Bull. Environ. Contam. Toxicol. (2006) 77:391–398

DOI: 10.1007/s00128-006-1078-8

Bulletin of Environmental Contamination and Toxicology

Variation in Pesticide Concentrations During Composting of Food Waste and Fowl Droppings

K. Kawata, K. Nissato, N. Shiota, T. Hori, T. Asada, K. Oikawa

Faculty of Applied Life Sciences, Niigata University of Pharmacy and Applied Life Sciences, 265-1 Higashijima, Niigata, Niigata 956-8603, Japan

Received: 25 May 2006/Accepted: 21 July 2006

Composting is a predominant method of recycling waste including food waste, livestock waste, wood waste, straw and husk, yard trimmings, municipal solid waste and sewage sludge. Pesticides could be applied to these wastes for the control of insects and weeds during composting. Thereby, pesticides are potentially present in the compost from various wastes. Several current insecticides (chlorpyrifos, diazinon, malathion, etc.) and herbicides (2,4-D, alachlor, atrazine, etc.) have been detected in the compost (Büyüksönmez et al. 2000).

A number of studies have been performed on pesticide degradations during composting. These investigations dealt with insecticides, such as chlorpyrifos (Fogg et al. 2003b, Vandervoort et al. 1997, Vischetti et al. 2004) and diazinon (Leland et al. 2003, Michel et al. 1997, Petruska et al. 1985), as well as fungicides, e.g., chlorothalonil (Fogg et al. 2003a, Fogg et al. 2003b) and metalaxyl (Vischetti et al. 2004), and herbicides, e.g., clopyralid (Vandervoort et al. 1997), imazamox (Vischetti et al. 2004) and isoproturon (Fogg et al. 2003a). The pesticide degradations have been evaluated during the composting of citrus pulp (Vischetti et al. 2004), pear moss with potassium hydroxide (Leland et al. 2003), sawdust (Petruska et al. 1985), vine-branch (Vischetti et al. 2004), winter wheat straw (Fogg et al. 2003a, Fogg et al. 2003b), turf grass (Vandervoort et al. 1997) and yard trimming (Michel et al. 1997). However, there are few investigations of the degradations of pesticides during the composting of food waste and fowl droppings, which are common raw materials of compost.

We have previously reported the determination of 14 pesticides in compost using a pressurized liquid extraction for the gas chromatographic/mass spectrometric (GC/MS) method. Furthermore, this method was used for the determination of chlorpyrifos and fenitrothion in compost samples prepared by adding the pesticides to food waste from a restaurant; fenitrothion was completely degraded by 100 days of composting with mixing every 20 days, whereas 25% of the chlorpyrifos remained in the compost during the same composting conditions (Kawata et al. 2005). This paper describes the degradation of organophosphorous insecticides during the composting of food waste and fowl droppings. Food waste, a major waste in Japan, is expected to be a candidate for compost, because

---

Correspondence to: K. Kawata

approximately 90 % of food waste is incinerated or disposed in landfills (Government of Japan 2002). Fowl droppings are a common waste for composting in Japan. The investigated insecticides included diazinon, EPN and fenitrothion as shown in Table 1 (Kanazawa 1996). They are designated as the Class I chemicals under the law concerning the pollutant release and transfer register in Japan, and commonly used in Asian countries including Japan.

MATERIALS AND METHODS

An ASE100 System (Dionex, Sunnyvale, CA, USA) with 11 mL stainless steel ASE vessels was used for the pressurized liquid extraction. A Finnigan POLARIS Q gas chromatograph–mass spectrometer (Thermo Electron, Waltham, MA, USA) equipped with a Combi Pal auto injection system (CTC Analytics, Zwingen, Switzerland) was used for the quantitative analysis. A 30 m×0.25 mm id (0.25 μm film thickness) fused-silica J&W DB-5MS column (Agilent, Palo Alto, CA) was used for the GC separation.

