CHAPTER 9

INFLUENCE OF SELECTED SOIL PROPERTIES ON THE PERSISTENCE AND HALF-LIFE OF ATRAZINE

Introduction

The persistence of herbicides and the availability of their residues for uptake by plants are important features of soil-applied compounds (Walker, 1991; Weber, 1991a,b). Many studies have therefore indirectly or directly focused on identifying compounds and conditions with which persistence problems are associated. Evidence in the literature and confirmation provided by work reported in previous chapters, identified soil pH as one of the important predictors of atrazine persistence. Soil pH exerts a strong influence on the adsorption and hydrolysis of atrazine. The bioavailability, mobility and stability of atrazine normally increase as soil pH increases.

Half-life values for herbicides are estimates of the length of time that a herbicide is present to exert an effect on plants. Weber (1991b) considers half-life values to be a relative index of the combined transformation processes involved in herbicide degradation. Leaching does not affect half-lives directly, but does contribute to the dissipation of a compound in soil. In the experiments reported on in this chapter, and glasshouse experiments reported earlier, leaching was eliminated. The objectives of the glasshouse experiments reported on here were: (a) to determine half-lives for atrazine in different soils by means of bioassays, and (b) to correlate atrazine half-life with selected soil properties.

A. Soil pH

Materials and Methods

Bioassays to assess the effect of soil pH on the persistence of atrazine were conducted in a glasshouse with soil samples of which essentially only the pH varied. Soil was collected at the Hatfield Experimental Farm of the University of Pretoria in plots of a long-term field trial which was conducted to evaluate the effects of soil acidity and liming on maize yield. Soil samples were taken from the top 200 mm soil layer in plots that had been treated annually with 2.25, 4.5 and 6.75 ton ha^{-1} pulverized calcitic lime (contains mainly $CaCO_3$ and less than 14% $MgCO_3$) for the past 15 years. Plots in which soil was collected were selected on the basis of pH(H_2O) levels that had been determined earlier for all plots. The aim was to obtain as wide a range of pH levels as possible within a limited number of soil samples. With the final selection of samples, six pH levels ranging from pH 4.8 to pH 7.0 were devised in a single soil. Selected properties of the six soil samples appear in Table 33.

Table 33 Selected properties of six samples of the loamy sand soil used in the study

Sample no.	Soil pH (H_2O)	% Clay	% C
1	4.8	20	0.31
2	5.3	18	0.28
3	5.5	22	0.33
4	5.7	19	0.34
5	6.3	18	0.29
6	7.0	18	0.29

The six soil samples were each treated with 0, 0.1 and 0.2 mg atrazine kg^{-1} on the day the experiment commenced, i.e. day 0. Pre-determined volumes of a 50 mg atrazine

L^{-1} solution were added to water, and a maximum of 30 cm^3 of this mixture was well mixed with the 500 g soil in each pot. Soil of control treatments (0 mg atrazine kg^{-1}) received 30 cm^3 water. Subsequently, additional water was added to attain 75% of the field capacity value of 17% (m/m). The soil water content at field capacity was determined gravimetrically. Pots were weighed immediately after watering to make allowance for subsequent replenishment of water losses through weighing. Soil was contained in plastic bags which prevented leaching.

Pots were allotted to each stage (days 0, 30, 60, 90 and 120 after treatment) at which a bioassay was to be done. The first bioassay was conducted on day 0, immediately after application of atrazine. Pots destined for bioassays at later stages were incubated in the dark at a constant 27/17°C (12/12 h day/night) temperature regime. Water loss during incubation was prevented by closing the plastic bags in which soil was held. Incubated pots were weighed weekly to check water loss, and when necessary, soil water content was adjusted with deionised water.

At each stage after atrazine application, pots destined for bioassaying were removed from incubation, and ten seeds of the test plant (oats cv SWK 001) were planted 20 mm deep in each pot. Those pots were moved to a glasshouse at a temperature regime of 27/17°C (12/12 h day/night regime) without supplemental lighting. Nutrients were supplied in the form of the nutrient solution of Nitsch (1972) which was applied in volumes of 50 cm^3 to all pots three times weekly. Plants were thinned to six in each pot after emergence and harvested fourteen days thereafter. Dry matter yield of the top growth was determined and expressed as percent damage (i.e. percent reduction in dry

matter relative to controls). Pots in the glasshouse and the adjoining darkroom were arranged in a completely random design with three replications. Standard analysis of variance was performed on percent damage data.

Use of a closed-system soil environment (leaching prevented) in the present experiment allowed the effects of leaching and soil pH to be separated. Another advantage of the procedure followed was the procurement of soil samples in which the pH was stabilised over several years. The use of a single soil in which essentially only the pH varied between samples (Table 33) afforded the rare opportunity to isolate the effect of this property from those of clay and organic matter content. It is unlikely that the slight variation in clay and organic matter contents between the soil samples used would have affected results.

The time span of this experiment (120 days) and the one reported on next (Experiment B - 150 days) was chosen in consideration of the conservation of biological activity in soils. Rates of atrazine degradation were shown to be markedly affected by the biological activity (biomass) of soils, with most rapid rates of loss occurring in fresh soil samples (Walker & Brown, 1981). It is generally accepted that prolonged incubation studies with pesticides should be avoided to conserve biological activity in soil (Anderson, 1987; Walker, 1989). Anderson (1987) concluded that incubation experiments with pesticides should be limited to a maximum duration of 90 days or until 50% of the biomass has been lost, whichever comes first.

Results and Discussion

Percentage reduction in dry mass of the test plant in response to atrazine, or its bioactive residues, over a 150-day period is presented in Table 34. Analysis of variance for percent reduction in dry mass detected significant interactions between soil pH, time and atrazine rate. The only effect that was not significant was the pH x Atrazine rate interaction, which indicated that the influence of soil pH on bioactivity resulting from application of either 0.1 or 0.2 mg atrazine kg^{-1} was similar.

The reduction in bioactivity of 0.1 mg atrazine kg^{-1} from day 0 to day 30 was significant at soil pH levels of 4.8, 5.3 and 5.5, but not at the higher pH levels of 5.7, 6.3 and 7.0 (Table 34). The time required for significant drops in activity of the 0.1 mg kg^{-1} rate to occur at the latter three pH levels increased with increasing soil pH. This trend was also evident for 0.2 mg atrazine kg^{-1}, with the difference that significant lowering of activity did not occur at either pH 6.3 or pH 7.0 at any stage after atrazine application.

The residual activity of atrazine at days 90 and 120 was not significantly different between pH levels of 4.8, 5.3 and 5.5 (Table 34). Residual activity at the latter pH level and pH 5.7 was similar at all stages after atrazine application. Initial differences in residual activity at pH 4.8, 5.3, 5.5 and 5.7 became progressively smaller from day 60 onward, and was eventually negligible at day 120. At days 90 and 120 the residual activity of both atrazine rates were significantly higher at pH 7.0 compared to activity at pH levels 4.8, 5.3, 5.5 or 5.7. At the same stages, differences in bioactivity between pH 6.3 and pH 7.0 were not significant.

Table 34 Effect of six soil pH levels on the residual activity of atrazine (based on percent reduction in dry mass of oats) in a sandy loam soil (ANOVA in Table 40A)

	Time (days after atrazine application)									
	0		30		60		90		120	
	Atrazine rate (mg kg^{-1})									
Soil pH (H_2O)	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2
	% damage		% damage		% damage		% damage		% damage	
4.8	74	83	19	62	1	13	0	14	-2	0
5.3	61	83	34	62	12	31	7	19	5	9
5.5	84	87	42	80	18	51	9	34	6	9
5.7	77	86	66	75	22	44	7	33	7	16
6.3	84	88	62	82	47	77	40	72	33	63
7.0	82	86	79	85	65	72	57	75	45	66
LSD_T (P=0.05)	pH x Time x Atrazine = 27									

Rough estimates of the half-lives of atrazine, based on comparison of the percentages reduction in dry mass on day 0 with those measured on specific days after application of 0.2 mg atrazine kg^{-1}, show that atrazine half-lives (x days) at different pH levels could be categorized as follows: $30 < x < 60$ at pH 4.8 and 5.3; $60 < x < 90$ at pH 5.5 and 5.7; $x > 120$ days at pH 6.3 and 7.0. As test plant response to atrazine rapidly declined below levels of 0.1 mg atrazine kg^{-1}, half-life estimates based on test plant response to residues of 0.1 mg kg^{-1} would be less accurate than approximations based on growth response to larger amounts of residues resulting from treatment with 0.2 mg atrazine kg^{-1}.

The effect of soil pH on the residual activity/persistence of atrazine first became apparent in the day 30 bioassay. This concurs with the findings of previous work in a glasshouse (Ehlers *et al.*, 1988) which indicated that the short-term bioactivity of atrazine (test species planted immediately after herbicide application) was not significantly influenced by soil pH. Results of the field study reported on in Chapter 4 also agree with the findings of Ehlers *et al.* (1988) as far as the activity of atrazine within 30 days of application is concerned. It was also shown in Chapter 5 that pH was an important predictor of atrazine bioactivity/persistence at 182 days after application. Results of the present study also appear to substantiate the extended persistence of atrazine that was found in the field in a montmorillonite clay type soil with pH 7.8 (see Chapter 6). In that soil, dissipation of atrazine would conceivably have been restricted by limited leaching due to the unique water-holding capacity of the soil type, and also by the high stability of atrazine at neutral pH levels (Armstrong *et al.*, 1967; Hiltbold

& Buchanan, 1977). Colbert *et al.* (1975) and Smit *et al.* (1979, 1980) reported that the adsorption and hydrolysis of atrazine generally decreased as soil pH was increased from relatively low pH to near neutral pH conditions.

B. Atrazine half-lives in 25 soils

Materials and Methods

Two sets of bioassays were conducted in a glasshouse.

Dose-response experiments

Experiments in the first grouping (Experiments I, II, III and IV) were conducted to obtain dose-response curves for each soil used. The equations that describe these best-fit curves (percent reduction in top growth dry mass plotted against atrazine concentration) were used for transforming residual bioactivity (expressed as percent reduction in top growth dry mass) in a soil into amount of bioactive residues present in that soil.

Differential dose thresholds for the test plant in different soils demanded that four ranges of atrazine rates be used for obtaining dose-response curves. Thus dose-response bioassays were grouped according to sets of soils treated with four ranges of rates (i.e. four experiments). The rates used appear in the sub-headings in Table 35. The choice of suitable atrazine rates (neither too high, nor too low) was based on preliminary experiments with some of the soils. A total of 34 soils were employed in these bioassays, but due to poor fit of data to dose-response curves and either too low

or too high bioactivity the data for 25 soils were eventually used. Certain key characteristics of those 25 soils appear in Table 35.

