Atrazine degradation and transport in runoff on a Black Vertosol

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Abstract. In Australia communities are concerned about atrazine being detected in drinking water supplies. It is important to understand mechanisms by which atrazine is transported from paddocks to waterways if we are to reduce movement of agricultural chemicals from the site of application. Two paddocks cropped with grain sorghum on a Black Vertosol were monitored for atrazine, potassium chloride (KCl) extractable atrazine, desethylatrazine (DEA), and desisopropylatrazine (DIA) at 4 soil depths (0–0.05, 0.05–0.10, 0.10–0.20, and 0.20–0.30 m) and in runoff water and runoff sediment. Atrazine + DEA + DIA (total atrazine) had a half-life in soil of 16–20 days, more rapid dissipation than in many earlier reports. Atrazine extracted in dilute potassium chloride, considered available for weed control, was initially 34% of the total and had a half-life of 15–20 days until day 30, after which it dissipated rapidly with a half life of 6 days. We conclude that, in this region, atrazine may not pose a risk for groundwater contamination, as only 0.5% of applied atrazine moved deeper than 0.20 m into the soil, where it dissipated rapidly. In runoff (including suspended sediment) atrazine concentrations were greatest during the first runoff event (57 days after application) (85 µg/L) and declined with time. After 160 days, the total atrazine lost in runoff was 0.4% of the initial application. The total atrazine concentration in runoff was strongly related to the total concentration in soil, as expected. Even after 98% of the KCl-extractable atrazine had dissipated (and no longer provided weed control), runoff concentrations still exceeded the human health guideline value of 40 µg/L. For total atrazine in soil (0–0.05 m), the range for coefficient of soil sorption (K_d) was 1.9–28.4 mL/g and for soil organic carbon sorption (K_{OC}) was 100–2184 mL/g, increasing with time of contact with the soil and rapid dissipation of the more soluble, available phase. Partition coefficients in runoff for total atrazine were initially 3, increasing to 32 and 51 with time, values for DEA being half these. To minimise atrazine losses, cultural practices that maximise rain infiltration, and thereby minimise runoff, and minimise concentrations in the soil surface should be adopted.

Additional keywords: available atrazine, desethylatrazine, desisopropylatrazine, leaching, runoff, sorption.

Introduction

Atrazine is a residual herbicide used to control weeds in summer grain crops. On the Darling Downs, Queensland, it is one of the most commonly used agricultural chemicals for sorghum and maize (Rayment and Simpson 1993). However, it is also a water contaminant and has been detected in surface water supplies on the Darling Downs more frequently than any other pesticide. Atrazine has been detected in 80–90% of all river water samples (CBWC 1999, 2002; Lucey 2004). The metabolites desethylatrazine (DEA) and desisopropylatrazine (DIA) have also been found recently (CBWC 2002; Lucey 2004).

Atrazine movement from the site of application is controlled by a variety of physical and chemical behaviours that are well described (Leonard 1990; Wauchope *et al*. 1992). The 2 most important processes controlling the fate of atrazine in the soil are the dissipation rate and soil-water partitioning (referred to as sorption). Losses of pesticides from soil may be due to volatilisation, biological or chemical degradation, diffusion, runoff, or leaching deeper into the soil. Losses of pesticides from soil are referred to here as dissipation, a term which does not imply any particular loss mechanism (Leonard and

Wauchope 1980). Dissipation of atrazine from the soil surface after application is an important determinant of losses in runoff, as concentrations in runoff are strongly related to pesticide concentration on rain-impacted soil surfaces (Leonard *et al*. 1979). Sorption properties are important because they control the phase of transport between the sediment bound and soluble water phases.

Although atrazine has been widely studied, there is clear evidence that dissipation and sorption characteristics may be different in Australian soils because of soil and environmental conditions (Kookana *et al*. 1998). Even within Australia, atrazine dissipation rates in soil (as described by half-life) range between 40 and 1162 days. Similarly, sorption coefficients (K_d) range between 0.24 and 24.9 mL/g and per unit of organic carbon (K_{OC}) range between 55 and 830 mL/g (Kookana *et al*. 1998).

Only a proportion of atrazine in the soil is available for weed control. This fraction depends on soil type and can range from 13 to 62% of the total atrazine (Walker *et al*. 1997). The half-life of available atrazine ranges from 40 to 80% of that of the total (Walker *et al*. 1997). This means that a significant proportion of atrazine will persist in the soil even after the available atrazine

concentration falls below the level needed to control weeds. We were interested to know if the total loss in runoff, and phase of transport of atrazine, were related to weed control availability.