The standard chemicals were purchased from Kanto (Tokyo, Japan) and Wako (Osaka, Japan). Solvents of pesticide analytical grade were purchased from Kanto. Each standard pesticide was dissolved in acetone to make up a 1 mg/mL stock standard solution. A standard solution of a mixture of the target pesticides (40 μg/mL) was prepared in acetone. An internal standard solution (40 μg/mL) of 9-bromoanthracene (Aldrich, Milwaukee, WI) was prepared in acetone. The purified water was from a Milli-Q system (Millipore, Bedford, MA, USA). The bamboo porous carbon was prepared using the same method as previously described (Asada et al. 2002), that is, Moso bamboo (*Phyllostachys pubescens*) was heated from room temperature to 100 °C at 1.3°C /min, then from 100 °C (held for 1 h) to 400 °C at 5 °C/min and was carbonized for 1 h using an electric charcoal kiln. The result carbon was sieved to a particle diameter of 25 - 125 μm.

Food waste from a restaurant and droppings of laying hens were used as the starting materials for the compost. To one kg of food waste was added 4.0 g of each of the pesticides. The treated food waste was mixed well with 99 kg of food waste. To one kg of fowl droppings was added 2.0 g of each of the pesticides and mixed well with 99 kg of fowl droppings. Each starting material was piled in a

Table 1. Properties of target pesticides.

	IUPAC name	Sw [a] (μg/L)	Log Pow	DT50 [b] (d)
Diazinon	*O*, *O*-diethyl *O*-2-isopropyl-6-methyl-pyrimidin-4-yl phosphorothioate	40	3.15	34-45
EPN	*O*-ethyl *O*-4-nitrophenylphenyl phosphonothioate	3110	3.85	7-16
Fenitrothion	*O*, *O*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate	21	3.45	11-22

[a] Water solubility. [b] 50% decline time in soil (Kanazawa 1996).

plastic greenhouse. The piles were stored for 100 d with good mixing every 25 d. The average air temperature during the composting was 24.1 °C. The concentrations of the three pesticides in the piles were determined at 0, 25, 50, 75 and 100 elapsed days (*n* = 5). The water contents of the food waste (75 %) and the fowl droppings (77 %) were reduced to 11 % and 14 %, respectively, after the composting.

The determination of the pesticides was performed using a previously published method (Kawata et al. 2005). Briefly, a 2 g sample was packed in the ASE vessel. The vessel was then closed and placed in the ASE system. The sample was extracted twice with acetonitrile. The extraction conditions were as follows: extraction temperature, 120 °C; extraction pressure, 11 MPa; static extraction time, 5 min; solvent flush volume, 6.6 mL; nitrogen purge time, 5 sec. The extract was evaporated to 5 mL and purified with 2 mL of hexane by shaking for 1 min. After the hexane layer was discarded, the acetonitrile layer was concentrated to 1 mL under a purified nitrogen gas stream. A 100 mg of the bamboo porous carbon was added to the acetonitrile solution. The solution was shaken for 1 min and filtered. Two mL of hexane and 3 mL of purified water were then added to the filtrate. After shaking for 2 min, the water layer was discarded. The hexane layer was washed with 3 mL of purified water by shaking for 1 min. After the hexane solution was dried over anhydrous sodium sulfate, the solution was concentrated to 1 mL under a purified nitrogen gas stream.

A 5 μL aliquot of the internal standard solution was added to the concentrated solution and 1 μL of the resulting mixture was injected into the GC/MS instrument. The monitored ions for quantification and identification were 152 and 199 for diazinon, 157 and 169 for EPN, 125 and 109 for fenitrothion, and 256 and 258 for 9-bromoanthracene, respectively. The ratios of the peak areas of the quantitative ions to those of the internal standards were used for quantification of the pesticides. The GC/MS conditions were as follows: column temperature, programmed from 50 °C (held for 1 min) to 280 °C (held for 10 min) at a rate of 15 °C/min; injector temperature, 200 °C; injection mode, splitless; helium carrier gas flow rate, 1.0 mL/min; MS transfer temperature, 290 °C; ion source temperature, 250 °C; ionization mode, electron impact; ionization energy, 70 eV; mass scan range, 50–450. The overall recoveries of the pesticides from the food waste compost fortified with standards (4 μg each) were 89 % for diazinon, 98 % for EPN and 85 % for fenitrothion. The relative standard deviations of diazinon, EPN and fenitrothion were 16 %, 6.1 % and 12 %, respectively.