Table 35 Selected properties of the 25 soils used

Exp. I: Soils treated with the lowest range of atrazine rates (0, 0.002, 0.004, 0.008, 0.016, 0.032, 0.064, 0.128, 0.256 mg kg^{-1})

	Soil properties				
Locality	Clay %	% C	pH(H_2O)	P-reversion (mg P kg^{-1})	CEC cmol(+) kg^{-1}
Colby	11	0.18	5.5	115	2.98
Fairdale	10	0.18	5.8	100	2.14
Nelspruit	4	0.29	6.8	170	2.62

Exp. II: Soils treated with the first intermediate range of atrazine rates (0, 0.0125, 0.025, 0.05, 0.075, 0.1, 0.125, 0.15, 0.2 mg kg^{-1})

Locality	Clay %	% C	pH(H_2O)	P-reversion (mg P kg^{-1})	CEC cmol(+) kg^{-1}
Bethal	13	0.40	5.1	109	3.10
Bothaville	15	0.20	4.9	137	2.50
Ermelo A	9	0.38	4.8	92	1.80
Leeudstd. A	7	0.32	5.3	105	1.20
Leeudstd. B	8	0.40	7.1	93	3.00
Nylstroom	13	0.40	5.1	75	3.10
Pretoria A1	20	0.31	4.9	120	5.32
Pretoria A2	18	0.28	5.3	110	4.38
Pretoria A3	19	0.34	5.7	117	5.73
Pretoria A4	18	0.29	6.5	123	4.17
Pretoria A5	18	0.29	7.2	118	4.22
Warmbad A	35	0.50	7.8	83	26.60

Continued overleaf

Table 35 continued

Exp. III: Soils treated with the second intermediate range of atrazine rates (0, 0.025, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35 mg kg^{-1})

	Soil properties				
Locality	Clay %	% C	pH(H_2O)	P-reversion (mg P kg^{-1})	CEC cmol(+) kg^{-1}
Carletonville	21	0.83	5.3	130	5.31
Ermelo B	16	0.80	5.3	82	8.50
Morgenzon	21	0.47	6.4	65	12.48
Redhill	50	0.98	5.0	5	3.30
Vryheid	53	2.04	5.5	25	15.80

Exp. IV: Soils treated with the highest range of atrazine rates (0, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 mg kg^{-1})

Potgietersrus	27	0.65	7.2	90	10.37
Pretoria B	41	1.06	5.9	70	14.11
Roodeplaat	17	0.41	6.9	40	12.22
Utrecht	27	1.18	5.8	115	11.33
Warmbad B	55	0.77	7.5	20	54.43

Bioassays for determining the degradation rates of atrazine

The second category of bioassays involved periodic measurement of bioactivity of atrazine residues in soils that were incubated for specific periods after treatment with 0.2 mg atrazine kg^{-1} on day 0. Except for those pots designated for bioassaying on day 0, all pots were incubated in the dark for specific intervals. The rate of 0.2 mg atrazine kg^{-1} was attained by mixing a pre-determined volume of a 50 mg atrazine L^{-1} stock solution with 500 g soil in each pot. Water only was added to the controls. Soil in pots were contained in plastic bags to prevent leaching of the herbicide out of the soil. Soils removed from incubation were thoroughly mixed before the test species was planted.

At specific intervals (30, 60, 90, 120 and 150 days after atrazine application), pots were removed from the incubator and bioassayed with oats (cv SWK 001). Atrazine half-life (days) in each soil were estimated by transforming the percentage reduction in top growth dry mass, which was recorded 0, 30, 60, 90, 120 and 150 days after herbicide application, to mg atrazine kg^{-1} soil by means of the logarithmic equation (see Appendix C) for each soil. This transformation involved entering the percentage reduction in dry mass (i.e. the dependent variable y) that was obtained for a certain soil, at a specific stage after application, in the dose-response equation for that soil, and solving the equation for mg atrazine kg^{-1} soil (i.e. x in the equation).

As bioactivity caused by 0.2 mg atrazine kg^{-1} varied from soil to soil, and from one stage of measurement to the next, it was necessary to dilute the amount of herbicide in

the incubated soils so as to ensure a measurable plant response. Dilution ratios of 100:0 (500 g treated soil:0 g untreated soil), 50:50 (250 g treated:250 g untreated) and 25:75 (125 g treated:375 g untreated) were brought about by mixing untreated soil with treated samples. The dilutions made it possible to avoid the insensitive extreme ends of dose-response curves when data (% reduction in growth) were transformed to herbicide amounts. The amounts of phytotoxic residues that were estimated with the 25:75 and 50:50 soil dilutions were transformed to full (100%) concentrations by multiplying the amounts estimated in the diluted soil by four and two, respectively.

Degradation rates in the 25 soils over the 150 day period were best described by the quadratic formula $y = ax^2 + bx + c$. Atrazine half-life in each of the 25 soils were estimated by means of these equations by calculating x (half-life in days) after inserting the value 0.1 (i.e. half the amount of atrazine applied) as the dependent variable (y). Regression analysis was performed on half-life data according to the Stepwise Procedure in the SAS programme, with the aim to identify variables (soil properties) for inclusion in a multiple regression model for the prediction of atrazine half-lives in soils. The real values of the soil variables (x), as well as their squares (x^2) were correlated with half-life data, in order to distinguish between linear and non-linear relationships.

General

Environmental conditions in the glasshouse were the same for both categories of bioassays. Water content of the soils in which the test plant was grown was adjusted

to 75% of the total water content per pot at field capacity by weighing pots on alternate days. The water content of the incubated soils was checked fortnightly. A volume of 30 cm^3 of the nutrient solution of Nitsch (1972) was applied to pots with test plants on days not designated for weighing of pots. A constant day/night temperature of 27/17°C (± 1°C) was maintained for a 12/12 h thermoperiod in a glasshouse. The same temperatures were maintained in the interconnected darkroom in which pots were incubated. Supplemental lighting was used to extend the daylight period in the glasshouse to a minimum of 12 hours. The growth period was 21 days, from seeding until harvesting of seedling top growth. The dry mass yield in each pot was calculated on a per plant basis (six plants per pot). Data were expressed as percent damage, i.e. percent reduction in shoot dry mass compared to untreated controls. Pots were arranged according to a completely randomized design in all the experiments. All treatments were replicated three times.

Results and Discussion

Logarithmic regression lines gave the best fit for dose-response data presented in Table 21B. The dose-response curves for the 25 soils are illustrated in Figures 1C-25C in Appendix C (p. 250). The amounts of phytotoxic atrazine residues that were estimated by means of the dose-response equations on days 0, 30, 60, 90, 120 and 150 after treatment are presented in Table 36. Analysis of variance of residual concentration data detected a significant Soil x Time (days) interaction. The atrazine concentration in most soils on day 0 was predicted fairly accurately, considering the inherent variation encountered in bioassays.

Table 36 Estimated amounts of atrazine, or its phytotoxic residue(s), which were available to the test plant at specific intervals after application (ANOVA in Table 45A)

	Number of days after atrazine application					
Locality	0	30	60	90	120	150
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Bethal	0.167	0.150	0.069	0.073	0.020	0.013
Bothaville	0.226	0.161	0.052	0.035	0.042	0.001
Carletonville	0.207	0.163	0.119	0.036	0.034	0.026
Colby	0.238	0.170	0.068	0.085	0.031	0.009
Ermelo A	0.161	0.124	0.080	0.025	0.009	0.000
Ermelo B	0.176	0.152	0.116	0.104	0.061	0.028
Fairdale	0.162	0.160	0.086	0.079	0.055	0.003
Leeudrgstd. A	0.149	0.165	0.093	0.031	0.043	0.006
Leeudrgstd. B	0.224	0.161	0.141	0.064	0.050	0.030
Morgenzon	0.217	0.168	0.091	0.079	0.031	0.033
Nelspruit	0.167	0.171	0.108	0.122	0.064	0.067
Nylstroom	0.163	0.156	0.069	0.072	0.019	0.009
Potgietersrus	0.177	0.189	0.167	0.110	0.112	0.062
Pretoria A1	0.190	0.171	0.061	0.061	0.045	0.009
Pretoria A2	0.167	0.133	0.047	0.013	0.035	0.010
Pretoria A3	0.227	0.133	0.121	0.089	0.026	0.025
Pretoria A4	0.222	0.146	0.142	0.046	0.052	0.011
Pretoria A5	0.192	0.190	0.137	0.089	0.088	0.015
Pretoria B	0.162	0.174	0.147	0.062	0.071	0.038
Redhill	0.185	0.170	0.065	0.081	0.045	0.008
Roodeplaat	0.206	0.179	0.116	0.095	0.071	0.050
Utrecht	0.224	0.163	0.152	0.051	0.067	0.022
Vryheid	0.168	0.179	0.121	0.086	0.074	0.025
Warmbad A	0.209	0.161	0.156	0.106	0.122	0.056
Warmbad B	0.193	0.157	0.162	0.166	0.067	0.090
LSD_T (0.05)			Soil x Days = 0.069			

The rate of degradation of atrazine in each of the 25 soils is illustrated in Figures 9-33. The r^2-values shown in Figures 9-33 were invariably significant at the 5% level. Differential degradation rates between soils can be best judged from the half-life data presented in Table 37.