Previous work on atrazine movement has concentrated on cane-growing areas (Rayment and Simpson 1993; Simpson *et al.* 2001), on soils of the Darling Downs in glasshouse studies (Walker *et al.* 1994, 1997), and on related compounds in rainfall simulation studies in cotton-growing areas (Silburn 2003). Preliminary work on atrazine dissipation with summer cropping on Vertosols has been reported by Connolly *et al.* (2000). To better understand availability, dissipation, sorption, and runoff of atrazine, DEA, and DIA on the Darling Downs the fate of atrazine was monitored during the growth of a sorghum crop.

Materials and methods

Site and soil

A set of nested catchments (Table 1 and Fig. 1), south-east of Toowoomba on the Darling Downs, Queensland, was monitored over the summer of 2001–02. The hill catchment contained mountain coolabah open woodland and the 2 monitored contour bays (steep and low slope bays) were cultivated and planted to sorghum, as were the adjacent contour bays. The soil was a self-mulching Black Vertosol (Isbell 1996). Selected soil properties are given in Table 2.

Cropping history and atrazine application

The contour bays were fallowed after a sorghum crop in 1999–2000. Leading up to herbicide application these bays were cultivated 5 times, initially with a chisel plough and the final cultivation using a scarifier. At planting the cover was 5% sorghum stubble. A current farming practice is to use atrazine as a pre-plant application to control weeds in later fallow and following a sorghum crop.

On 19 September 2001 (day 0), Gesaprin 500 (containing 500 g/L of atrazine active ingredient) was sprayed at an estimated 5 L/ha (2.5 kg/ha of atrazine) and followed by a light cultivation. Subsequent analysis of the atrazine in soil samples indicate that the application rate was more likely 3.4 kg/ha. Fertiliser applications were urea (46% N) at 250 kg/ha and Starter Z (10.9% N, 19.2% P, 2.2% S, 2.5% Zn) at 30 kg/ha. Following 29 mm of rainfall in the previous week, sorghum was planted on 15 October. In late November, thornapple (*Datura* spp.) became a weed problem and Starane 200 (200 g/L of fluroxypyr as the methylheptyl ester active ingredient) was sprayed aerially on 4 December 2001. Sorghum yielding 5.8 t/ha was harvested on 28 April 2002.

Table 1. Nested catchment site details

Catchment and runoff sampling position	Land use	Catchment area (ha)	Land slope (%)	Channel slope (%)
Low slope bay (3)	Sorghum	7.3	1.8	0.3
Steep slope bay (2)	Sorghum	4.3	7.0	0.3
Hill catchment (1)	Pasture–woodland	21.6	30.4	0.5
Waterway catchment (4)	All above	38.2	–	7.0–2.0

Rainfall and runoff measurement

A tipping bucket pluviometer and manual rain gauge were used to measure rainfall. A water depth sensor (pressure transducer) was installed at each runoff sampling point (Fig. 1, black arrows show locations). Runoff volume was estimated from flow depths, measurements of the cross section of the flow sections, and Manning's equation (Manning 1891, 1895).

Sampling

Soil

Soil was sampled from within the steep and low slope bays using a 50-mm-diameter corer, with samples taken at 6–8 randomly selected locations for each bay and bulked for each bay. Sampling depth increments were 0–0.05, 0.05–0.10, 0.10–0.20, and 0.10–0.30 m. Soil sampling was conducted 2, 16, 30, 57, 90, and 128 days after herbicide application on 19 September. Soil cores were frozen directly after collection. All soil samples were delivered to an analytical laboratory within 5 days of collection and were extracted within 1 week of arrival at the laboratory. Average herbicide concentrations in soil were calculated for the 2 contour bays and these values were used in subsequent analyses.

Runoff water (including sediment)

Runoff water was sampled opportunistically by hand using 1-L glass Schott bottles, which were chilled to 4°C immediately after collection. Four locations were used to sample runoff
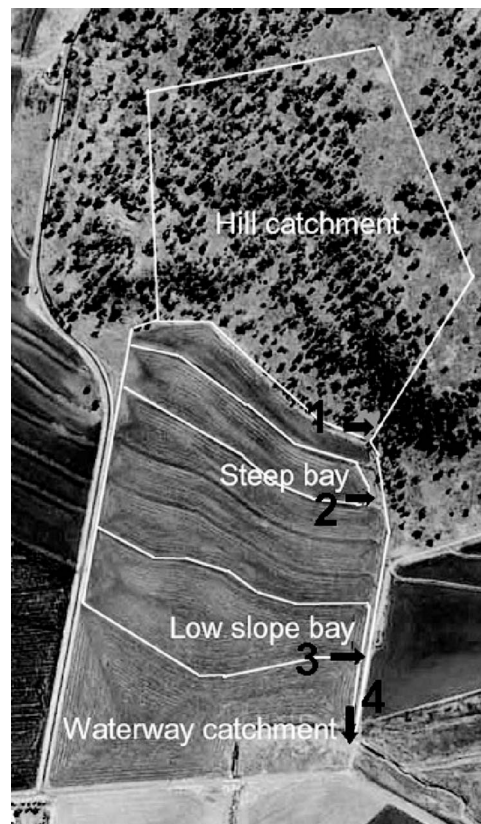

Fig. 1. Aerial photograph showing location of runoff sampling positions (numbered arrows).