RESULTS AND DISCUSSION

The residue concentrations ± standard deviation (dry base) of the pesticides in the food waste and the fowl droppings upon composting are given in Figure 1. The average concentrations and relative standard deviations of diazinon, EPN and fenitrothion in the food waste were 41 μg/g and10 %, 36 μg/g and13 %, and 37 μg/g and 11 %, respectively (*n* = 5). These values were 101 % of diazinon,

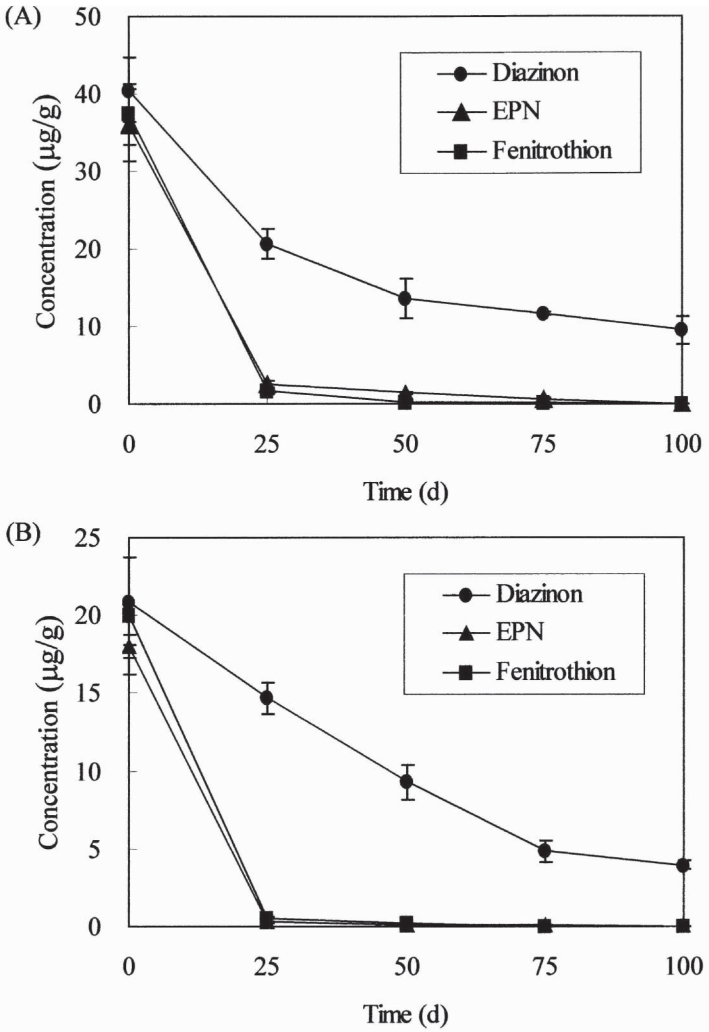

Figure 1. Pesticide residue concentrations on composting. (A) food waste, (B) fowl droppings.

90 % of EPN and 93 % of fenitrothion fortified in the food waste. The concentrations of diazinon, EPN and fenitrothion decreased to 14, 1.4 and 0.31 μg/g after 50 d, respectively. Diazinon decreased to 9.5 μg/g after 100 d, while fenitrothion and EPN were not detected (<0.05).