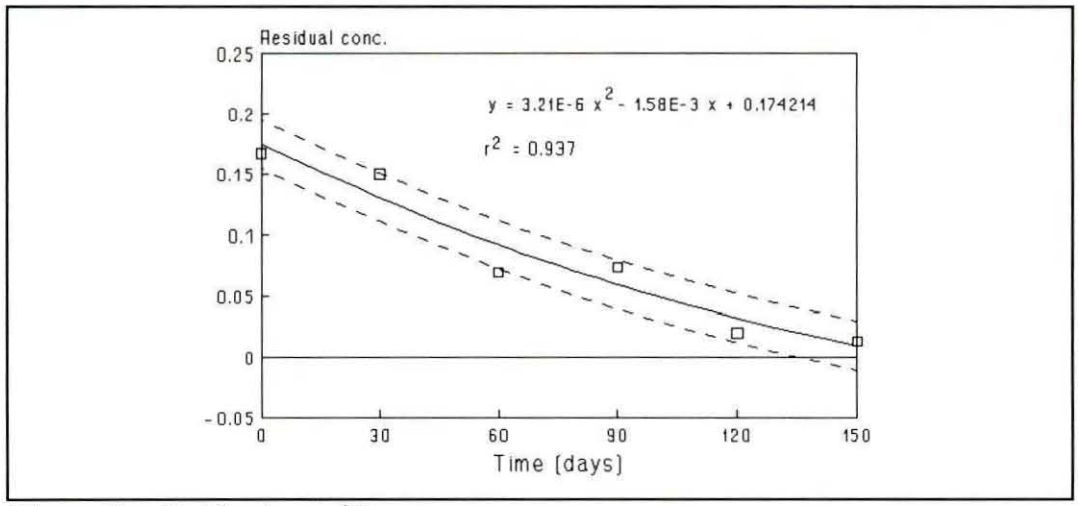

Fig. 9 Bethal soil

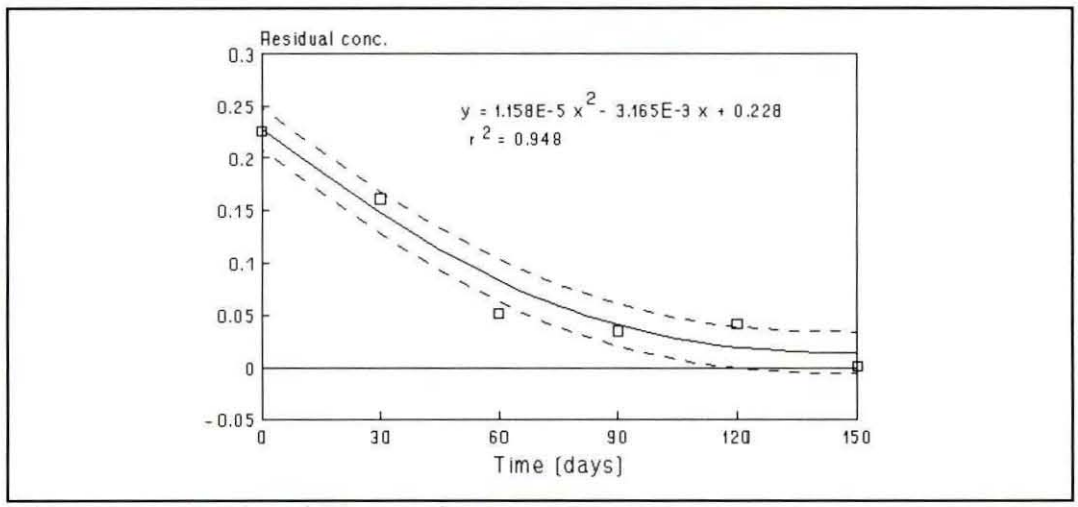

Fig. 10 Bothaville soil

Figure 9 & 10 Rate of atrazine degradation in the Bethal and Bothaville soils (Broken lines denote quadratic relationships for upper and lower 95% confidence limits)

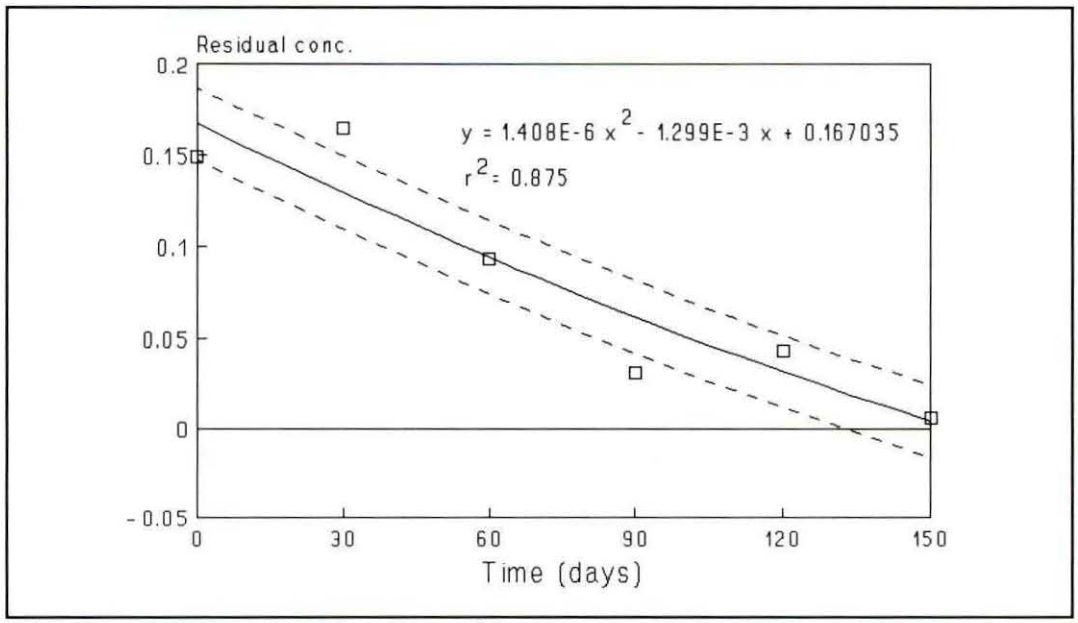

Fig. 11 Leeudrgst. A soil

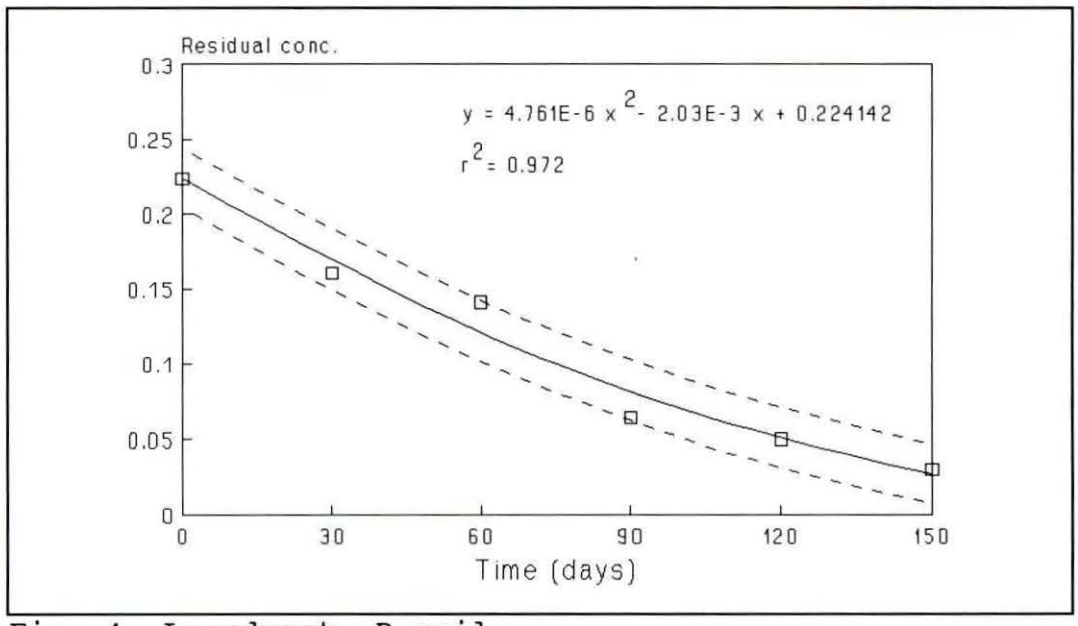

Fig. 4 Leeudrgst. B soil

Figures 11 & 12 Rate of atrazine degradation in the Leeudoringstad A and Leeudoringstad B soils

