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Dissipation of Atrazine Residues from Soils

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Between 1970 and 1980 corn production in Ontario rose 87% from 0.67 to 1.26 x 10^6 ha (OMAF 1970; 1980). During this period Roller (1975, 1978) reported that atrazine was applied to 84 and 87% of the corn produced in 1973 and 1978 respectively (Table 1). The average application rate was 1.6 kg/ha ai. Frank et al. (1966 and 1983) and Eagle (1978) reported that carry-over residues greater than 0.10 µg/g could damage susceptible crops following corn in the rotation. The experiments and field monitoring program reported in this paper were designed to identify initial rates of application of atrazine that would give carry-over residues below the phytotoxic threshold to susceptible crops grown next in the rotation.

Table 1. Corn grown and treated with atrazine in Ontario, 1973 and 1978 (Roller 1975, 1978)

Year	Corn Production (ha)		Atrazine Used	
	Total	Treated[1]	x 10^3 kg	kg/ha
1973	759	553	949	1.72
1978	1020	875	1410	1.61

[1] 1973 84% treated, 1978 87% treated.

MATERIALS AND METHODS

A randomized design of four replications was located on a clay loam soil which contained 32% clay, and 4.8% organic matter and had a pH of 7.0. Field corn was seeded into plots 6 x 12 m on May 27 and atrazine at 1.1, 2.2 and 3.3 kg/ha ai was applied immediately

using a tractor mounted sprayer delivering 40 L/ha of water (Table 2). Soil on the plot was sampled at three depths, namely 0-6, 6-13 and 13-25 cm, 0.2, 2.0, 3.5, 5 and 12 months after application using a probe. The experimental plots were plowed in late October, 5.5 months after application.

A split plot randomized block design of four replications was located on a loam soil which contained 24% clay and 3.5% organic matter and had a pH of 7.5. Atrazine at 0.56, 2.2 and 4.5 kg/ha ai was applied on May 25 with a tractor mounted sprayer delivering 45 L/ha of water (Table 3). Split plots (6 x 12 m) were treated with activated charcoal 22 days after spraying and the charcoal was incorporated by rototiller. The experimental area was plowed in the 5th and 17th month after spraying. Following the second plowing in late October the second year, samples were taken at three depths namely 0-5, 5-10 and 10-15 cm for analysis.

Between 1970 and 1980 surficial soil samples (0-6 cm) were collected from a large number of sites across the province where known rates of atrazine had been applied. These included experimental farms and commercial farms. The data recorded included the rate and time of application and the date of sampling.

The analytical procedure described by Sirons et al. (1973) was used for the extraction and quantitation of atrazine and its metabolite de-ethylatrazine. Air dried soil samples (100 g) were extracted with 600 ml of a 2:1 acetonitrile-water mixture by mechanical shaker. The initial shake was 40 min and after standing overnight a second shaking for 40 min was given. The extract (ca 500 ml) was filtered through a coarse porosity sintered glass funnel into a second flask. The acetonitrile was evaporated on a rotary evaporator and the water phase was transferred into a separatory funnel with 600 ml of water. The pH was adjusted to 9 by the addition of 0.4 ml of 2N NH_4OH. Atrazine and its metabolite were partitioned into chloroform. After filtering, the chloroform was evaporated to almost dryness by rotary evaporation at 50°C. Isooctane (10 ml) was added and the last remnants of chloroform were evaporated off. The residue was dissolved in methanol (5 ml) and injected into a GLC for qualitative and quantitative analysis.

