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Degradation of Ethoprophos in Three Physicochemically Different Soils Treated with Composted Manure and Chemical Fertilizer

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Ethoprophos (O-ethyl S,S-diprophyl phosphorodithioate) is a non-systemic, non-fumigant nematicide. In Korea, it has widely been applied to the surface soil at sowing or transplanting of a range of vegetable crops. The dosage range recommended is 3-10 kg a.i./ha, depending on soil type, crop, pest organism and soil management. The half-life ($t_{1/2}$) of ethoprophos in soils varies from 3 to 30 days, depending on soil and environmental conditions (Jones and Norris, 1998). Particularly, the enhanced degradation of ethoprophos occurred in soils previously received multiple ethoprophos treatment (Karpouzas and Walker, 2000). Besides, the input of either organic or inorganic nutrients may affect the way of pesticide degradation by changing its mobility and microbial activity in soil (Perrin-Ganier et al., 2001). Compost application generally enhances pesticide sorption through increased hydrophobic interaction between pesticide and humified sites in compost (Perrin-Ganier et al. 2001), thus limiting the degradation of pesticides by reducing their partitioning to the soil liquid phase (Guo et al., 2000). Similarly, soil organic matter may inhibit the degradation of ethoprophos presumably due to increased binding to soil particles (Jones and Norris, 1998). At the same time, however, an increase in soil organic matter and nutrient availability stimulates soil microbial activity (Marinari et al., 2000), and thus increases pesticide biodegradation (Soulas and Lagacherie, 2001). Soil clay content, on the other hand, may affect biodegradation of ethoprophos. Ladd et al. (1996), working with labeled chemical compounds, showed that soil organic matter decomposition and its turnover was faster in soils with lower clay content. Therefore, an aerobic incubation was conducted to determine the short-term effect of fertilization (compost, chemicals, or both) on the degradation of ethoprophos in soils having different organic matter and clay contents.

MATERIALS AND METHODS

Three soils were obtained from different agricultural sites of Korea: soil A (mesic family of Typic Dystrudepts), soil B (mixed, mesic family of Typic Udifluvents), and soil C (artificially disturbed soils). While two soils (soils A and B) had no history of ethoprophos treatment, soil C had previous history of persistent use due to intensive monocultures of horticultural crops under plastic-film soil condition.

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Soil samples were taken from a depth between 0 and 20 cm of each soil, air-dried, and sieved through a 2-mm mesh for an aerobic incubation experiment, and commercially available composted manure produced with a mixture of sawdust and manure (pig and poultry) by aerobic fermentation were used (Table-1).

Table 1. Mean physicochemical properties of soils and composted manure used.

Soil Properties		Soil A	Soil B	Soil C	Composted manure
pH [a]		4.97	5.04	5.66	7.23
Electrical conductivity[a] (dS m^{-1})		0.13	1.19	0.29	10.77
Organic C (g kg^{-1})		8.12	14.99	32.37	302.82
Total N (g kg^{-1})		0.58	1.33	2.78	25.33
NH_4-N (μg g^{-1})		8.27	48.34	18.75	510.0
NO_3-N (μg g^{-1})		5.02	57.14	9.82	2372.0
Total P_2O_5 (g kg^{-1})		0.56	1.17	8.85	43.05
Soil texture (g kg^{-1})	Sand	624.1	440.0	607.9	-
	Silt	270.9	413.2	292.7	-
	Clay	105.0	146.8	99.4	-
Soil moisture at 33 kPa tension (g kg^{-1})		179.5	269.2	225.4	-

[a] The ratio of 1:1 (sample-to-water) was used for soils and that of 1:5 was used for composted manure.

