CHAPTER 8

DISSIPATION AND MOBILITY OF ATRAZINE

Introduction

Previous chapters contain citations of numerous reports on the influence of climatic and edaphic factors on the persistence of atrazine in soil. The methodology in own experiments involved measurement of atrazine residues by biological means in bioassays (Chapters 5 & 6), as well as residue determination by means of chemical analysis in the absence of plants (Chapter 7).

Bioassays have the advantage that they measure only the plant-available residue fraction in soil. Their disadvantage is that they are non-specific, i.e. a particular test species may be affected by a wide range of herbicides. In contrast, the detection methods used for analytical determination of residues have greater specificity and require less time to produce results (Duffy, 1991). Results from chemical analyses are however more difficult to interpret since the amount detected is not necessarily available for uptake by plants. Analytical methods are therefore ideally suited to herbicide degradation studies in which the effect of herbicide residues on crops is not the main objective.

Walker (1989) states that degradation is only one component of the complex which determines pesticide persistence and activity in soil. Leaching is another important avenue for loss (dissipation) of herbicides in the field. In the present study the role of leaching in the dissipation of atrazine was assessed. The primary aim was to quantify

phytotoxic atrazine residues in different layers of a sandy clay loam soil by means of bioassays.

Materials & Methods

Bioassays with oats (cv SWK 001) as test species were conducted in parallel in the field and in the glasshouse with a sandy clay loam soil of the Hutton form with 22% total clay content, 0.31% organic C, P-reversion 117 mg kg^{-1}, and soil pH(H_2O) 6.3. The soil was from a cultivated field which had not been treated with herbicides during the last three years. A broadcast application of 37.5 kg N ha^{-1}, 25 kg P ha^{-1}, and 12.5 kg K ha^{-1} in the form of fertilizer [3:2:1 (25) + Zn] applied at a rate of 300 kg ha^{-1} was made three months before the experiment commenced.

Field bioassays

Six adjacent plots, each 4 m (width) by 8 m (length), were laid out on a fallow field. Each plot was divided into two sub-plots (each 4x4 m). One set of sub-plots served as controls, and were therefore not treated with atrazine. All plots denoted for treatment, except the day -1 plot (i.e. one day prior to application), were treated on day 0 with a single atrazine rate of 0.25 kg ha^{-1} (0.5 L Gesaprim® 500 FW ha^{-1}). A small plot sprayer which delivered 151 L water ha^{-1} at 300 kPa was used to apply the herbicide. On designated days (i.e. -1, 1, 30, 60, 90 and 120 days after atrazine application), four rows of oats were hand-seeded with a spacing of 500 mm x 40 mm on one half (2x4 m) of each sub-plot. The remaining 2x4 m section of each sub-plot was not seeded, and was kept free of weeds by hand-weeding. Soil samples for bioassays in the glasshouse were taken on these plant-free sections. On sub-plots seeded with oats, ten

neighbouring plants were harvested (15 days after emergence) at three randomly selected positions in a plant row. Three rows in every sub-plot were harvested this way. Plants were cut at ground level and oven-dried for determination of dry mass.

Bioassays in the glasshouse

Determination of leaching

Soil samples were collected from the 0-100 mm, 100-200 mm and 200-300 mm layers of the soil profile at days -1, 30, 60, 90 and 120 after application of atrazine. Only the top soil layer was sampled on day 1, since leaching of atrazine beyond that depth was not expected within one day after application. As atrazine could conceivably have been leached beyond the 200-300 mm zone by day 120, the 300-400 mm layer was sampled at that stage only. Sixty 50 mm diameter soil samples were taken with a field sampler from each soil layer in the unplanted sub-plots (2x4 m) at appointed intervals. Samples from a specific layer were combined before being air-dried and sifted (3 mm sieve). One kilogram of each sample was added to 1 L (100x100x100 mm) polyethylene pots lined with plastic bags to prevent drainage. Three pots (replicates) were prepared for each sampling depth at each stage after application of atrazine. Pots were arranged according to a completely randomized design. Eight ungerminated oats (cv SWK 001) seeds were planted in each pot, and plants thinned to six after emergence. Temperatures (day/night) in the glasshouse were maintained at 27/17°C on a 12/12 hour basis, without supplementary lighting. Pots were watered daily, and weighed on alternate days to bring the soil water content to 75% of the field capacity value (17% m/m). The nutrient solution of Nitsch (1972) was used to eliminate possible disparity in nutrients across soil samples by adding 0.05 L of the solution biweekly to the soil in all pots.

