spray history is known and in terms of the most toxic insecticide registered if the spray history is unavailable.

The method reported herein is a prototype and has been subjected to further refinement (Gunther et al., 1980). For example, a battery-operated, factory-thermostated heating unit has supplanted the camp stove used herein.

California Assembly Bill 1090 (AB 1090) allows growers more flexibility by making provisions for testing groves for safe conditions rather than having to automatically wait until the expiration of a preset reentry interval. Knaak et al. (1980) have suggested toxicological safe levels for azinphosmethyl, methidathion, and parathion as being 3.1, 0.6, and 0.09 $\mu g/cm^2$ for citrus. The field method can readily determine these levels. However, each insecticide will require specific instructions as to the volumes of salt water and hexane to be added and removed for use. If the final measurement obtained by the analyst is below the absorbance value provided with the kit and the procedure, then the field can be deemed safe for worker entry. The absorbance value must be determined by using the actual reagents and equipment used in the final field kit. Prototype kits will be field tested more extensively.

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Effects of Atrazine Treatment of a Corn Field Using Different Application Methods, Times, and Additives on the Persistence of Residues in Soil and Their Uptake by Oat Plants

Shahamat U. Khan,* Paul B. Marriage, and Allan S. Hamill

Treatment of corn fields with the herbicide atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine] resulted in the formation of its 2-hydroxy analogue as the only measurable metabolite in a clay loam soil. The time and method of atrazine application (preplant incorporated, preemergence, and postemergence) and the presence of oil/surfactant additives in the herbicide formulation had no long-term effect on its persistence. However, postemergence application and the presence of additives resulted in a slightly greater initial degradation rate of atrazine in soil. Both atrazine, in less than phytotoxic amounts, and hydroxyatrazine persisted into the following growing season from all treatments. The residues from the field-treated soil were taken up, metabolized, and conjugated by oats seeded in the spring.

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine] is a widely used selective herbicide for weed control in corn. Applications may be made prior to planting with soil incorporation, immediately after planting before crop and weed emergence, and after crop and weed emergence. In the latter instance the addition of oils, surfactants, and their mixtures is recommended to enhance atrazine penetration into the leaf surface of weeds. In addition, atrazine for application at planting is now available in wettable powder and flowable formulations with the latter containing various additives.

It has been suggested that atrazine application in oil–water emulsions could affect and possibly decrease the persistence of atrazine (Sylwester, 1966; Sweet et al., 1979). Time and/or method of application may also effect atrazine persistence and degradation. It has been observed that treatments applied after corn emergence generally result in greater atrazine persistence or carry over than earlier treatments (Peters and Keeley, 1964; Frank, 1966; Burnside, 1976; Burnside and Schultz, 1978), and this may be related to soil moisture conditions.

In a previous study it was suggested that atrazine degradation products could persist beyond the growing season following a single atrazine application (Khan and Marriage,

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1977). These residues may be absorbed by various subsequently planted crops. This study was undertaken to determine the effects of time, method, and type of application in corn on the degradation and persistence of the herbicide atrazine. Furthermore, the subsequent uptake of residues by oat plants seeded in the treated field plots in the following spring was also investigated.

EXPERIMENTAL SECTION

Soil Treatment. The times and methods of atrazine application and the different wetting agents used in the formulations of atrazine with the rates involved are shown in Table I. The field plots were located at Woodslee, Ontario, on a Brookston clay loam. The soil has 4.1% organic matter and a pH of 5.6. The experimental plots were 3 × 12 m established in a field free from detectable atrazine residues. The design was a randomized block of four replicates for each treatment. The herbicide formulations were sprayed on May 24, 1978, for preplant incorporated and preemergence treatments and on June 14, 1978, for postemergence treatments. The plots were seeded to corn. Rainfall in millimeters for the 1978 growing season at this location and its expression as percent of normal rainfall in parentheses are as follows: May, 76.1 (108); June, 100.4 (129); July, 51.6 (63); Aug, 30.4 (39); Sept, 76.2 (128); Oct 61.2 (100).

Soil and Crop Sampling. Soil samples were collected from the 0- to 15-cm layer on May 24, June 2, 12, and 28, July 12, and Sept 28, 1978, for preplant and preemergence treatments (Table I). From the postemergence treated plots, soil samples were taken on June 15 and 28, July 12, and Oct 13, 1978. For all treatments 10 samples were taken at random from each plot and combined. The samples were air-dried, screened, passed through a 20-mesh sieve, and stored in the freezer until analyzed.