Soil depth (m)	pH[A]	Organic C[B] (%)	Sand (%) 2.0–0.02 mm	Silt (%) 0.02–0.002 mm	Clay (%) <0.002 mm
0–0.05	7.4	1.3	7	26	67
0.10–0.20	8.0	1.1	9	19	72
0.40–0.80	8.6	0.8	14	20	66

[A] Soil : water 1 : 5.
[B] Organic carbon—Walkley and Black procedure.

(Fig. 1), representing an untreated natural vegetation catchment (position 1), steep and low slope cultivated catchments (positions 2 and 3), and a waterway (position 4) that integrated runoff from the natural vegetation catchment and 7 cultivated catchments (all cultivated catchments had the same atrazine application). In the laboratory, and within 5 days of collection, samples were buffered to pH 7 with a phosphate buffer (standard practice as recommended by the USA Environmental Protection Agency). All runoff samples (water and sediment) were extracted within 1 week of arrival at the laboratory. Where possible, sediment (material $>1.2\,\mu m$) was filtered through a GF/A filter paper placed above a GF/C filter paper (retentions 1.6 and $1.2\,\mu m$, respectively), sediment concentrations were determined, and herbicides in water and sediment were analysed separately. Where there was insufficient sediment for analysis ($<0.2\,g$) the sediment and water were analysed as 1 sample. Average herbicide and sediment concentrations in runoff were calculated for each event using a flow weighted average.

Herbicide analysis

Soil, runoff water, and sediment samples were all analysed for atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3, 5-triazine) and its metabolites DEA (2-chloro-4-amino-6-isopropylamino-1,3,5-triazine) and DIA (2-chloro-4-ethylamino-6-amino-1,3,5-triazine), the sum of these being termed total atrazine. The limits of quantitation for atrazine, DEA, and DIA were each 0.01 mg/kg in soil and sediment samples, below which they were reported as not detected. For runoff samples the limits of quantitation were $0.05\,\mu g/L$ for atrazine and $0.02\,\mu g/L$ for DEA and DIA.

Total atrazine in soil

Soils were extracted with acetone/hexane (50 : 50 v/v) by 1 of 2 procedures. The first was in a soxhlet apparatus refluxing with the solvents overnight. The second was by shaking 15 g of soil with 50 g sodium sulfate and 50 mL acetone/hexane, and this is the procedure used most often in this study.

Available atrazine in soil

Soil (50 g) was extracted with 0.02 M potassium chloride solution (100 mL) by shaking for 1 h, after which the filtrate was passed through a carbograph cartridge from which atrazine and its metabolites were recovered in acetone (K. P. Spann, unpublished procedure). The choice of 0.02 M potassium chloride solution as an extractant for the soil was based on the premise of Stalder and Pestemer (1980) that an aqueous extract indicates the proportion of atrazine available to plants and therefore effective as a herbicide. This extraction procedure was adopted by Walker *et al.* (1994, 1997) as a measure of available atrazine in soils.

Sediment analysis

Wherever there was sufficient sediment ($>0.2\,g$), the runoff samples were filtered through pre-weighed GF/A and GF/C filter papers under low vacuum. The filter papers were then wrapped around the sediment for extraction with acetone/hexane in an extraction thimble. Finally, the sediment in the filter paper was dried and weighed to calculate g/L of sediment. Herbicide concentrations in sediment are reported in mg/kg or in runoff $\mu g/L$ (calculated by multiplying mg/kg by g/L).

Runoff water

When atrazine and its metabolites were analysed, runoff water (diluted to 500 mL if necessary) was extracted 3 times with ethyl acetate (3×50 mL). When only atrazine concentrations were required, dichloromethane was used as the extractant (3×50 mL).

Atrazine analyses to determine the soil sorption coefficient (K_d)

A 10-g subsample of the soil used to measure total atrazine (see above) was extracted with 1 L of deionised water using the shaking procedure to determine available atrazine (see above). The water was decanted, the volume measured, and from this the atrazine was extracted 3 times with ethyl acetate (3×75 mL) (see previous paragraph). The atrazine concentration in the water was reported in $\mu g/L$, which corresponded to the total extracted from the soil. The atrazine remaining adsorbed to the soil was calculated by difference. This, when divided by the μg extracted in the water, gave the sorption coefficient K_d in mL/g.

