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Fate of Toxic Compounds During Composting

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Composting has gained acceptance in recent years as a means of converting wastes into a useful product (Steuteville 1996, Ballister-Howells 1996). One example is the increasing use of compost as greenhouse potting media for a variety of plants (Bugbee and Frink 1989; Beaver 1994; Bugbee 1996). However, the possible presence of toxic compounds in waste materials continues to raise concerns about the release of such compounds, either during the composting process or when the finished compost product is used.

PCDD/F are known to be spread through the environment by atmospheric transport and depositional processes (Eitzer and Hites 1989; Brzuzy and Hites 1996). Such processes lead to the presence of these compounds on plant material and soil, albeit at low concentrations. Since plant materials form a major feedstock in composting, it is important to determine the fate of these compounds during the composting process. Using laboratory scale bioreactors, Krauß et al. (1994) found that some dioxins appear to increase in concentration and absolute amount during composting. However, the authors state that their results are close to the precision of their methods. PCDD/F concentrations have been seen to increase in maturing garden compost, and remain stable or slightly decrease in household organic waste compost (Oberg et al. 1994).

In our previous work on volatile organic chemicals in MSW compost (Eitzer 1994) there was some evidence for formation and release of aldehydes and/or ketones during the composting process. Unfortunately, the sorbent trapping/thermal desorption method used in that study worked poorly for these compounds. Methods and analyses specific for aldehydes and ketones would therfore be of use to confirm these prior findings.

The purpose of this study was to determine the fate of toxic materials present in a waste compost generated at the Connecticut Agricultural Experiment Station (CAES). The potentially toxic heavy metals were determined and compared to the regulatory limits governing agricultural use of sewage sludge based on its heavy metal content (EPA 1993). The concentration of PCDD/F in mixed wastes was determined before and after composting in small static piles. A new method specific for aldehydes and ketones was developed and used to determine if these compounds were produced during the composting process. In this study the agricultural utility of the compost produced was also assessed.

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MATERIALS AND METHODS

Organic waste materials were collected from lunchrooms and greenhouses at CAES during the summer of 1995. Wastes generated in lunchrooms included fruit, vegetables, coffee grounds and filters, but excluded meats. Greenhouse waste included non-diseased plant material and spent potting media. Waste materials were collected twice per week and weighed. Food wastes were held in closed 32 gallon LDPE trash barrels, and greenhouse wastes in 64 ft^3 pressure-treated lumber (PTL) bins open to the air, until enough material had been amassed to form a pile. Three piles were formed during the summer trials.

Collected materials were shredded and mixed using a wood chipper and formed into 24 ft^3 piles in 64 ft^3 PTL bins open to the atmosphere. Once a week the piles were aerated by hand turning. The temperature of the piles was monitored daily; when the temperature had returned to ambient it was assumed that the composting process had been completed. Perforated 4 in. diameter PVC pipes were inserted into Pile 3 in order to increase aeration. Each pile was sampled at formation and upon completion of composting. The samples were held frozen at -4 °C until analysis.

Carbon-to-nitrogen ratio (C:N) for each pile at formation and completion of composting was determined as follows. Carbon was measured by loss on ignition at 550 °C for 3 hours. Total nitrogen analysis was performed using an automated Kjeldahl method with a Tecator 1030 Kjeltec Auto Analyzer (Tecator,Hoganas, Sweden), using a copper catalyst.

A greenhouse germination and growth study was conducted using compost from Pile 2 to determine if the compost generated during this study had horticultural value. Tomato seeds *(Lycopersicon esculentum* Mill., cv Celebrity) were sown in one of three media: Promix BX (Premier Horticulture, Inc., Red Hill, PA); Mix-1, consisting of compost, sphagnum, vermiculite in a 3:3:4 ratio; and Mix-2, consisting of compost: sphagnum:vermiculite in a 5:2:3 ratio. Standard 0.2 L square plastic pots were used for the germination studies. They were arranged in flats of 24 with five seeds per pot and 24 pots per treatment. Flats were kept in clear polyethylene bags to retain moisture. Seed germination and moisture were monitored daily. Within each treatment, moisture was maintained by delivering equal volumes of deionized distilled water to each pot. Bags were removed when they began to interfere with plant growth. Plant fresh weights were determined 25 days after sowing.