Each soil was pre-incubated for 7 days at 25±2℃. During pre-incubation, soil moisture content was kept at 3% (w/w) lower than that equivalent to a soil moisture tension of 33 kPa. Four treatments for each soil were designed (Table-2). In all treatments, three replicates of each soil (65 g) were sprayed with a 0.8 mL of 440 μg ethoprophos mL^{-1} in water, which was diluted from liquid ethoprophos (96.5%, Aventis crop science, France), to give a concentration of 5.4 μg a.i. g^{-1} dry soil. The concentration of 440 μg mL^{-1} was a measured value using the same method as ethoprophos residue determination in soil (described below). For chemicals treatment (U), 2 mL of a stock solution containing 8084 mg L^{-1} urea and 4792 mg L^{-1} KH_2PO_4 were treated with each soil sample. For composted manure alone treatment (CM), 296.2 mg of solid composted manure were used. For the combination treatment of composted manure plus urea (CM-U), 2 mL of 4889 mg L^{-1} urea solution together with 116.1 mg of solid composted manure were treated with each soil sample. Control was chosen as the treatment in which no input of urea, composted manure, and KH_2PO_4 was made.

Distilled water was added to each soil mixture to reach soil moisture tension of 33 kPa, and the mixtures were individually covered with perforated aluminum foil to ensure gas exchange and then incubated at 25±2℃ for the desired time of incubation (0, 7, 14, 28, and 42 days). Soil moisture content was maintained constant throughout the incubation by addition of distilled water when necessary to adjust its initial moisture content. At the desired time, pH and ethoprophos concentration of each mixture were measured.

Table 2. Details of fertilizer treatments.

Treatments	N application (μg N g^{-1}) Composted manure	Urea	KH_2PO_4 application (μg P_2O_5 g^{-1})	Ethoprophos (a.i. μg g^{-1})
Control	0	0	0	5.4
U[a]	0	115	154	5.4
CM	115	0	0	5.4
CM-U[b]	45	70	0	5.4

[a]Equivalent to 150 kg N ha^{-1}, 100 kg P_2O_5 ha^{-1} at bulk density 1.3 Mg m^{-3}.
[b]P-based compost plus supplemental urea application make to 150 kg N ha^{-1}.

For ethoprophos extraction, each soil mixture (30 g) was shaked with 50 mL of acetone for 1-hr and then extracted under negative pressure of -80 kPa. The extract was put in a 500 mL separation funnel with 250 mL of distilled water, 25 mL of dichloromethane (J.T. Baker, USA), and 25 mL of saturated sodium chloride solution. This funnel was shaken vigorously for 2-3 min and the lower dichloromethane layer was separated into a round flask via a glass column pre-filled with anhydrous sodium sulfate layer over a plug of glasswool. The partitioning was repeated using fresh portion of 25 mL of dichloromethane.

Dried two dichloromethane extracts were combined in a round flask, and concentrated in a vacuum rotary evaporator at 40°C. The residue was dissolved in hexane for GC analysis. The ethoprophos concentration was measured with Hewlett Packard 5890 series-II gas chromatograph, equipped with packed inlet, a flame photometric detector (FPD), a capillary column SPB-5 (15m × 0.53 mm i.d., film thickness 0.5 μm) (Supelco, Inc.), HP 7673 automatic sampler, and HP 3365 chemstation. Operating parameters were column temperature, 180°C; inlet temperature, 230°C; detector temperature, 250°C; and sample size, 2 μL. High purity helium and nitrogen were used as carrier amd make-up gas at 10 and 30 mL min^{-1}, respectively. Hydrogen and air were used as fuel gas at 75 and 100 mL min^{-1}, respectively. Under these conditions, the retention time of ethoprophos was 1.68 min. Recoveries of ethoprophos residues in soil samples fortified at 0.6, 2.0, and 5.4 μg g^{-1} ranged from 83 to 103%.

Equilibrium sorption coefficient of ethoprophos of each treatment and soil was estimated by fitting the Freundlich equation ($S=K_FC^n$, where K_F is Freundlich coefficient; S and C are quantity adsorbed, μg g^{-1}, and equilibrium solution concentration, μg mL^{-1}, respectively) to the respective sorption isotherm data. Sorption isotherm of ethoprophos in the soil was measured by the batch method following the procedure of Dowling et al. (1994). Ethoprophos extracts were prepared following the same procedure as described above.

Data were analyzed using Generalized Linear Models procedures (SAS Institute, 1989). Significance effects of the treatment on the degradation of ethoprophos were separated by least square difference (LSD) test.

RESULTS AND DISCUSSION

Irrespective of treatment, the pH of each soil sample remained virtually the same as the initial value during incubation, thus negating ethoprophos hydrolysis due to increased pH (Tomlin, 1997). During GC analysis, no degradation of ethoprophos was observed. The retention time, and peak area and height of the chromatogram were used to estimate of ethoprophos residues.