Analyses by gas chromatography/mass spectrometry

The extracts were analysed using a Hewlett Packard 6890 gas chromatograph with a 30 m by 0.25 mm, $0.25\,\mu M$ HP-5MS column and a Hewlett Packard 5973 series mass selective detector. For the column the initial temperature was 50°C and initial time 1 min, followed by a ramp temperature to 100°C at 25°C/min, then ramping to 295°C at 5°C/min with a hold time of 5 min. The retention times for atrazine, DEA, and DIA were 18.7, 16.9, and 16.6 min, respectively.

Quality assurance/quality control

For each of the extraction procedures for atrazine, DEA, and DIA every batch of samples analysed included internal and surrogate standards, a laboratory reagent blank, and a fortified recovery sample. Soils with atrazine, DEA, and DIA from

the field and fortified control soils were analysed before and after freezing and there was no significant difference between the results (K. P. Spann, pers. comm.). For the fortified soil samples, recoveries were >90% for atrazine, DEA, and DIA. Confirmatory recovery tests were carried out for water analyses using both deionised water and alkaline bore water fortified with atrazine, DEA, and DIA; recoveries were >94% for atrazine and >90% for DEA and DIA.

Derived parameters for atrazine

Half-life

Half-life ($t_{1/2}$) is defined as the time to dissipate to half of the initial concentration. For atrazine, this was calculated by fitting a first-order exponential decay function to concentrations in soil (Leonard and Wauchope 1980). The equation (Wauchope *et al.* 1992) that relates concentrations in soil at times t1 and t2 (days) and the rate constant k (days^{-1}) is:

$$C_{t2} = C_{t1}\, e^{-k(t2-t1)}$$

The half-life (days) is calculated as:

$$t_{1/2} = \ln_e(2)/k = 0.693/k$$

Soil sorption coefficient (K_d)

The sorption coefficient K_d (mL/g) is the ratio of concentration of pesticide bound to the solids (C_s) to the concentration in the water phase (C_w) (Leonard 1990):

$$K_d = C_s/C_w$$

The sorption coefficient is often reported as a value normalised for soil organic carbon (OC) (%) (Wauchope *et al.* 2002).

$$K_{OC} = 100 * K_d/OC$$

The sorption coefficients were measured by comparing the atrazine retained by 10 g of soil with that extracted in 1 L of deionised water (see *Atrazine analysis to determine the soil sorption coefficient* above). Thus, the sorption coefficients were determined for soil sampled in the field at various times after application.

Partition coefficient for the sediment (K_p)

Concentrations of atrazine in the water (C_w) and associated sediment (retained by filtration) (C_s) were used to calculate the partition coefficient in runoff:

$$K_p = C_s/C_w$$

(see *Sediment analysis* and *Runoff water* above). If the weight of sediment available for analysis was <0.2 g, the partition coefficient could not be calculated. This situation occurred more frequently as crop cover increased and, as a consequence, sediment concentrations in runoff decreased.

Conversions from atrazine concentrations to g/ha

The mass of herbicide in each soil layer was calculated using a bulk density of 1.0 and 1.1 t/m^3 for the 0–0.10 and 0.10–0.30 m layers, respectively The proportions of the total and KCl-extractable atrazine and metabolites at each depth could

then be calculated and also the percentage of the applied atrazine remaining at various times.

Results

Hydrology

The first rainfall event occurred 20 days after applying the atrazine and total rainfall for the study period was 465 mm (Fig. 2). The first runoff was observed from the cropped bays 50 days after herbicide application. Over the next 40 days, 5 runoff events were recorded but a long gap followed to the last measured runoff on day 145. Total runoff from the cropped bays was 130 mm during the summer (28% of rainfall), while runoff from the hill catchment was <2 mm. Rainfalls of 98, 146, 110, 8, and 103 mm for October, November, December, January, and February, respectively, were 1.7, 2.1, and 1.2 times the medians for the first 3 months (as recorded at the Cambooya meteorological station not far away). However, January was exceptionally dry but the rainfall for February was 1.5 times the median.

Decreases in atrazine and distribution through the soil profile

In the soil surface (0–0.05 m), mean concentrations (from the steep and low slope bays) of total and KCl-extractable atrazine declined more or less exponentially after application (Fig. 3). However, just 2 days after application, a small proportion of the total atrazine was present at 0.05–0.10 m and 16 days after application some was measured at 0.10–0.20 and 0.20–0.30 m (Fig. 4), possibly due to incorporation. The increase in total atrazine at 0.05–0.10 m between 16 and 30 days (Fig. 4) may be attributed to infiltration of rainfall of approximately 80 mm after 20 days (Fig. 2). This increase in atrazine at depth is also reflected in the distribution with depth data, given in Table 3. Data in Table 3 assume that the total atrazine (g/ha), at day 2, corresponded to 100%, and is used as a baseline against which later residual concentrations were calculated. Table 3 also shows that there was minimal movement of atrazine below the surface 0.05 m, and very small concentrations below 0.10 m.