Metals were analyzed using the procedures of Stilwell (1993). In brief, compost samples were digested with concentrated nitric acid in a CEM MDS-81D microwave digester (CEM, Matthews, NC). Elemental analysis was carried out on the digest using either an AtomScan 16 Inductively Coupled Plasma Spectrometer (Thermo Jarrel Ash, Franklin, MA) for Cu and Zn; or, a Perkin-Elmer 5100PC Graphite Furnace Atomic Absorption Spectrometer (Perkin-Elmer, Wilton, CT) with Zeeman background correction for As, Cd, and Pb. Standard conditions and wavelengths were employed for both instruments.

PCDD/F were determined using standard procedures described in EPA Method 1613 (EPA 1994). In brief, compost samples were spiked with carbon-13 labeled PCDD/F internal standards, Soxhlet extracted, and subjected to a multi-step clean-up procedure. This included partitioning against sulfuric acid and aqueous sodium hydroxide and two stages of column chromatography (alumina and carbon). Samples were concentrated under nitrogen to a final volume of less than 2OµL and a C-13 labeled recovery standard was added. Reported sample concentrations exceeded blanks by at least a factor of 2.5.

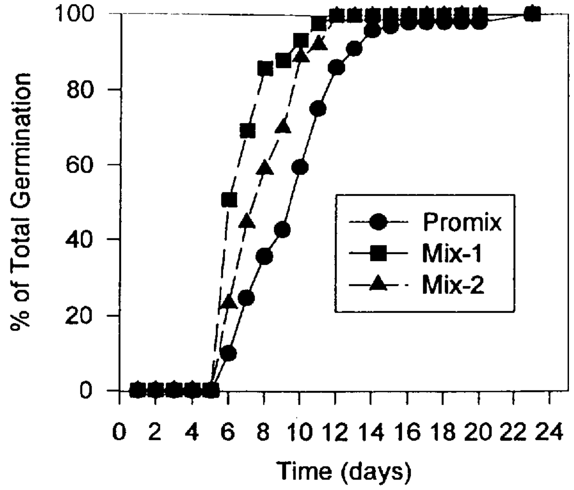

Figure 1. Germination rates expressed as percent germination normalized to total germination for each treatment.

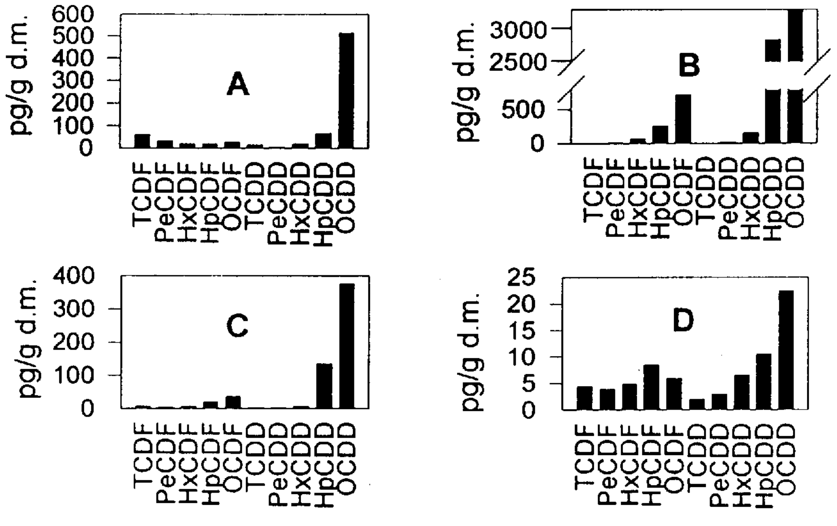

Figure 2. Homolog profiles for composts: institutional, this study (A); yard waste, Malloy et al. (1993) (B); household, Kraub et al. (1994) (C); and garden/household, Oberg et al. (1994) (D).

Table 1, Compost pile composition, C:N ratio, and maximum temperature and date maximum temperature reached from pile formation

Pile	% Food	% Plant	% Promix	Initial C:N	Final C:N	Max.T (ºC)	Days to Max. T
1	12.7	23.6	63.7	70.7	55.0	37	7
2	271	27.1	45.8	82.7	30,2	57	12
3	52.8	13.0	34.2	50.9	38,7	39	11

Table 2. Tomato germination and biomass

Treatment	t½ Germination (days)	% Germination	Avg. Fresh Wgt./Seedling
Promix BX	9.4	84	0.46
Mix-1	5.9	76	0.44
Mix-2	7.3	75	0.40

Table 3. Average concentration of heavy metals in finished compost in mg/Kg dry weight.

Element	Pile 1	Pile 2	Pile 3	EPA 503 Limit*
As	12.8	9.8	13	41
Cd	0.6	0,3	0.4	39
Cu	33	33	41	1500
Pb	26	30	33	300
Zn	95	87	101	2800

*EPA in the Federal Register Feb 19, 1993 p9392.

