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Fate of Selected Pesticides Applied to Turfgrass: Effect of Composting on Residues

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Alternative uses for yard waste are essential with the diminishing landfill capacity in the United States. Grass clippings have been estimated to take up as much as 20% of landfill space. Grass clippings should be returned to the turf as an efficient nutrient recycling practice; however, there are cases where returning clippings is not practical. Instead of disposing of clippings, composting is a viable practice that produces a useful, organically rich material (Martin and Gershuny, 1992). Addition of compost to soil can improve soil physical properties such as structure, water holding capacity, and aeration status (Martin and Gershuny, 1992). Cisar and Snyder (1992) observed faster sod establishment on solid-waste compost than for sod establishment on unamended soil.

Since compost is to be used for growing plants, the fate of any anthropogenic compounds in the compost must be known. Pesticides are used with some regularity on turfgrass and the fate of these products during the compost process is not well-understood (Racke and Frink, 1989; Lemmon and Pylypiw 1992). Lemmon and Pylypiw (1992) evaluated the decomposition of the preemergence herbicide pendimethalin and three insecticides, diazinon, chlorpyrifos, and isofenphos, in grass clipping compost. They found all pesticides were present at concentrations below 1 mg kg^{-1} by three weeks after compost initiation. Racke and Frink (1989) measured the degradation of carbaryl and the polyaromatic hydrocarbon phenanthrene during the composting of sewage sludge. Phenanthrene was quite persistent with 89-93% remaining after composting whereas only 3-4% carbaryl remained after composting.

Composted grass clippings would make an excellent soil amendment (Martin and Gershuny, 1992). The objective of this research was to assess the persistence of several pesticides applied to turfgrass foliage that was subsequently used for compost.

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MATERIALS AND METHODS

On June 12, 1991, five pesticide products were applied to 0.07 ha plot of a mixed stand of Kentucky bluegrass *(Poa pratensis),* perennial ryegrass *(Lolium perenne),* **and fine fescue *(Festuca* sp). The turf was an old stand and varietal identification was not known. The pesticides applied were chlorpyrifos at 1.6 kg ai ha^{-1}, triclopyr plus 2,4-D at 1.07 plus 0.41 kg ha^{-1}, triclopyr plus clopyralid at 0.22 plus 0.65 kg ha^{-1}, isoxaben at 0.84 kg ai ha^{-1}, and flurprimidol at 0.84kg ai ha^{-1}. The plots treated with isoxaben were watered in immediately with a pressurized sprayer. Clippings were harvested using a rotary mower set at 3.8 cm. The clipping were collected and separated into compost piles (@ 0.5 m^3) for each pesticide. The total clippings from each pesticide treatment, including a control, were divided into two compost piles of equal size. One pile was turned regularly while the other was left unturned for the duration of the study. The piles were sampled at compost initiation and at 14, 28, 56, 128, and 365 days after treatment. Grab samples were taken from the interior and exterior of each pile, placed in 0.96 L mason jars, transported to the laboratory and stored at ~-10 C.**

All standards were purchased from Chem Service (W. Chester, PA) or obtained directly from the manufacturer. The purity of the standards ranged from 92.5 to 99.8%. A standard curve for the pesticide in question was run to determine linearity of the range to be quantified. All samples were analyzed with High Performance Liquid Chromatography (HPLC) or Gas Chromatography (GC) to determine the amount of pesticide in the sample. A single point calibration standard was used to quantify the amount of pesticide in the sample.

Determination of chlorpyrifos (O,O-Diethyl-O-[3,5,6-trichloro-2-pyridyl]-phosphorothioate) in grass was with an Electron Capture Detector (ECD) GC. About 10 g of grass was extracted for each analysis. The grass was homogenized with 100 ml of acetone for more than 5 minutes and then filtered with 0.5 cm of HyFlo Super Cel (Johns-Manville) in 150 ml sintered glass funnel on a vacuum filtering assembly. The extraction was repeated with 100 ml of acetone. The filtrates were combined and taken to dryness. The extract was transferred with 20 ml of hexane to a column for cleanup. The extract was placed on a column containing 1.5 g of 60-100 mesh silica gel (oven dried at 110° C for 4 hours) with a glass wool (solvent extracted) pledget in the bottom of a 1 cm i.d. glass column. Three 20 ml portions of hexane was used to elute the sample through the column. The hexane elute was taken to dryness with a Turbo-Vap and brought to a volume of about 2 ml with acetone for the GC injection. Gas chromatography was performed with a Perkin-Elmer 8500 instrument equipped with Ni^{63} ECD. The oven temperature was 200° C, the injector temperature was 250° C, and the detector was 345° C. The carrier gas (helium) flow rate was 15 psig and the

makeup gas (N_2) at 20 psig. A DB-5 capillary column 0.25-um film thickness 30m long with and i.d. of 0.32 mm was employed.

