Degradation of pirimiphos-methyl during thermophilic composting of greenhouse tomato plant residues

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Ghaly, A.E., Alkoaik, F. and Snow, A, 2007. **Degradation of pirimiphos-methyl during thermophilic composting of greenhouse tomato plant residues**. Canadian Biosystems Engineering/Le génie des biosystèmes au Canada **49**: 6.1 - 6.11. The effectiveness of invessel thermophilic composting on the destruction of pirimiphos-methyl (12, 24, and 36 mg/kg dry matter) was evaluated. The bioreactor operated on a mixture of tomato plant residues, wood shavings, and municipal solid compost. Water was used to adjust the moisture content to 60% (wet basis); urea was used as a nitrogen source to adjust the C:N ratio to 30:1; and used cooking oil was added as a bioavailable carbon source. The composting process successfully destroyed 81-89% of pirimiphos-methyl within the first 54 h of operation. Complete destruction of the pesticide required approximately 438 h. The rate constant (*k*) for the degradation of pirimiphos-methyl was determined to be a function of the bioreactor temperature. A rate constant of 0.026, 0.003-0.010, and 0.002-0.009 h^{-1} was observed for the rising temperature mesophilic phase (25-45°C), thermophilic phase (45-63-45°C), and declining temperature mesophilic phase (45-25°C), respectively. A number of physical, chemical, and biological mechanisms contribute to the degradation of pirimiphos-methyl in the environment including mineralization or hydrolysis, abiotic transformations, adsorption, leaching, humification, and volatization. During composting of greenhouse wastes, the degradation of pirimiphos-methyl is accelerated by high temperatures, organic matter content, moisture, and biological activity. **Keywords:** pirimiphos-methyl, thermophilic, compost, degradation.

L'efficacité de destruction du pirimiphos-méthyl (12, 24, et 36 mg/kg matière sèche) par le compostage thermophilique en contenant a été évaluée. Le bioréacteur était alimenté de résidus de plants de tomates, de copeaux de bois et de compost solide de source municipale. De l'eau était utilisée pour maintenir la teneur en eau à 60% (base humide), de l'urée était utilisée comme source d'azote pour ajuster le ratio C:N à 30:1 et des huiles de cuisson usées étaient ajoutées comme source de carbone bio-disponible. Le compostage a permis de détruire de 81 à 89% du pirimiphos-méthyl dans les premières 54 h du processus. Approximativement 438 h ont été nécessaires pour une complète destruction du pirimiphos-méthyl. Il a été déterminé que la constante du taux (*k*) de dégradation du pirimiphos-méthyl variait en fonction de la température du bioréacteur. Des taux constants de 0,026, 0,003-0,010 et 0,002-0,009 h^{-1} ont été observés pour la phase mésophilique (25-45°C) d'augmentation de température, la phase thermophilique (45-63-45°C) et la phase mésophilique de diminution de température (45-25°C) respectivement. Différents mécanismes physiques, chimiques et biologiques contribuent à la dégradation du pirimiphos-méthyl dans l'environnement incluant la minéralisation ou hydrolyse, les transformations abiotiques, l'adsorption, le ruissellement, l'humidification et la volatilisation. Durant le compostage de résidus de serre, la dégradation du pirimiphos-méthyl était accélérée par des températures élevées, le contenu en matières organiques, la teneur en eau et l'activité biologique. **Mots clés**: pirimiphos-méthyl, thermophilique, compost, dégradation.

INTRODUCTION

Greenhouse tomato production represented 58% of the total greenhouse vegetable production in Canada in 2000, with a production area of 1550 hectares yielding 182,736 tonnes (AAFC 2001). A typical vegetable greenhouse operation produces 40-60 tonnes of organic residues per hectare per year from trimming and harvesting the crop. This residue must be disposed of properly (ODAF 2004). A tomato crop is susceptible to various types of insects and diseases under greenhouse environments, where optimum conditions for most pathogens are met and is, therefore, subject to intensive pesticide applications.

The term pesticide is defined as any substrate that prevents, destroys, repels, or mitigates a pest. It generally covers insecticides, fungicides, and herbicides (Bűyűksőnmez et al. 1999). Most of the pesticides used in greenhouses are insecticides or fungicides. Insecticides are the most hazardous class of pesticides due to their inhibition of the nerve system and enzymes in humans, animals, birds, and fish in addition to the targeted insects. Insecticides are classified into five categories based on their chemical structure: organochlorines, organophosphates, carbamates, pyrethroids, and a general category that includes petroleum oils, soaps, botanical extracts, microbial toxins, insect growth regulators, and inorganic mineral dusts. The ban on organochlorine insecticides (DDT, chlordane, and dieldrin), because of their resistance to biological and chemical degradation and accumulation in body fat, was followed by the development of organophosphate compounds (pirimiphos-methyl, chlorpypifos, diazinon, and malathion).

Pirimiphos-methyl is a fast-acting broad spectrum insecticide with both contact and fumigant action. It shows activity against a wide variety of insects including ants, aphids, beetles, caterpillars, cockroaches, fleas, flies, mites, mosquitoes, moths, and thrips. Pirimiphos-methyl has a half-life of 117 days in water (Yamada 2005; Bullock 1974), 180-270 days on greens and seeds, and 130 days in soil (Bowker et al. 1972). It has been reported to cause cholinesterase inhibition (in the liver) in