Samples were analyzed using high resolution gas chromatography (GC)/high resolution mass spectrometry (MS). A Hewlett-Packard 5890 GC (Hewlett-Packard, Avondale, PA) with a 60 m x 0.32 mm-O.25 µm film thickness J8W DB-5 capillary column (J&W, Folsom, CA) was used with splitless injection and the following temperature program: 200 ºC for 2 min., 5 °C /min to 220 °C hold for 16 min., 5 º C/min to 235 °C hold for 7 min., 5 °C/min. to 330 ºC hold for 5 min. The GC was interfaced to a Kratos Concept 1S MS (Kratos, Manchester, England), which was operated with an electron impact ion source at 35 eV ionizing potential, 250 ºC. and 8 KV accelerating voltage. Selected ion monitoring at resolution equal to or greater than 10,000 was used. Five groups of 10 ions each were monitored (two ions for each homolog) with magnet switching between groups.

Air samples were collected for aldehyde/ketone analysis by using a portable sampling pump to draw air at a rate of 0.67 L/min through an LPD-DNPH sampling cartridge (Supelco, Bellefonte, PA). These cartridges were placed in a bottomless carboy set into the compost pile to assure that the air sampled came from the pile (Eitzer 1994). These cartridges contain dinitrophenylhydrazine reagent impregnated on silica to derivatize and stabilize the carbonyl moiety present in aldehydes and ketones. The cartridges were analyzed with two 2 mL aliquots of acetonitrile, with the eluate brought to a final volume of 5 mL. The cartridges ware analyzed by high performance liquid chromatography (HPLC) with ultraviolet detection at 360 nm on a Perkin-Elmer Integral 4000 (Perkin Elmer, Norwalk, CT) using a Supelco LC-18, 25 cm x 4.6 mm column, a 20 µL injection and a flow rate of 1 mL/min. The initial mobile phase of water:acetonitrile:tetrahydrofuran (60:30:10) was held for 1 min and linearly ramped over 25 min to water:acetonitrile (40:60) which was held for 2 min. Samples were quantified using an external standard containing DNPH-derivatized aldehydes and ketones.

RESULTS AND DISCUSSION

The feedstock composition and maximum temperature achieved for each of the three piles is given in Table 1. Pile 2 achieved a maximum temperature of 57 °C. This is near the 60 °C optimum temperature for oxidation of organic matter to CO_2 and H_2O as reported by Poincelot (1975). It is possible that the low maximum temperature reached by Pile 1 was due to the large proportion of spent potting media in that pile. Pile 3 contained a relatively high percentage of food wastes, much of which was water. The initial moisture content of the pile appeared to limit its heating. This was corrected through aeration of the pile on day 7 by inserting perforated PVC pipes into the pile. The pile responded with a 17 °C increase in temperature but the maximum temperature reached was still below optimum.

Final C:N for all piles are within a range considered reasonable for agricultural use. Beaver (1994) composted separated cow manure (SCM) alone and with coal ash at rates of 5.4% to 31.8% C:N ratio of finished composts was 23.5 for SCM and ranged from 26 to 29 for SCM/coal ash composts. Bugbee (1996) utilized yard waste and biosolid compost with a C:N ratio of 65 in potting mixtures in various proportions. Growth of rhododendron, arborvitae, and black-eyed susan in unamended potting medium was not different from those containing compost.

The compost from pile 2 in this study was used as a component of two potting mixes for the growth of tomato plants. Germination as a function of time for plants in the three patting media are shown in Figure 1. Germination in Mix-1 was found to be significantly different from that in Promix BX by the Kolmogorov-Smirnov one sided-two sample test (p=O.O5). Mix-2 was not significantly different from Promix BX, but still reached 50% germination ($t_{½}$) more quickly than did Promix BX (Table 2). Overall total percent germination was higher for Promix BX, but as this was a single trial the difference could not be tested for significance. Fresh weights in the 3 media were not found to be significantly different from one another by a one-way analysis of variance.

The concentrations of heavy metals in the finished composts are reported in Table 3. Note that all of these values are well below the EPA 503 regulatory limits for heavy metals in sewage sludge intended for agricultural application (EPA 1993), indicating that there are no regulatory problems associated with use of this compost due to heavy metal content.

