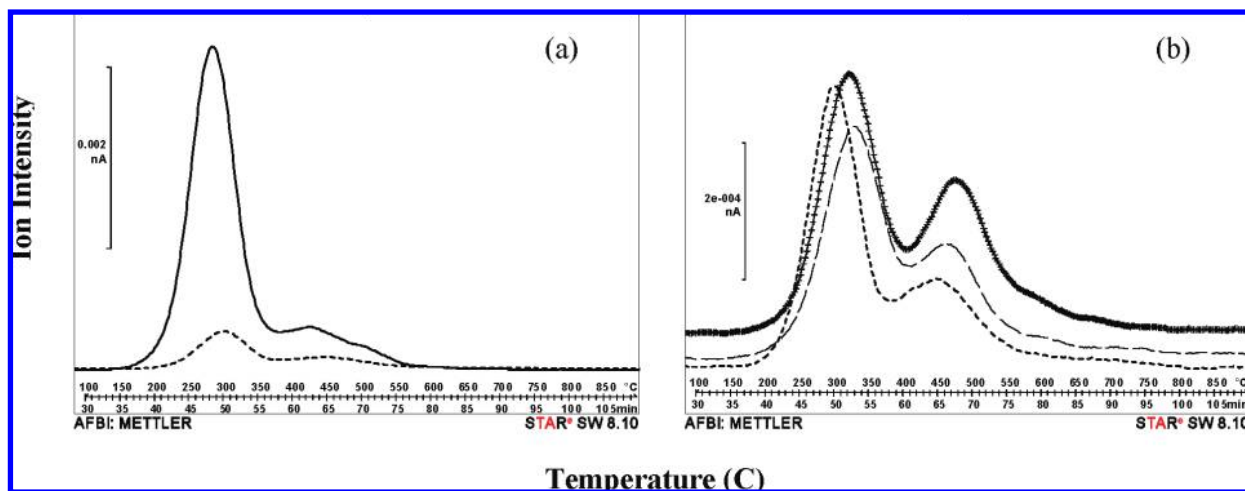


Figure 7. Typical mass spectral evolution profiles for m/z 74 for (a) aerated (---) and nonaerated (—) samples from sites 6 and 10, respectively, and (b) site 6 sample (---) as compared to two samples from PCA cluster 3 (+++ and ---).

564 °C for nonaerated sites (Table 4), and aerated sites produced a higher intensity peak (Figure 5c). Overall, the intensity was higher for nonaerated sites (Table 5). Interestingly, samples found in PCA cluster 3 (Figure 4) displayed intermediate properties to those described previously for peak temperature evolution of water (Figure 5d) and CO₂ (Figure 5e), suggesting that char decomposition shared characteristics of both aerated

and nonaerated samples. Other ion currents measured for members of this cluster provided results similar to aerated systems (apart from propionic acid).

Maximum production of methanethiol (m/z 47) took place between 280 and 300 °C for all samples; however, aerated samples displayed secondary and tertiary processes at 500 and 625 °C as compared to similar processes at 560 and 740 °C in

nonaerated samples (Figure 5f). Peak evolution temperatures for acetic acid (m/z 60) and sulfur dioxide (m/z 64) (Figure 6a,b) were similar for all sites, but intensity values were higher for nonaerated samples, and the onset temperature of sulfur dioxide production was lower for nonaerated samples. Dimethyl sulfide (m/z 62) evolved with a single process at 300 °C for aerated samples and two distinct processes at 280 and 425 °C for nonaerated RCL, with similar intensity values for both (Figure 6c).