In the fowl droppings, the average concentrations (relative standard deviation) of diazinon, EPN and fenitrothion were 21 μg/g (13 %), 18 μg/g (4.1 %) and 20 μg/g (19 %), respectively. These values were 104 % of diazinon, 90 % of EPN and 100 % of fenitrothion fortified in the fowl droppings. The concentrations of

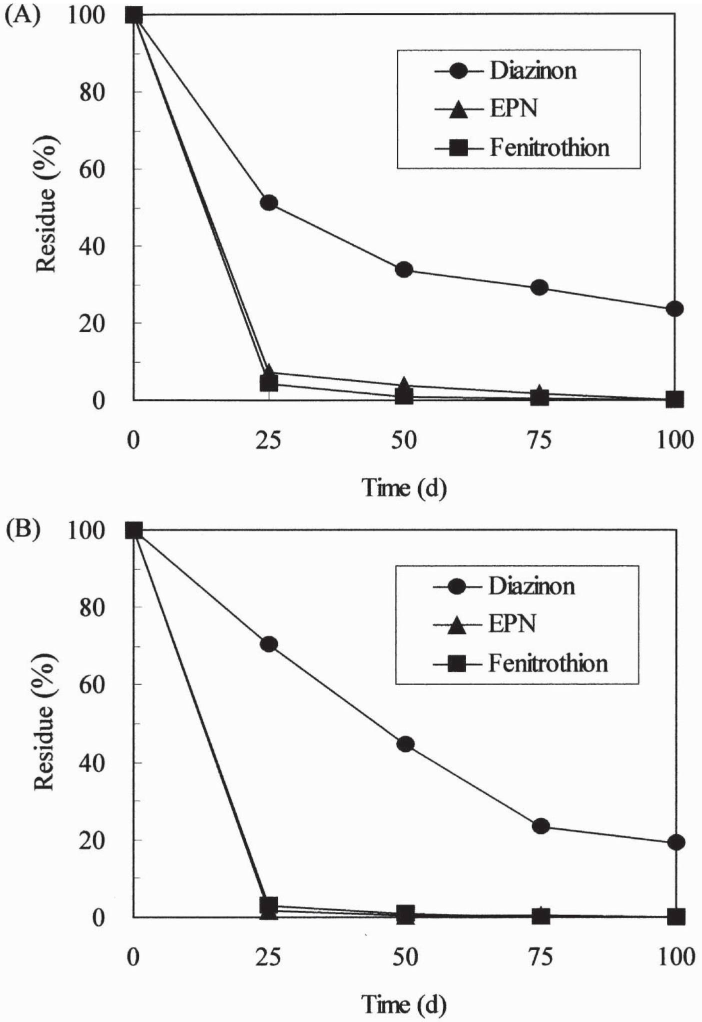

Figure 2. Residues of pesticides on composting. (A) food waste, (B) fowl droppings.

diazinon, EPN and fenitrothion decreased to 9.3, 0.11 and 0.21 μg/g after 50 d, respectively. Diazinon decreased to 4.0 μg/g, after 100 d, while EPN and fenitrothion were not detected after 100 d and 75 d, respectively.

The percentile degradations of the pesticides upon composting are given in Figure 2. Diazinon in the food waste and the fowl droppings decreased to 51 and 70 % after 25 d, 34 and 44 % after 50 d, and 23 and 19 % after 100d, respectively. Several reports have been published on the degradation of diazinon under aerobic conditions; the reported degradation rates were affected by the starting materials of the compost and composting conditions. Petruska et al. (1985) studied the composting of a mixture of cattle manure and sawdust; during 3 weeks of composting, about 21% of the ^{14}C-diazinon was recovered as a volatile organic material. Michel et al. (1997) reported that <1 % of the ^{14}C-diazinon was extracted after 54 days of composting yard trimmings in a laboratory compost. Leland et al. (2003) evaluated the degradation of ^{14}C-diazinon upon the composing of pear moss added potassium hydroxide. They reported that 95% of the diazinon was degraded after 60 d of composting. The degradation rates of this study were lower than those reported values, while the rate for the food waste was approximately similar to that for the fowl droppings as described below. Hence, it is likely that the difference in these degradation rates mainly depended on the compositing conditions.

EPN in the food waste and the fowl droppings decreased to 7.1 and 1.5 % after 25 d, and 3.9 and 0.6 % after 50 d, respectively. There is no paper describing the EPN degradation during composting. On the other hand, 210 μg/g of fenitrothion in food waste from a restaurant was completely degraded by composting for 100 days with mixing every 20 days based on our previous report (Kawata et al. 2005). In this study, fenitrothion in the food waste and the fowl droppings decreased to 4.3 and 2.8 % after 25 d, and 0.8 and 1.0 % after 50 d, respectively, and <0.1 % after 100 d.