Determination of clopyralid (3,6-Dichloro-2-pyridinecarboxylic acid) (Galoux, 1982) in grass was done with a ECD-GC. About 10 g of grass was homogenized for 5 minutes with 150 ml of 0.25 M KOH. The extract was transferred to a 500 ml separatory funnel through a Whatman # 1 filter. One hundred ml of diethyl ether, 5 g of NaCl and 20 ml of H_2SO_4 were added to the separatory funnel. The diethyl ether layer was collected and the extraction was repeated. The combined extracts were put through about 5 g anhydrous Na_2SO_4 and the volume was reduced to about 1 ml. The clopyralid extract was then esterified with diazomethane, the volume reduced to < 0.5 ml and then brought to a volume of ~ 2 ml for GC analysis. The clopyralid samples were run with the same GC conditions as chlorpyrifos.

Triclopyr (3,5,6-Trichloro-2-pyridinooxyacetic acid) in grass was determined with an ECD-GC. A 10 g sample was shaken for 10 minutes with 6 g of NaCl, 1 ml of 9 M H_2SO_4, 50 ml of diethyl ether and 50-100 ml of H_20. The extract was vacuum filtered through a Whatman # 1 filter. The filtrate was then transferred to a separatory funnel and the ether portion was retained. The aqueous portion and filter paper was then shaken with 50 ml of diethyl ether for 10 minutes. The ether portion was separated and combined with the previous ether portion. The extract was washed twice with 20 ml of 10 % NaCl w/v, and dried over ~ 5 g of anhydrous Na_2SO_4. The volume was then reduced to near dryness. A silica gel column was prepared by adding 3 g of silica gel to a 1 cm i.d. glass column in a hexane slurry. The column was washed with 100 ml of toluene and hexane (1:9) v/v. The extract was added and then eluted with 100 ml toluene and hexane (35:65) v/v. The volume was reduce to <0.5 ml and esterified with BF_3 in methanol and held at 80 °C for 1 hour. The sample was then transferred with hexane to a separatory funnel, washed twice with 20 ml of 10 % NaCl w/v, and dried over ~ 5 g of anhydrous Na_2SO_4. The sample was reduced in volume to ~ 2 ml for the GC analysis. The GC conditions were the same as for the chlorpyrifos samples.

Flurprimidol (alpha-(1-methylethyl)-alpha-[4-(trifluromethoxy)phenyl]-5-pyrimidinemethanol) in grass was analyzed with ECD-GC after solid phase extraction with a basic alumina column (Alltech 500 mg). The grass was refluxed for 1 hour in 4:1 methanol: water v/v in a reflux condenser. After cooling, the extract was filtered through a Whatman # 7 filter into a separatory funnel with 30 ml of 5 % NaCl w/v. This solution was extracted three times with 50 ml of hexane and the hexane extract was passed through ~ 5 g of anhydrous Na_2SO_4. The hexane extract was taken to dryness and brought to 3 ml with dichloromethane and put on an Alumina Sep-Pak cartridge. The flurprimidol was eluted with 3:1 dichloromethane: methanol v/v solution. The extract was taken to dryness in a Turbo-Vap tube and brought

to ~ 2 ml in hexane for GC analysis. The Perkin-Elmer GC was used with the same conditions as were used for the chlorpyrifos.