Carbon disulphide (m/z 76) production was observed as two processes: primary production for aerated sites was between 240 and 315 °C with a secondary event at 470 °C, as compared to nonaerated samples with primary production between 240 and 350 °C and a secondary process at 425 °C (Figure 6d). Propionic acid (m/z 74) was produced in two processes, the first and major peak occurred at ~300 °C for aerated and 275 °C for nonaerated samples, with a smaller peak noted for all samples at 450–470 °C (Figure 7a). Nonaerated samples produced a higher intensity peak. Samples from PCA cluster 3 had higher main peak evolution temperatures for m/z 74 (320–340 °C) and intensities similar to aerated samples (Figure 7b). No difference in peak evolution temperature or ion intensity value was found between aeration and nonaeration for dimethyl disulphide/phenol (m/z 94) production.

To summarize, aeration of RCL by a submerged air supply was found to accelerate the organic fraction decomposition in dry matter, therefore improving substrate quality. Analogous effects have been reported for piggery slurry volatile emissions (22), where increasing the duration of aeration reduced the oxygen demand of the water (less negative redox potential) but did not affect pH. RCL dry matter content can be reduced by washing less poultry manure out of the prewet area and by applying some of the poultry manure later in the composting process. The solid material in leached poultry manure also can be screened out of the RCL, but dissolved components will be retained in the leachate. The effects of these treatments on the quality of RCL can easily be measured on-site by determining the electrical conductivity or dry matter content and redox potential.

The main benefit of lower dry matter content and greater organic fraction decomposition is the reduction of emissions and odors from the RCL storage area and when the liquid is used to wet compost (20). TGA discriminated between samples from aerated and nonaerated sites based on thermal decomposition profiles. Investigation of dry matter organic fraction composition by TG–MS highlighted differences in the degree of decomposition that had occurred in the RCL storage pits. Peak evolution temperatures and relative intensities of the ion currents studied indicated that greater mineralization of macromolecules had taken place in RCL storage pits where aeration and solid content had been effectively managed. Monitoring of evolution temperature and ion current intensity for methane, fatty acids, methanethiol, dimethyl sulfide, sulfur dioxide, and carbon disulphide by thermal decomposition identified compounds that could act as specific markers of RCL quality.

ACKNOWLEDGMENT

We acknowledge the cooperation of all members of the project consortium. G.L. thanks Colin McRoberts for assistance with MS analysis and Dr. Sally Watson for help with statistical data.