The plots were plowed in the fall of 1978. In the spring of 1979 the area was double disked in two directions at right angles and oats were planted on May 10. Final soil samples were collected on May 10 in the seeded field at the 0–15-cm depth. Oats were planted at right angles to previous corn planting in plots. The plants were harvested prior to heading while in vegetative stage on June 25, 1979, by using a forage harvester which removed a 75-cm swath in the center of the previous corn plot. The plant samples were stored in plastic bags at −20 °C until they were analyzed.

Chemicals. All solvents were of pesticide grade and used as received. Reference standards of atrazine and metabolites were used from an earlier study (Khan and Marriage, 1977).

Determination of Residues. Residues of atrazine and metabolites in soil and oat samples were determined as described in an earlier publication (Khan and Marriage, 1977).

Performance of the Method. The recoveries of the residues by the method used were determined by adding known amounts of the compounds to soil or oat samples. The samples were then processed as described earlier (Khan and Marriage, 1977).

All field samples were analyzed in duplicate and average values are reported. The results reported here are not corrected for recovery. Soil residue is reported on an oven dry basis and crop residue is on a fresh weight basis.

Gas Chromatography (GC). The gas chromatograph was a Pye Series 104, Model 64, fitted with an alkali-flame ionization detector having an RbCl annulus. A capillary column 30 m × 0.5 mm i.d. quartz tube with 3% Carbowax 20M coated on 80–100-mesh Chromosorb WHP was used. The operating conditions were as follows: on column in-

Table I. Residues of Atrazine and Hydroxyatrazine in Field-Treated Soils

treatment[a]	rate,[b] kg/ha	application[c]	compd[e]	ppb[d] at day 0	% of initial ppb[e] at days after treatment						atrazine half-life, days, for 0–4 period
					9	14	19	28	35	49	121–127	
atrazine	1.68	ppi	atrazine	443 ± 6	87 ± 7		76 ± 8		65 ± 4	53 ± 5	27 ± 2	67
			hydroxyatrazine		T[f]		10		16	19	30	
atrazine (flowable)	1.68	pre	atrazine	365 ± 15	79 ± 13		70 ± 3		56 ± 8	50 ± 10	26 ± 4	65
			hydroxyatrazine		T		10		15	20	29	
atrazine (wettable powder)	1.68	pre	atrazine	415 ± 17	90 ± 9		80 ± 7		62 ± 6	48 ± 5	28 ± 5	69
			hydroxyatrazine		T		10		23	29	40	
atrazine + Super Spred	1.68 ± 0.25%	post	atrazine	420 ± 15		77 ± 8		61 ± 9			23 ± 2	57
			hydroxyatrazine			10		23			29	
atrazine + Atplus 411F	1.68 ± 1.0%	post	atrazine	399 ± 17		72 ± 5		57 ± 4			23 ± 3	56
			hydroxyatrazine			13		24			33	
atrazine + Kornoil	1.68 ± 4.0%	post	atrazine	383 ± 14		77 ± 7		59 ± 4			25 ± 4	60
			hydroxyatrazine			10		23			33	
atrazine	1.68	post	atrazine	350 ± 16		82 ± 4		66 ± 3			24 ± 2	59
			hydroxyatrazine			16		21			27	

[a] Atrazine applied as wettable powder formulation where not specified. Super Spred, surfactant; Atplus 411F, oil/surfactant blend; Kornoil, mineral oil. [b] Surfactant/oil concentrations expressed as percent of total spray voluem. [c] ppi, preplant incorporated application; pre, preemergence application; post, postemergence application. [d] Mean values ± standard errors for duplicate samples from four replicates. [e] Mean values ± standard deviations for duplicate samples from four replicates as percentages of initial soil concentration for atrazine and as percentages of initial atrazine concentration for hydroxyatrazine with coefficients of variation ranging from 10 to 15% for hydroxyatrazine. [f] T = <10 ppb.

