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Assessing Atrazine Persistence in Soil Following a Severe Drought

Richard A. Leavitt,[1] James J. Kells,[1,2] Jeffrey R. Bunkelmann,[1] and Robert M. Hollingworth[1]

[1]Pesticide Research Center and [2]Department of Crop & Soil Sciences, Michigan State University, E. Lansing, Michigan 48824, USA

Much of the corn production region in the United States, including Michigan, experienced a severe drought during the 1988 growing season. The severity of the drought for Michigan is indicated in Table 1 by rainfall accumulations far below the normal monthly averages for May and June. This was the driest May-June period since comparative records began in 1895 for all but weather district 2 (U.S. Dept. of Commerce, 1988). The very little rainfall coupled with temperatures above normal created extremely dry soil conditions during the period when soil moisture is usually adequate in Michigan and raised concern about herbicide carryover.

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine] is the most widely used herbicide with potential to persist in sufficient quantity to injure sensitive rotational crops. This herbicide is a member of the *s*-triazine family and is used primarily for weed control in corn. Atrazine can persist in the soil for one or more years following application and may cause crop injury when rotating to atrazine-sensitive crops such as soybeans or alfalfa.

Atrazine is degraded in soil by both chemical hydrolysis and microbial breakdown with these processes occurring much more rapidly under conditions of adequate soil moisture and relatively warm temperature (McCormick and Hiltbildt 1966; Roeth et al. 1968; Talbert and Fletchall 1964). Thus, it is generally accepted that the risk of atrazine carryover is greater following a year of low rainfall, since microbial activity is favored by adequate soil moisture. The 1988 drought created a critical need for an assessment of atrazine concentration in soil to advise producers on crop management options related to atrazine sensitive crops.

Send reprint requests to Dr. Richard A. Leavitt at the above address.

Table 1. Average monthly precipitation (cm) composites for the lower peninsula of Michigan.

Weather Districts	May		June	
	1988[1]	30 yr avg[2]	1988	30 yr avg
2,3 (North)	2.35	6.88	3.09	7.65
4,5,6 (Central)	1.63	6.82	2.07	7.84
7,8,9 (South)	2.84	7.39	1.53	9.19

[1] (U.S. Dept. of Commerce, 1988).
[2] 1951-1980 (U.S. Dept. of Commerce, 1981).

Typical laboratory analysis for atrazine involves lengthy solvent extraction of soil followed by gas-liquid chromatography (GLC) (Sirons et al. 1973; Lee and Chau 1983; Smith 1981) or high performance liquid chromatography (HPLC) (Vickery et al. 1980; Ferris and Haigh 1987; DiCorcia et al. 1987) analysis. Recently, immunoassay techniques have been developed for specific pesticides, including the *s*-triazines, which are relatively inexpensive and can be quickly conducted in the laboratory or at field locations (Dunbar et al. 1985; Huber 1985; Bushway 1988; Schlaeppi et al. 1989).

The objectives of this study were to assess: 1) atrazine residue levels in Michigan soils following the 1988 drought, and 2) the suitability of the immunoassay technique over a wide variety of soils.

MATERIALS AND METHODS

Soil samples were collected by Cooperative Extension Service personnel from 30 Michigan counties in November and December, 1988. The sample sites were representative of the major corn production regions in Michigan (Figure 1). Sites were selected from untilled fields where corn had been grown in 1988 and which had received known rates of atrazine in 1988 and no atrazine treatments in 1986 or 1987. Sites were selected which had received atrazine at rates ranging from 1.1 to 4.4 kg/ha and represented a wide range of soil characteristics including pH, organic matter, and cation exchange capacity. Each sample was a composite of 20 subsamples taken from bare soil between corn rows with a soil probe from a depth of 0 to 15 cm. Field headlands and borders where sprayer overlap may have occurred and areas of standing water were avoided. Samples were thoroughly mixed before being split for the separate analysis methods and for soil characteristics testing. Samples were maintained at -20°C until used for analysis.