After 16 days, the total atrazine concentration had halved (Table 3). On a log scale (Fig. 4) there was an almost linear decrease in total atrazine at 0–0.05 m, consistent with first-order
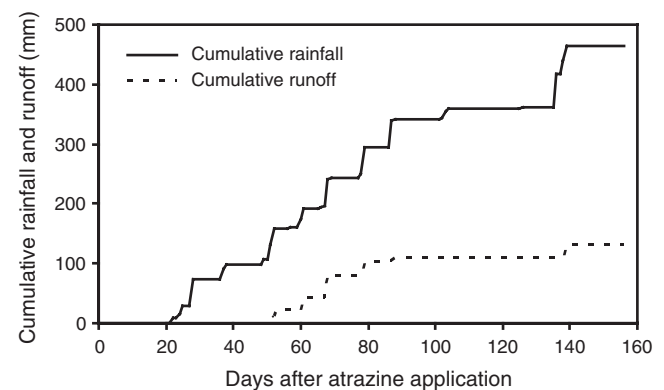
Fig. 2. Cumulative rainfall and runoff at the bottom of the waterway catchment waterway (sampling position 4).

exponential loss as indicated in Fig. 3. Exponential equations fitted to the concentrations of total atrazine (g/ha) gave half-lives (coefficients of determination in parentheses) of 16 (0.97), 18 (0.97), and 20 (0.94) days for atrazine at 0–0.05, 0–0.10, and 0–0.30 m, respectively. KCl-extractable atrazine had a half-life of 15 (0.97), 20 (0.99), and 20 (0.99) for the 3 depth intervals for the period 2–30 days, and 6 days for the period 30–57 days.
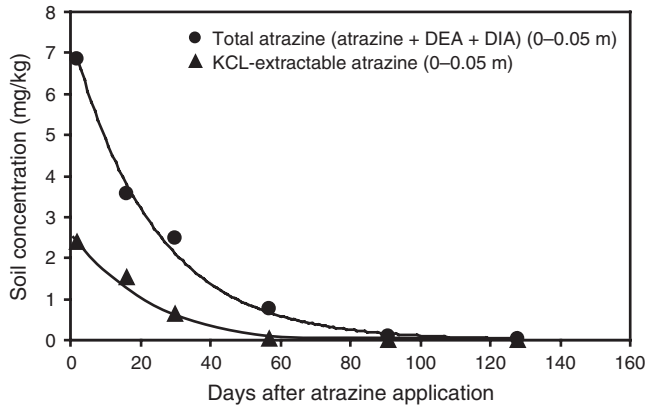

Fig. 3. Total and KCl-extractable atrazine dissipation at 0–0.05 m in the soil with fitted exponential lines.
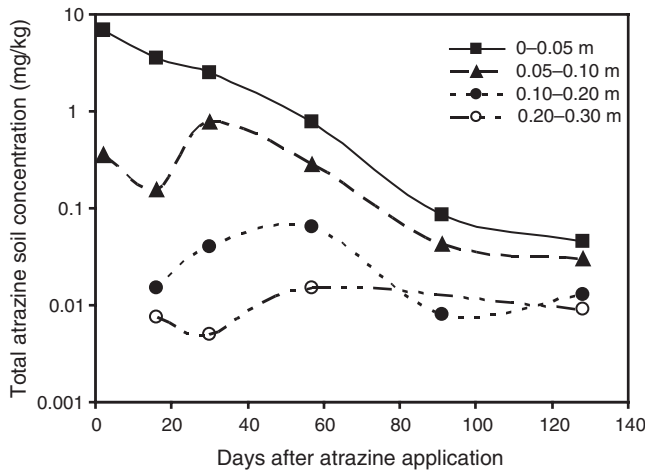

Fig. 4. Time series of total atrazine concentrations at four depths (limit of quantitation 0.01 mg/kg).

Table 3.   Distribution of total atrazine (% of total at day 2) at various depths in the soil profile

Soil depth (m)	Days after application					
	2	16	30	57	91	128
0–0.05	95.1	49.5	34.4	10.8	1.2	0.6
0.05–0.10	4.9	2.1	10.7	3.9	0.6	0.4
0.10–0.20	0.0	0.5	1.3	2.2	0.3	0.4
0.20–0.30	0.0	0.2	0.2	0.5	0.0	0.3
0–0.30	100	52	47	17	2	2

KCl-extractable atrazine and metabolites

KCl-extractable atrazine concentrations decreased rapidly after 30 days and by 90 days were not measurable (Fig. 5). The more rapid decline after day 30 coincided with runoff events after 50 days (Fig. 2). DEA was already present 2 days after application and increased until 57 days, after which time it decreased. However, the concentrations of both the total atrazine and DEA showed minimal decreases between 90 and 128 days, a period of minimal rainfall and no runoff (Fig. 2). DIA was found after 16 days, again increasing until 57 days and thereafter it was below the limit of quantitation.