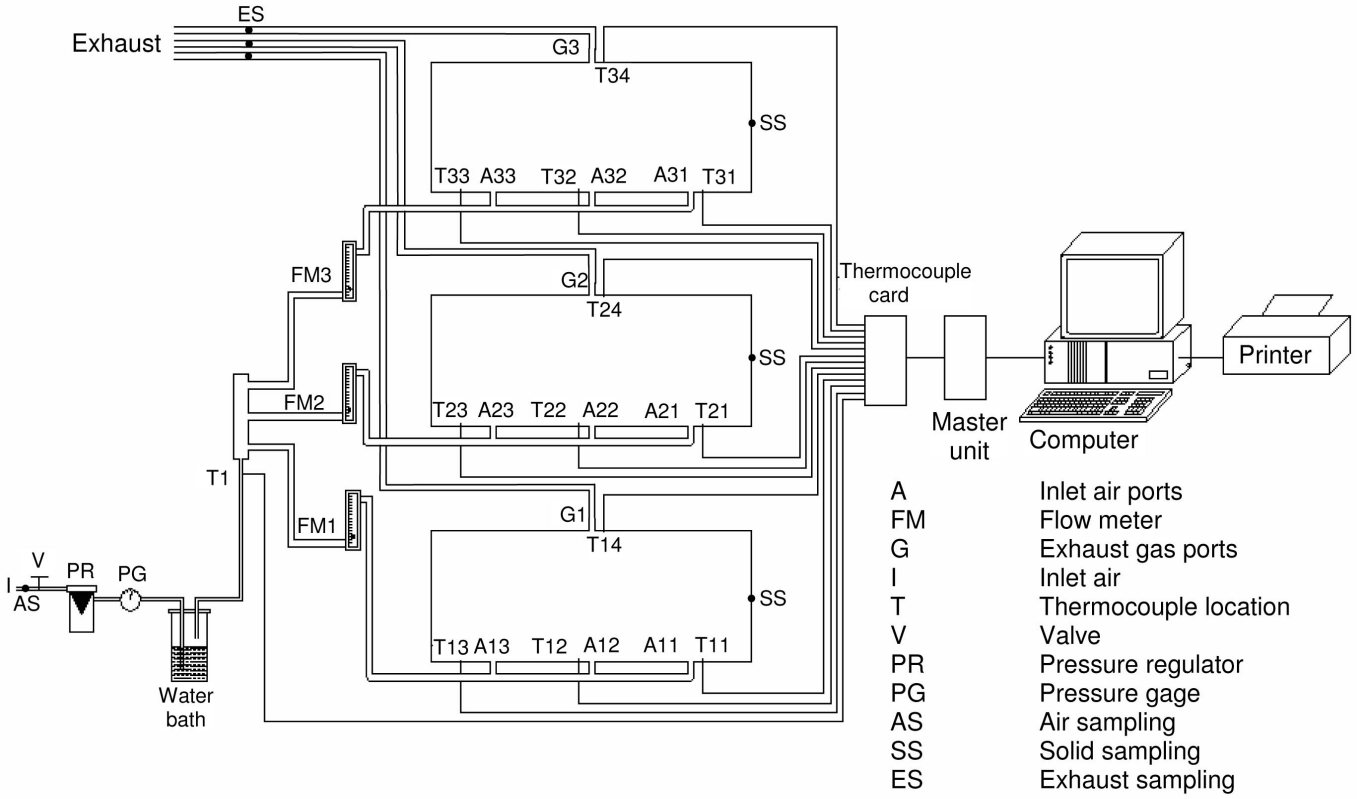


Fig. 1. Experimental setup.

humans which at high dose rates results in nausea, dizziness, and confusion and at high exposure (accidents, major spills) results in respiratory paralysis and death (Abo-Elsaad et al. 2001). Rapid absorption and bioaccumulation of pirimiphos-methyl has been reported in tissues of rats and dogs (Bratt and Jones1973; MacPherson 1998), goats (Bowker et al. 1973; Skidmore et al. 1985), cows (Bullock et al. 1974; Swaine 1982), and hens (Green et al. 1973; Earl et al. 1990) which resulted in inhibition of cholinesterase in brain, red cells, and plasma (Clark 1970), reduction in mating performance and pregnancy rates in animals, and increases in the number of dead chicks in eggshells (Palmer and James 1972).

According to NSMAFF (2004) and OMAFRA (2004), composting of greenhouse wastes is considered the preferred organic waste management method, especially for the destruction of plant pathogens and degradation of pesticides. Composting is an aerobic biological decomposition of organic matter (Haug 1993; Liang et al. 2003) whose end product (compost) can be used to restore and preserve the environment (Stentiford 1996).

The aim of this study was to investigate the effectiveness of controlled thermophilic composting of greenhouse tomato plant residues on pirimiphos-methyl degradation.

EXPERIMENTAL APPARATUS

The experimental set up shown in Fig. 1 consisted of a frame, three bioreactors, mixing unit, air supply unit, and data acquisition system. The frame was made of aluminum sheets and angles (3.2 mm thick) and was used to hold the mixing motors, flow meters, air and exhaust gas manifolds, tubing, and thermocouple wires.

Each bioreactor was constructed of a polyvinyl chloride (PVC) tube having a length of 520 mm, an inside diameter of 203 mm and a wall thickness of 5 mm (Fig. 2). A removable circular plexiglas plate of 203-mm diameter and 6-mm thickness was recessed and secured into one side of the cylinder by means of six stainless steel screws (6 mm). A rubber gasket lining (O-ring, 2.5-mm thick) was added to the inner side of the circular plate to keep it tight. There was a small circular window (64 mm in diameter) on the removable circular plate, which was closed with a rubber stopper (No.13) and used as a sampling port. A fixed circular PVC plate of 203-mm diameter and 6-mm thickness was glued into the other side of the tube. Each reactor was fitted into an aluminum ring, which was fastened into the frame by means of four bolts (6 mm) and nuts. There were three holes at the bottom and one at the top of the bioreactor, which were drilled and threaded to take a 12-mm nylon hose barb. The holes at the bottom were connected to a manifold by 6.4-mm diameter Tygon tubing and used for aeration, whereas the one at the top was used for the exhaust gas. Both circular plates were insulated with 38.1-mm thick styrofoam layer, while the tube was insulated with a 38.1-mm thick fiberglass. A removable 10.5-mm diameter solid stainless steel shaft, (having five stainless steel collars in which five bolts of 69-mm length and 6-mm diameter each were mounted) was mounted on two bearings inside each bioreactor. The shaft was rotated by a thermally protected electric motor (Model No. 127P1486/B, D. C., Sigma Instruments Inc., Braintree, MA). Air was supplied continuously to the bottom of the bioreactor from the laboratory

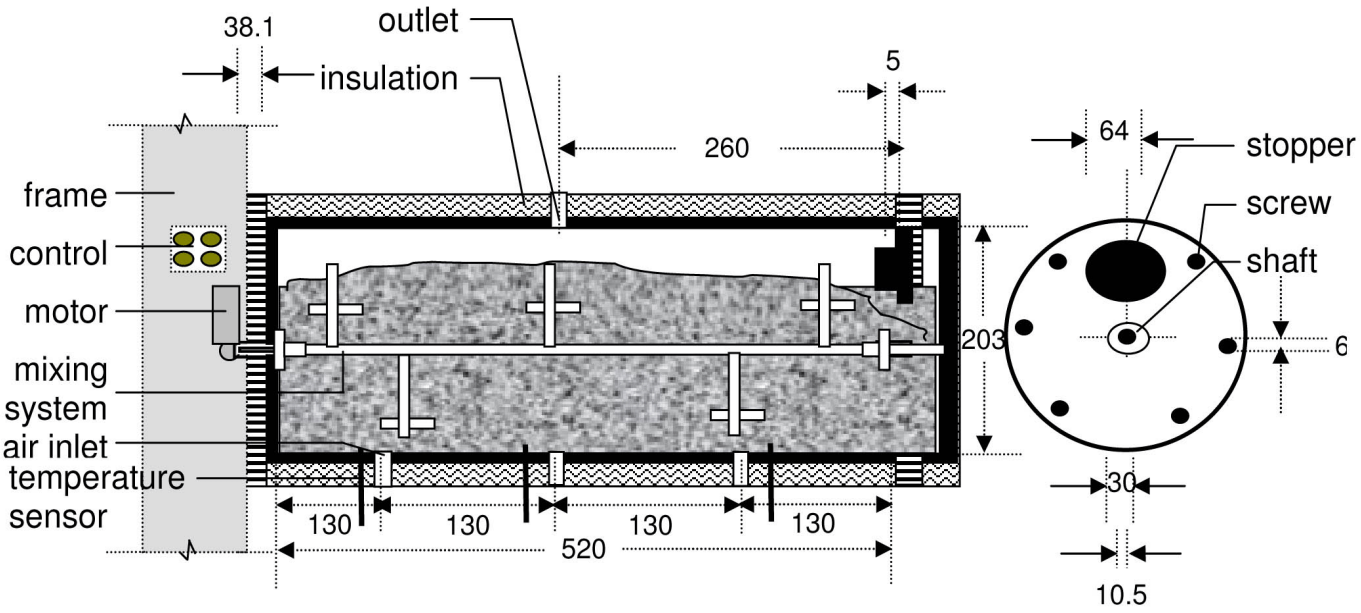


Fig. 2. Detailed schematic of a bioreactor.

air supply. It passed through a pressure regulator and a pressure gage (to maintain the pressure at approximately 5 kPa) and then through a water bath to be humidified (to a measured 100% saturation), and finally through a flow meter (Model 32461-14, Cole-Parmer Instrument Company, Vernon Hills, IL) capable of measuring a flow in the range of 0.0566-0.566 m^3/h.

Table 1. Some characteristics of the composting materials used.