Determination of isoxaben (N-[3-(1-Ethyl-1-methylpropyl)-5-isoxazolyl]-2,6-dimethoxybenz-amide) in grass was analyzed with HPLC. The grass was ground and extracted with 150 ml of methanol by shaking for one hour on a gyratory shaker. The extract was then vacuum filtered through a Whatman # 1 filter. The plant material and filter paper were returned to a pint jar and shaken for half an hour with 100 ml of methanol. Again the extract was filtered and the filtered extracts were combined and transferred to a 1000-ml separatory funnel. 75 ml of a 5% NaCl solution and 200 ml of water were added to the separatory funnel. The solution was extracted with two 125 ml portions of hexane and the hexane was discarded. This was followed with three 70 ml extractions with CH_2Cl_2. The CH_2Cl_2 was passed through ~ 5 g of anhydrous Na_2SO_4. The CH_2Cl_2 extract was evaporated to dryness and transferred to a column made up of 13 ml of alumina, 5 ml of florisil, and 4 ml anhydrous Na_2SO_4 with CH_2Cl_2. The column was washed with 50 ml of 4:1 CH_2Cl_2/ethyl acetate v/v and 25 ml of 99:1 v/v CH_2Cl_2/methanol and the eluate was discarded. Fifty ml of 99:1 v/v CH_2Cl_2/methanol was put on the column and the eluate was collected. The solvent volumes necessary for proper elution of the isoxaben was verified with each new batch of alumina and florisil. The eluate was evaporated to dryness and 2 ml of 2 % $KMnO_4$ w/v and the mixture was swirled. Two ml of 2 M KOH was added followed by 4 ml of CH_2Cl_2 and the mixture was shaken vigorously. The mixture stood for 5 minutes, the CH_2Cl_2 layer was separated and dried over ~ 5 g of anhydrous Na_2SO_4 The addition of CH_2Cl_2 was repeated twice and CH_2Cl_2 washes were combined. The CH_2Cl_2 was evaporated to dryness and brought to volume of ~ 2 ml for HPLC analysis. The mobile phase was 6:4 methanol/water at 2 ml/min. HPLC was performed using 50 µl *Rheodyne* injector, *Bischoff* HPLC pump, *Milton Roy* SpectroMonitor 3100 UV/Visible spectrophotometer set at 254 nm, *Brownlee Labs* Spheri-5 RP-18 column (220 X 4.6 mm) and a *Spectro-Physics* integrator.

Determination of 2,4-D (2,4 dichlorophenoxy acetic acid) was done by extraction of 10 g of grass with 5 ml of H_2O, 8 ml of H_2SO_4, and 50 ml of methanol by shaking for 20 minutes. The extract was filtered through a Whatman #1 Filter. The process was repeated on the filter paper. The combined filtrates were reduced to the aqueous portion. The aqueous extracts were extracted with two portions of 50 ml of CH_2Cl_2 and reduced to about 1 ml with a N_2 stream. A 1 cm i.d. Florisil column was prepared with 3 g of Florisil and about 2-4 mm of Na_2SO_4 and 30 ml of petroleum ether was eluted through and discarded. The sample extract was placed on the column, followed by 15 ml of petroleum ether and the eluate was discarded. 2,4-D was eluted with 25 ml of 1:1 v/v petroleum ether and ethyl ether. The eluant was reduced to < 0.5 ml. The 2,4-D was esterified to the methyl ester

by reaction with diazomethane. The extract was reduced to < 0.5 ml and brought up to volume of ~ 2 ml in hexane for ECD-GC analysis. The same parameters for the GC as were used for chlorplyrifos.

The percent recovery for each pesticide was: chlorpyrifos, 83 %; isoxaben, 66 %; flurprimidol, 143 %; triclopyr, 72 %; clopyralid, 132 %, 2,4-D, 107 %. The limit of detection was 0.01 ppm for the pesticides.

RESULTS AND DISCUSSION

Patterns of chemical loss in the compost piles was similar for all of the pesticide treatments. Isoxaben (Table 1), flurprimidol (Table 2), triclopyr (Table 3), and chlorpyrifos (Table 4) all were below the detection limit of 0.01 ppm of the methods used after 365 days. The data on 2,4-D (Table 5) showed a decline from a high of 183 ppm to less than 2 ppm in 365 days. 2,4-D was applied to bluegrass turf at 0.73 kg ai/acre in a laboratory experiment (Extoxnet, 1993) and a half-life of ten days was determined. Other studies have shown half-lives of 1.5 to 16 days in non-sterile soils. EPA has included 2,4-D in a list of chemicals likely to leach from soil and this agrees with the water solubility of 890 mg/l but the persistence as indicated in the half-lives implies that it will generally breakdown before becoming a ground water problem.

Studies have shown chlorpyrifos (Table 4) to be relatively persistent as compared to 2,4-D in that the half-life can range from 2 weeks to over a year. This research confirms the long half-life in that at 56 days chlorpyrifos was still detectable at 0.7 ppm and 0.1 ppm at 128 days. Some of the persistence can be related to its strong sorption to soil particles and grass. The mean of all samples from inside of the pile compared to the mean of all from outside of the piles showed that the inside concentration was on the average lower than the outside of the pile concentration. The means of turned versus not turned showed a lower concentration in the turned than in the unturned pile. All of the chemicals except 2,4-D and clopyralid (Table 6) were below the method limit of detection at 365 days, although 2,4-D had a high concentration of 183 ppm at initiation it was down to 1.4 ppm after 365 days. Clopyralid declined from 32 ppm to less than 1.4 ppm after 365 days. The obvious choice would be for the pesticides to breakdown to innocuous products. The compounds that bind are still of concern because of the possibility of future bioavailability to another organism. The release of an intact pesticide or a toxic pesticide metabolite is a real concern because of the potential damaging effects. The rate of release may be so slow, so as to be inoffensive to the environment, or may be rapid and cause damage. Clopyralid (Table 6) and 2,4-D (Table 5) were reduced to 1.4 ppm and 1.3 ppm respectively after 365 days.