Plants were harvested fifteen days after emergence for determination of top growth dry mass.

Dose-response curves

Transformation of the measured residual activities (i.e. % reduction in dry matter yield relative to controls) into herbicide concentrations required comparison of these activities with those obtained in dose-response bioassays, which were performed concurrently with bioassays conducted on soil samples from the field experiment, under identical conditions in the glasshouse. Soil from the 0-200 mm layer in control plots was used to obtain dose-response curves. For this purpose, herbicide concentrations of 0, 0.025, 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 mg atrazine kg^{-1} were established in potted soil. Treatments were replicated three times. The growth response (dry matter yield) of the test plant to different atrazine rates was expressed as percent reduction in growth relative to growth in the control treatment (0 atrazine), and plotted against herbicide rate. Dose-response curves were obtained for days 1, 30, 60 and 90 after atrazine application in the field.

The procedure for estimating the amount of phytotoxic atrazine residues in different soil layers at specific intervals in the field was similar to that employed by Streibig (1988). Non-linear regression analysis of the data from the dose-response bioassays was carried out in order to obtain dose-response curves at certain intervals after herbicide application in the field. Residual atrazine concentrations in soil samples taken from the field at certain intervals were estimated by means of a single equation that described the relationship between test plant response (% reduction in dry matter yield) and atrazine

rate. The equation employed is given in the next section under the sub-heading *Glasshouse bioassays*.

Results and Discussion

Field bioassays

Damage caused by 0.25 kg atrazine ha^{-1} applied in the field was assessed visually at each stage after application by comparing the general growth of plants on treated plots with that of plants on the adjacent control plots. Concurrently, damage was determined by measuring the top growth dry mass at set intervals after herbicide application. Visual assessments indicated that residual atrazine caused 0%, 95%, 80%, 70%, 30% and 0% damage to the test plants at days -1, 1, 30, 60, 90 and 120, respectively. At corresponding stages after atrazine application, concurrent plant dry mass measurement showed that damage caused by residues was -2%, 86%, 90%, 65%, 51% and 0%, respectively (Table 31). Plant fresh weight data corresponded even better with the visual ratings. Both fresh and dry mass data indicated that amount of residues available to the test plant dropped significantly between days 30 and 60, and again between the latter stage and day 90. Lethal quantities of herbicide residues apparently persisted until about 90 days after application (Table 31).

Table 31 Persistence of atrazine in the field at different time intervals after application (ANOVA in Table 37A)

Days after treatment	Freshweight	Dry mass
	% damage	% damage
-1	1.0	-2.2
1	95.3	86.6
30	87.0	90.0
60	63.5	65.5
90	48.5	51.4
120	0.3	0.04
LSD_T (P=0.05)	13.8	12.1

Glasshouse bioassays

As the dose-response curves for days 1, 30, 60 and 90 were well matched (Figure 6), data from the dose-response bioassays were combined to derive a single equation that could be used throughout. The amount of phytotoxic atrazine residues in different soil layers at certain intervals after application was calculated with the equation:

$$y = 23.2 + 47.2\ (\log(100x)) \qquad \text{------ 5}$$

[where y = % damage in oats dry mass); x = amount of atrazine in soil (mg kg^{-1})]

