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CHAPTER 7

DEGRADATION OF ATRAZINE IN SOILS AT DIFFERENT WATER LEVELS AND TEMPERATURES

Introduction

Results of the field studies reported in Chapters 5 & 6 illustrated the variability in the rate of atrazine degradation in different soils. Many researchers have tried to predict persistence by describing the relationships between environmental factors and herbicide persistence in soil. However, establishing exact relationships are difficult because the rate at which a herbicide degrades is influenced by several soil and weather factors (Harris *et al.*, 1969; Hurle & Lang, 1981; Walker, 1987; Weber, 1991a).

According to Walker (1989), appreciable variability in herbicide degradation rate between soils necessitates extensive field testing at different sites and in different years. For this reason, comparison of herbicide degradation in different soils is often made in the laboratory where factors such as temperature and soil moisture can be carefully controlled.

The aims of the present laboratory investigation was to substantiate the noted variation in atrazine persistence between soils in the field, and to determine the combined effects of temperature and soil water on the degradation rate of the herbicide. In contrast to the two previous field studies, the methodology employed here negated the effect of leaching.

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Materials & Methods

The degradation rate of atrazine (Gesaprim® 500 FW) was measured over a 60-day period in a fine-textured soil and a coarse-textured soil incubated under different temperature and soil water conditions in walk-in Conviron® growth cabinets. The heavier soil contained mostly montmorillonite clay (80%) and had a total clay content of 55%, 0.7% organic C, 48 cmol(+) kg^{-1} CEC, and a pH(H_2O) of 7.3. The coarse-textured soil contained mainly kaolinite clay, with 7% total clay, 0.34% C, 0.8 cmol(+) kg^{-1} CEC, and a pH(H_2O) of 5.4. Atrazine was applied to both soils at 1 and 2 mg kg^{-1} on day 0 by thoroughly mixing a pre-determined volume of a 50 mg atrazine L^{-1} solution into the soil. Each pot contained 0.5 kg air-dried and sifted (3 mm sieve) soil. Residual atrazine concentration was measured in soil samples 0, 30 and 60 days after application by means of high pressure liquid chromatography (HPLC). On day 0, ten pots from each of the 1 and 2 mg atrazine kg^{-1} treatments were randomly selected for determination of initial atrazine concentrations. At days 30 and 60 after application all treatment combinations were analyzed.

Potted soil was incubated in the dark in three growth chambers at temperature regimes of 30/16 °C, 30/8 °C and 16/8 °C on a 12/12 hour basis. Soil water levels were attained by applying half the required volume of water to the surface of the soil in each pot, prior to herbicide application, and the rest thereafter. Pots were weighed regularly and water added to ensure that original weights were maintained. Soil water contents of about 1% (air-dried soil), the water content at field capacity (13% and 26% for the coarse- and fine-textured soils, respectively) and 2x field capacity were maintained by weighing pots on alternate days and replenishing water lost through evaporation.

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Water loss over, for example, an 8-day period was minimal due to the pots having been sealed in plastic bags immediately after the initial waterings.

Pots in the growth chambers were arranged according to a completely randomized design. Two soil samples from each treatment combination were analyzed. Separate analyses of variance were performed for day 30 and day 60 data.

For HPLC determination, soil samples were extracted according to the methods described by Mattson, Kahrs & Murphy (1970) and Sirons, Frank & Sawyer (1973), which were modified by extracting soil samples (50 g) for two hours with acetonitrile:water 9:1 (v/v; 150 ml). The acetonitrile:water:soil slurry was centrifuged at 5 000 r.p.m. for 5 minutes. The supernatant was filtered through a Whatman no 5 filter paper. A Millipore teflon filter disc (0.5 μm pore diameter) was used to filter 5 ml of this filtrate. The final filtrate was stored at -5°C until analyzed.

The final filtrate was used as such for analysis. A Spectra-Physics model SP 8000B equipped with a data system, autosampler and a 10 mm lightpath length flow-through cell fixed wavelength detector (254 nm) was used. A 10 μl sample loop and an Altex ODS 250x2.6 mm column were used. The instrument was operated isocratically at 1 ml min^{-1} with methanol:water (80:20). Apostolides *et al.* (1982) found that the HPLC technique described above was more suitable for determining atrazine concentrations similar to those encountered in this study than either thin layer chromatography, spectrophotometry in the ultraviolet region, or gas chromatography with a flame ionization detector or a nitrogen phosphorous detector.

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Results and Discussion

Chemical analyses showed that initial (day 0) concentrations in both soils were close to the intended levels of 1 and 2 mg atrazine kg^{-1} (Tables 19B & 20B). Percentages atrazine remaining in the soils at day 30 are shown in Table 29, and data for day 60 in Table 30. Percentage data will be discussed.

