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Degradation of Parent Compounds of Nine Organophosphorus Insecticides in Ontario Surface and Ground Waters under Controlled Conditions

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Organophosphorus insecticides are widely used for insect control on field crops and fruit in southern Ontario. The combined uses of these compounds in 1988 totalled 259,000 kg (Moxley 1988). Occasional contaminations with organophosphorus insecticides have been reported in river waters in Ontario (Braun and Frank 1980, Frank and Logan 1988), in farm wells (Frank et al 1987, 1990a), and in farm ponds (Frank et al 1990b).

Normal pH levels of surface and ground waters in agricultural watersheds in southern Ontario range from 8.0 to 8.5. In addition climatic conditions are such that ground waters are maintained at cool temperatures. This study was carried out in an attempt to determine the rate of disappearance of nine organophosphorus insecticides in water under conditions of light and dark and 4, 21 C and ambient temperature regimes. Analytical measurements over time were made only on the parent compounds.

MATERIALS AND METHODS

In the first experiment river water was collected from the Eramosa River, Guelph, Ontario on 21 May 1988 and placed into 4-L bottles; the pH was determined as 8.5. Well water was collected on the same date and the pH was measured as 8.3. The ionic contents of the river water were as follows (mg/L): Ca^{++} - 109; Mg^{++} - 14; K^{+} - 47; SO_4^{--} - 25; and Cl^{-} - 28. The calculated hardness was 320, conductivity at 25° was measured as 530 umoh/cm^3 and alkalinity as $CaCO_3$ measured 222. Ionic concentrations in well (tap) water were as follows (mg/L): Ca^{++} - 91; Mg^{++} - 32; K^{+} - 1.4; SO_4^{--} - 115; and Cl^{-} 28; hardness was 361, conductivity 741 umoh/cm^3, and alkalinity 245 as $CaCO_3$.

A mixture of nine organophosphorus insecticides was made up from analytical reference standards in acetone; this mixture included chlorpyrifos, diazinon, dimethoate, ethion, fensulfothion, methidiathion, mevinphos, phosmet, and terbufos. This mixture was added to the collected waters on 5 June 1988 in amounts to fortify

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the waters at a level of 50 ug/L with respect to each of the compounds. Bottles were divided into two groups and stored in the dark (in amber glass and cardboard containers) and in ambient outdoor light (in clear glass protected from direct sunlight). Each treatment was replicated four times. Bottles were sampled at regular intervals by removing 50 ml from each replicate and compositing into two sub-replicates for analysis. The last samples were taken at 164 days at which time the pH was measured at 8.2 and 8.1 respectively for the river and well waters.

In Experiment II, well (tap) water was drawn on 26 September 1989 and placed in four 4-L bottles. The pH was 8.2 and the ionic contents were similar to those determined for well water in Experiment I. A mixture of the same nine organophosphorus insecticides in acetone was added on 28 September at fortification levels of 50 ug/L., Bottles were stored in a cooler at 4° in the dark and at 21° under ambient indoor fluorescent light conditions. Two replicate 50 ml samples were collected at regular intervals for analysis with the final samples being taken at 125 days on 31 January 1990. The pH of the water at termination was 8.0 for both storage conditions.

Water samples (100 ml) were extracted by shaking twice for 60 sec with 50 ml dichloromethane after the addition of 10 ml saturated aqueous sodium chloride solution. The extracts were dried and combined by passage through anhydrous sodium sulfate, evaporated just to dryness with rotary vacuum, and re-dissolved in 5.0 ml acetone to give a 20x concentration factor.

Determinations were made with gas-liquid chromatography with flame photometric detection (P-mode) and using a 15 m x 0.53 mm fused silica column coated with 2.5 um thickness of OV-1 equivalent phases. Oven temperature was programmed at 5°/min with 0 hold time from 150° to a final temperature of 200°; helium carrier gas was set at ca 8 ml/min.

Recoveries were established as being better than 90% for all compounds on the basis of values obtained for the day 0 samples (50 ug/L) and also by ten-fold dilution of the day 0 samples followed by extraction according to the described procedure.