Characteristics	Tomato residues	Wood shavings	Municipal compost	Used cooking oil*
Moisture content (% wet basis)	76.0	8.0	58.6	NA
Total solids (mg/g DM)				
Volatile solids	693.0	997.4	854.6	999.45
Ash	307.0	2.6	145.4	0.55
Nitrogen (mg/g DM)				
Total Kjeldahl nitrogen	27.0	1.0	18.0	0.22
Ammonium nitrogen	2.2	0.2	5.2	0.004
Carbon (mg/g DM)				
Total	327.0	499.0	440.0	775
Organic	260.0	390.0	350.0	620
Elemental composition (mg/g DM)				
Ca	51.0	0.8	20.0	0.057
Na	0.7	0.0	6.2	0.301
Fe	0.4	0.0	2.8	0.140
Mg	4.7	0.1	1.8	0.008
Zn	0.0	0.0	0.1	ND
K	57.6	0.6	7.8	0.010
Cl	0.07	0.0	0.3	0.742
P	10.5	0.0	2.7	0.010
S	7.9	0.9	2.3	2.324
Others	174.1	0.2	101.4	0.161
C : N	12.1:1	499:1	24.4:1	3523:1

* NA = not applicable
ND = not detectable

The data acquisition unit consisted of a master unit (Multiscan 1200, Omega, Stanford, CT), a thermocouple scanning card with 24 isolated differential input channels (MTC/24, Omega, Stanford, CT), software, type T (copper-constantan) temperature sensors (Cole Parmer, Chicago, IL), a personal computer (IBM Pentium IV), and a printer (Hewlett Packard Laser Jet 4). The Tempview Software used was a Microsoft Windows based setup and acquisition application software that featured a graphical spreadsheet style user interface which allowed easy configuration of hardware, acquisition, and display of parameters and provided a nonprogrammable approach for data collection and display. Three thermocouples were located at the bottom of the bioreactor and were used to measure the temperature of the compost mass whereas the fourth was located at the top of the bioreactor, near the outlet air exit (21 mm away) and was used to measure the temperature of the exhaust gas. Thermocouple locations, on the bottom of all bioreactors, were chosen to be far enough from the inlet air (65 mm away).

EXPERIMENTAL PROCEDURE

Compost mixture preparation

The materials used in this study included tomato plant residues, wood shavings, municipal solid waste compost, urea, and used cooking oil. Some characteristics of these materials are shown in Table 1. The moisture content, solids, nitrogen, carbon, and elemental analysis were

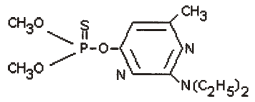
Table 2. Constituents of the mixture.

Item	Tomato residues	Wood shavings	Compost	Oil*	Mixture
Moisture content (% wet basis)	76	8	58	NA	36
Wet mass (kg)	0.65	0.97	0.18	0.06	1.86
Dry mass (kg)	0.16	0.89	0.08	0.06	1.19
Total carbon (g/g)	327	499	440	775	459
Total nitrogen (g/g)	27	1	18	0.2	5.60
C : N	12.1:1	499:1	24.4:1	3875:1	81.9:1

* NA = not applicable
Oil density = 0.9 Mg/m^3

determined according to the procedures described in the Standard Methods for the Examination of Water and Wastewater (APHA 1998). The tomato plant remains (leaves, stems and some fruits) were collected from a greenhouse at an average moisture content (MC) of approximately 90% and left over night at room temperature (≈ 25°C) to partially dry to a MC of 76%. They were then chopped into small pieces using a shredder (Model 242A645-515, 5HP, Briggs and Stratton, Plainfield, NJ), mixed with wood shavings (tomato plant residues : wood shavings ratio of 1 : 1.5 dry basis) and then ground in a hammer mill (Model C-H, Horvick Manufacturing, NCC, Moorhead, MN) to an average size of 6.0 mm. A 15-day-old municipal solid waste compost obtained from a local municipal composting facility (Miller Composting Corporation, Dartmouth, NS) was added to the tomato trimmings mixture in order to introduce a wide range of active composting microorganisms. Used cooking oil was added to the mixture as a bioavailable carbon source. Since the C : N ratio of the mixture was very high (Table 2), urea [$CO(NH_2)_2$] was used as a nitrogen source (46% nitrogen) to adjust the C : N ratio to 30 : 1 as suggested by Alkoaik and Ghaly (2005). Water was used to adjust the moisture content to 60%.

Table 3. Properties of pirimiphos-methyl (Yamada 2005).

Property	Description
Chemical name	O-(2-diethylamine-6-methylpyrimidin -4-yl) O,O-dimethyl phosphorothioate
Synonyms	PP 511, Actellic
Formulated products	Emulsified concentrates (8, 25, 50% ai) or dust (2% ai)*
Chemical formula	$C_{11}H_{20}O_3N_3PS$
Chemical structure	
Molecular mass	305.4 g
Density	1.17 Mg/m^3 at 20°C
Melting temperature	15-18°C
Stability	6-48 months at 20°C or 14 days at 54°C
Solubility	200 mg/L in most organic solvents at 20°C) (water solubility = 10mg/L)
Vapor pressure	20 µPa at 60°C
Henry's law constant	7.01 x 10^{-7} atm m^3/mole
Hydrolysis	by strong acid or alkali
Hydrolysis at 25°C	half life in neutral aqueous solution of 117 days
Photolysis	half life in neutral aqueous solution of 0.47 h
Dissociation constant	pKa = 4.30 at 20°C
Odor	strong mercaptance like odor

* ai = active ingredient

Insecticide application

An analytical grade (240 µL) of pirimiphos-methyl (actellic) [O-(2-diethylamino-6-methylpirimidin-4-yl) O, O-dimethyl phosphoro-thioate] with 99.0% purity (Cat No. PS644, Sigma-Aldrich Canada Ltd, Oakville, ON) was used in this study. The pure substance is soluble in most organic solvents but has a low water solubility of 10 mg/L at 20°C. Some characteristics of pirimiphos-methyl are shown in Table 3.

Antonious and Snyder (1994) reported that pirimiphos-methyl residues on the leaves of greenhouse tomato plants 14 days after spraying was 12 mg/kg. Since trimming usually takes place two weeks after spraying, a minimum concentration of 12 mg/kg is expected to be on greenhouse tomato trimmings. Therefore, three concentrations (12, 24, and 36 mg/kg) were chosen for this study. Thus 62.64, 125.28, and 187.92 mg active ingredient of pirimiphos-methyl were applied to three identical final composting mixtures (3.5 kg of tomato trimming, wood shavings, and municipal solid compost at 60% MC wet basis). This resulted in initial concentrations of pesticide, after mixing all ingredients, of 15.8 (low), 31.6 (medium), and 47.4 (high) mg/kg, respectively.

Composting protocol

Approximately 64 mL of used cooking oil and the required amount of insecticide were added to each 1.8 kg of the initial mixture of tomato residues: wood shavings: municipal solid waste compost (1: 1.5: 0.28 ratio) as shown in Table 2. Water and urea were then used to adjust the moisture content to 60% (wet basis) and the C:N ratio to 30:1. The final mixture (3.5 kg) was mixed well and placed in the bioreactors. It occupied 75% of the total volume of the bioreactor (or 0.012 m^3). The plexiglas side wall was put in place and visual inspection of the bioreactor was done to detect any leakage before placing the insulation cover on the side wall. The mixing unit was started at 5 rpm and the system was operated at a constant aeration rate of 0.15 m^3/h (0.17 vvm) during all experiments. The temperature was continuously monitored. Once the temperature peaked (after 30 h), a volume of 36 mL of the used cooking oil was added every 12 h in order to compensate for heat losses and extend the thermophilic phase (maintain the temperature above 55ºC) as recommended by Alkoaik and Ghaly (2006). The amount of used cooking oil added to the bioreactor was determined from the heat losses from the system, which was 51.2 kJ/h and the energy content of the used cooking oil, which was 36 kJ/mL (Alkoaik and Ghaly 2006). Samples were collected every 24 hours to assess the destruction of the insecticide pirimiphos-methyl.