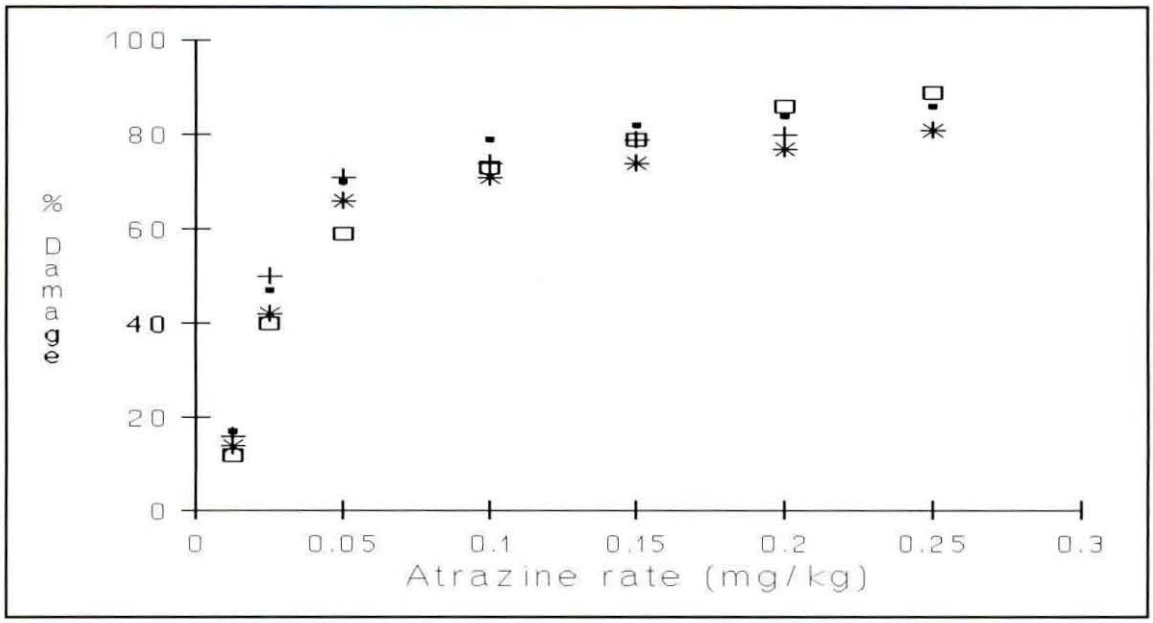

Figure 6 Dose-response curves derived from test plant response (percent reduction in top dry mass) to a range of atrazine rates in separate bioassays conducted in a glass-house at 1 (■), 30 (□), 60 (*) and 90 (+) days after atrazine application in the field

The estimated residual amount detected in the 0-100 mm soil layer was 0.177 mg atrazine ha^{-1} on day 1 after herbicide application (Table 32), which conforms well with the expected amount of about 0.179 mg kg^{-1}. The latter concentration was derived with expression [5] by taking into account the specific weight of the soil (i.e. 1.4 g cm^{-3}), and assuming that the atrazine applied in the field (i.e. 0.25 kg atrazine ha^{-1}) was distributed evenly in the top 100 mm soil layer.

$$x = \frac{0.25x10^6}{1.4x10^6}$$

[where x = mg atrazine kg^{-1} after application of 0.25 kg ai ha^{-1}]

Table 32 Percent damage caused by atrazine residues in soil sampled in different soil layers at certain stages after herbicide application, and the estimated amount of residue responsible for damage to the test plant (ANOVA's in Tables 38A & 39A)

	Damage (%) and estimated residue conc. (mg kg^{-1})									
	Soil layer (mm)									
Day	0-100		100-200		200-300		300-400		Mean	
	% damage	mg kg^{-1}	% damage	mg kg^{-1}	% damage	mg kg^{-1}	% damage	mg kg^{-1}	% damage	mg kg^{-1}
1	82	0.177	-	-	-	-	-	-	82	0.177
30	65	0.080	50	0.038	69	0.097	-	-	61	0.071
60	38	0.021	19	0.008	10	0.005	-	-	22	0.011
90	23	0.010	15	0.007	-2	0.003	-	-	12	0.007
120	3	0.004	17	0.007	9	0.005	22	0.010	13	0.007
$LSD_{T\ 0.05}$			**% damage**: Day x Depth = 15			**mg kg^{-1}**: Day x Depth = 0.033				

* Dash (-) denotes soil layer not monitored.