RESULTS AND DISCUSSION

No significant differences were observed in insecticide decline between river and well water samples and hence these data are combined in the results. Original and final concentrations of the nine organophosphorus insecticides in Experiment I appear in Table 1. The ambient monthly temperatures over the test period of 6 June to 17 November appear in Table 2. The combined data were subjected to regression analysis and the results appear in Table 3.

Little or no apparent differences were observed for the degradation of the parent compounds during storage in ambient

Table 1. Initial and final residues in water of nine organophosphorus insecticides (Experiment 1).

Organophosphorus Insecticide	Residue in water ug/L					
	Initial		Final		Day	
	Dark	Light	Dark	Light	Dark	Light
Chlorpyriphos	53	49	9	5	164	164
Diazinon	45	49	24	18	164	164
Dimethoate	53	50	25	17	164	164
Ethion	51	55	5	8	164	164
Fensulfothion	50	52	0.1	0.1	164	164
Methadithion	50	51	9	2.6	164	164
Mevinphos	50	51	0.1	1.3	164	164
Phosmet	53	58	0.1	0.1	1	2
Terbufos	52	51	0.1	0.1	17	17

Table 2. Ambient temperature over the test period, 6 June - 17 November, 1988 (Experiment 1).

Month	Outdoor ambient air temperature (°C)				
	Average	Mean Maximum	Mean Minimum	Range	
				Min	Max
June (6-30)	19.0	27.0	9.8	2.1	36.5
July	22.7	29.6	15.5	7.1	37.0
Aug.	21.5	26.9	15.9	6.5	35.0
Sept.	16.1	22.2	10.2	2.7	31.5
Oct.	6.6	11.8	1.7	-3.8	28.8
Nov. (1-17)	5.3	9.1	1.9	-2.0	14.4
Period	15.9	21.9	9.8	-3.8	37.0

light vs. dark conditions. Of the nine compounds studied, phosmet degraded the most rapidly with concentrations from the initial 50 ug/L down to 0.1 ug/L requiring only one to two days. Terbufos required 17 days to degrade to a level of 0.1 ug/L while fensulfothion and mevinphos required 164 days (the terminal samples) to decline to similar levels. Diazinon and dimethoate appeared to be the most stable with half-life disappearance of 67 and 99 days, respectively.

Comparisons of the effects of storage temperature are shown in Table 4 with regression analyses on breakdown of the parent compounds appearing in Table 5. Degradation of all nine insecticides was significantly affected by temperature suggesting that hydrolysis was the main mode of degradation. Phosmet, chlorpyrifos, and terbufos degraded rapidly at 21° with half-life

Table 3. Degradation of nine organophosphorus insecticides in water at ambient temperatures (Experiment 1).

Insecticide	Condition	Regression Equation Log y	Significance[1] F	Correlation r^2	Half Life Disappearance (days)	Rate of Loss/day (%)
Chlorpyrifos	dark	1.503-0.005x	50	0.85	56	1.3
	light	1.461-0.007x	66	0.88	46	1.5
Diazinon	dark	1.586-0.003x	63	0.88	99	0.7
	light	1.540-0.003x	32	0.79	88	0.8
Dimethoate	dark	1.492-0.003x	21	0.73	87	0.8
	light	1.574-0.004x	119	0.93	67	1.0
Ethion	light	1.541-0.006x	83	0.92	51	1.4
	light	1.536-0.005x	42	0.83	58	1.2
Fensulfothion	dark	1.625-0.016x	252	0.96	18	3.8
	light	1.505-0.016x	378	0.98	19	3.7
Methadithion	dark	1.470-0.007x	43	0.83	44	1.6
	light	1.401-0.009x	48	0.85	34	2.0
Mevinphos	dark	1.429-0.010x	71	0.89	30	2.3
	light	1.463-0.002x	187	0.96	14	5.1
Phosmet	dark	1.618-1.363x	54	0.99	0.2	94
	light	1.896-1.341x	13	0.99	0.2	94
Terbufos	dark	1.894-0.138x	57	0.94	2.2	32
	light	1.946-0.152x	132	0.97	2.0	35

[1] All F values significant at probability of 0.005.