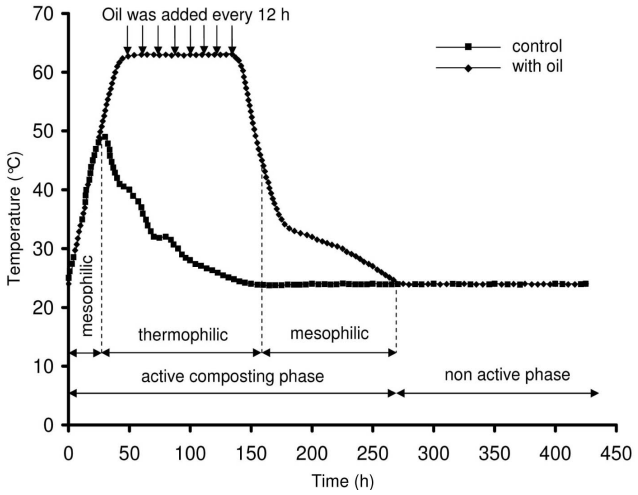


Fig. 3. Temperature profiles

Experimental design

To not cause heat losses during sampling, several bioreactors were used during the experiment. Mixtures were assigned to the reactors at random and each reactor was used once. The duration of the entire experiment was 270 hours. Every 24 hours, a reactor operation was terminated and samples were obtained for analysis.

Identification of insecticide in compost

The pesticide residue in the contaminated composting mixture was determined using a gas chromatograph (GC) (Model No. 5890-SII, Hewlett Packard, Atlanta, GA). The GC was first calibrated by injecting 10.0 µL of the hexane extracted pesticide of different concentrations onto a 25 m X 0.2 mm, 0.33 µm film thickness, 5% diphenyl siloxane megabore capillary column to establish a standard curve for the pesticide. The injection port was set at 180ºC and the flame ionization detector was set at 250ºC. The oven containing the column was first held isothermally at 40ºC for 4 minutes and then increased at a rate of 10 ºC/min until a final temperature of 350ºC was reached. The final temperature was held for 5 minutes. Helium was used as a carrier gas and was held at a constant flow rate of 1.2 mL/min. The pesticide residue was calculated with the aid of the computer program (GS Software) using the peak area method and the results were saved as output files. The pirimiphos-methyl recovery using this procedure was 94% and the minimum detectable limit used in the standard calibrations for this set of experiments was 0.1 ppm of pirimiphos-methyl.

For the pirimiphos-methyl contaminated compost, a known mass (approximately 10 g) was quantitatively transferred into a volumetric flask. Hexane (100 mL, 99.9 %) was added and the entire solution was first shaken 15 times and then vortexed for 30 seconds. The solution was kept for 1 hour to allow for complete dissolution of pirimiphos-methyl. The solvent layer was then extracted and injected onto the GC.

RESULTS and DISCUSSION

Temperature

The profiles of average temperatures are presented in Fig. 3. The average bioreactor temperature increased gradually due to microbial metabolism of organic material. The microorganisms utilized the bioavailable carbon for energy (respiration) and synthesis (growth) of new microbial cells according to Eqs. 1 and 2 (Alkoaik and Ghaly, 2006).

Table 4. Changes in biological parameters.

Parameter	Initial	Final	Reduction (%)
Moisture content (% wet basis)	61.7	61.3	0.6
Volatile solids (g/kg)	868	721	17
Fixed solids (g/kg)	132	131	0.7
Total carbon (%)	43.7	39.6	9.4
Total Kjeldahl nitrogen (%)	1.46	1.41	3.4
Ammonium nitrogen (%)	0.6	0.6	0.0
C : N	30:1	28:1	6.7

Energy:

$$C_X H_Y O_2 \xrightarrow{microbes} CO_2 + H_2O + heat \quad (1)$$

Growth:

$$C_X H_Y O_2 + NH_4 \xrightarrow{microbes} new\ microbial\ cells \quad (2)$$

The generated heat raised the temperature of the material in the bioreactor and caused the evaporation of moisture (latent heat). Also some heat was lost with the exhaust gas (sensible heat) and through the body and side walls of the reactor (conductive heat). The temperature in the control reactor reached 49°C after 30 h and declined quickly due to lack of bioavailable carbon. The addition of used cooking oil (36 mL) as a bioavailable carbon source every 12 h starting at 30 h increased the peak temperature and its duration. Thermophilic temperatures (of 63.10 ± 1.44ºC, 63.30 ± 1.61ºC, and 63.29 ± 1.59ºC) were maintained for 72 hours (after the peak time of 30 h) in the bioreactors receiving low, medium, and high concentrations of pirimiphos-methyl, respectively. The temperature results indicated that the higher concentration of pirimiphos-methyl did not seem to have any inhibitory effects on the microbes. When the addition of used cooking oil ceased (after 132 hours), the temperature started to decline reaching the mesophilic range (< 40ºC) within a day and then continued to decline reaching room temperature (25°C) after 10 days.

Biological parameters

The change in the moisture content, volatile and fixed solids, total carbon, total nitrogen, and C : N ratio are presented in Table 4.

Moisture content The initial and final moisture content values (wet basis) were 61.7 ± 0.36 and 61.3 ± 0.86%, respectively. Even though aeration was provided, little change in the moisture content was observed (0.6%). This was due to the equilibrium between the water produced by microbial respiration and the water lost with the exhaust gas. McKinley and Vestal (1984), Tiquia et al. (1998), Richard et al. (2002), Liang et al. (2003), and Ghaly et al. (2006) emphasized the importance of moisture content and stated that the optimum moisture content for composting is in the range of 50 – 70% (wet basis) depending on the type of composted material. In this study, the moisture

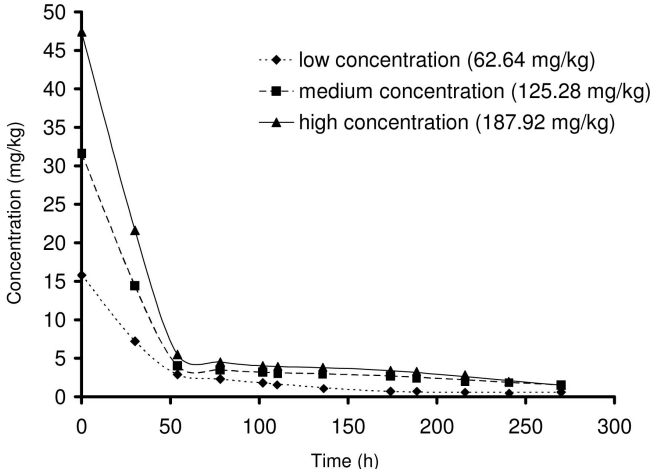


Fig. 4. Pirimiphos-methyl insecticide concentrations.

content of the mixture remained within this range during the composting process.

Total solids The initial volatile and fixed solids were 868 and 132 g/kg and the final volatile and fixed solids were 721 and 131 g/kg, respectively. The reduction in the volatile solids was 16.9 % while the reduction in the fixed solids was insignificant (0.7 %). Schwab et al. (1994) reported 34% reduction in the volatile solids after 85 days for simulated municipal solid waste that included rabbit chow, shredded newspaper, sand, and composted cow manure (3 : 2 : 1.5 : 1). Hänninen et al. (1995) reported 21.7% reduction in the volatile solids after 60 days of composting. Wang et al. (2003) reported 25% reduction in the volatile solids after 12 days of composting municipal sludge and vegetable waste. The lower reduction in volatile solids observed in this study was due to the low bioavailable carbon in wood shavings, which made up the bulk (52%) of the mixture.