With incubation time, residues of ethoprophos recovered by soils decreased (Figure-1). Residues of ethoprophos in soils were detected throughout the measurement period for soils B and C, but below detectable limit (0.005 $\mu g\ g^{-1}$) after 28 days of incubation for soil A. Rapid degradation of ethoprophos in soil A relative to other soils was attributable to increased chemical hydrolysis (Jones and Norris, 1998), since ethoprophos was partitioned more to solution phase due to lower K_F of 0.44 (Table-3). This observation corroborates the increased persistence of ethoprophos with higher soil organic matter (Jones and Norris, 1997) and clay (Ladd et al., 1996) contents.

Table 3. The first-order rate constant (*k*), half-life ($t_{1/2}$), and Freundlich parameters (K_F, n) of ethoprophos in four treatments of three soils.

				Feundlich parameters	
Soil	Treatments	k (d^{-1})	$t_{1/2}$ (d)	K_F^a	n
Soil A	Control	0.147 (0.98)	4.71	0.47 (0.99)	0.76
	U	0.151 (0.97)	4.61	0.43 (0.95)	0.78
	CM	0.150 (0.97)	4.63	0.44 (0.99)	0.79
	CM-U	0.145 (0.95)	4.77	0.40 (0.94)	0.81
	LSD^b	0.010	0.33	0.07	0.11
Soil B	Control	0.030 (0.97)	22.79	1.59 (0.98)	0.44
	U	0.027 (0.95)	24.89	1.72 (0.95)	0.49
	CM	0.030 (0.98)	23.34	1.70 (0.98)	0.52
	CM-U	0.030 (0.99)	23.40	1.95 (0.98)	0.58
	LSD^b	0.003	2.54	0.43	0.08
Soil C	Control	0.035 (0.99)	19.86	3.15 (0.98)	0.54
	U	0.048 (0.99)	14.46	2.88 (0.93)	0.75
	CM	0.045 (0.99)	15.50	2.66 (0.95)	0.65
	CM-U	0.042 (0.99)	16.36	3.14 (0.94)	0.79
	LSD^b	0.007	2.70	0.47	0.11

[a] Unit: $(\mu g)^{1-n}\ g^{-1}\ (mL)^n$

[b] Least square difference between treatments ($P<0.05$)

Numbers in parentheses denote coefficients of determination (r^2).

There was no treatment-related difference in the overall pattern of ethoprophos residues for soils A and B, except for data at 7 days of incubation for soil B.