Table 5. Degradation of nine organophosphorus insecticides in water at 4 and 21C.

Insecticide	Temperature	Regression equation Log y	Significance[1] F	Correlation r^2	Half life disappearance (days)	Rate of loss/day (%)
Chlorpyrifos	21 C	1.916-0.063x	56	0.96	4.8	14.6
	4 C	1.728-0.011x	310	0.99	27	2.5
Diazinon	21 C	1.715-0.021x	403	0.99	14	4.8
	4 C	1.744-0.007x	158	0.97	45	1.5
Dimethoate	21 C	1.671-0.009x	47	0.92	34	2.1
	4 C	1.641-0.002x	17	0.81	142	0.5
Ethion	21 C	1.672-0.08x	49	0.92	34	2.1
	4 C	1.713-0.004x	25	0.86	84	0.8
Fensulfothion	21 C	1.713-0.017x	140	0.97	18	3.8
	4 C	1.674-0.004x	41	0.91	82	0.8
Methadithion	21 C	1.733-0.015x	161	0.97	20	3.6
	4 C	1.654-0.002x	14	0.78	139	0.5
Mevinphos	21 C	1.640-0.0016x	261	0.98	19	3.6
	4 C	1.668-0.002x	15	0.79	150	0.5
Phosmet	21 C	1.517-0.166x	57	0.98	1.8	39
	4 C	1.608-0.079x	26	0.93	3.8	19
Terbufos	21 C	1.706-0.133x	266	0.99	2.3	31
	4 C	1.646-0.009x	112	0.96	34	2.1

[1] All F values significant at 0.005 probability.

disappearances at 1.8 to 4.8 days. At the cool temperature of 4°, dimethoate, methadithon, and mevinphos were slow to degrade, requiring 139 to 150 days for half-life disappearance. Phosmet exhibited the highest degradation rate with half-lives of 1.8 and 3.8 days at 21° and 4°, respectively.

Table 4. Initial and final residues in water of the parent compound of nine organophosphorus insecticides held at 4 and 21 C (Experiment 2).

Organophosphorus Insecticide	21 C			4 C		
	Initial	Final	Days	Initial	Final	Days
Chlorpyrifos	58	0.1	39	56	1.9	125
Diazinon	57	0.1	125	57	7.4	125
Dimethoate	50	2.5	125	47	26	125
Ethion	52	3.7	125	53	21	125
Fensulfothion	48	0.3	125	49	14	125
Methadithion	49	0.5	125	52	26	125
Mevinphos	50	0.5	125	49	22	125
Phosmet	50	0.1	15	50	0.1	29
Terbufos	50	0.1	20	50	4.9	125

The data support previous reports which list diazinon as one of the few organophosphorus insecticides which has been found in surface waters in Ontario (Braun and Frank 1980, Frank and Logan 1988). From farm surveys diazinon, terbufos, and phosmet are reportedly the most heavily used OP insecticides in Ontario (Moxley 1988).

Bowman and Sans (1982) found that terbufos disappeared rapidly in natural water (t 1/2 = 3 days) but that the sulfoxide and sulfone persisted longer with t 1/2 = 18 and 40 days. Miles et al (1981) studied the persistence of fensulfothion in water and its degradation to the sulfoxide and sulfone. Fensulfothion disappeared in water at 8-12 weeks with almost complete conversion to the sulfone. In this study, residues of parent fensulfothion were present at both 21° and 4° after 125 days but the analysis did not include the metabolites.

Hurlbert et al (1970) reported rapid degradation of chlorpyrifos when applied to fresh water ponds in California i.e. from 0.2 mg/L to 0.006 mg/L within 7 days. In this study, chlorpyrifos was calculated to have a half-life of 1.8 days at 21° water temperature.

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