Total carbon The initial and final total carbon (TC) of the mixture (without cooking oil) were 43.7 and 39.6% of the total weight, respectively. Sommer and Dahl (1999) studied the fate of carbon during 197 days of composting three types of deep litters (compressed litter, mixed after 30 days and untreated) and reported carbon reductions in the three treatments of 43, 54, and 52%, respectively. Beck-Friis et al. (2001) reported a total carbon reduction of 65% after 31 days of composting a source separated organic household waste and a chopped wheat straw. Michel et al. (1995) reported a total carbon reduction of 24% during composting of yard trimmings waste consisting of leaves and grass (2 : 1 dry weight basis). Wang et al. (2003) reported a reduction of organic carbon of 14% after 12 days of composting sewage sludge and vegetable food waste. The lower reduction reported in this study (9.4%) was due to the fact that most of the carbon in the wood shavings was non-bioavailable for microbes.

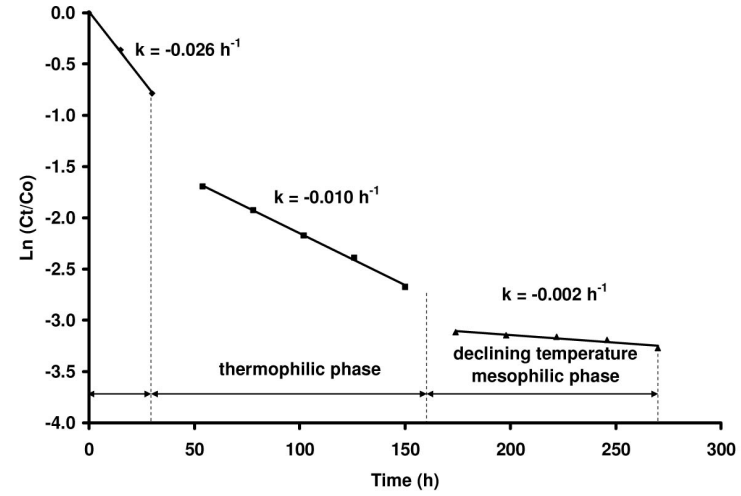
Total nitrogen The initial and final total Kjeldahl nitrogen (TKN) were 1.46 and 1.41%, respectively. This resulted in a reduction of 3.4% in the TKN. The initial and final ammonium nitrogen (NH_4-N) concentration (which is the suitable nitrogen form for microorganisms) was relatively constant as a result of the microbial conversion of organic nitrogen into NH_4-N (mineralization process) and the conversion of NH_4-N back to organic nitrogen in the form of microbial cells (microbial synthesis process). Tiquia and Tam (2000) reported that a part of NH_4-N can be biologically converted to NO_2-N and NO_3-N (nitrification process) and Fang et al. (1999) reported the loss of NH_4-N from the reactor in the form of NH_3-N (volatilization). In this study, neither the smell of NH_3 in the exhaust gas nor the presence of NO_2-N or NO_3-N in the compost mixture was detected. The absence of NO_2-N and NO_3-N was due to the inhibition of the nitrification process by the high temperature as reported by Morisaki et al. (1989).

C : N ratio At the start of the experiments, the C : N ratio was adjusted to the optimum range of 30 : 1 as recommended by Livshutz (1962) and Hamoda et al. (1998). It was slightly reduced to 28 : 1 at the end of the experiments. Keller (1962) stated the change in the C : N ratio during the composting process is an indicator of the decomposability of the material and the reduction in C : N indicates rapid biodegradation of carbon. Hamoda et al. (1998) reported total organic carbon reduction of 8, 8.7, and 11% at C : N ratios of 15 : 1, 20 : 1, and 30 : 1, respectively. Larsen and McCartney (2000) investigated the influence of C : N ratio on the performance of a bench-scale bioreactor treating pulp and paper biosolids using four C : N ratios of 107 : 1, 55 : 1, 29 : 1, and 18 : 1 and found the initial C : N ratio of 29 : 1 to be the most suitable as judged by the best volatile solid reduction as well as least odor generation. The C : N ratio reduction in the present study was 6.7%, which is less than the value of 60% reported by Lopez-Real and Baptisa (1996) and Michel et al. (1996) in a large-scale bioreactor and the value of 33.1% reported by Sadaka and El-Taweel (2003) in a laboratory-scale bioreactor. This is due to the non-bioavailability of carbon in the mixture. Since the C : N ratio in this study slightly decreased, it can be concluded that nitrogen was not a limiting factor during these composting experiments.

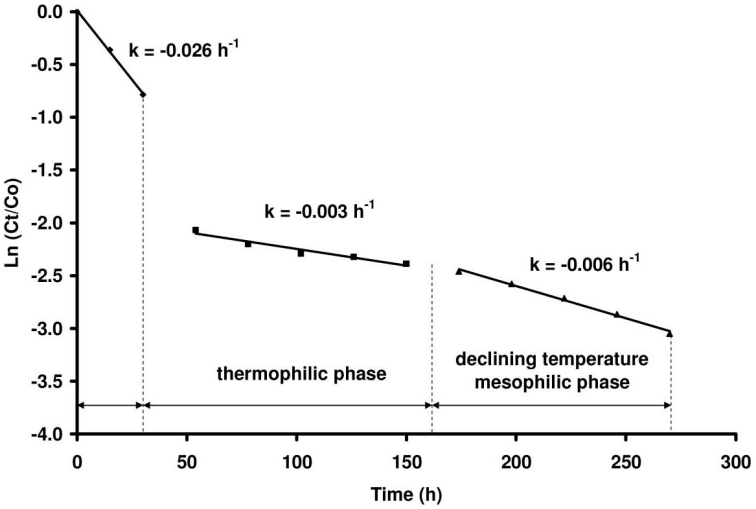
Pirimiphos-methyl concentration

Figure 4 shows the concentrations of pirimiphos-methyl during the composting process. The majority of pirimiphos-methyl (81.6, 87.3, and 89.0% for mixtures containing low, medium, and high concentrations, respectively) was lost in the first 54 h (30 h mesophilic phase + 24 h in the thermophilic phase). The removal efficiency was affected by the initial concentration. The lower concentration reached a non-detectable level after 12 days, while the medium and highest concentrations were reduced to 0.37 mg/kg (99.2% removal) by the eighteenth day.

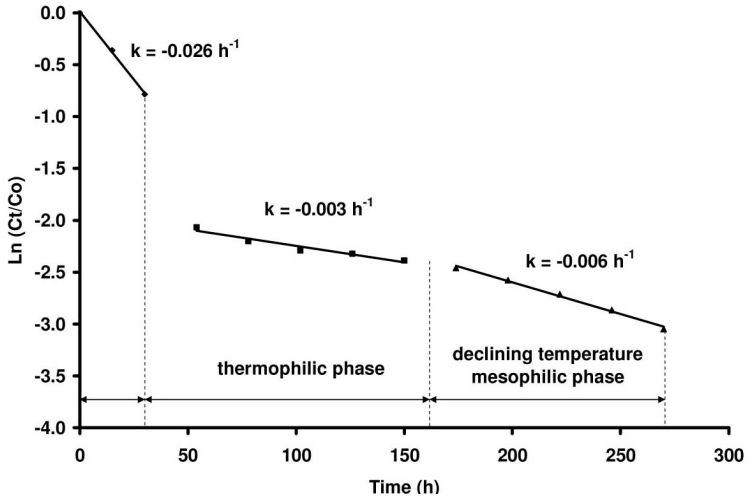
A number of mechanisms (mineralization, biotic transformations, humification, and volatilization) have been reported to contribute to the degradation of pesticides in the environment. Büyüksonmez et al. (1999), Reddy and Michel (1999), Valzano (2000), and Fogg et al. (2003) reported that microbial communities are involved in the mineralization and biotransformation of pesticides during the composting process and biodegradation is accelerated by high temperature, organic matter content, moisture, and biological activity that can make pesticides more bioavailable. Walker (1974), Walker and Barnes (1981), Bollag and Liu (1990), Rocha and Walker (1995), and Wu and Nofziger (1999) stated that degradation of pesticides is the result of chemical and biological reactions that depend on temperature. Fogarty and Tuovinen (1991) stated that volatilization can also play a role in pesticide removal in laboratory studies.