Table 2. Residues of atrazine in soil 0.2, 2, 3.5, 5 and 12 months after application on a clay loam soil (Field Experiment I)

Atrazine kg/ha	Soil[1] Depth (cm)	Residue of atrazine[2] in dry soil (µg/g) Months after application					Half Life Dissipation (Months)	Regression Equation
		0.2	2	3.5	5	12[3]		
1.1	0- 6	0.83 f[4]	0.50 d	0.37 c	0.23 b	0.08 a	3.6	Log Y = -0.13 - 0.08 χ
	6-13	0.04 a	0.02 a	0.07 a	0.08 a	0.03 a		r^2 = 0.98
	13-25	0.01 a	0.02 a	0.07 a	0.05 a	0.05 a		F = 125.5
2.2	0- 6	1.38 g	0.90 f	0.60 e	0.40 c	0.09 a	3.0	Log Y = 0.14 - 0.10 χ
	6-13	0.04 a	0.03 a	0.07 a	0.03 a	0.09 a		r^2 = 0.99
	13-25	0.01 a	0.02 a	0.05 a	0.01 a	0.06 a		F = 1044.
3.3	0- 6	2.23 h	1.29 g	0.90 f	0.61 e	0.20 b	3.5	Log Y = 0.29 - 0.09 χ
	6-13	0.19 b	0.07 a	0.06 a	0.04 a	0.08 a		r^2 = 0.98
	13-25	0.01 a	0.07 a	0.06 a	0.02 a	0.06 a		F = 126.0

[1]Soil characteristics 32% clay, 4.8% organic matter, 7.1 pH

[2]Atrazine residues included atrazine and its de-ethyl metabolite

[3]Plowed in late October, 5.5 months after application

[4]Significantly different at P 0.05 by Duncan's Multiple Range Test

Table 3. Residues of atrazine[1] 17 months after initial applications. Charcoal was applied 22 days after herbicide treatment.

Atrazine (kg/ha)	Initial Residue 0-5 cm	Residues of atrazine in soil (µg/g) Soil - No Charcoal[2] 0-5 cm	5-10 cm	10-15 cm	Soil - Charcoal[2] 0-5 cm	5-10 cm	10-15 cm
0	0.02	0.03 a	0.02 a	0.01 a	0.06 a	0.03 a	<0.01 a
0.56	0.67	0.09 ab	0.04 a	0.02 a	0.16 c	0.08 a	0.01 a
2.24	2.84	0.16 b	0.09 b	0.02 a	0.60 e	0.28 cd	0.04 a
4.48	5.57	0.22 c	0.15 ab	0.04 a	1.12 f	0.55 e	0.10 ab

[1]Atrazine residues included atrazine and its de-ethyl metabolite.

[2]Plowed in 5th and 17th month just prior to sampling, soil had pH 7.5, 3.5% organic matter, and 24% clay.

A Tracor 550 GLC fitted with a Coulson conductivity detection system operating in the nitrogen mode was used. Two columns each operated at 210°C were used. The first was 183 cm x 4. mm i.d. glass packed with 6% Carbowax 20M on Aeropak 30 (80-100 mesh), and the second was 61 cm x 4. mm i.d. glass packed with 1.5% cyclohexane dimethanol succinate (CHDMS) on Gas Chrom Q (80-100 mesh). Other instrument temperatures were: injector, 245°; transfer line, 220°; and pyrolyzer, 860°. The bridge potential was set at 30V. The quartz pyrolyzer tube was 6.35 mm x 25.4 mm with a 12.7 mm length of strontium hydroxide scrubber. The carrier gas was purified helium set at a flow rate of 70 ml/min for 6% Carbowax 20M column and 200 ml/min for 1.5% CHDMS column. Hydrogen was used in the pyrolyzer at a flow rate of 50 ml/min. The ion-exchange resin used was AG50W-X8 with a mesh size of 20-25 in the hydroxide and hydrogen form. The water flow rate through the cell was 3 ml/min.

Recoveries of atrazine from fortified samples were 86 to 90%.

RESULTS AND DISCUSSION

Atrazine levels in the soil declined exponentially over the 12 month period following a first order regression equation. The half-life dissipation in the upper 0-6 cm varied from 3.0 to 3.6 months (Table 2). Atrazine was observed to increase in concentration in the lower depths of the soil, however these residues were only a tenth of surficial residues collected at 0.2 and 2 months after application. By the end of the 12 month period surficial residues had declined and approached residues in the sub-surface layers.