The pesticides tend to show a biphasic degradation. There was generally an initial rapid dissipation rate followed by a slower process. The first phase may be related to volatilization and photolysis while the second phase loss by microbial degradation. Table 7 shows the first-order decay constants, k (day^{-1}) (Frederick, 1994), for each pesticide. The values are calculated between the first detection (initial concentration or A) and the next interval with a detected concentration (X) sample interval. The initial recovery for each chemical is A, where X equals the concentration at time t. These values were determined by the equation:

$$X = Ae(-kt)$$

Table 1. Isoxaben residue concentration-days since applied (ppb)

Isoxaben	1	14	28	56	128	365
Turned, inside	8120	14720	590	2220	980	nd
Unturned, inside	36830	4990	13680	1900	3200	nd
Turned, outside	4980	12990	5090	10580	10170	nd
Unturned, outside	175510	32350	76270	49990	810	nd

Table 2. Flurprimidol residue concentration-days since applied (ppb)

Flurprimidol	1	14	28	56	128	365
Turned, inside	2240	nd	4190	1140	1730	nd
Unturned, inside	nd	3670	1530	970	2210	nd
Turned, outside	430	1690	550	1000	2520	nd
Unturned, outside	2360	5500	170	2350	1750	nd

Table 3. Triclopyr residue concentration-days since applied (ppb)

Triclopyr	1	14	28	56	128	365
Turned, inside	nd	nd	450	nd	nd	nd
Unturned, inside	940	40	30	260	480	nd
Turned, outside	120	3180	20	170	nd	nd
Unturned, outside	70	50	10	nd	170	nd
Turned, inside	50	190	70	50	nd	nd
Unturned, inside	300	190	40	260	70	nd
Turned, outside	4540	nd	nd	nd	210	nd
Unturned, outside	220	7130	50	150	110	nd

The sampling of the compost piles had inherent difficulties. The piles were not homogeneous masses. Within the piles there could be aggregate population of degrading organisms and this produced unequal rates of decline of the chemicals within the piles. The sampling suffered from aggregate distribution of chemical and microbes and may account for a

portion of the variation seen in the results. If the sampling occurred in an area where the population of degrading organisms was high, then the chemical may be absent or at a low concentration and the converse would occur at low population of organisms. The physical appearance of the samples appeared to be great. The determination of percent water confirmed the variation in physical appearance. The percent water ranged from < 1 % to greater than 70 %. For all the chemicals applied, the composting environment was a good degrader of pesticides. The initial concentrations could cause damage to plants if applied immediately after composting but within several months the compost provides an excellent soil amendment. All of the values given for the pesticide concentrations are

Table 4. Chlorpyrifos residue concentration-days since applied (ppb)

Chlorpyrifos	1	14	28	56	128	365
Turned, inside	40	nd	10	nd	40	nd
Unturned, inside	230	10	nd	nd	nd	nd
Turned, outside	820	nd	50	210	110	nd
Unturned, outside	6800	170	nd	730	110	nd

Table 5. 2,4-D residue concentration-days since applied (ppb)

2,4-D	1	14	28	56	128	365
Turned, inside	38120	97020	3710	nd	nd	nd
Unturned, inside	86610	nd	250	nd	nd	nd
Turned, outside	26320	nd	75790	nd	620	510
Unturned, outside	183150	41540	11420	6060	nd	1370

TABLE 6. Clopyralid residue concentration-days since applied (ppb)

Clopyralid	1	14	28	56	128	365
Turned, inside	1560	16800	300	500	31900	1300
Unturned, inside	7200	1000	46900	300	9600	600
Turned, outside	32000	nd	200	200	10600	900
Unturned, outside	6800	700	7700	400	4700	100

Table 7. First-order decay constants for the pesticides applied

Pesticide	k value(day $^{-1}$)	Std Dev	CV
Chlorpyrifos	0.159	0.10	0.63
Triclopyr	-0.039	0.17	4.36
2,4-D	0.053	0.13	2.45
Clopyralid	0.104	0.10	0.96
Isoxaben	0.183	0.36	1.97
Flurprimidol	-0.030	0.07	2.33

given in dry grass weight. Future studies should control the variability by taking more samples, identify the metabolites and degradation products as well look at the depth of penetration of the pesticide within the turf. This would bring some understanding as to where the pesticide goes after application.

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