The ratios of DIA to DEA at 0–0.05 m after 30 and 57 days were 40% and 50%, respectively, and the corresponding ratios at 0.05–0.10 m were 50 and 30% and for 0–0.30 m were 30 and 40% (Table 4).

Atrazine in runoff and in soil

Atrazine was found in all runoff, decreasing exponentially from the first runoff event after 50 days after herbicide application, a pattern similar to that for total atrazine at 0–0.05 m in the soil (Fig. 6). However, the exponential decrease in KCl-extractable
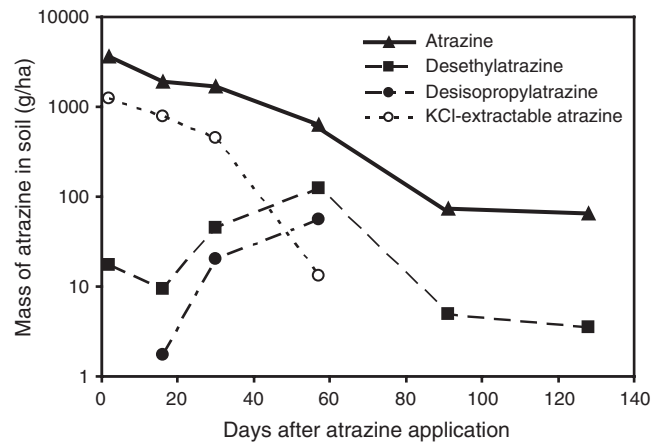

Fig. 5. Time series of atrazine, metabolites, and KCl-extractable atrazine in 0–0.30 m soil.

Table 4.   Distribution of KCl-extractable atrazine, DEA, and DIA (% of total at day 2) at various depths in the soil profile

Atrazine form	Days after application					
	2	16	30	57	91	128
	0–0.05 m					
KCL-extractable	33.2	21.2	8.8	0.4	0.0	0.0
DEA	0.4	0.2	1.0	2.0	0.1	0.1
DIA	0.0	0.0	0.4	1.1	0.0	0.0
	0.05–0.10 m					
KCL-extractable	0.7	0.5	3.5	0.0	0.0	0.0
DEA	0.1	0.1	0.2	1.4	0.1	0.0
DIA	0.0	0.0	0.1	0.4	0.0	0.0
	0–0.30 m					
KCL-extractable	33.9	21.8	12.5	0.4	0.0	0.0
DEA	0.5	0.3	1.9	3.9	0.1	0.2
DIA	0.0	0.0	0.6	1.5	0.0	0.0

atrazine, extrapolated to zero before 90 days, was more marked. Similar concentrations in runoff and a strong relationship with time after application were obtained at the contour bay outlets (data not shown). Extrapolating the fitted exponential equation back to the day of application gives an estimate of potential atrazine runoff concentration of 300 µg/L if a runoff event had occurred at that time. While this is only a rough estimate, it is consistent with the high pesticide concentrations observed in runoff shortly after application (Silburn 2003).

There was a close relationship ($R^2 = 0.94$) between the total atrazine in runoff water from both the cropped bays and the waterway and the total atrazine at 0–0.05 m in the soil (Fig. 7). The tendency is for runoff concentrations to be greater (relative to soil concentration) at greater soil concentrations, as indicated by the exponent being >1.0 for the fitted equation.

Soil sorption coefficients for atrazine in soil

Soil from 0–0.05 m sampled up to 57 days after application contained measurable atrazine. The derived sorption coefficients, K_d, for samples taken 2, 16, 30, and 57 days after application were 1.9, 1.3, 2.9, and 28.4 mL/g, respectively,
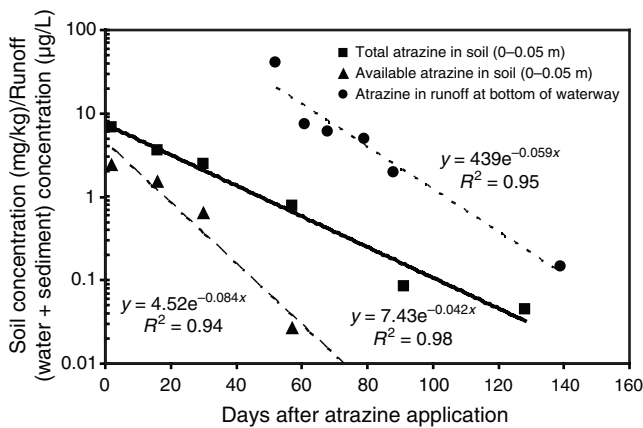