The concentrations of individual 2,3,7,8-substituted PCDD/F congeners (considered to be the toxic congeners) are reported in Table 4. There were no statistically significant differences in concentration between initial and final samples from each individual compost pile. Although no differences are reported, it must be pointed out that the relatively high variability (typical for PCDD/F measurements at these extremely low concentration levels) necessitates a concentration change of a factor of 2 to 3 for significance During the composting process the organic carbon as a percentage of dry weight was reduced by approximately 10.15% as a result of the conversion of organic matter to carbon dioxide; therefore, if the composting process did not effect PCDD/F we might expect to see a small increase in absolute PCDD/F concentration but, as noted, this increase would not be significant given the variability of the data.

It is useful to compare the concentrations observed here with those observed by other workers. The average homolog profiles (the sum of all congeners at a given level of chlorination) from these composts are displayed in Figure 2 along with those of a mature garden compost (Oberg et al. 1994), a household compost (Krauß 1994), and the average of yard waste composts (Malloy 1993).

Table 4. Concentration of 2,3,7,8-substituted PCDD/F and average (all samples before and after) TEQ in pg/g dry weight.

Congener	Pile 1 Initial	Pile 1 Final	Pile 2 Initial	Pile 2 Final	Pile 3 Initial	Pile 3 Final	Avg. TEQ
2,3,7,8-TCDF	4.3±1.5	3.0±1.3	2.3±0.3	2.0±0.4	1.4±0.1	1.9±0.2	0.25
2,3,7,8-TCDD	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.00
1,2,3,7,8-PeCDF	3.9±3.9	3.0±1.8	1.2±0.7	1.5±1.0	0.7±0.1	0.6±0.2	0.09
2,3,4,7,8-PeCDF	1.3±1.3	0.7±0.2	0.9±0.2	0.8±06	0.6±0.2	0.8±02	0.42
1,2,3,7,8-PeCDD	0.0±0.0	0.3±0.2	0.0±0.0	0.0±0.0	0.5±0.2	0.5±0.3	0.10
1,.2,3,4,7,8-HxCDF	4..4±1.6	2.4±0.7	2.6±1.0	2.0±0.9	1.4±0.7	1.5±0.4	0.24
1,2,3,6,7,8-HxCDF	3.3±0.l	2.0±0.7	1.3±0.l	1.4±0.3	1.5+1.0	1.4±0.3	0.18
1,2,3,7,8,9-HxCDF	0.3±O.3	1.2±0.4	0.7±0.1	0.4±0.1	0.8±0.5	0.6±0.1	0.07
2,3,:6,7,:8--HxCDF	0.7±0.7	0.5±0.2	0.0±0.0	0.0±0.0	0.1±0.1	0.0±0.0	0.02
1,2,3.4,7,8-HxCDD	0.9±0.9	0.8±0.2	0.7±0.l	0.6±0.1	0.5±0.2	0.4±0.1	0.06
1,2,3,6,7,8-HxCDD	1.1±1.1	2.2±0.9	1.9±0.5	1.3±0.3	4.1±3.6	1.9±0.3	0.21
1,2,3,7,8,9-HxCDD	1.3±1.3	1.9±0.3	2.6±0.l	I.4±O.3	1.9±0.8	I.5±0.3	0.17
1,2,3,4,6,7,8-HpCDF	9.8±3.1	11±2	7.9±0.7	6.4±1.O	9.2±5.1	9.2±2.4	.0.09
1,2,3.4,7,8.9-HpCDF	1.3±0.6	1.0±0.4	0.8±0.2	0.5±0.4	0.8±0.5	0.7±0.5	0.01
1,2,3,4,6,7,8-HpCDD	19 ± 13	40±13	27 ± 1	20 ± 3	58±45	33±7	0.33
OCDF	16±6	42 ± 46	16±1	17±4	18 ± 8	23±4	0.02
OCDD	260±160	670±140	410±60	340±70	690±210	530±60	0.48
						Total TEQ	2.75

The concentrations reported in this study fall in the middle of the reported concentration range. Note that the homolog profiles for all of these composts are quite similar, being dominated by the OCDD content, a profile consistent with the environmental background caused by atmospheric deposition as reported elsewhere (Eitzer and Hites 1989; Brzuzy and Hites 1996).

The data should also be examined in terms of toxicity and the proposed agricultural use of compost. In Table 4 the average 2,3,7,8-substituted PCDD/F concentration of all piles (averaged over both before and after composting since no significant differences were observed) is combined with international toxic equivalency factors (TEF) to produce an average toxic equivalency (TEQ) in pg TEQ/g dry weight.