(a) low concentration (62.64 mg/kg)



(b) medium concentration (125.28 mg/kg)



(c) high concentration (187.92 mg/kg)

Fig. 5. Determination of the rate constant (*k*) for pirimiphos-methyl degradation.

There are no reported studies in the literature on the degradation of pirimiphos-methyl during composting. However, the fate of several pesticides during composting has been investigated by several researchers. Lemmon and Pylypiw (1992) found that three organophosphate insecticides (diazinon, chlorpyrifos, and isofenphos) disappeared from grass clippings during the composting process reaching a concentration less than 1 mg/kg after 21 days of composting. Vandervoort et al. (1997) investigated the fate of several pesticides (the organophosphate insecticide chlorpyrifos, the four herbicides 2,4-D, isoxaben, triclopyr, clopyralid, and the plant growth inhibitor flurprimidol) during composting of grass clippings and found the pattern of pesticide loss to be similar for all pesticides and concluded that the destruction process of pesticides was biological in nature. Fogg et al. (2003) found that the composting process was able to degrade a complex mixture of pesticides (isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazola, and dimethoate).

In this study, the reduction in pirimiphos-methyl was biological in nature and volatilization did not contribute to the removal mechanism as the exhaust sample did not show any trace of pirimiphos-methyl. According to Lyman et al. (1990), Wang and Hoffman (1991), Haug (1993), and Eneji et al. (2002), the biodegradation of organic substrates can be described using a first order model (Eq. 3)

$$C_t = C_0 e^{-kt} \tag{3}$$

where:

C_t = concentration of the organic substrate at time t (mg/kg),

C_0 = initial concentration of the organic substrate (mg/kg), and

k = rate constant (h^{-1}).

According to these authors, a plot of ln (C_t /C_0) versus time yields a straight line with a slope equal to k. However, plotting the data obtained from the present study did not fit a straight line for the entire active composting period because the rate constant (k) is a function of temperature. The linear relationship between ln (C_t/C_0) and time for the biological degradation of pirimiphos-methyl is only true for specific temperature zones within the active microbial phase as shown in Fig. 5.

The results shown in Table 5 indicate that a degradation rate constant of 0.026 h^{-1} was observed during the initial rising temperature mesophilic phase (first mesophilic phase, 0-30 h) regardless of the initial concentration of pirimiphos-methyl. The relationship between the reaction rate and substrate concentration for biological reactions is described by the Michaelis-Menton kinetic equation (Eq. 4) (Doran 1995).

$$k = \frac{k_{\max} S}{K_S + S} \tag{4}$$

Table 5. Rate constant for pirimiphos-methyl degradation.

Phase/time	Temperature (°C)	k (h^{-1})		
		low	medium	high
Rising temperature mesophilic phase (0 - 30 h)	25 - 45	-0.026	-0.026	-0.026
Thermophilic phase (30 - 160 h)	45 - 63 - 45	-0.010	-0.003	-0.003
Declining temperature mesophilic phase (160 - 270 h)	45 - 25	-0.002	-0.006	-0.009

where:

S = substrate concentration (mg/kg),

k_{max} = maximum reaction rate for given substrate microbial system (h^{-1}), and

K_S = substrate concentration at half the maximum rate constant (mg/kg).

Figure 6 shows the effect of substrate concentration (S) on the reaction rate (k). At low substrate concentrations (Zone A), the reaction follows first order kinetics in which the reaction rate increases with increases in substrate concentration. However, at high substrate concentrations, the reaction rate follows zero order kinetics and approaches a maximum value that is independent of substrate concentration (Zone B). At higher substrate concentrations, the reaction rate becomes inhibited (Zone C). These results indicated that the pesticide was used as a bioavailable substrate and the activities of the mesophilic microorganisms were not substrate limited. Also, the high concentration of pirimiphos-methyl did not seem to inhibit the activity of the mesophilic microorganisms.

During the thermophilic stage (30 – 160 h), the temperature increased from 45 to 63°C (30 – 45 h) and remained constant at 63°C (45 – 140 h) due to the addition of cooking oil and then declined from 63 to 45°C (140 – 160 h). The degradation rate constant for the thermophilic phase was much lower than that of the initial mesophilic phase and was affected by the initial concentration of pirimiphos-methyl. Michel et al. (1995) and Reddy and Michel (1999) suggested that thermophilic microbial communities are involved in the mineralization and biotransformation of pesticides during composting. The results obtained from this study suggest that either the majority of the thermophilic microorganisms do not posses the enzymes required for the degradation of pirimiphos-methyl or they are less tolerant to its inhibitory effect as compared to the mesophilic microorganisms. The reduction in the k value as a result of the increased concentration of pirimiphos-methyl seems to favor the latter.

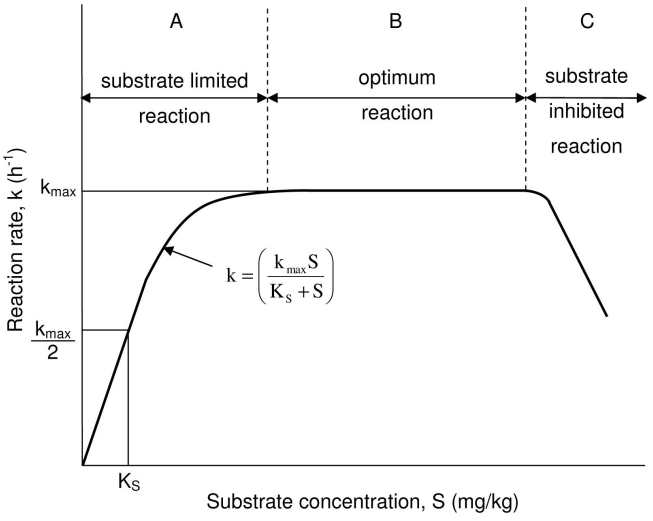


Fig. 6. Effect of substrate concentration on reaction rate (*k*).

The degradation rate constant of the declining temperature mesophilic phase (second mesophilic phase, 160 – 270 h) was higher than that of the thermophilic phase and was also affected by the initial concentration of pirimiphos-methyl (in a positive way). The surviving mesophilic microorganisms utilized the remaining portion of pirimiphos-methyl as a bioavailable substrate. However, the concentration of the pesticide during this phase was below the growth limiting concentration (Zone A in Fig. 6) and, therefore, affected the degradation rate constant; the remaining substrate from the higher pesticide concentration resulted in a higher degradation rate constant.

Eneji et al. (2002) and Bowker et al. (1972) monitored the disappearance of pirimiphos-methyl in different soils and reported an average rate constant (k) of 0.003 h^{-1}. The achieved average degradation rate constant (k) in this study was 8.6 times that reported in soil. The higher values of the degradation rate constant obtained in this study are due to the higher temperatures. In the soil system, psychophilic bacteria (-10 to 25°C) ate the most active group while in the composting system the mesophilic bacteria (15 to 45°C) appeared to be the most effective group in degrading pirimiphos-methyl. *Pseudomonas* species were reported to be an active mesophilic group during the composting process (Hayes 1968; Stanek 1971; Fermor et al. 1979). The results are also in agreement with those reported by Hegazy et al. (2000) who investigated the fate of pirimiphos-methyl under different temperature regimes (20, 30, 40, and 50°C) for 192 h and found increased destruction of pirimiphos-methyl in the mesophilic range.