Seventeen months after application atrazine residues were significantly higher in soil where charcoal had been used than where no charcoal had been added. The area was plowed twice during the period and substantial residues of atrazine were found in the 5-10 cm especially where charcoal had been applied (Table 3).

Field monitoring revealed that atrazine residues declined exponentially following the equation $Y = a + b \text{ Log } \chi$ where Y was the herbicidal residue in the soil and χ the times that had elapsed following application. Breakdown of the herbicide in the first 5 months appeared more rapid than in the later 7 months. This first 5 month period coincided with late spring and summer temperatures and the later 7

months with fall, winter and early spring temperatures. The half-life disappearance of atrazine ranged from 2.4 to 3.0 months (Table 4).

Sheets (1970) pointed out that the persistence of s-triazine herbicides was dependent on a number of soil factors including pH, moisture, temperature and microbiological activity. Breakdown of atrazine in the field appeared to be slower under winter than summer conditions. Hence dissipation of residues in the first 5 months following application in May of each year appeared more rapid than in the next 7 months. This was not reflected in Field Experiment I where dissipation took longer than in the field monitored samples. In the field monitored samples half-life dissipation appeared to be 1.4 months in the summer and increased to 3 to 4 months in the winter. Khan et al. (1981) reported half-life disappearance of approximately 2 months for atrazine over the first six months after application i.e. during the late spring, summer and early fall months.

Eagle (1978) and Frank et al. (1983) have reported that residues of atrazine below 0.1 µg/g did not affect the growth of susceptible crops, however, at levels between 0.1 and 0.2 µg/kg injury could occur. With levels between 0.2 and 0.3 µg/g injury could be severe and above 0.4 µg/g plant failure occurred. The data presented indicated that on soils where application rates of up to 1.1 kg/ha were used susceptible crops like winter wheat could be planted five months later. However, variations in soil residue after five months were such, namely 0.13 ± 0.10 µg/kg that crop injury could ensue. Twelve months after application, residues from 1.1 kg/ha were at or below 0.10 µg/g (i.e. 0.06 ± 0.04 µg/g) and soils could be safely planted to susceptible crops. Applications of 2.2 kg/ha left residue of 0.10 ± 0.09 kg/ha that could cause crop injury. The higher application rates of 3.3 kg/ha left residues that could kill susceptible crops. The wide standard deviation of the mean residues 12 months after application appeared to depend on soil temperatures and moisture in summer and the degree of frost in the soil in winter. Charcoal treatments appeared to protect atrazine against microbiological breakdown.

Table 4. Decline of atrazine in a wide range of soils collected from many locations

Period After Application (months)	Atrazine Residues in Dry Soil (µg/g) Initial Application (kg/ha) mean and range					De-ethylated Atrazine (%)
	1.1 (0.6-1.6)	2.2 (1.7-2.7)	3.3 (2.8-3.8)	4.4 (3.9-4.9)	5.5 (5.0-6.0)	
0.12 Mean	1.10	2.30	3.10	4.10	5.60	3.3
1.0 Mean	0.70	1.24	1.93	2.38	3.34	8.7
2.5 Mean	0.37	0.65	0.93	1.30	2.10	15.3
5.0 Mean	0.13	0.30	0.45	0.64	0.81	21.3
SD	0.10	0.11	0.12	0.20	-	
8.0 Mean	0.10	0.17	0.29	0.46	0.50	22.6
SD	0.05	0.11	0.11	0.18	-	
12 Mean	0.06	0.10	0.15	0.21	0.25	22.1
SD	0.04	0.09	0.10	0.10	0.13	
Half-life (Mo) Dissipation	2.4	2.7	2.8	3.0	2.7	
Regression Equation $Y = a + b \log \chi$						
a	0.61	1.21	1.70	2.24	3.11	
b	-0.57	-1.15	-1.56	-2.02	-2.80	
r^2	0.98	0.93	0.94	0.99	0.99	
F	183	53	61	448	383	
Months to reach 0.10	8	12	14-16	16-18	18-20	

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