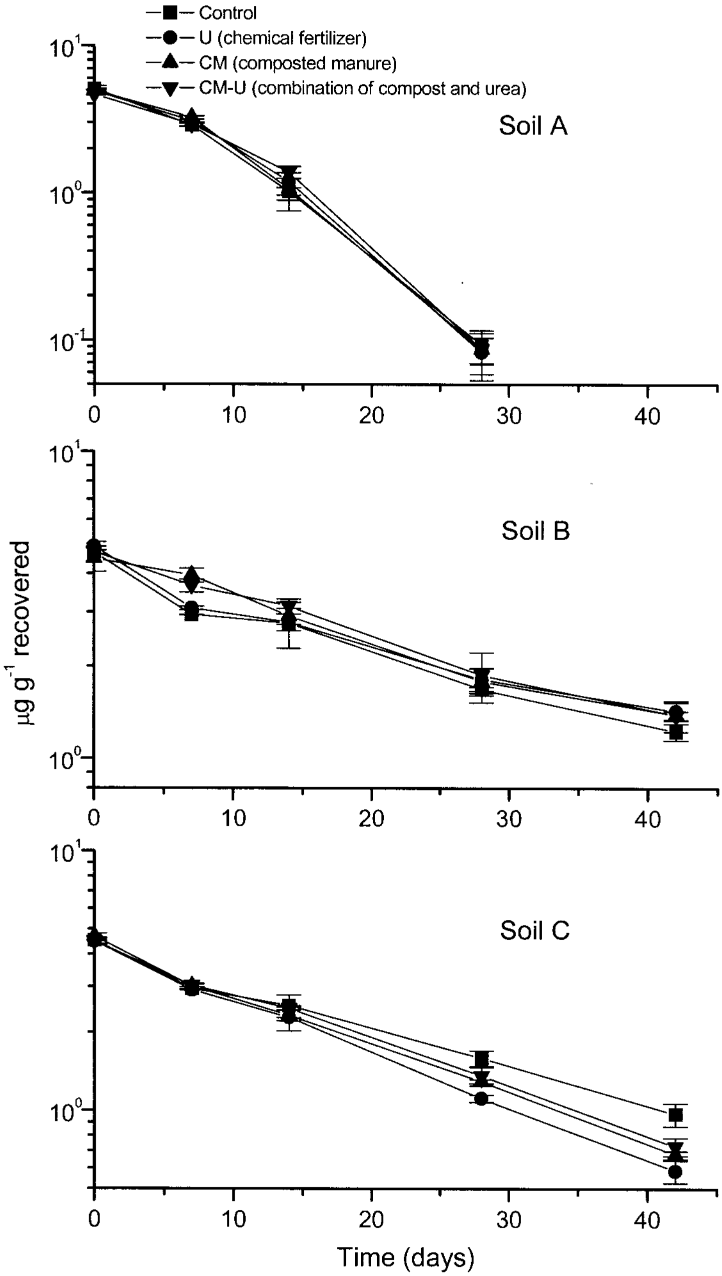

Figure 1. Ethoprophos recovered from soil samples treated with four fertilization types in three soils. Vertical bars represent standard deviation.

However, for soil C, ethoprophos residues of treated samples were significantly lower than those of control over the period since 14 days of incubation. This result suggested that the effect of fertilization on ethoprophos would be variable depending on soil clay and organic matter contents, the decomposition of composted manure, and N mineralization affecting the availability of C and inorganic N for soil microbes. Recous et al. (1995) showed that initial soil N level below a certain critical value (60 mg kg^{-1}) regulates C decomposition.

The half-life of ethoprophos degradation was estimated by fitting first-order kinetics to temporal variations in ethoprophos residues for each treatment and soil (Beulke and Brown, 2001). The half-life of ethoprophos degradation was lowest in soil A and highest in soil B (Table-3). Compared to soil A of similar texture (Table-1), soil C had greater half-life due to higher soil organic matter and K_F. The exponent of Freundlich equation (n) was lower than unity: 0.79 for soil A, 0.51 for soil B, and 0.68 for soil C. This implies that the initial substance retained on the surface of all soils inhibits subsequent retention (van Loon and Duffy, 2000). Assuming n=1, K_{oc}, a ratio of K_F to soil organic carbon content (kg kg^{-1}), of each control soil was 58 for soil A, 106 for soil B, and 97 for soil C ($LSD_{0.05}$=29), indicating that higher clay content of soil B had no significant effect on ethoprophos sorption in soil. However, C decomposition can be significantly retarded by physical protection (Sorenson et al., 1996) such as entrapment inside micropores in soils having higher clay and silt content. In addition, the possibility of enhanced degradation (Karpouzas and Walker, 2000) in soil C due to persistent use could not be eliminated. Therefore, despite higher soil organic matter content, faster degradation of ethoprophos in soil C than in soil B could be attributed either to lower clay and silt contents or to enhanced degradation.

The half-life of ethoprophos degradation between the fertilization treatments was significantly different in soil C, but not in soils A and B (Table-3). For soil C, the half-life of ethoprophos degradation in treated soils was significantly lower than that in control soil, with lowest value at the treatment of chemical fertilizer (U). This result suggested that fertilizers input, particularly in the form of chemical fertilizers, would facilitate short-term ethoprophos degradation in soils having relatively high easily decomposable C and low inorganic N contents, presumably due to increased soil microbial activity. However, since no measure of contribution of clay and silt fraction or soil microbial biomass at the beginning and at the end of the experiment was made, this study lacks supporting information to explain the facilitation of ethoprophos degradation in soil C under this experimental condition. Nevertheless, this study showed that the short-term pattern of ethoprophos degradation was affected primarily by soil types varying in soil organic matter and clay contents, and this could be further modified by the addition of fertilizers influencing the activity of decomposer organisms in various ways.

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