An analytical standard of atrazine (98.2% pure) was obtained from EPA, Pesticides & Industrial Chemical Repository, Research Triangle Park, NC 27709. Stock solutions were prepared by

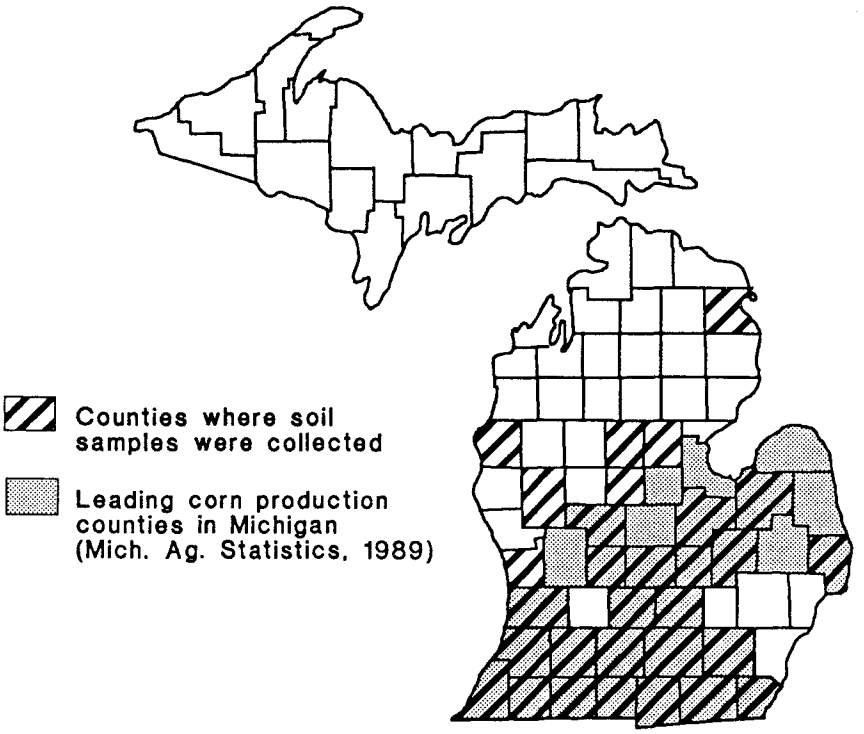

Figure 1. Distribution of soil sampling and corn producing areas in Michigan.

weighing approximately 0.01 g atrazine into a 50 mL volumetric flask and filling to the mark with either methanol or acetonitrile for GLC or immunoassay analyses, respectively. Working standards in the range of 0.1 to 2 ppm and 0.5 to 10 ppb were prepared by serial dilution of standard stock solutions.

For the GLC analyses, using general procedures described by Smith, et al., 1980, 20 g wet soil samples were extracted for 23 hr with 90% methanol in distilled water using Soxhlet extractors. Following removal of methanol by vacuum rotoevaporation (water bath at 40°C), the soil extracts were further cleaned up by partitioning from water into methylene chloride. The methylene chloride was evaporated to dryness and residues were then redissolved in isooctane and filtered through glass wool for GLC analysis.

The atrazine residues were quantified using a Tracor 560 gas chromatograph equipped with a nitrogen/phosphorous detector and a 1.8 m x 2 mm i.d. glass column containing 1.5% OV-17 + 1.95% QF-1 on Chromosorb W-HP 80/100 packing. Operating temperatures were 250, 220, and 185°C for the detector, injector, and column, respectively. Gas flows were 40 mL/min helium for the column and

4 mL/min hydrogen and 100 mL/min air for the detector. Under these conditions, the retention time for atrazine was about 4.5 min. Samples were quantified by comparison to atrazine standards with similar GLC peak heights and were corrected for soil moisture content.

For the immunoassays, Res-I-Mune ATRAZINE Immunoassay kits with specificity for *s*-triazines were purchased from ImmunoSystems, Inc., Biddeford, ME 04005. Each kit contained detailed instructions for use and consisted of 20 atrazine antibody-coated tubes, solutions of atrazine-enzyme conjugate, and solutions which develop color in the presence of the atrazine-enzyme conjugate.