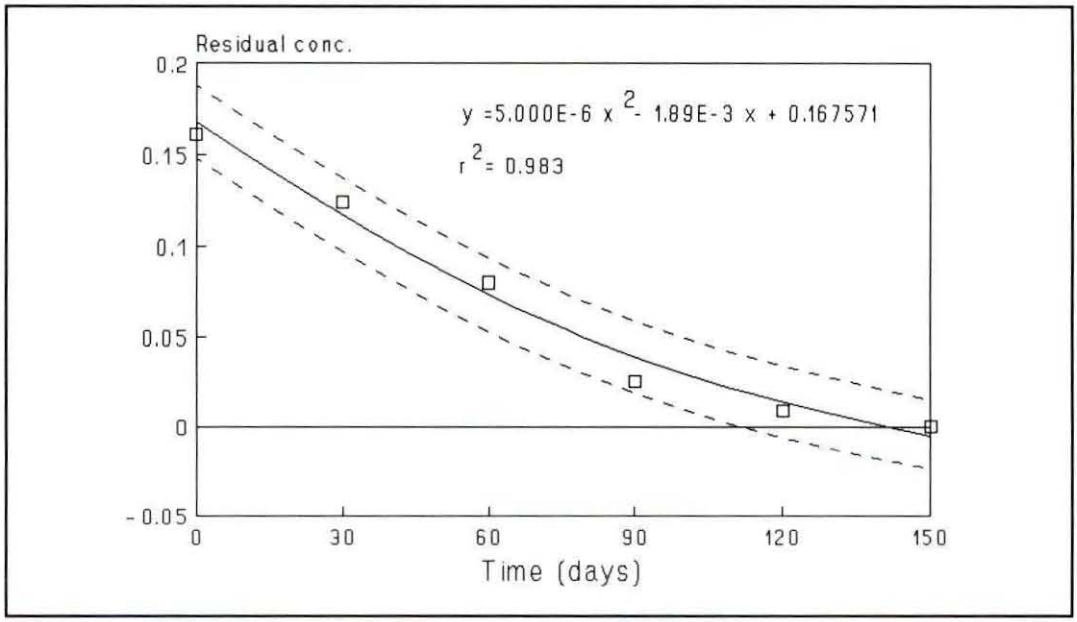

Fig. 13 Ermelo A soil

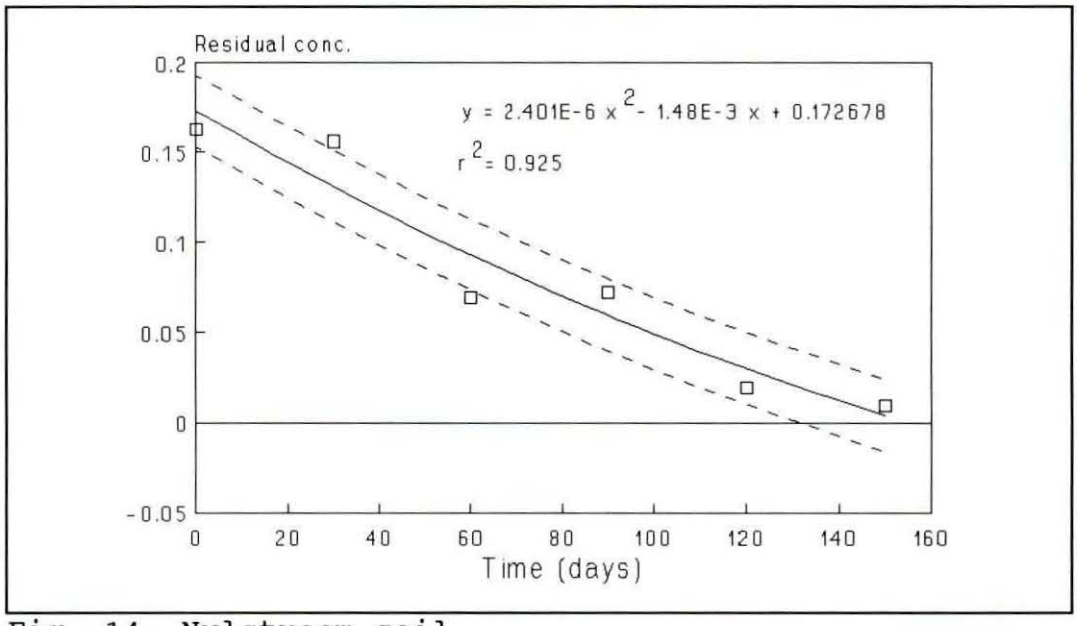

Fig. 14 Nylstroom soil

Figures 13 & 14 Rate of atrazine degradation in the Ermelo A and Nylstroom soils

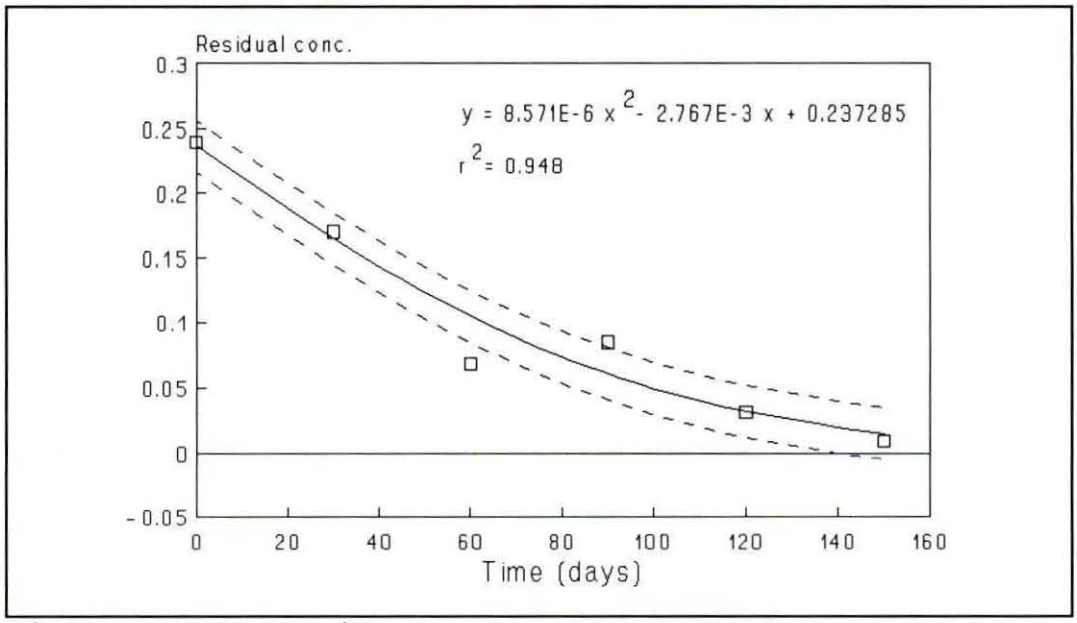

Fig. 15 Colby soil

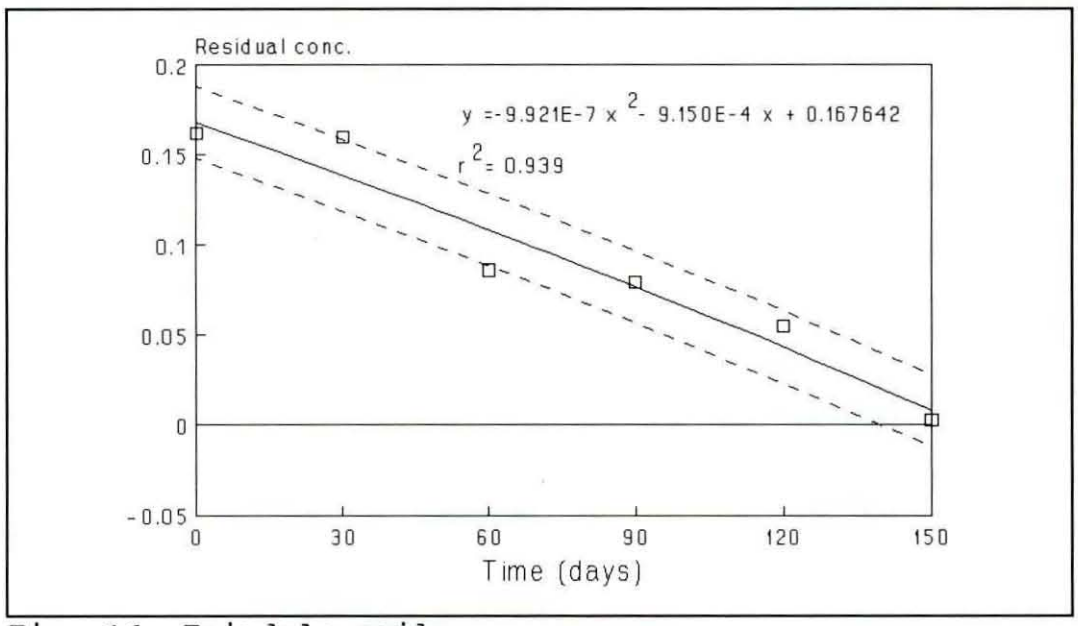

Fig. 16 Fairdale soil

Figures 15 & 16 Rate of atrazine degradation in the Colby and Fairdale soils

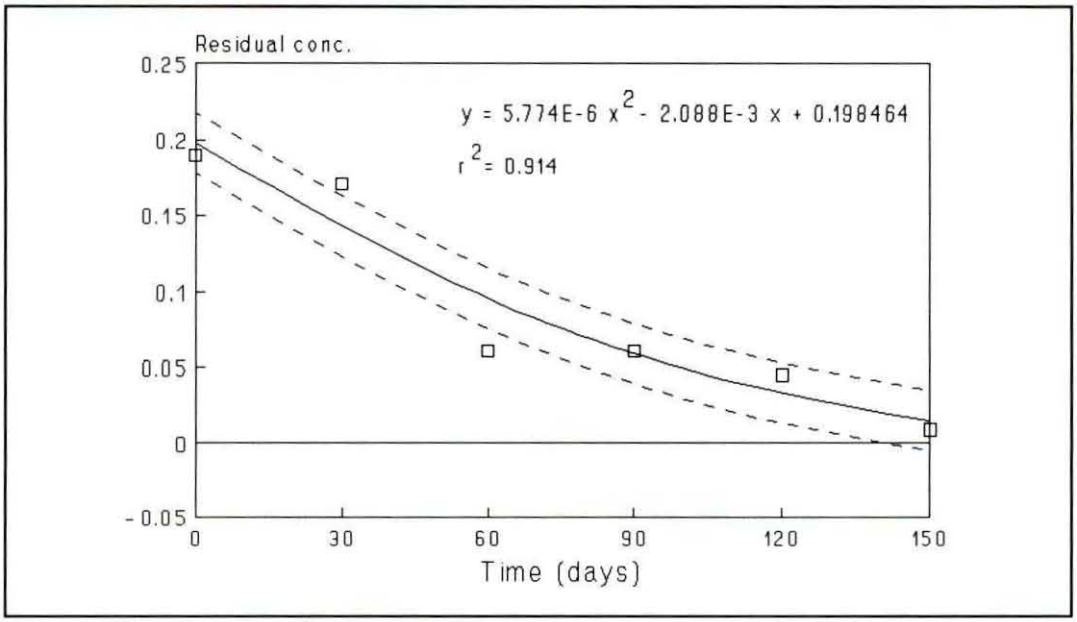

Fig. 17 Pretoria A1 soil

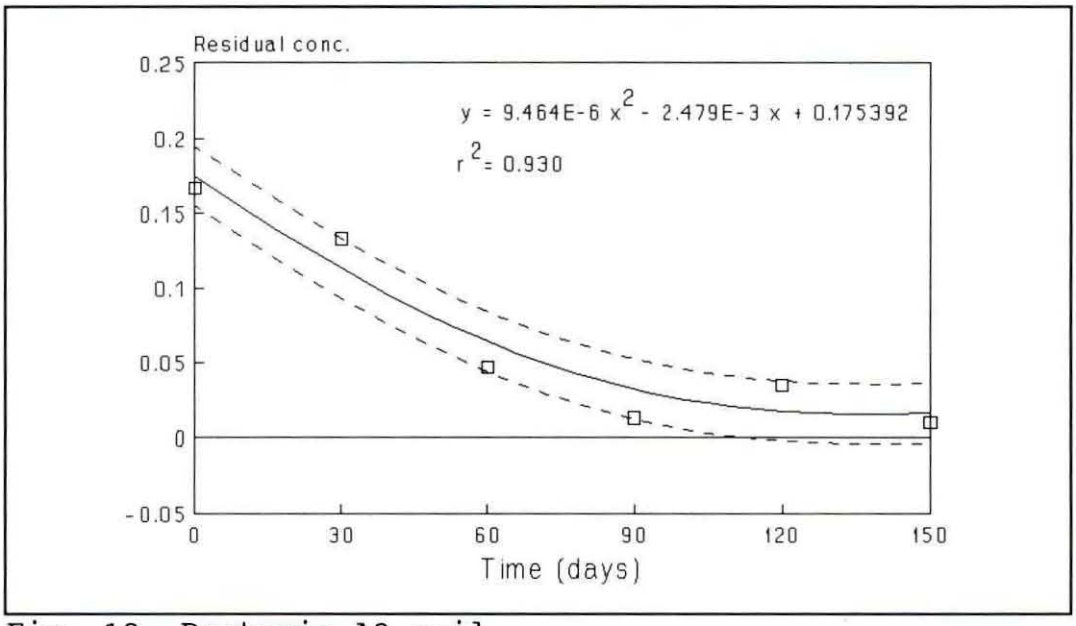

Fig. 18 Pretoria A2 soil

Figures 17 & 18 Rate of atrazine degradation in the Pretoria A1 and Pretoria A2 soils