Fig. 6. Relationship between total and KCl-extractable atrazine in soil and of total atrazine in runoff.
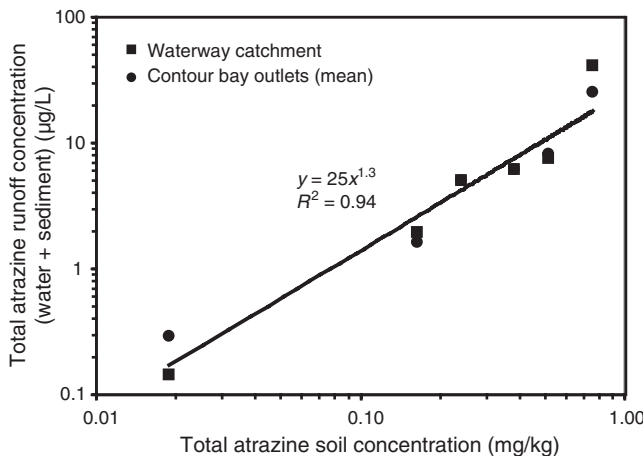

Fig. 7. Relationship between total atrazine concentration in the surface soil (0–0.05 m) and total atrazine in runoff (water + sediment).

and the corresponding K_{OC} values are 146, 100, 223, and 2184 mL/g (OC = 1.3%).

Partition coefficients for sediment

Partition coefficients (K_p) of atrazine in runoff increased with time after application (Table 5). Low sediment concentrations in runoff limited the ability to determine K_p later in the trial.

Measurable DEA was found in runoff and sediment 61 and 68 days after application. K_p values were lower for DEA than for total atrazine, indicating lower sorption. No DIA was measured in sediment or runoff samples, so K_p values could not be derived.

Estimated atrazine losses for the season

The total atrazine lost in runoff for the season was estimated at 14.2 g/ha and represents approximately 0.4% of the initial application. Of this, 13.6 g/ha or 96% was in the water phase (Table 6).

The first event was the major contributor to the total load lost in runoff for the season and most of the atrazine was transported in the water phase. The rainfall in this first event was low intensity, resulting in low erosion and sediment concentrations in runoff of only 0.4 g/L. Sediment concentrations in the subsequent events ranged from 1.3 to 5.3 g/L. Atrazine concentrations on sediment ranged from 0.02 to 0.18 mg/kg and were slightly lower than the soil concentration of total atrazine which ranged from 0.02 to 0.75 mg/kg (Fig. 7).

Discussion

Half-lives for atrazine and KCl-extractable atrazine

The decrease in total atrazine in soil was exponential, following first-order kinetics as would be expected for Australian soils (Kookana *et al*. 1998). Taking into account the small proportion of atrazine below 0.05 m (Table 3) raised the calculated half life from 16 to 20 days, considerably shorter than the values given by Kookana *et al*. (1998) whose values are closer to that of 60 days used for modelling (Wauchope *et al*. 1992). Walker *et al*. (1997), in glasshouse experiments, derived half-lives for

Table 5. Atrazine partition coefficient (K_p) between sediment and water at the contour bay outlet at various times after application

Days after application	Total atrazine	Desethylatrazine
52	3	—[A]
61	32	16
68	51	28

[A]Below the limit of quantitation.

Table 6. Sediment bound, water phase and total atrazine load in runoff (g/ha) at the waterway outlet, showing the first event to be the dominant event

i.d., Insufficient data

Atrazine	Days after application						Total
	52	61	68	79	87	139	
Sediment bound	<0.1	0.2	0.3	0.1	i.d.	<0.1	0.6
Water phase	9.2	1.2	1.1	1.0	i.d.	<0.1	13.6
Total	9.2	1.4	2.4	1.1	0.1	<0.1	14.2

atrazine of 61–143 days for Vertosols (Black Earths, 70% clay) and 31–63 days for KCl-extractable atrazine. Popov *et al.* (2005) studied the degradation rate of atrazine in soils from the Liverpool Plains, NSW, under laboratory incubation and in glasshouse bioassay and derived half-lives of 2–7 days for cropped soil and 8–22 days for grassland soils. Preliminary work on atrazine dissipation with summer cropping on Vertosols by Connolly *et al.* (2000) derived a half-life of 30 days for total atrazine. The large variability between various studies determining half-lives for atrazine indicates the great influence the experimental conditions have on the value that is calculated and problems of trying to transpose data generated from the laboratory or glasshouse to the field situation.