For each sample, 25 g of wet soil was shaken, using a wrist-action shaker, for 15 min with 25 mL of 90% acetonitrile in distilled water. After settling for 10 min, a 1 mL aliquot was withdrawn and diluted to 50 mL with distilled water. From the diluted sample, 160 μL was pipetted into an antibody-coated tube and immediately followed by 160 μL of the atrazine-enzyme conjugate solution. After 5 min, the tubes were rinsed with water and the color developing reagents were added. Absorbance measurements were made at 450 nm with either a Gilford 2600 UV/VIS spectrometer using 1 mm cells or a portable battery powered Artel differential photometer available from ImmunoSystems, Inc. Samples were quantified by comparison to atrazine standards (0.5 to 10 ppb in 1.8% acetonitrile in distilled water) which went through the same procedure as the samples except for the initial extraction.

Method validation studies for both techniques were conducted using control soil samples that had not received atrazine treatments. For each technique, three replicate samples were fortified at two atrazine concentrations in methanol which was allowed to evaporate before proceeding with the initial extractions. Both methods showed excellent recovery of atrazine from control samples fortified at 0.0784 and 0.1568 ppm. Recoveries averaged 93.3% ± 5.4% and 88.0% ± 5.8% for the Soxhlet-GLC and Immunoassay methods, respectively.

Soil characterization tests for pH, organic matter, and cation exchange capacity were conducted by the Michigan State University Soil Testing Laboratory. This data was correlated with atrazine concentration to assess which factors most strongly influenced atrazine persistence.

RESULTS AND DISCUSSION

Table 2 shows the distribution of atrazine concentration values detected by the Soxhlet-GLC method from soil treated within four application rate ranges. In general, the concentration of atrazine detected was not greatly different from what was expected following a more normal growing season. For example,

89% of the fields treated with 1.1 to 1.7 kg/ha of atrazine had atrazine concentrations less than 0.1 ppm, an amount generally safe for soybeans. In addition, 82% of the fields treated with 1.7 to 2.8 kg/ha of atrazine had atrazine concentrations less than 0.1 ppm. Concentrations greater than 0.2 ppm were detected in the soil only where atrazine was applied at rates of 4.0 to 4.5 kg/ha. On a statewide basis, atrazine levels remaining in the soil were not unusually high in late fall, despite the severe summer drought. Information from this project was very useful to Michigan producers in planning crop rotations for the 1989 growing season.

Previous research has shown that soil characteristics affect the persistence of atrazine. For example, as soil pH increases, atrazine persistence becomes greater (Kells et al. 1980; Pawlak et al. 1987). In addition, these same factors affect the availability of atrazine for plant uptake. In general, higher clay content, higher organic matter, and lower soil pH correlate

Table 2. Atrazine concentration[1] in soil in late fall, 1988, following application the previous spring.

Atrazine application rate, kg/ha	No. of samples	Atrazine concentration, ppm			
		<0.05	0.05-0.10	0.10-0.20	>0.20
		(% of samples)			
1.1-1.7	35	69	20	11	0
1.8-2.8	38	45	37	18	0
2.9-3.9	14	50	29	21	0
4.0-4.5	13	15	15	55	15

[1] Quantification by the Soxhlet-GLC method.

to less availability of atrazine and thus less risk of plant injury (Kells et al. 1980). Therefore, a given concentration of atrazine may cause crop injury in one soil and not in another.

In this study, the greatest correlation with atrazine persistence was observed with cation exchange capacity ($Y = 0.14 + 0.96 X$; $R^2 = 0.30$; $N = 75$). No significant correlation between atrazine persistence and other soil characteristics was observed. This suggests that environmental factors such as soil moisture and temperature were the greatest factors influencing atrazine persistence under Michigan field conditions in 1988.