The total TEQ of 2.75 pg TEQ/g is lower than the 5 pg TEQ/g recommended limit for unrestricted agricultural use of compost in Germany (Malloy et al., 1993). The total TEQ from our study can also be compared to the criteria for land application of sludge developed by Thiel et al (1995). They proposed that the mass of 2,3,7,8-TCDD + 0.0013 times the mass of 2,3,7,8-TCDF not exceed 1.3 mg/hectare. As a conservative estimate we used the average TEQ for the compost reported here (including all congeners and 2,3,7,8-TCDF at a 0.1 equivalency factor) and assumed compost applied at a rate of 50 tons/acre. The resultant mass loading yields a value of 0.3 mg TEQ/hectare, well below the proposed guideline,

Four compounds were observed in the air samples taken with the LPD-DNPH cartridges; acetone, 2-butanone, formaldehyde, and acetaldehyde. Analysis of samples taken from Pile 1 indicated that the 15 minute sampling time used led to low concentrations in the extract that were difficult to quantify. Samples taken for Piles 2 and 3 were conducted with 60 minute sampling times to improve detectable amounts. The air concentration data for these four compounds are presented in Table 5. It should be noted that all of these concentrations are below threshold weighted average limits for workplace air as set by the American Conference of Governmental Industrial Hygenists (1992).

Table 5. Concentrations of aldehydes and ketones in air samples in µg/m3. When two samples are shown for a given day they represent before (*) and after (**) turning of the pile. (nd-not detected)

Pile	Day	Formaldehyde	Acetaldehyde	Acetone	2-butanone
1	1	15.4	nd	54.7	nd
1	2	15.4	nd	74.6	nd
1	3	11.4	nd	49.8	nd
1	6*	3.2	nd	3.9	nd
1	6**	2.0	nd	19.0	28.6
1	13*	2.1	nd	nd	nd
1	13**	4.0	nd	15.9	nd
2	0	34.8	1069.7	nd	14.9
2	1	4.0	4.1	65.8	nd
2	2	2.4	3.7	6.1	nd
2	4	2.2	5.1	7.1	nd
2	7*	2.5	4.2	11.3	nd
2	7**	8.1	4.9	14.6	14.6
2	10	2.5	6.6	7.8	nd
2	14*	0.9	nd	5.2	nd
2	14**	1.5	nd	nd	nd
3	1	5.0	13.4	718.9	42.8
3	2	8.3	3.0	38.7	4.0
3	3	6.4	1.6	11.2	nd
3	6	3.9	0.7	18.8	nd
3	9	26.1	22.9	325.9	126.2
3	10	21.5	7.3	50.2	30.6
3	13*	1.0	2,1	21.0	nd
3	13**	5.5	6.1	342.5	200.6

Table 5 shows that there is usually an increase in observed air concentrations for all compounds immediately after turning (turning dates: Pile 1, days 6 and 13; Pile 2, days 7 and 14; Pile 3, days 7 and 13). For example, 2-butanone changes from not detected before turning to a concentration of 28.6 µg/m3 after turning in air sampled from Pile 1 on day 6. This is consistent with the fact that turning exposes interior surfaces and allows volatilization of chemicals from those surfaces. Significant concentrations were also observed after the second turning of each pile. In fact, in some cases these concentrations were higher than after the first turning. This observation suggests that these compounds were generated in the central core of the pile during the composting. The possibility of generating aldehydes and ketones is also supported by the data from Pile 3 in which we did not achieve a good temperature increase until after day 7 when the perforated PVC pipe was used to aerate the pile. Note how the concentrations of aldehydes and ketones dramatically increased after this point (day 9 as compared to day 6). The concentrations in the samples after the next turning (day 13**) remain very high, lending support to the theory that they were produced during good composting conditions. All of these data are consistent with our earlier work that suggested the formation of aldehydes and ketones by the composting process (Eitzer 1994). The anomalous high values for acetaldehyde and formaldhyde in air from Pile 2 might be an artifact.

Our data showed that successful composting of a portion of the organic waste stream at an institution such as the Connecticut Agricultural Experiment Station can produce a useable product.

These data showed that the compost has horticultural value. Toxic materials were below levels of concern in the compost. In addition, seedlings grew as well in the compost mixtures as in the Promix BX. By replacing a portion of the purchased material (Promix BX) with recycled material (waste compost) the compost mixture was more cost effective. For example, Promix alone costs 64% more than the 3:3:4 compost:sphagnum:vermiculite ratio used in Mix-1.

The data on the fate of PCDD/F although somewhat variable, supported the contention that only minor changes to the concentrations of PCDD/F take place during composting and that the source of these compounds should be attributed to their presence in the starting materials. In addition, the data lent support to the theories that aldehydes and ketones can be generated by the composting process.

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