Thirty days after atrazine application in the field, concentrations causing reductions ranging from 50% to about 80% in the shoot dry mass of oats were detected in the 0-100 mm, 100-200 mm and 200-300 mm soil layers (Table 32; Figure 7a). The percentages damage recorded at that stage were transformed with the equation for the dose-response curves to 0.080, 0.038 and 0.097 mg atrazine kg^{-1} (in the 0-100 mm, 100-200 mm and 200-300 mm layers, respectively). This distribution pattern most likely resulted from 165 mm rainfall during the 30 day period after application (Figure 8). Disparity between the cumulative amount of atrazine residues present in the three soil layers monitored at day 30, and the amount applied at day 0, accentuate a restriction in the use of bioassays for quantifying herbicide residues. It is to be expected that the inherent biological variation in bioassays, and the multi-step methodology involved would make the procedure less accurate than chemical analysis. However, as pointed out earlier, bioassays allow plant-available residues to be estimated.

Beyond day 30, a further 180 mm of rainfall during the period ending on day 60 probably contributed to further reductions in the amount of atrazine residues in the respective layers to 0.021, 0.008 and 0.005 mg atrazine kg^{-1} (Table 32; Figure 7b). Results presented in Figures 7 & 8 indicate that atrazine leached quite rapidly in response to substantial rainfall. It is not only the total amount of rainfall which determines the leaching of a herbicide, but also the frequency and intensity of water received (Ammon, 1985).