All soil samples were analyzed by both methods and significant variation did exist for individual samples ($Y = 0.01 + 0.824 X$; $R^2 = 0.78$; $N = 75$). However, in general, each technique detected similar levels of atrazine in a wide range of soil types. Figure 2 shows the correlation between the two techniques for the 75 samples which had atrazine concentrations ≥ 0.01 ppm by both

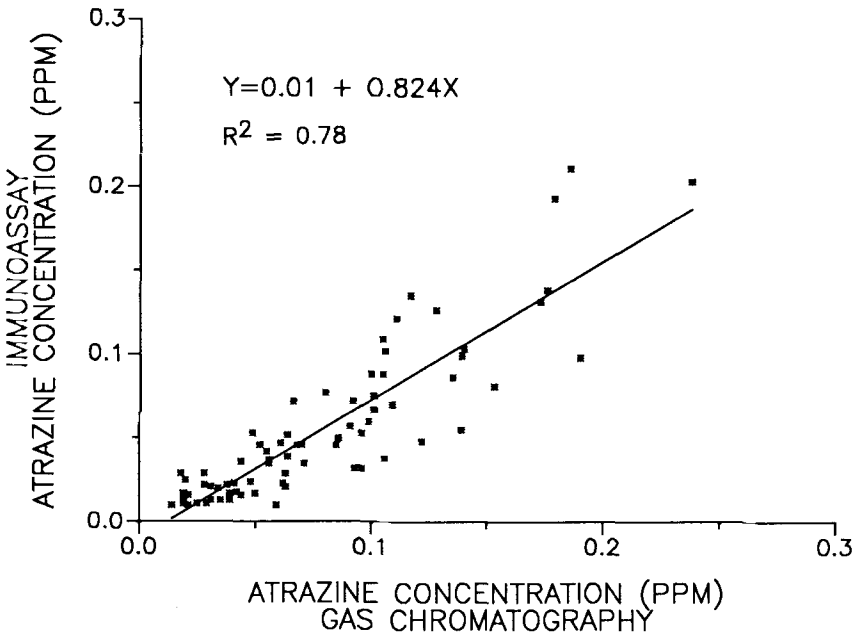

Figure 2. Comparison of gas chromatography and immunoassay analysis techniques for quantitation of atrazine in 75 soil samples collected in Michigan.

methods. The immunoassay method values were on average 20% less than those determined by the Soxhlet-GLC method run on the same soil sample. Even though fortified sample recoveries were similar, for the weathered samples the difference between the two techniques may be due to the initial extraction times of 15 min and 23 hr for the immunoassay and Soxhlet-GLC methods, respectively. The relative difference in atrazine detection between the two techniques was not influenced by soil characteristics. No significant interaction between atrazine detection and soil characteristics was observed in this study. This suggests that both techniques were equally effective in detecting atrazine residues across a wide range of soil properties.

Selected samples representing atrazine concentrations of 0.01 to 0.05 ppm were use for comparison of the Gilford spectrometer and the Artel photometer. Both instruments gave comparable absorbance measurements ($Y = 0.001 + 0.96\ X$; $R^2 = 0.96$; $N = 10$) but the Artel photometer was much easier to use since it gave the differential absorbance for sample versus control using the antibody-coated tubes directly and could easily be used in the field.

In general, both the immunoassay and Soxhlet-GLC techniques

provided adequate estimates of atrazine residue levels in soil for making decisions on rotational crop selection. The immunoassay technique detected approximately 20% less atrazine in soil, probably due to differences in initial extraction efficiency. The immunoassay technique examined in this study is inexpensive, provides quick results and is relative easy to use. It accurately detected atrazine at concentrations as low as 0.01 ppm. The results of this study suggest that this technique is a reasonable alternative to the traditional Soxhlet-GLC procedure for atrazine analysis in soil in situations where maximum precision in analysis is not critical and could be used to assay *s*-triazine residues under field conditions. This technique could be adopted by public or private testing services to provide a rapid, inexpensive assessment of atrazine or other *s*-triazines in soil.

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