The degradations could be interpreted using first-order reaction kinetics (Fogg et al. 2003a) in the following equation:

$$\ln R = k\,t + C \qquad [1]$$

where R is the residue of the pesticides (%), k is the degradation rate (/d) and t is the time (d). Figure 3 shows ln R versus elapsed time with the regression line using the least-squares method. The calculated k values and the determination coefficients (r^2) are given in Table 2. The degradation plots of diazinon were extremely well fitted to the first order reaction given by equation [1]. On the other hand, the plots of EPN and fenitrothion were rather less fitted to the first order reaction compared to those of diazinon.

To evaluate the degradation rates of the pesticides, the 50% decline times (DT_{50}) were estimated using the established relations (Table 2). The DT_{50} values of diazinon (38 - 30 d) were much greater than those of EPN and fenitrothion (11 - 5.8 d). The pesticide degradations were faster in the food waste than in the fowl droppings. Fogg et al. (2003a) reported that the degradation rates of the herbicide isoproturon (11 - 456 μg/g) and fungicide chlorothalonil (7-287 μg/g) decreased

Table 2. DT_{50} of pesticides during composting.

	Food waste			Fowl droppings		
	DT_{50} (d)	k	r^2	DT_{50} (d)	k	r^2
Diazinon	38	-0.0138	0.913	30	-0.0177	0.980
EPN	11	-0.0499	0.871	7.4	-0.0713	0.807
Fenitrothion	7.7	-0.0685	0.884	5.8	-0.0914	0.903