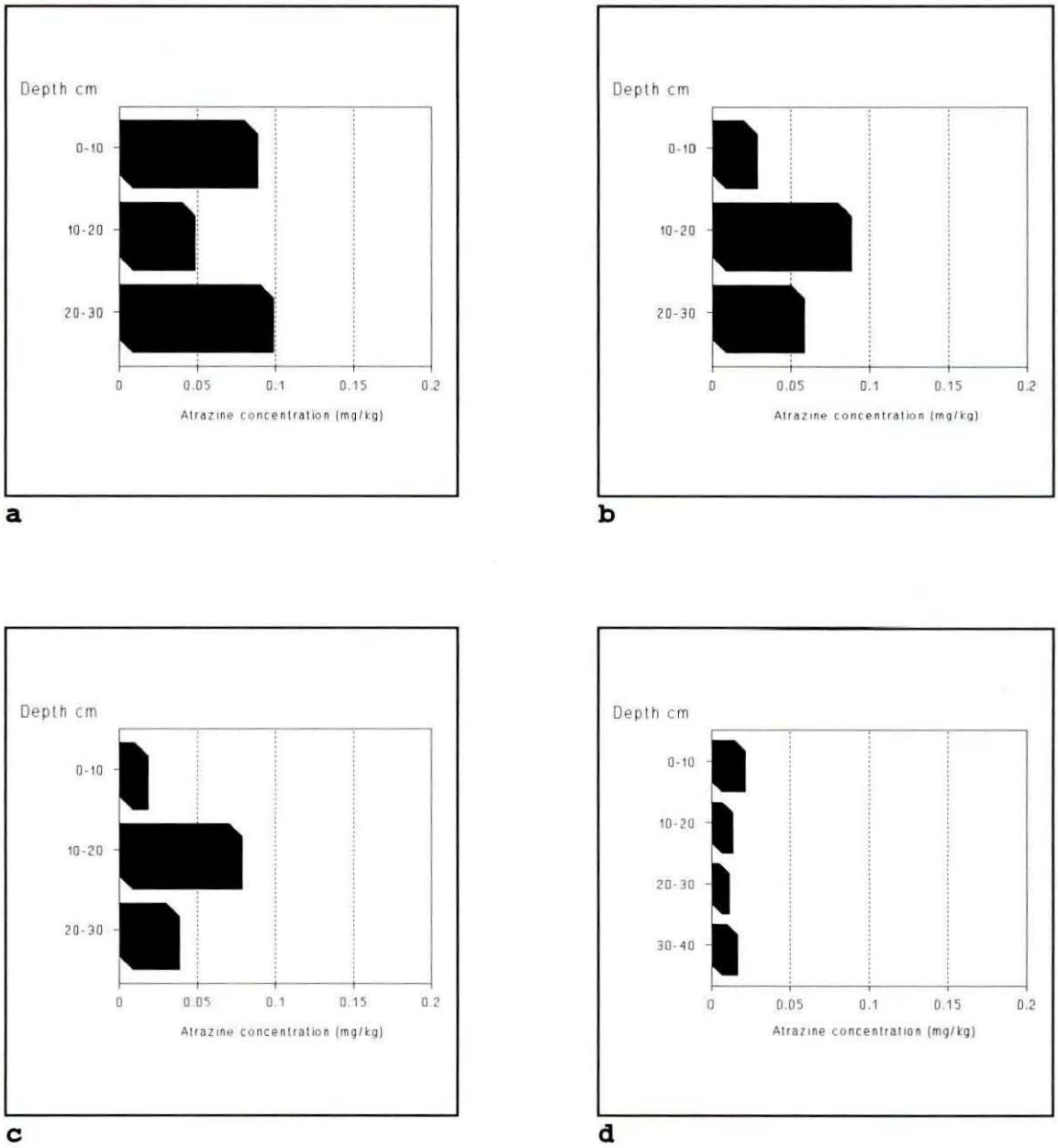

Figure 7 Leaching pattern of atrazine as depicted by estimated residual atrazine in different soil layers: (a) 30 days after treatment (d.a.t.); (b) 60 d.a.t.; (c) 90 d.a.t.; (d) 120 d.a.t.