CONCLUSIONS

The composting process was able to destroy 81.6, 87.3, and 89.0% of the pesticide within the first 54 hours for the three initial concentrations of pirimiphos-methyl, 15.8, 31.6, and 47.4 mg/kg, respectively. Complete destruction of the pesticide at an initial concentration of 15.8 mg/kg required approximately 12 days while initial pesticide concentrations of 31.6 and 47.4 mg/kg were reduced to 0.37 mg/kg. The rate constant (k) for pirimiphos-methyl degradation was determined to be a function of the bioreactor temperature, initial pesticide concentration, and time. A rate constant of 0.026 h^{-1} was observed during the rising temperature mesophilic phase (25-45°C) regardless of pesticide concentration. During the thermophilic phase (45-63-45°C), a rate constant of 0.010 h^{-1}

was observed at an the initial pesticide concentration of 15.8 mg/kg and decreased to 0.003 h^{-1} at pesticide concentrations of 31.6 and 47.4 mg/kg. During the declining temperature mesophilic phase (45-25°C), the rate constant increased from 0.002 to 0.009 as the initial pesticide concentration increased from 15.8 to 47.4 mg/kg. During composting of greenhouse wastes, the degradation of pesticides is accelerated by high temperatures, organic matter content, moisture, and biological activity.

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REFERENCES

AAFC. 2001. Profile of the Canadian greenhouse tomato industry. Industry Highlights Report. Ottawa, ON: Agriculture and Agri-Food Canada. http://www.agr.gc.ca/misb/hort/index_e.cfm?s1=prof&page=tom (2006/11/24).

Abo-El-Saad, M., M. Al-Eed and M. Shawir. 2001. Detection and elimination of certain insecticide residues in cucumber fruits. *Journal of Pharmaceutical Sciences* 15(2): 116-120.

Alkoaik, F. and A.E. Ghaly. 2005. Effect of inoculum size on the composting of greenhouse tomato plant trimmings. *Compost Science and Utilization* 13(4): 262-273.

Alkoaik, F. and A.E. Ghaly. 2006. Determination of heat generated by metabolic activities during composting of tomato plant residues. *Journal of Environmental Engineering and Science* 5: 1-14.

APHA. 1998. *Standard Methods for the Examination of Water and Wastewater*, 20th edition. Washington, DC: American Public Health Association, American Water Works Association and Water Environment Federation.

Antonious, G.F. and J.C. Snyder. 1994. Residues and half-lives of acephate, methamidophos and pirimiphos-methyl in leaves and fruit of greenhouse-grown tomatoes. *Bulletin of Environment Contamination and Toxicology* 52: 141-148.

Beck-Friis, B., S. Smårs, H. Jönsson and H. Kirchmann. 2001. Gaseous emissions of carbon dioxide, ammonia, nitrous oxide from organic household waste in a compost reactor under different temperature regimes. *Journal of Agricultural Engineering Research* 78(4): 423-430.

Bollag, J.-M. and S.-Y. Liu. 1990. Biological transformation processes of pesticides. In *Pesticides in the Soil Environment: Processes, Impacts, and Modeling*, ed. H.H. Cheng, 169-211. Madison, WI: Soil Science Society of America.

Bowker, D.M., D. Riley and R.P. Gratton. 1972. Pirimiphos-methyl: Fate in soil. Report No. TMJ 809 A. Basel, Switzerland: ICI Plant Protection Ltd.

Bowker, D.M., B.F. Griggs and P. Harper. 1973. Pirimiphos-methyl (PP 511): Excretion by a goat. Report No. AR2458 B. Basel, Switzerland: ICI Plant Protection Ltd.

Bratt, H. and L.A. Jones 1973. Pirimiphos-methyl (PP 511): Metabolism in rats and dogs. Unpublished report. Basel, Switzerland: ICI Industrial Hygiene Research Laboratories.

Bullock, D.J.W. 1974. Pirimiphos-methyl: Residues in stored grain bread, flour and milled products. Report No. AR 2537 A. Basel, Switzerland: ICI Plant Protection Limited.

Bullock, D.J.W., S. Day, R.J. Hemingway and T. Jegatheeswaran 1974. Pirimiphos-methyl: residue transfer study with cows. Unpublished report. Basel, Switzerland: ICI Plant Protection Ltd.

Büyüksönmez, F., R. Rynk, T.F. Hess and E. Bechinski. 1999. Occurrence, degradation and fate of pesticides during composting. *Compost Science and Utilization* 7(4): 66-82.

Clark, D.G. 1970. The toxicity of PP511 [O-(2-diethylamino-6-methylpyrimidin-4-yl) O,O-dimethylphosphorothioate] Unpublished report. Basel, Switzerland: ICI Industrial Hygiene Research Laboratories.

Doran, P.M. 1995. *Bioprocess Engineering Principles*. London, UK: Academic Press Limited.

Earl, M., H. Swaine, P. Pain, G.J. Hayward, S.R. Burke and S. Robertson. 1990. Pirimiphos-methyl: Residue levels of the hydroxypyrimidine metabolites of the insecticide in the tissues and eggs of hens fed on a treated diet. Report No. M5119B. Basel, Switzerland: ICI Agrochemicals.

Eneji, I.S., E. Buncel and G.W. vanLoon. 2002. Degradation and sorption of pirimiphos-methyl in two Nigerian soils. *Journal of Agricultural and Food Chemistry* 50: 5634-5639.

Fang, M., J.W.C. Wong, K.K. Ma and M.H. Wong. 1999. Co-composting of sewage sludge and coal fly ash: Nutrient transformations. *Bioresource Technology* 67: 19-24.

Fermor, T.R., J.F. Smith and D.M. Spencer. 1979. The microflora of experimental mushroom compost. *Journal of Horticulture Science* 54: 137-147.

Fogarty, A.M. and O.H. Tuovinen. 1991. Microbiological degradation of pesticides in yard waste composting. *Microbiology Reviews* 55: 225-233.

Fogg, P., A.B. Boxall, A.Walker and A. Jukes. 2003. Pesticide degradation in a biobed composting substrate. *Pest Management Science* 59(5): 527-537.

Ghaly, A.E., F. Alkoaik and A. Snow. 2006. Thermal balance of invessel composting of tomato plant residues. *Canadian Biosystems Engineering* 48: 6.13-6.22.

Green, T., I.H. Monks and P.J. Phillips. 1973. Pirimiphos-methyl (PP 511): Sub-acute oral and residue studies in hens. Report No. HO/IH/P/65B. Basel, Switzerland: ICI Industrial Hygiene Research Laboratories.

Hamoda, M.F., H.A. Abu Qdais and J. Newham. 1998. Evaluation of municipal solid waste composting kinetics. *Resources, Conservation and Recycling* 23: 209-223.

Hänninen, K., O. Tolvanen, A. Veijanen and K. Villberg. 1995. Bioaerosols in windrow composting of source separated biowastes. In *Biomass for Energy, Environment, Agriculture and Industry*, eds. P. Chartier, A.A.C.M. Beenackers and G. Grass, 2: 1212-1221. Proceedings of the 8th European Biomass Conference. New York, NY: Pergamon Press.

Haug, R.T. 1993. *The Practical Handbook of Composting Engineering*. Boca Raton, FL: Lewis Publisher.