The second-order soil by atrazine by water interaction was significant for the day 30 (Table 29) and day 60 data (Table 30). The rate of degradation was not significantly influenced by an increase in water content from f.c. to twice that amount. At both stages after atrazine application, degradation was significantly faster in the coarse-textured soil than in the fine-textured soil (Tables 29 & 30).

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Table 29 Effect of temperature and soil water on percent atrazine remaining 30 days after application to two soils (ANOVA in Table 33A; original data appear in Table 19B)

		Temperature regime (day/night)											
		30/16 °C			30/8 °C			16/8 °C			Mean		
	Atrazine	Soil water content											
Soil	(mg kg$^{-1)}$	0	fc	2xfc	0	fc	2xfc	0	fc	2xfc	0	fc	2xfc
		% atrazine			% atrazine			% atrazine			% atrazine		
Sand	1	94	76	71	92	72	74	93	85	81	93	78	75
	2	97	65	64	96	63	67	98	82	79	97	70	70
Clay	1	99	92	95	103	87	93	97	101	96	100	93	95
	2	100	95	96	100	97	96	98	95	98	99	96	97
LSD_T (P=0.05)											Soil x Atrazine x Water = 6		

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Table 30 Effect of temperature and soil water on percent atrazine remaining 60 days after application to two soils (ANOVA in Table 34A; original data appear in Table 20B)

		Temperature regime (day/night)											
		30/16 °C			30/8 °C			16/8 °C			Mean		
	Atrazine	Soil water content											
Soil	(mg kg^{-1})	0	fc	2xfc	0	fc	2xfc	0	fc	2xfc	0	fc	2xfc
		% atrazine			% atrazine			% atrazine			% atrazine		
Sand	1	86	45	45	82	60	51	94	70	64	87	58	53
	2	90	45	45	93	53	49	95	66	64	93	55	53
Clay	1	96	73	71	96	74	63	94	80	76	95	76	70
	2	97	78	76	98	79	75	98	86	81	98	81	77
LSD_T (P=0.05)											Soil x Atrazine x Water = 6		

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Half-lives for atrazine can be inferred from the data in Table 30. In the sandy loam soil it appears that the half-life of atrazine was somewhat less than 60 days at 30/16°C with water content at the field capacity value. At 60 days after atrazine application to the clay soil at least 75% of the initial amount was still detectable, thus implying a halflife well beyond 60 days.

Soil characteristics were clearly determining the persistence of atrazine in the two soils. The assertion of Allen & Walker (1983) and Walker, *et al.* (1983) that increased adsorption provides protection against degradation, ostensibly explains the longer persistence of atrazine in the montmorillonite clay soil (Tables 29 & 30). In addition, atrazine molecules are highly stable under neutral pH conditions (Armstrong *et al.*, 1967). The clay soil had a near neutral pH (pH 7.3). However, the potential role of the high adsorptive capacity of the montmorillonite clay in this soil would presumably be partially negated by the fact that atrazine exists in the molecular form at high pH (Weber & Whitacre, 1982). In the neutral state, atrazine molecules would be relatively weakly bonded to negatively charged colloids which predominate under high pH conditions. In contrast to clay minerals, organic matter has both hydrophilic and lipophilic characteristics (Weber, 1991a), and therefore is likely to adsorb both atrazine molecules and cations. It is also possible that atrazine molecules can be temporarily trapped inside the expandable layers of montmorillonite clay. It seems likely that soil pH and adsorption on organic matter were the main determinants of the rate of atrazine degradation in the clay soil. Typical features of local montmorillonite soils include pH levels near or above pH 7 and relatively high clay and organic matter contents.

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Soil water content and temperature both influenced the degradation of atrazine. The big differences in the magnitude of soil water levels, in contrast to the order differences for temperature, probably resulted in water content appearing to be more important than temperature. In laboratory experiments with many pesticides, Briggs (1983) and Walker & Allen (1984) reported a 2 to 2.5 fold increase in half-life with a 10°C decrease in temperature and a 1.5 to 2.5 fold increase in half-life if soil moisture is reduced by a factor of two. Grover (1965) contended that adsorption of *s*-triazines on the hydrophillic adsorptive sites of clay minerals, under high soil water conditions, will be insignificant because atrazine molecules would be desorbed from these sites by the overwhelming number of highly polar water molecules. Little or no degradation of atrazine occurred in air-dry soil, probably because both chemical and biological degradation processes occur in aqueous medium.

Results presented above suggest that weather conditions can have a marked influence on rates of atrazine loss in the field. In addition, the combination of high soil pH levels and adsorption on organic matter could be conducive to excessive persistence, and therefore, injury to sensitive follow-up crops. It is recognized that leaching is involved in the dissipation of atrazine from soil in the field. This aspect was considered in a subsequent investigation aimed at evaluating a bioassay technique for monitoring the movement of the herbicide, or its phytotoxic residues, in soil.

The work reported in this chapter has been published (Reinhardt & Nel, 1993).