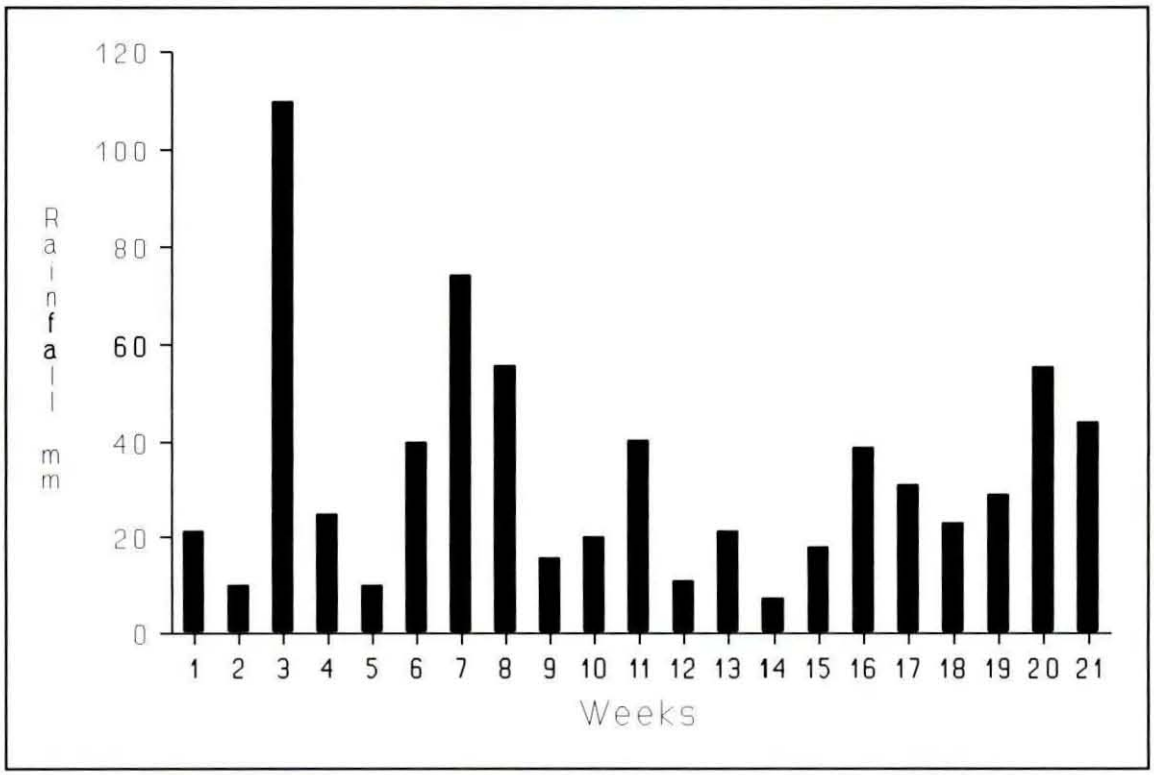

Figure 8 Total weekly rain and irrigation after atrazine application

Sampling on day 90 revealed a similar herbicide distribution pattern as that obtained 30 days previously (Figure 7c), but with reductions in residue concentration in all three soil layers tested (Table 32). On day 120, atrazine residues had decreased notably in the 100-200 mm and 200-300 mm soil layers from the levels detected 30 days previously, whilst little change in concentration was evident in the top soil layer (Table 24; Figure 7d). The upward movement of atrazine in capillary water in response to water evaporation from the soil surface as reported by Spencer & Cliath (1973) and Hubbs & Lavy (1990), could have been responsible for maintaining phytotoxic residues in the top soil layer for the duration of the experiment.

Phytotoxic atrazine residues (i.e. 5.6% of the amount applied) was also detected in the 300-400 mm soil layer at day 120 (Table 32; Figure 7d). From the results of previous bioassays it appears that atrazine residues might have been leached into the 300-400 mm layer earlier on in the experiment, due mainly to high rainfall during the 60 day period following herbicide application. The relatively low atrazine adsorption capacity of the soil (22% total clay of the kaolinite type; 0.31% C; pH 6.3) is expected to have contributed to the substantial leaching of the herbicide. According to Leonard *et al.* (1988), atrazine can be classified as moderately to slightly mobile in most soils. Dissipation of atrazine through leaching can be expected to accelerate under near neutral and alkaline soil conditions (McGlamery & Slife, 1965; Smit & Nel, 1977), particularly in soils with low adsorption capacities.

In the present study, application of a relatively small amount of atrazine (0.25 kg ha^{-1}) in the field made it possible to derive dose-response curves with a range of atrazine rates which elicited computable responses from the test plant. Experience gained in a previous study with the same atrazine rate and test plant on the same soil was useful for determining which herbicide rates to use in the present study. Without experience of the magnitude of a test plant's response to a given amount of a herbicide applied to a particular soil, the applicability of dose-response curves for quantifying herbicide residues could be disputed.

Ideally, dose-response curves should be obtained for each soil layer, since the availability of residues for plant uptake could conceivably be governed by differences

in certain soil properties (e.g. % clay, % C, nutrients and pH) down the soil profile. However, the number of observations required if dose-response curves for each soil layer at specific intervals after herbicide application are to be obtained is prohibitive. A collaborative study involving bioassays for monitoring the dissipation of metsulfuron-methyl and metribuzin in different soils was confronted with the same constraint (Krauskopf +25 others, 1991).

The bioassay technique proved useful for making projections of the amount of phytotoxic atrazine residues in different soil layers. It must be stressed, however, that the suitability of bioassays for quantifying atrazine residues could be tenuous under circumstances which differ from those that prevailed in the present study. There is agreement with the view of Krauskopf *et al.* (1991) that the technique does provide a relatively simple, time- and cost-effective procedure with which residual activities can be measured, thereby facilitating projections of the potential for sensitive follow-up crops to be injured.

As an alternative to direct measurements of the residual herbicide concentration in the root zone for defining the risk of carry-over, various computer simulation models are used to predict dissipation, as well as the likelihood of injury to sensitive following crops. A useful piece of input information is the half-life of a compound in a particular soil. Research reported in the following chapter was aimed at formulating a regression model based on the relationships between half-life of atrazine and selected soil properties.