Hayes, W.A. 1968. Microbiological and biochemical changes in composting straw/horse manure mixtures. *Mushroom Science* 7: 173-186.

Hegazy, M.E.A., A.S. Shokr, A. Abdel-Samei, MY. Mohamed and D. Neveen. 2000. Efficiency of some technological processes on reducing the residues of malathion and pirimiphos methyl in mature broad bean seeds. Central Agricultural Pesticides Laboratory, Agricultural Research Centre, Dokki, Giza, Egypt. http://nile.enal.sci.eg/ArcJournal/pro.htm (2006/11/24).

Keller, P. 1962. Methods to evaluate maturity of composts. *Compost Science* 2(3): 20-26.

Larsen, K.L. and D.M. McCartney. 2000. Effect of C:N ratio on microbial activity and N retention: Bench-scale study using pulp and paper biosolids. *Compost Science and Utilization* 8(2): 147-159.

Lemmon, C.R. and H.M. Pylypiw, Jr. 1992. Degradation of diazinon, chlorpyrifos, isofenphos, and pendimethalin in grass and compost. *Bulletin of Environmental Contamination and Toxicology* 48: 409-415.

Liang, C., K.C. Das and R.W. McClendon. 2003. The influence of temperature and moisture contents regimes on the aerobic microbial activity of a biosolids composting blend. *Bioresource Technology* 86: 131-137.

Livshutz, A. 1962. New developments in windrow composting. *Compost Science* 3 (3): 26-29.

Lopez-Real, J. and M. Baptista. 1996. A preliminary study of three manure composting systems and their influence on process parameters and methane emission. *Compost Science and Utilization* 4 (3): 71-82.

Lyman,W.J., W.F. Reehl and D.H. Rosenblatt. 1990. *Handbook of Chemical Property Estimation Methods.* Washington, DC: American Chemical Society.

MacPherson, D. 1998. Pirimiphos-methyl: Biotransformation in the rat, central toxicology laboratory. Zeneca Report No. CTL/P/5345. Basel, Switzerland: Central Technology Laboratory.

McKinley, V.L. and J.R. Vestal. 1984. Biokinetic analysis of adaptation and succession: Microbial activity in composting municipal sewage sludge. *Applied and Environment Microbiology* 47: 933-941.

Michel, F.C, Jr., C.A. Reddy and L.J. Forney. 1995. Microbial degradation and humification of the lawn care pesticide 2,4-dichlorophenoxyacetic acid during the composting of yard trimmings. *Applied and Environment Microbiology* 61: 2566-2571.

Michel, F.C. Jr., D. Grarber, L.J. Forney and C.A. Reddy. 1996. The fate of lawn care pesticides during composting. *BioCycle* 37(3): 64-66.

Morisaki, N., C.G. Phae, K. Nakasaki, M. Shoda and H. Kubota. 1989. Nitrogen transformation during thermophilic composting. *Journal Fermentation and Bioengineering* 67: 57-61.

NSMAFF, 2004. *Environmental Guidelines for Nursery and Turf Industry*. Best Agricultural Waste Management Plans. Halifax, NS: Nova Scotia Ministry of Agriculture, Food and Fisheries.

OMAFRA. 2004. Best Management Practices. Horticultural Crops. Toronto, ON: Ontario Ministry of Agriculture, Food and Rural Affairs.

Palmer, A.K. and P. James. 1972. Effect of PP 511 on reproductive function of multiple generations in the rat. Unpublished report. Huntingdon, Cambridgeshire, UK: Huntingdon Research Centre.

Reddy, C.A. and F.C. Michel, Jr. 1999. Fate of xenobiotics during composting. In *Proceedings of the 8th International Symposium on Microbial Ecology*, 485-491. Orlando, FL: Magnolia Publishing.

Richard, T.L., H.V.M. Hamelers, A.H.M. Veeken and T. Silva. 2002. Moisture relationships in composting processes. *Compost Science and Utilization* 10(4):286-302.

Rocha, F. and A. Walker. 1995. Simulation of the persistence of atrazine in soil at different sites in Portugal. *Weed Research* 35:179-186.

Sadaka, S. and A. El-Taweel. 2003. Effects of aeration and C:N ratio on household waste composting in Egypt. *Misr Agricultural Engineering Journal* 11(1): 36-40.

Schwab, B.S., C.J. Ritchie, D.J. Kain, G.C. Dobrin, L.W. King and A.C. Palmisano. 1994. Characterization of compost from a pilot plant-scale composter utilizing simulated solid waste. *Waste Management and Research* 12: 289-303.

Skidmore, M.W., J.P. Leahey, B. Haywood and C. Elliott. 1985. Pirimiphos-methyl: Quantification and characterisation of radioactive residues in milk and tissues of a goat dosed with 14C pirimiphos-methyl. Report No. RJ0430B. Basel, Switzerland: ICI Plant Protection Division.

Sommer, S.G. and P. Dahl. 1999. Nutrient and carbon balance during the composting of deep litter. *Journal of Agricultural Engineering Research* 74: 145-153.

Stanek, M. 1971. Microorganisms inhabiting mushroom compost during fermentation. *Mushroom Science* 8: 797-811.

Stentiford, E.I. 1996. Composting control: Principles and practice. In *The Sciences of Composting*, eds. M. De Bertoldi, P. Sequi, B. Lemmes and T. Papi, 49-59. Glasgow, UK: Blackie Academic and Professional.

Swaine, H. 1982. Pirimiphos-methyl: Residue levels of the hydroxypyrimidine metabolites of the insecticide in the tissues and milk of cows fed on a treated diet containing 94 mg kg-1 pirimiphos-methyl. Report No. RJ0135B. Basel, Switzerland: ICI Plant Protection Division.

Tiquia, S.M. and N.F.Y. Tam. 2000. Fate of nitrogen during composting of chicken litter. *Environmental Pollution* 110: 535–541.

Tiquia, S.M., N.F.Y. Tam and I.J. Hodgkiss. 1998. Changes in chemical properties during composting of spent pig litter at different moisture contents. *Agriculture, Ecosystem and Environment 67*: 79-89.

Vandervoort, C., M.J. Zabik, B. Branham and D.W. Lickfeldt. 1997. Fate of selected pesticides applied to turf grass: Effects of composting on residues. *Bulletin of Environmental Contamination and Toxicology* 58 (1): 38–45.

Valzano, F. 2000. A Literature review on the composting of composite wood products. Sydney, NSW, Australia: The University of New South Wales. http://www.resource.nsw.gov.au/data/wood/ROU%20Literature%20Review.pdf (2006/11/24).

Walker, A. 1974. A simulation model for prediction of herbicide persistence. *Journal of Environmental Quality* 3:396-401.

Walker, A. and A. Barnes. 1981. Simulation of herbicide persistence in soil: A revised computer model. *Pesticide Science* 12:123-132.

Wang, T.C. and M.E. Hoffman. 1991. Degradation of organophosphorus pesticides in coastal water. *Journal of the Association of Official Analytical Chemists* 74(5): 883-886.

Wang, J.Y., O. Stabnikova, S.T.L. Tay, V. Ivanov and J.H. Tay. 2003. Intensive composting of sewage sludge and food waste by Bacillus thermoamylovorans. *World Journal of Microbiology and Biotechnology 19*: 427–432.

Wu, J. and D. L. Nofziger. 1999. Incorporating temperature effects on pesticide degradation into a management model. *Journal of Environmental Quality* 28:92-100.

Yamada, Y. 2005. Pirimiphos-methyl. http://www.fao.org/WAICENT/FAOINFO/AGRICULT/AGP/AGPP/Pesticid/JMPR/Download/2003_eva/pirimiphos-methyl%202003.pdf (2006/11/23).