Table II. Residues of Atrazine and Hydroxyatrazine in the Field-Treated Soils the Year following the Herbicide Application and Their Uptake

		soil residues,[b] ppb		oat plant residues, ppb	
treatment[a]	application[a]	atrazine	hydroxy-atrazine	hydroxy-atrazine	deisopropyl-hydroxyatrazine
atrazine	ppi	35 ± 5	16 ± 1	205	165
atrazine (flowable)	pre	32 ± 1	19 ± 2	305	340
atrazine (wettable powder)	pre	37 ± 1	11 ± 1	295	245
atrazine + Super Spred	post	37 ± 1	17 ± 2	270	365
atrazine + Atplus 411F	post	35 ± 1	12 ± 1	305	355
atrazine + Kornoil	post	41 ± 3	11 ± 1	250	360
atrazine	post	41 ± 4	25 ± 5	285	145

[a] Treatment and application details are as described in Table I. [b] Mean values ± standard errors for duplicate samples from four replicates.

jections; injector port, column, and detector temperatures, 260, 176, and 300 °C, respectively; the helium carrier gas, makeup gas, hydrogen, and air flow rates, 5, 40, 5, and 150 mL/min, respectively.

RESULTS AND DISCUSSION

The capillary column separated atrazine and metabolites with good resolution. The compounds gave a 50% full-scale deflection in the 3.4–26.7-ng range.

Recoveries of atrazine, hydroxyatrazine [2-hydroxy-4-(ethylamino)-6-(isopropylamino)-*s*-triazine], and their dealkylated analogues added to untreated soil at the 0.05-, 0.1-, and 0.2-ppm levels ranged from 62 to 98%. Similarly, recoveries of these compounds from the oat samples fortified at the 0.05- and 0.1-ppm levels ranged from 64 to 80%. In general, the recoveries of hydroxy compounds from fortified soil and plant samples were low partly due to poor efficiency of methylation (Khan and Marriage, 1977).

GC analysis of extracts of experimental samples showed peaks having retention times identical with those of some of the reference standards. The identities of the peaks were confirmed by cochromatography with authentic standards and finally by gas chromatography–mass spectrometry (Khan and Marriage, 1977).

Decline of atrazine residues in soil in all the treatments resulted in the formation of hydroxyatrazine as the only measurable metabolite (Table I). With all application times and methods, the degradation rate of atrazine was faster during the first month after treatment than over the remaining 3-month growing season. This was evidenced by the percent of the herbicides remaining in soil over these two periods (Table I). The slow degradation rate is probably attributable to the dry conditions in July and Aug of 1978 (Walker, 1978). It is unlikely that loss of atrazine through volatilization or photodecomposition at the time of application (Jordan et al., 1964; Burt, 1974) or through leaching beyond the 15-cm soil depth during the growing season (Burnside et al., 1969) will contribute significantly to the decline in atrazine concentration.

The decrease in atrazine residue levels with each date and method of atrazine application was accompanied by an increase in and accumulation of hydroxyatrazine. However, a progressive decline in each treatment of the total residue levels (ppb of atrazine plus hydroxyatrazine) was observed which may partly be accounted for by low hydroxy atrazine recovery. It is also possible that atrazine and hydroxyatrazine were further degraded to some other compounds which were not detectable by the techniques employed in this study. The cleavage of the triazine ring structure seems very unlikely based on the known slow rate of ring cleavage of triazine herbicides and the failure to detect either 2-chloro or 2-hydroxy dealkylated products in the soil as intermediates preceding this reaction (Esser et al., 1975; Khan and Marriage, 1977).

Time and method of application of atrazine did not have a major effect on atrazine degradation or persistence (Table I). Postemergence treatments of atrazine made 3 weeks after the applications at planting had generally faster degradation rates than preplant and preemergence treatments as evidenced by the half-life values for atrazine (Table I). The higher mean daily temperatures for the monthly period following the postemergence applications may partly account for the more rapid dissipation of atrazine (Walker, 1978). During this period the moisture conditions were adequate due to the 70 mm of rainfall distributed over the 3 weeks after treatment. These relative degradation rates resulted in essentially equivalent amounts of atrazine residues, approximately one-quarter of the initial amount, at the end of the growing season for all treatments. In contrast to these findings, previous observations have indicated that postemergence atrazine applications may be expected to degrade more slowly and persist longer than preemergence or preplant treatments, but this may be associated with drier conditions following such treatments (Burnside, 1976; Burnside and Schultz, 1978). Preemergence and preplant incorporated treatments of atrazine as the wettable powder formulation were degraded at the same rate over the 4 months after application. These observations are in agreement with those reported by Buchholtz (1965) and Buchanan and Hiltbold (1973) but differ from the findings of Burnside (1976) where less atrazine persistence occurred when it was applied as a preplant incorporated treatment.