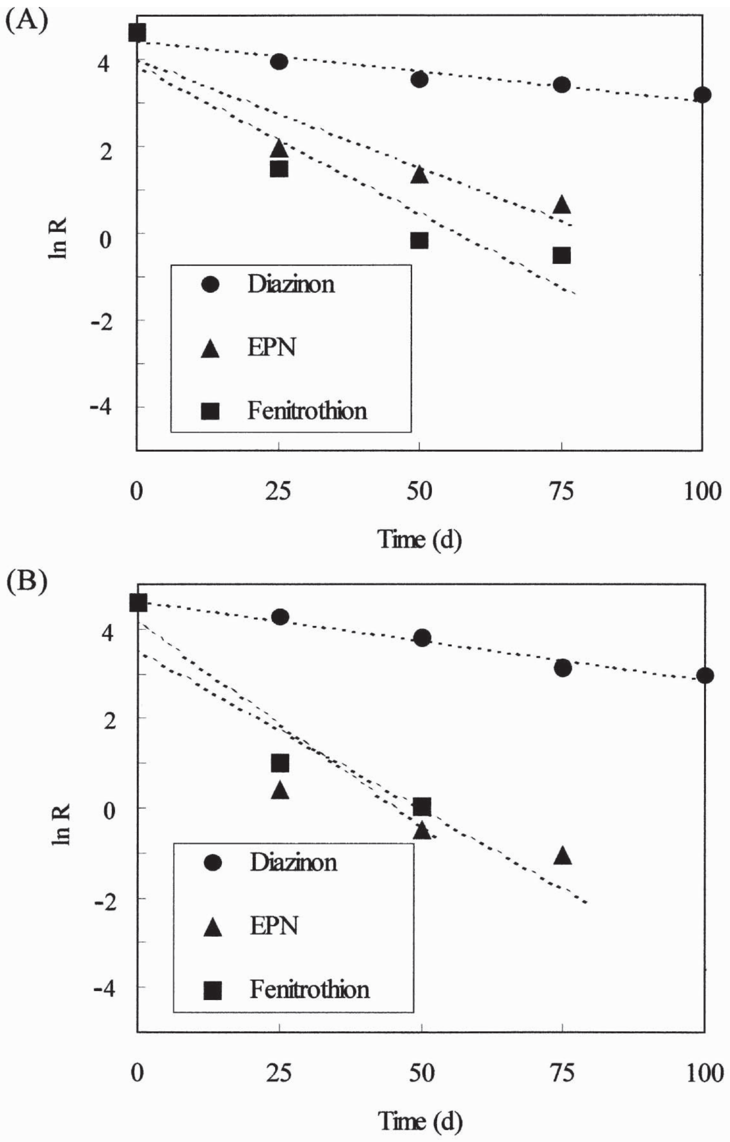

Figure 3. ln R *vs*. time with regression lines by using the least-squares method. (A) food waste, (B) fowl droppings.

with the increasing concentration up to 20 times. In this study, the initial concentrations of the pesticides in the food waste were only twice as high as those in the fowl droppings. The starting materials for the compost, therefore, affected the differences in the degradation rates in this study. Moreover, the composting conditions accelerated the degradations of EPN and fenitrothion, but not that of diazinon.

The obtained DT_{50} values (Table 2) during the composting were compared to those in soil (Table 1). The ratios (*R*s) of the diazinon's DT_{50} values to those in soil were 0.84 - 1.1 (0.96 in mean) for the food waste and 0.67 - 0.88 (0.76 in mean) for the fowl droppings; the *R*s of EPN were 0.69 - 1.6 (0.96 in mean) for the food waste and 0.44 - 1.0 (0.61 in mean) for the fowl droppings. These results show that the composting conditions for the food waste were extremely analogous to soil for the decomposition of diazinon and EPN, and that the conditions for the fowl droppings were considerably analogous to soil. On the other hand, the *R* values of fenitrothion were lower than the other pesticides: 0.35 - 0.70 (0.47 in mean) for the food waste and 0.26 - 0.53 (0.35 in mean) for the fowl droppings. This indicates that the composting conditions were suitable for the decomposition of fenitrothion compared to soil.

REFERENCES

Asada T, Ishihara S, Yamane T, Toba A, Yamada A, Oikawa K (2002) Science of bamboo charcoal: study on carbonizing temperature of bamboo charcoal and removal capability of harmful gases. J Health Sci 48: 473-479

Büyüksönmez F, Rynk R, Hess TF, Bechinski E (2000) Occurrence, degradation and fate of pesticides during composting. Compost Sci Utili 8: 61-81

Fogg P, Boxall ABA, Walker A (2003a) Degradation of pesticides in biobeds: the effect of concentration and pesticide mixtures. J Agric Food Chem 51: 5344-5349

Fogg P, Boxall ABA, Walker A, Jukes AA (2003b) Pesticide degradation in a ‘biobed’ composting substrate. Pest Manag Sci 59: 527–537

Government of Japan (2002) Biomass Nippon strategy. Cabinet Meeting, Government of Japan, Tokyo

Kanazawa J (1996), Environmental character and toxicity data of pesticides. Godo-shuppan, Tokyo

Kawata K, Asada T, Oikawa K (2005) Determination of pesticides in compost by pressurized liquid extraction and gas chromatography–mass spectrometry. J Chromatogr A 1090: 10–15

Leland JE, Mullins DE, Berry DF (2003) The Fate of ^{14}C-diazinon in compost. Compost-Amended Soil, and Uptake by Earthworms. J Environ Sci Health B 38: 697 - 712

Michel FC, Reddy CA, Forney L (1997) Fate of C-14 diazinon during the composting of yard trimmings. J Environ 26: 200-205

Petruska JA, Muains DE, Young RW, Collins ER (1985) A benchtop system for evaluation of pesticide disposal by composting. Nucl Chem Waste Manag 5: 177-182

Vandervoort C, Zabik MJ, Branham B, Lickfeldt DW (1997) Fate of Selected Pesticides Applied to Turfgrass: Effect of Composting on Residues. Bull Environ Contam Toxicol 58: 38-45

Vischetti C, Capri E, Trevisan M, Casucci C, Perucci P (2004) Biomassbed: a biological system to reduce pesticide point contamination at farm level. Chemosphere 55: 823-828