LITERATURE CITED

- (1) Sharma, H. S. S. Compositional analysis of neutral detergent, acid detergent, lignin, and humus fraction of mushroom compost. *Thermochim. Acta* **1996**, *285*, 211–220.
- (2) Lyons, G.; McCall, R. D.; Sharma, H. S. S. Physical degradation of wheat straw by the in-vessel and windrow methods of mushroom compost production. *Can. J. Microbiol.* **2000**, *46*, 817–825.
- (3) Miller, F. C.; Macauley, B. J. Odors arising from mushroom composting: A review. *Aust. J. Exp. Agric.* **1998**, *28*, 553–560.
- (4) Derikx, P. J. L.; Op den Camp, H. J. M.; Van der Drift, C.; van Griensven, L. J. L. D.; Vogels, G. D. Identification and quantification of odorous compounds emitted during production of mushroom compost. *Appl. Environ. Microbiol.* **1990**, *56*, 563–567.
- (5) Op den Camp, H. J. M.; Pol, A.; Van der Drift, C.; Vogels, G. D.; van Griensven, L. J. L. D. Production of odorous sulphur compounds during indoor compost preparation and overview of possible air treatments. *Mushroom Sci.* **1995**, *14*, 181–187.
- (6) Perrin, P. S.; Macauley, B. J. Positive aeration of conventional (Phase I) mushroom compost stacks for odor abatement and process control. *Mushroom Sci.* **1995**, *14*, 223–232.
- (7) Noble, R.; Hobbs, P. J.; Mead, A.; Dobrovin-Penington, A. Influence of straw types and nitrogen sources on mushroom composting emissions and compost productivity. *J. Ind. Microb. Biotechnol.* **2002**, *29*, 99–110.
- (8) Pecchia, J. A.; Beyer, D. M.; Wuest, P. J. The effects of poultry manure based formulations on odor generation in phase I mushroom composting. *Mushroom Sci.* **2000**, *15*, 335–339.
- (9) Fermor, T. R.; Randle, P. E.; Smith, J. F. Compost as a substrate and its preparation. In *The Biology and Technology of the Cultivated Mushroom*; Flegg, Spencer, and Wood, Eds.; Wiley: New York, 1985; pp 81–109.
- (10) Duns, G. J.; Ripley, B. D.; Rinker, D. L. Monitoring the production of odorous compounds during Phase I mushroom composting. *Mushroom News* **1999**, *47*, 12–23.
- (11) Heineman, P.; Engels, L. Toxicite des acides organiques sur le mycelium d'*Agaricus hortensis* et especes voisines en culture pure. *Mushroom Sci.* **1953**, *2*, 49–51.
- (12) Pietro, M.; Castaldi, P. Thermal analysis for the evaluation of the organic matter evolution during municipal solid waste aerobic composting process. *Thermochim. Acta* **2004**, *413*, 209–214.
- (13) Otero, M.; Calvo, L. F.; Estrada, B.; Garcia, A. I.; Moran, A. Thermogravimetry as a technique for establishing the stabilization progress of sludge from wastewater treatment plants. *Thermochim. Acta* **2002**, *389*, 121–132.
- (14) Peuravuori, J.; Paaso, N.; Pihlaja, K. Kinetic study of the thermal degradation of lake aquatic humic matter by thermogravimetric analysis. *Thermochim. Acta* **1999**, *325*, 181–193.
- (15) Lyons, G. A.; Sharma, H. S. S.; Kilpatrick, M.; Cheung, L.; Moore, S. Monitoring of changes in substrate characteristics during mushroom compost production. *J. Agric. Food Chem.* **2006**, *54*, 4558–4667.
- (16) Jakab, E.; Faix, O.; Till, F. Thermal decomposition of milled wood lignins studied by thermogravimetry/mass spectrometry. *J. Anal. Appl. Pyrolysis* **1997**, *40–41*, 171–186.
- (17) Gomez, C. J.; Meszaros, E.; Jakab, E.; Velo, E.; Puigjaner, L. Thermogravimetry/mass spectrometry study of woody residues and an herbaceous biomass crop using PCA techniques. *J. Anal. Appl. Pyrolysis* **2007**, *80*, 416–426.
- (18) Remmler, M.; Kopinke, F.-D.; Stottmeister, U. Thermoanalytical methods for characterising hydrocarbon–sludge–soil mixtures. *Thermochim. Acta* **1995**, *263*, 101–112.
- (19) Conesa, J. A.; Marcilla, A.; Moral, R.; Moreno-Caselles, J.; Perez-Espinosa, A. Evolution of gases in the primary pyrolysis of different sewage sludges. *Thermochim. Acta* **1998**, *313*, 67–73.

- (20) Noble, R. Improving the efficiency and environmental impact of mushroom composting. M 3e Horticulture LINK Project CSA6365/HL0163LMU, HDC, U.K., 2006; p 89.
- (21) Geyer, W.; Hemidi, F. A.-H.; Bruggemann, L.; Hanschmann, G. Investigation of soil humic substances from different environments using TG-FTIR and multivariate data analysis. *Thermochim. Acta* **2000**, *361*, 139–146.
- (22) Burton, C. H.; Sneath, R. W.; Misselbrook, T. H.; Pain, B. F. The effect of farm scale aerobic treatment of piggery slurry on

odor concentration, intensity, and offensiveness. *J. Agric. Eng. Res.* **1998**, *71*, 203–211.

Received for review February 15, 2008. Revised manuscript received May 9, 2008. Accepted May 12, 2008. This work was carried out as part of Horticulture LINK Project CSA6365/HL0163LMU, and HDC, Defra, and DARD NI are thanked for funding and support.

JF800487E