The presence of oils and/or surfactants in the herbicide formulations resulted in a more rapid initial degradation. This is shown by the percentage decrease in atrazine concentration in the soil for flowable atrazine applied preemergence and postemergence treatments containing surfactant and/or oil. It has been suggested that such emulsion could reduce the persistence of atrazine by decreasing the rate of adsorption of atrazine by soil particles (Sylwester, 1966; Sweet et al., 1979). Our data demonstrate that such effects would be expected primarily in the initial stages of degradation. Other factors may also, however, be involved since Fusi and Corsi (1969) observed that surfactants had no effect on atrazine adsorption or desorption by the soils they examined. On a long-term basis (4 months) the presence or absence of surfactants/oils at application time had no discernible effect on atrazine persistence. This observation is in agreement with the results of Parochetti et al. (1977).

In general, the rate of atrazine degradation observed in our study agreed with that obtained by previous investigators (Harris, 1967; Nearpass et al., 1978; Walker, 1978; Dao et al., 1979), although Birk and Roadhouse (1964) observed more rapid and Marriage et al. (1978) slower degradation at equivalent application rates. Residue levels

of atrazine and hydroxyatrazine present in the spring of the year following treatment were uniform over all treatments. Fall plowing disrupted the soil profile and altered herbicide distribution (Buchholtz, 1965). Thus, atrazine and metabolite losses over the winter through both slow degradation and leaching would be anticipated (Burnside et al., 1969; Nearpass et al., 1978). The only metabolite of atrazine observed in the soil in the spring of 1979 was hydroxyatrazine, and, in contrast to the previous fall (121–127 days after treatment, Table I), its concentration was less than that of atrazine (Table II).

Oats sown in early May of 1979 on plots treated with atrazine the previous year and harvested at the vegetative stage in June contained in the shoot residues of hydroxyatrazine and one of its monodealkylated analogues, namely, deisopropylhydroxyatrazine [2-hydroxy-4-(ethylamino)-6-amino-*s*-triazine] (Table II). These compounds were present in the conjugated form as evidenced by their release in the plant extracts only after hydrolysis. No treatment-related differences in atrazine metabolites were observed in the oat samples. Furthermore, no unaltered atrazine was detected in the oat shoots although its presence was anticipated based on the residue levels in the field-treated soil (Table II). Both atrazine and hydroxyatrazine are likely to have been absorbed by the oat plants (Shimabukuro, 1968; Khan and Marriage, 1977) and were rapidly metabolized by the reactions involving dealkylation and/or hydroxylation (Shimabukuro, 1967, 1968; Khan and Marriage, 1977). The level of atrazine in the soil was below that at which measurable phytotoxic effects on oat growth would be expected (Marriage, 1975). Furthermore, atrazine phytotoxicity is destroyed by hydroxylation (Kaufman and Blake, 1970) which may explain the lack of visible effects on the oat plants due to the previous year's atrazine treatment. The residue levels of hydroxyatrazine observed in the field-grown oat shoots the year following a single atrazine treatment ranged from 205 to 305 ppb. These levels are broadly comparable to the levels found in oats grown in a bioassay study using soil which had been repeatedly treated with atrazine and had accumulated a significantly higher level of hydroxyatrazine (Khan and Marriage, 1977).

CONCLUSIONS

This study indicates that under the parameters of the experiment, atrazine in nonphytotoxic amounts and its hydroxy analogue will persist in the soil beyond the growing season. It is anticipated that under different environmental and edaphic conditions, atrazine degradation rate and metabolites produced may vary, and seasonal weather may have less influence on residue carry over than soil properties. In addition, it appears that the application of atrazine at different dates and by various methods and the formulation of atrazine with oil/surfactant additives will have no notable effect on the degradation and persistence of atrazine and its metabolites. It has been demonstrated that crops grown in the field the year following a single application of atrazine will absorb atrazine and metabolite residues, in this case hydroxyatrazine, which in turn are subject to conjugation in plant tissues. The data also indicate that the herbicide absorbed by plants is metabolized and detoxified via 2-hydroxylation and N-dealkylation.

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