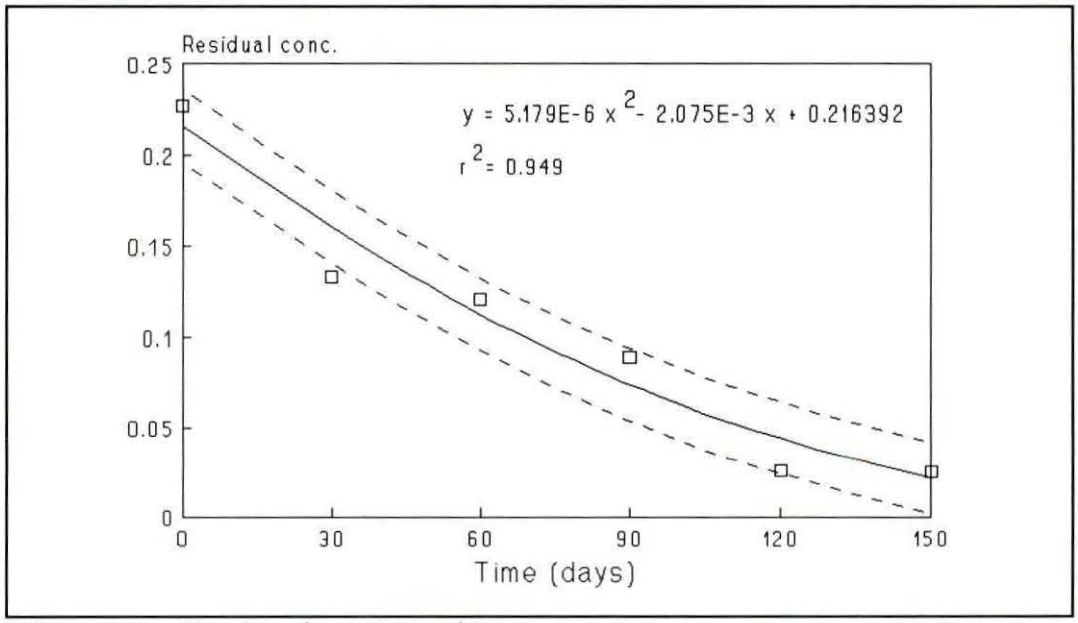

Fig. 19 Pretoria A3 soil

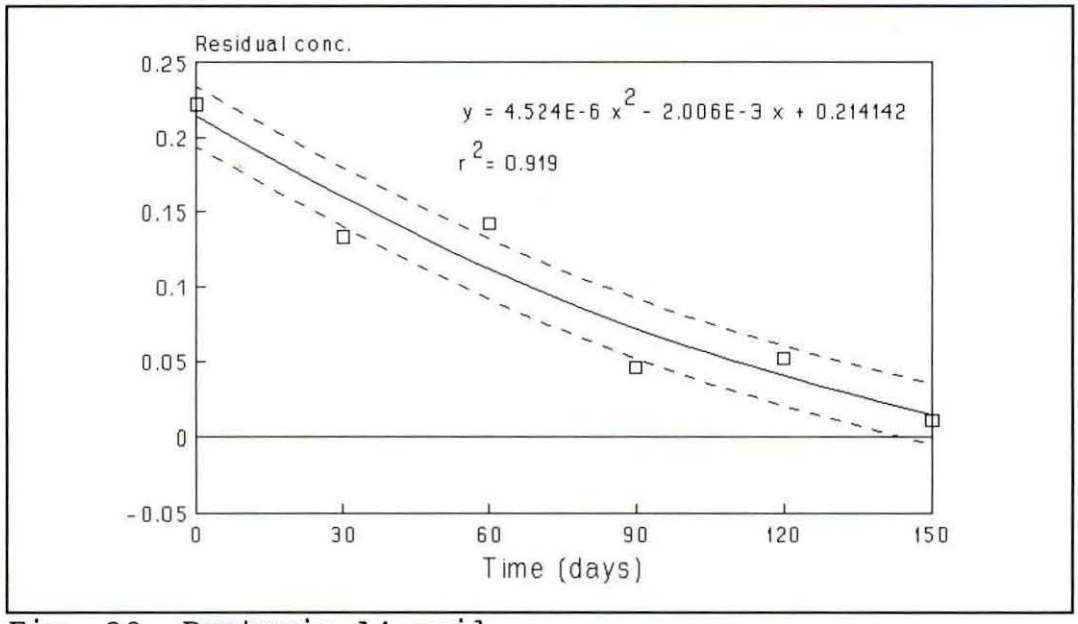

Fig. 20 Pretoria A4 soil

Figures 19 & 20 Rate of atrazine degradation in the Pretoria A3 and Pretoria A4 soils

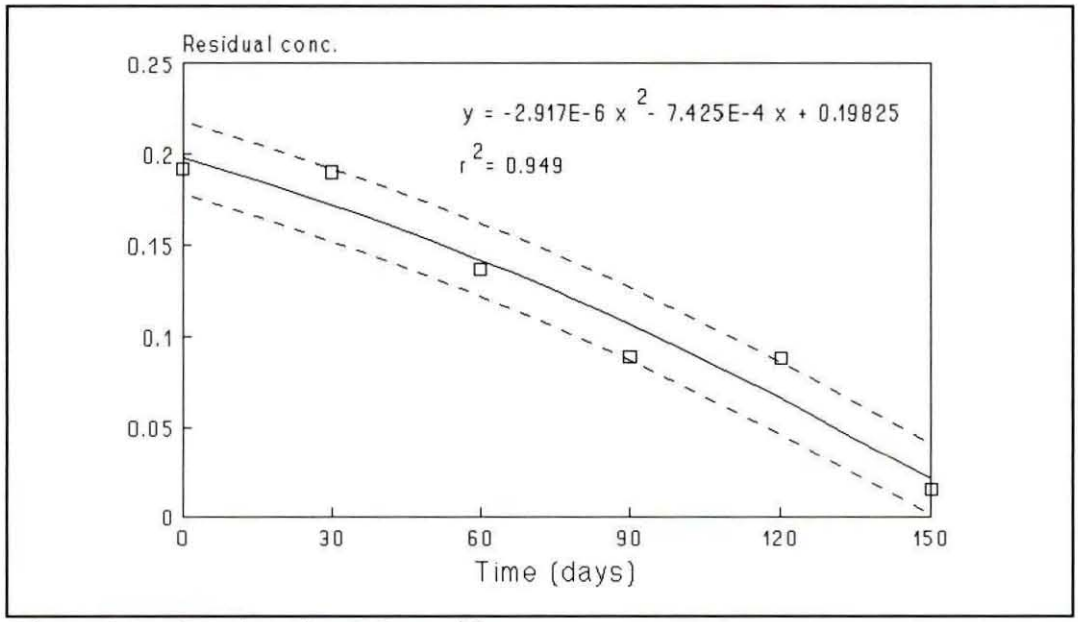

Fig. 21 Pretoria A5 soil

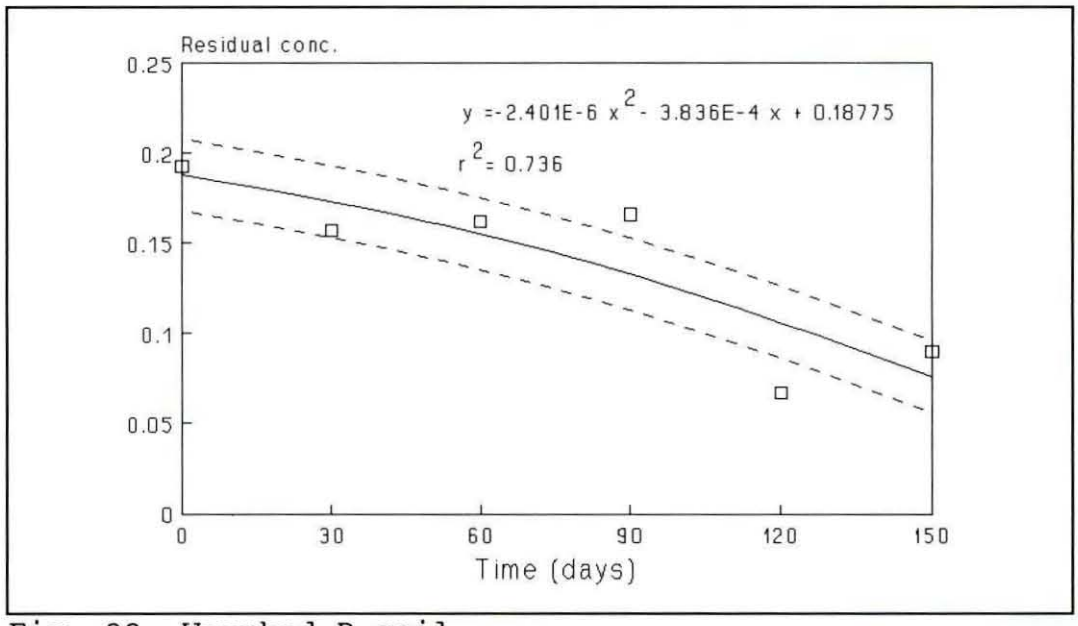

Fig. 22 Warmbad B soil

Figures 21 & 22 Rate of atrazine degradation in the Pretoria A5 and Warmbad B soils

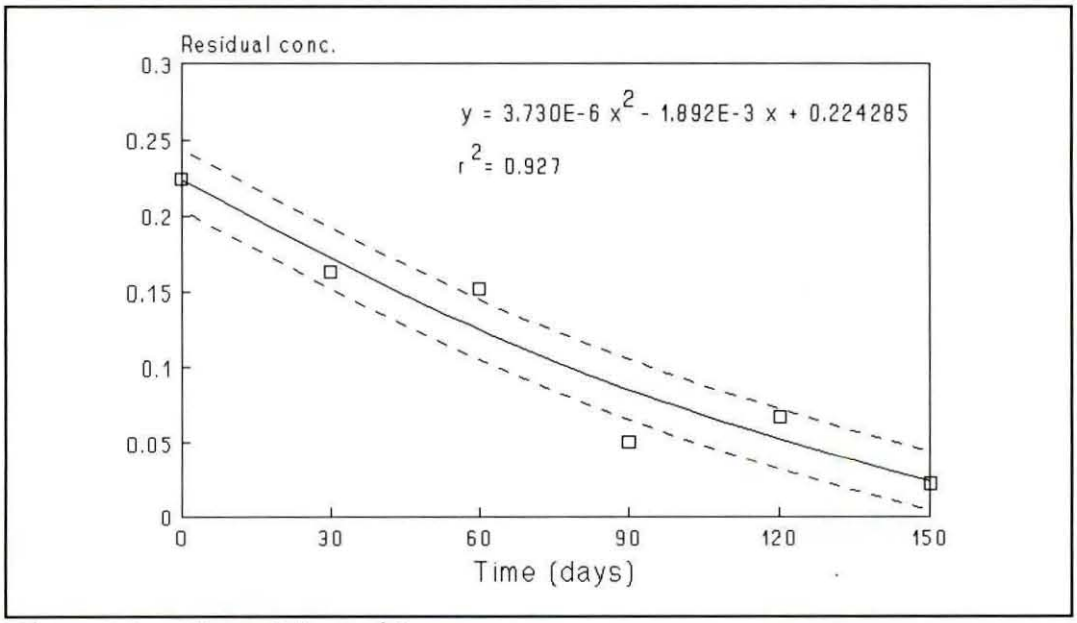

Fig. 23 Utrecht soil

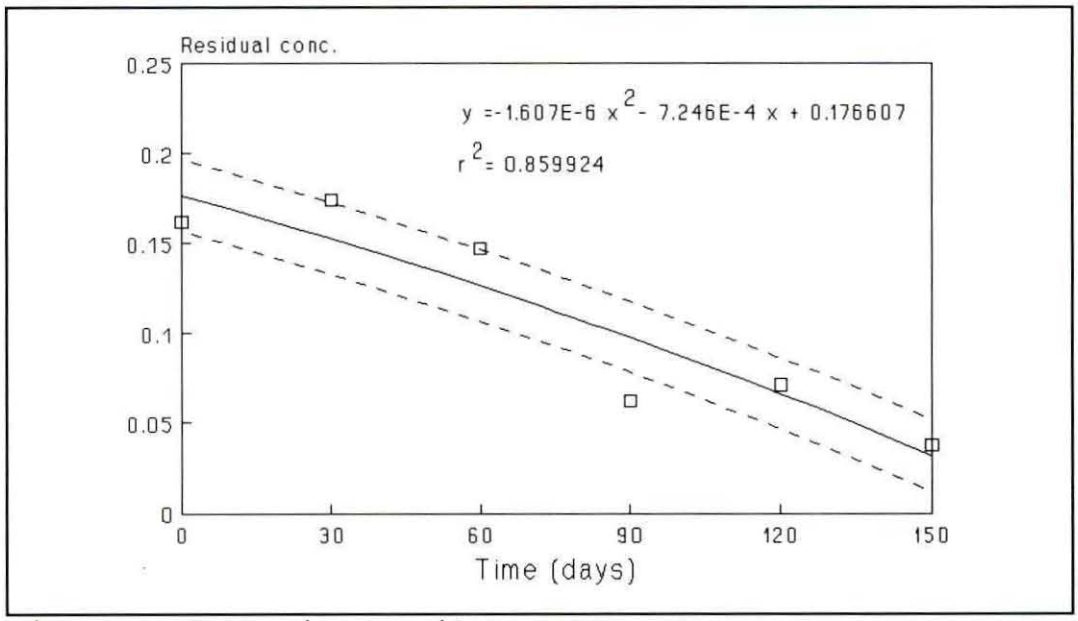

Fig. 24 Pretoria B soil

Figures 23 & 24 Rate of atrazine degradation in the Utrecht and Pretoria B soils

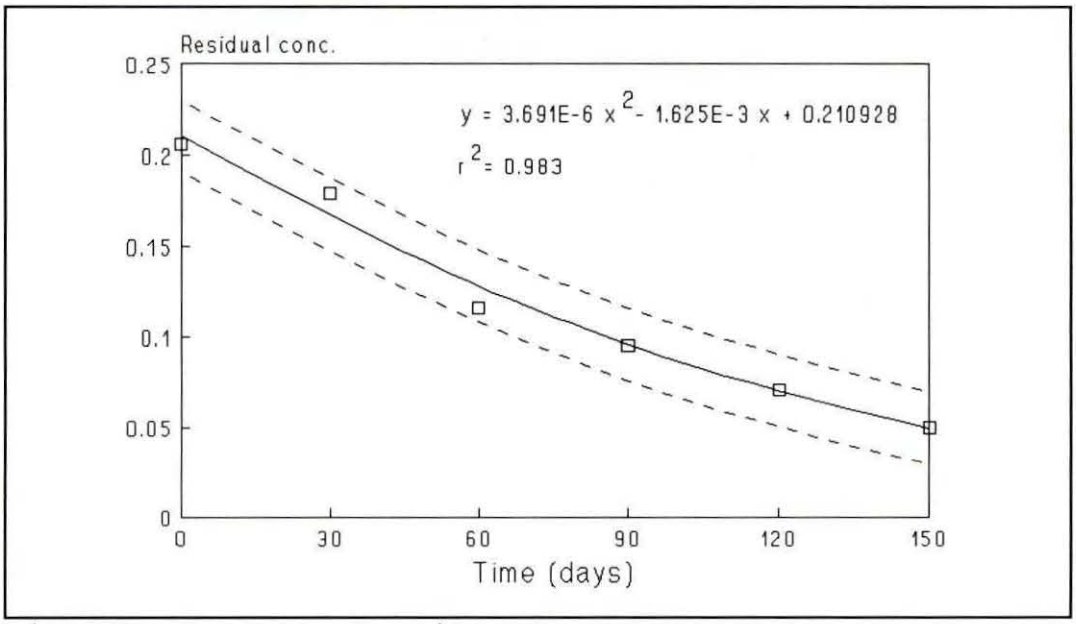

Fig. 25 Roodeplaat soil

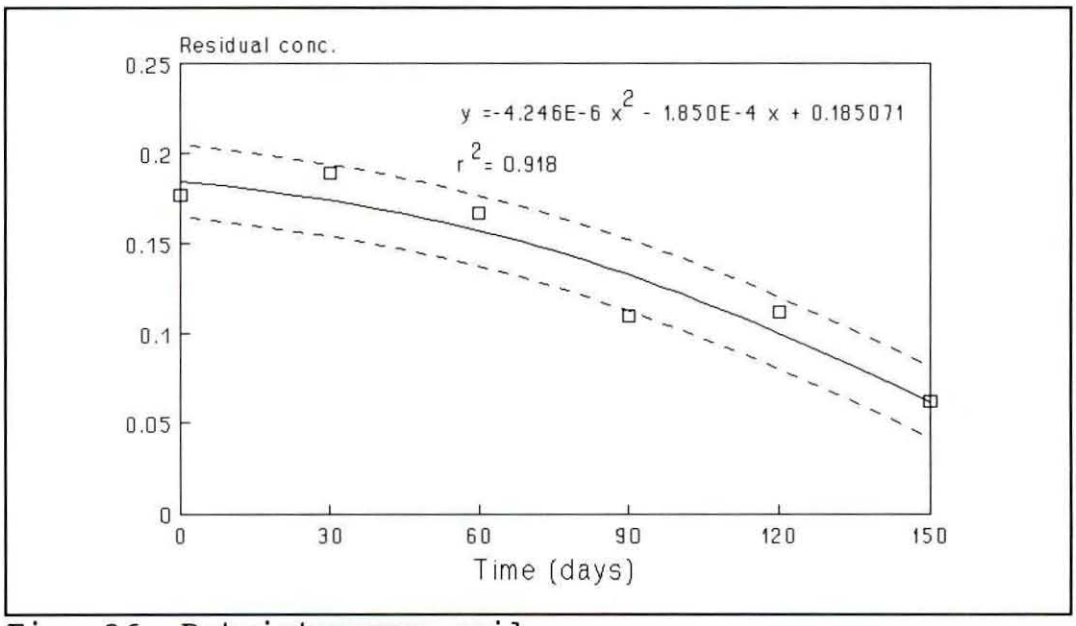

Fig. 26 Potgietersrus soil

Figures 25 & 26 Rate of atrazine degradation in the Roodeplaat and Potgietersrus soils

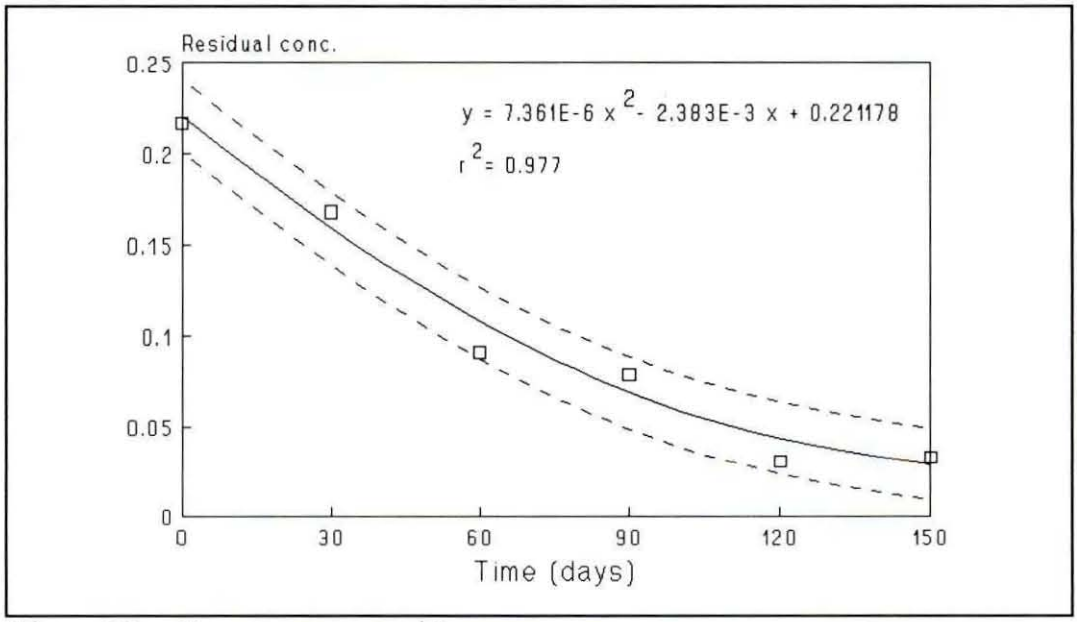

Fig. 27 Morgenzon soil

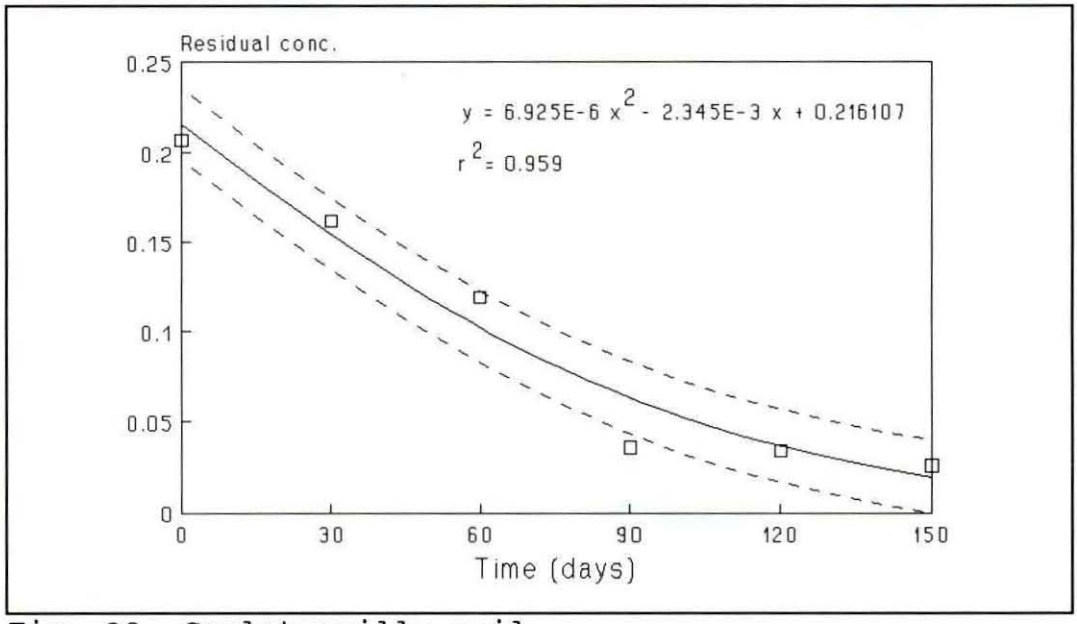

Fig. 28 Carletonville soil

Figures 27 & 28 Rate of atrazine degradation in the Morgenzon and Carletonville soils

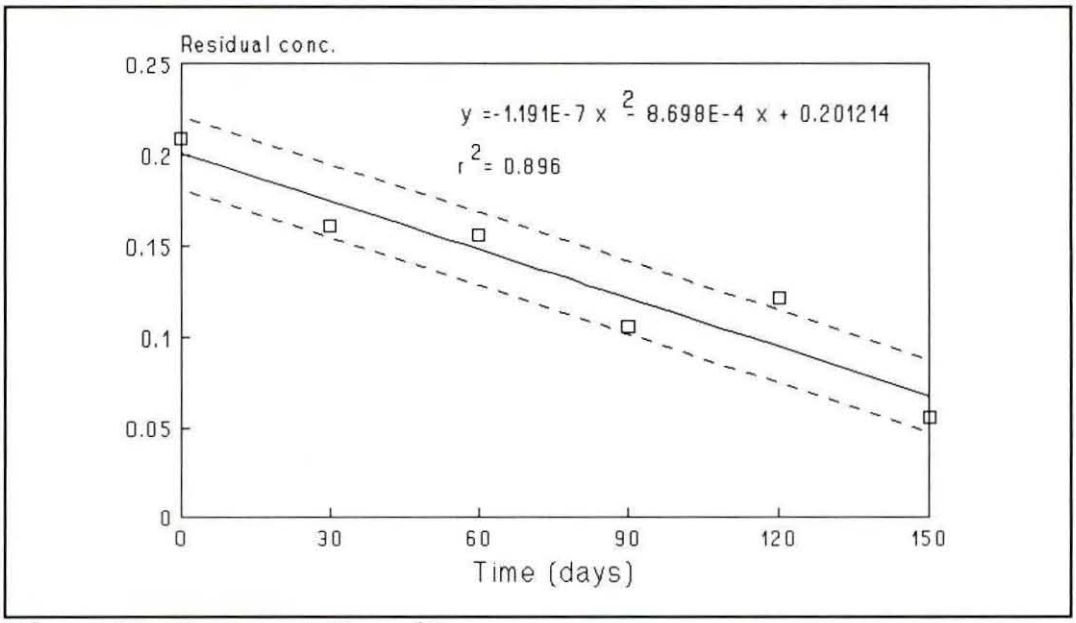

Fig. 29 Warmbad A soil

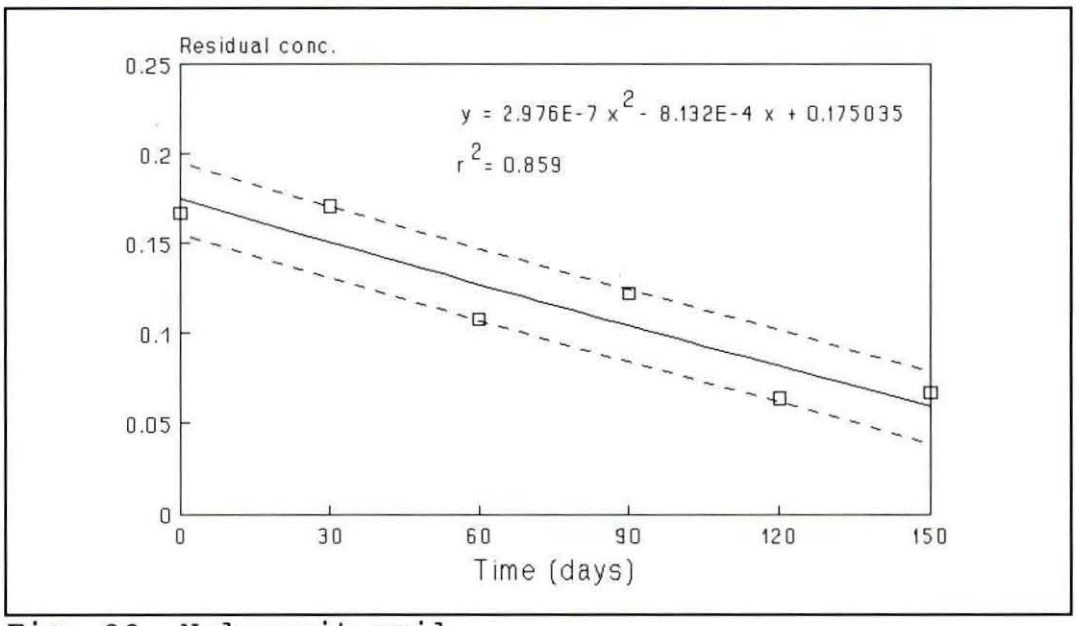

Fig. 30 Nelspruit soil

Figures 29 & 30 Rate of atrazine degradation in the Warmbad A and Nelspruit soils

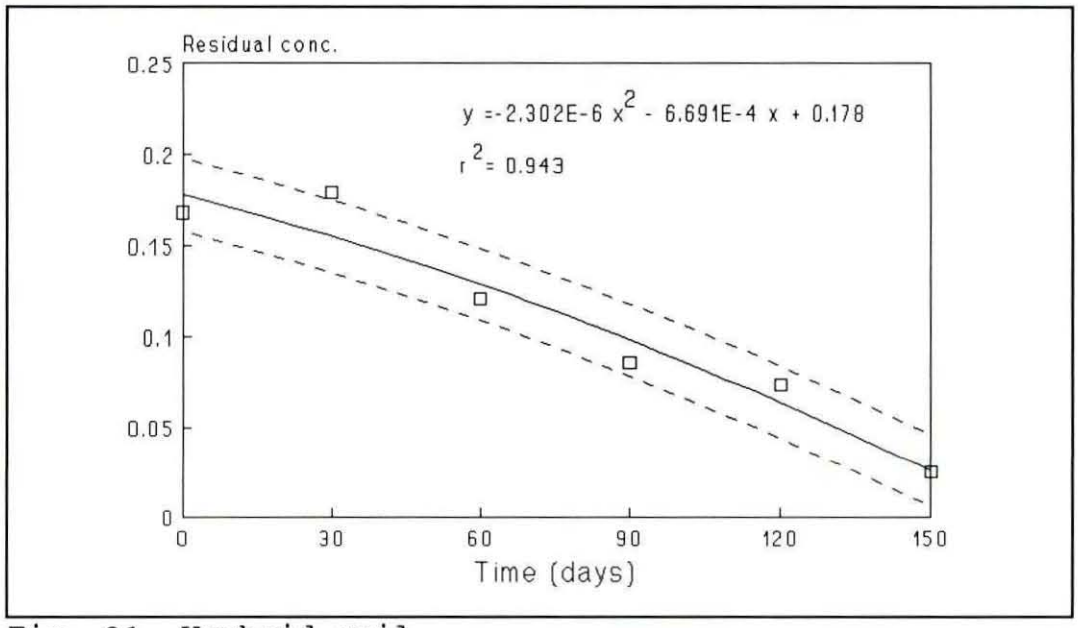

Fig. 31 Vryheid soil

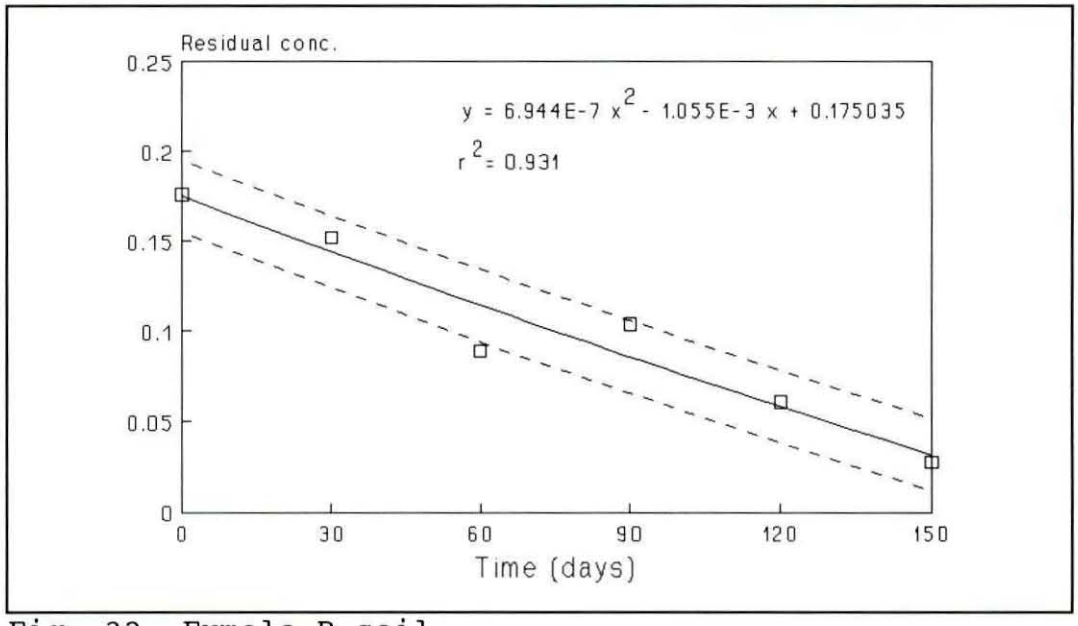

Fig. 32 Ermelo B soil

Figures 31 & 32 Rate of atrazine degradation in the Vryheid and Ermelo B soils

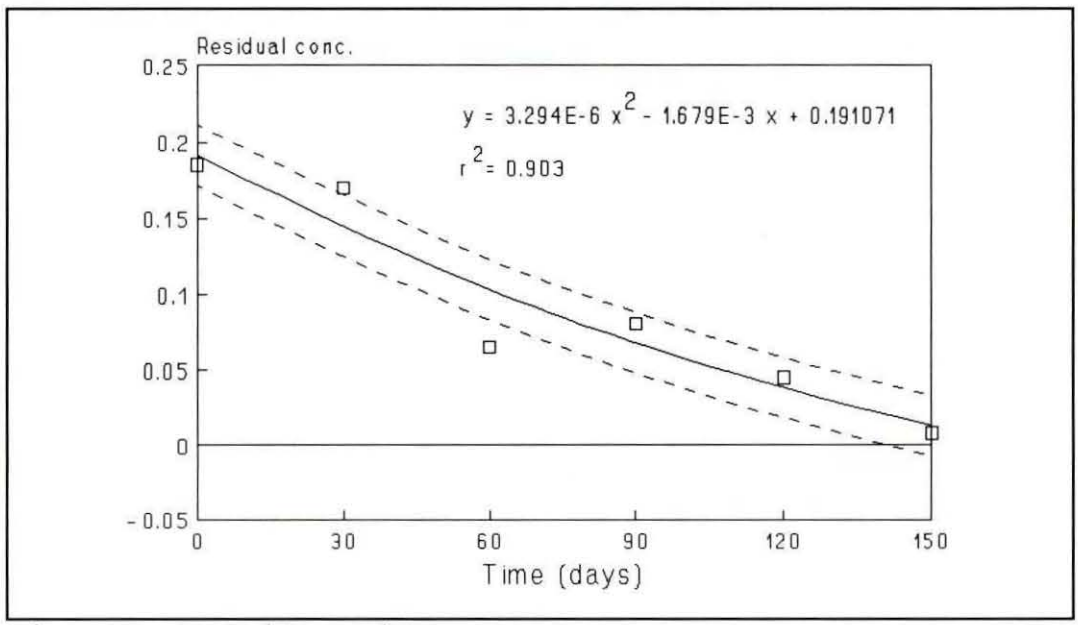

Fig. 33 Redhill soil

Figure 33 Rate of atrazine degradation in the Redhill soil

Considering the methodology employed, the quadratic regression lines fitted the data fairly well. The confidence bands indicate that the variation in the estimated half-life of atrazine can be substantial (Figures 9-33). The atrazine half-lives that were estimated by means of the quadratic formula for each soil (Figures 9-33) are given in Table 37.

Table 37 Atrazine half-lives extrapolated from Figures 9-33

Soil	Half-life (days)	Soil (cont.)	Half-life (days)	Soil (cont.)	Half-life (days)
Bethal	63	**Morgenzon**	78	**Redhill**	69
pH 5.1/0.40% C		pH 6.4/0.47% C		pH 5.0/0.98% C	
Bothaville	54	**Nelspruit**	107	**Roodeplaat**	102
pH 4.9/0.20% C		pH 6.8/0.29% C		pH 6.9/0.41% C	
Carletonville	63	**Nylstroom**	58	**Pretoria B**	86
pH 5.3/0.83% C		pH 5.1/0.40% C		pH 5.9/1.06% C	
Colby	75	**Potgietersrus**	102	**Utrecht**	81
pH 5.5/0.18% C		pH 7.2/0.65% C		pH 5.8/1.18% C	
Ermelo A	50	**Pretoria A1**	57	**Vryheid**	88
pH 4.8/0.38% C		pH 4.9/0.31% C		pH 5.5/2.04% C	
Ermelo B	85	**Pretoria A2**	50	**Warmbad A**	120
pH 5.3/0.8 % C		pH 5.3/0.28% C		pH 7.8/0.50% C	
Fairdale	71	**Pretoria A3**	71	**Warmbad B**	147
pH 5.8/0.18% C		pH 5.7/0.34% C		pH 7.5/0.77% C	
Leeudrgstd. A	64	**Pretoria A4**	75		
pH 5.3/0.32% C		pH 6.5/0.29% C			
Leeudrgstd. B	86	**Pretoria A5**	85		
pH 7.1/0.40% C		pH 7.2/0.29% C			

The half-lives that were determined for atrazine in different soils (Table 37) demonstrate the appreciable effect that soil type can have on rates of degradation. As all experimental conditions, except soil type, are considered to have been equal, the variation in atrazine half-life between soils is ascribed to differences in soil properties

which affect atrazine persistence. Results of the Stepwise Procedure that was used to identify the soil characteristics which give the best prediction of atrazine half-life appear in Table 38.

Table 38 Summary of the Stepwise Procedure that was used for determining the model which gives the best prediction of the dependent variable, atrazine half-life (The complete procedure is given in Table 46A)

	Variable (soil property)					
Step no.	Entered	Removed[1]	Partial R^2	Model R^2	F-value	Prob > F
1	$(pH)^2$		0.6939	0.6939	52.13	0.0001
2	% C		0.1331	0.8270	16.93	0.0005
3	$(CEC)^2$		0.0162	0.8432	2.17	0.1558
4		$(CEC)^2$	0.0162	0.8270	2.17	0.1558

[1]All variables left in the model are significant at the 5% level. No other variables met the required significance level for entry into the model.

The best predictor of atrazine half-life was the square of soil pH (partial $r^2=0.69$)(Table 38). This indicated that soil pH was not linearly correlated with the half-life of the herbicide. The next best predictor was soil organic matter (partial $r^2=0.13$). The Stepwise Procedure eliminated all other variables from the multiple regression model for prediction of atrazine half-life (Table 38). Thus the model giving the best prediction of half-life, with a model R^2-value of 0.8270, included only the square of soil pH and organic matter content (% C).

The multiple regression model which best described atrazine half-life in soil was the following:

$$y = -2.29 + 1.77x_1 + 20.81x_2$$

[where y = half-life in days; x_1 = [soil pH(H_2O)]^2; x_2 = % C]

The important role shown for soil pH (Table 38) substantiates those results reported in section A of this chapter and those presented in Chapter 5. It is abundantly clear that soil pH was the main determinant of atrazine persistence. This finding concurs with those of many authors who reported that the stability of atrazine against hydrolysis to inactive hydroxyatrazine increases progressively as soil pH increases to around neutral (Armstrong *et al.*, 1967; Jordan, Farmer, Goodin & Day, 1970; Best & Weber, 1974 and Hiltbold & Buchanan, 1977). The second-best predictor of persistence was soil organic matter content, which appears to confirm that adsorption on these colloids does provide some protection against degradation of atrazine. According to Walker (1987), the organic matter content of soil might be expected to influence the degradation rate of pesticides, since it is the most important variable controlling adsorption, and hence their distribution between the solid and solution phases. The leaching of atrazine can be expected to be governed by its adsorption on soil colloids, especially organic matter, and therefore soil organic matter content would probably have been better correlated with atrazine half-life if the work had been conducted in the field. This view is confirmed by the equally important roles of soil pH and % C in the persistence of atrazine that was reported for the field study in Chapter 5.

It is suggested that the regression equation presented above could contribute towards categorizing atrazine half-lives in soils more accurately, e.g. in cases where published half-life categories are the only alternative sources of information. Walker (1987) states that the half-life concept is valuable in comparing loss rates in different situations, but that its use is often an oversimplification, and therefore its use to characterize dissipation rates in the highly variable field environment should be avoided. Walker (1987) does acknowledge that the only way to take account of soil type on degradation is by regression analysis, provided the data base from which equations are arrived is large enough. Granted that half-life data have limited value in forecasts of persistence if considered alone, it is suggested that their inclusion in existing simulation models might improve the prediction of, in this instance, atrazine persistence. Computer models that can advise on, for example, recropping intervals after atrazine use in maize would signify a tremendous improvement in the way recommendations are made in this country. In the light of the findings reported in Chapters 3 & 6, the most suitable models in the case of atrazine would be those which also take account of the differential growth response of susceptible crops to specific concentrations of the herbicide in different soils. In practical terms, validation of any model requires data from numerous field sites with variations in soil type and weather patterns. Unfortunately, such studies are often beyond the scope of individual research laboratories.

Some applications of the use of simulation models for the prediction of herbicide persistence have been described by Walker & Barnes (1981), Walker & Eagle (1983), Gottesbüren *et al.* (1991) and Walker (1991). Of these models, only the model of

Gottesbüren *et al.* (1991) contains a module which predicts the effects of herbicide residues on succeeding crops. Walker (1991) acknowledges that in addition to the stability of specific herbicides, information on the critical soil residue levels in terms of rotational crop safety is required for reliable risk assessments. Walker (1991) used a simple mathematical model (Walker & Barnes, 1981) to make generalized predictions of atrazine persistence in four soils in South Africa. Using a half-life of 45 days for atrazine, Walker (1991) estimated that the herbicide would persist from 8 to 12 months following application in spring. Past reports of damage caused by atrazine residues, and own results reported in Chapter 6 (Table 28) attest that atrazine persistence often exceeds 12 months. From the predictions made by Walker (1991) it appears that atrazine persistence in the Warmbad soil was underestimated. Predicted atrazine losses for Warmbad were similar to those for Kroonstad, but results reported in Chapter 6 showed that atrazine residues in the same Warmbad soil caused significant damage to sunflower and dry beans at both 12 and 24 months after atrazine application. In contrast, negligible damage occurred at Kroonstad at the 12 month stage. The weather and soil data used by Walker (1991) as inputs in the model of Walker & Barnes (1981) were data which were recorded during the first 12 months at the two trial sites. It is suggested that if the regression model presented here had been available to predict atrazine half-lives in the two soils, more accurate predictions of persistence might have ensued. The regression model estimates of the half-lives for atrazine in the Kroonstad (pH 5.6; 0.36% C) and Warmbad (pH 7.9; 0.53% C) soils are 36 and 119 days, respectively. The estimated half-life of atrazine in the Kroonstad soil corresponds with the value of 45 days (irrespective of soil type) that was used in the model of Walker &

Barnes (1981). However, their model underestimated persistence in the Warmbad soil, probably because the half-life input of 45 days was inaccurate for this soil.

Further demonstration of the worth of the regression model in the prediction of atrazine persistence is given in Table 39 where atrazine half-lives that were determined by Walker & Zimdahl (1981) in a laboratory incubation study are compared with those predicted by the regression model developed in own work.

Table 39 Half-lives for atrazine in three soils (adapted from a laboratory study by Walker & Zimdahl (1981)), and the half-lives as predicted with the regression model developed in own work

		Atrazine half-life (days)		
Soil % C	Soil pH	Laboratory[1]	Regr. model[2] (% C + square pH)	Regr. model[3] (square pH alone)
1.45	8.0	41-87	141	120
1.51	6.4	28-50	101	80
0.64	7.3	47-100	105	102

[1]Adapted from Walker & Zimdahl (1981). The lower values were determined at 25°C and 16.8% soil water content, and the upper values at 15°C and 17.9% soil water.
[2]Multiple regression model: $y = -2.29 + 1.77(pH)^2 + 20.81(\%\ C)$ - from Table 46B.
[3]Simple regression model: $y = 10.6 + 1.73(pH)^2$ - from Table 46B.

Atrazine half-life predicted by the multiple regression model (pH^2 + % C) for the soil with the lowest organic matter content (Table 39) closely matched the maximum value reported for that soil by Walker & Zimdahl (1981). Compared to the laboratory measurements, the multiple regression model overestimated atrazine half-life in the other soils. The predictions given by the model which contained only square pH

corresponded slightly better with the laboratory measurements of Walker & Zimdahl (1981) for all three soils (Table 39). It is not surprising that both the regression models employed in Table 39 were not consistent in their prediction of half-lives determined in an unrelated study, since it is unlikely that simple empirical models based on limited environmental factors will be applicable in a wide range of weather and soil conditions. The environmental conditions were not exactly the same in the two studies that are compared in Table 39. As shown in Chapter 7, and as has been extensively reported in the literature, the persistence of atrazine is affected by various soil (Hiltbold & Buchanan, 1977; Walker, 1987, 1991) and weather factors (Roeth, Lavy & Burnside, 1969; Walker & Zimdahl, 1981; Walker, 1987, 1991). The regression model is expected to be valid for different atrazine rates. Hiltbold & Buchanan (1977) provided evidence to support the theory of first-order kinetics in atrazine degradation. They found that degradation rates of 1.12, 2.24 and 3.36 kg atrazine ha^{-1} did not differ significantly.

Experimentally derived atrazine half-lives (Table 37) and those values predicted with the model for each of the 25 soils are compared in Table 40. Presentation of the data in Table 40 should not be regarded as an attempt to validate the model - it merely serves to illustrate the variation inherent in the techniques that were used. The methodology of the present study involved time-consuming and relatively inaccurate bioassays. Chemical analysis would have generated data quicker and more accurately. Nonetheless, it is proposed that bioassays could be useful in work of this nature, should the available facilities dictate that the technique be used.

Table 40 Comparison of atrazine half-lives, which were determined experimentally for 25 soils, with those values predicted with the multiple regression model

Soil organic matter (% C)	Soil pH(H_2O)	Atrazine half-life (days)	
		Measured	Predicted
0.40	5.1	63	52
0.20	4.9	54	44
0.83	5.3	63	64
0.18	5.5	75	54
0.38	4.8	50	46
0.80	5.3	85	63
0.18	5.8	71	60
0.32	5.3	64	53
0.40	7.1	86	95
0.47	6.4	78	79
0.29	6.8	107	86
0.40	5.1	58	52
0.65	7.2	102	102
0.31	4.9	57	46
0.28	5.3	50	52
0.34	5.7	71	62
0.29	6.5	75	78
0.29	7.2	85	95
0.98	5.0	69	62
0.41	6.9	102	90
1.06	5.9	86	81
1.18	5.8	81	81
2.04	5.5	88	93
0.50	7.8	120	115
0.77	7.5	147	113