The half-life of KCl-extractable atrazine was calculated as 20 days for the initial 2–30 days after application, whereas it was reduced to 6 days for the period 30–57 days. Presumably this reduction is attributable to rainfall that promoted increased microbiological activity and plant uptake. After 2 days the KCl-extractable atrazine was 34% of the total atrazine, reduced to 21% after 16 days. These figures are comparable with the range of 14–26% for KCl-extractable to total atrazine found when Walker *et al.* (1994) incubated Vertosols (Black Earths) at field capacity in an environmental cabinet for 8 days. The clay content of 66–72% for the soil profile in the present study lies within the range of 53–79% clay for the Vertosols of Walker *et al.* (1994).

The large decrease in KCl-extractable atrazine between 30 and 57 days after atrazine application to finally being immeasurable after 91 days (Fig. 5 and Table 4) cannot be attributed to leaching by rainfall (Table 4) or loss in runoff (Table 6). Little leaching of KCl-extractable atrazine below 0.10 m was observed with 0.3% detected below 10 cm at day 30 and negligible amounts at day 57 (Table 4). Runoff of soluble atrazine accounts for only 0.3% of loss for this period (Table 6). The rapid loss of KCl-extractable atrazine is more likely to be attributable to degradation and uptake by plants.

Rates of 1.8–2.25 kg atrazine/ha would be expected to control thornapple and in this study 2.5 kg/ha was applied. There may be 2 explanations for the apparent failure of atrazine to control thornapple, which had to be sprayed with Starane 85 days later. The first explanation is that seeds can be buried to the depth of cultivation, nominally 0.05–0.10 m (S.R. Walker pers. comm.) and the atrazine in this study was concentrated at 0–0.05 m. Alternatively, there may have been insufficient atrazine left. Even after 57 days (about 3 half lives for atrazine, calculated as 16–20 days depending on whether the concentrations at 0–0.05, 0–0.10, or 0–0.30 m were used) only 17% of the total remained and only 1.5% was present as KCl-extractable atrazine (Tables 3 and 4). By then, the KCl-extractable atrazine concentration was well below 0.1 mg/kg (Fig. 6), a limit for broadleaf weed control proposed by Walker *et al.* (1997).

Atrazine and its metabolites

Microbial transformation of atrazine in soils can be expected to proceed by N-dealkylation (Graham-Bryce 1981; Erickson and Lee 1989; Vanderheyden *et al.* 1997), which involves the loss of the ethyl group to give DEA and of the isopropyl group to give DIA. The solubilities of atrazine, DEA, and DIA are quoted by Erickson and Lee (1989) as 0.15, 2.0, and 1.2 mM in water,

respectively, and the greater solubilities of the metabolites would be expected to give increased mobility and lower K_d values compared to atrazine. In this study the K_p values for DEA were half those for atrazine, which is in agreement with the water solubilities of these compounds.

Soil concentrations decreased in the order atrazine $\gg$ DEA > DIA, which is the same order as concentrations found in waterways of the Condamine-Balonne Catchment (CBWC 2002). The ratio of 30–50% for DIA to DEA found in this study is comparable with the ratios of 31% reported by Shipitalo and Owens (2003) and of 40–52% that they quote for other runoff studies.

KCl-extractable atrazine, K_d and K_p

Both soil sorption (K_d) and runoff partition (K_p) coefficients increased markedly with time after application. The rapid loss of KCl-extractable atrazine also explains the 10-fold increase in K_d for total atrazine, from 2.9 mL/g at day 30 to 28.4 mL/g at day 57 and also the 10-fold increase in K_p, from 3 at day 52 to 32 at day 61, followed by a further increase for both total atrazine and DEA by day 68 (Table 5). In the overlap of K_d and K_p data, it was noted that there was consistency between the 2 measures with time, which indicates that K_d may provide a useful surrogate for K_p. Further testing of this hypothesis would be useful as field values of K_d are considerably easier to collect than K_p that is used to explain phase distribution of atrazine loss in runoff.

These sorption coefficients are the ratio of atrazine in soil or sediment to that in solution. So if atrazine in the water phase decreases dramatically there will be an apparent considerable increase in the sorption coefficients. The prevailing view (e.g. Leonard and Wauchope 1980; Leonard 1990) is that increases in coefficients with time are due to increasing sorption into clay and organic carbon matrices in the soil while the atrazine in solution remains unchanged. Indeed, Wauchope *et al.* (2002) refer to 'ageing', a slow reaction which irreversibly removes pesticides from solution. While 'ageing' could be the reason for less KCl-extractable atrazine with time, it may well be reinforced by degradation of the KCl-extractable atrazine.

K_d and K_{OC} values

The K_d values for atrazine of 1.3–2.9 mL/g measured from days 2 to 30 and before runoff events in this soil (67% clay, 1.3% organic carbon) are close to the values of 2.5–4.4 mL/g for the Black Earths (69–71% clay, 1.0–1.8% organic carbon) cited by Walker *et al.* (1994), who also recorded for atrazine a higher correlation with clay than with organic carbon for soils from south-east Queensland. However, organic carbon is one of the main constituents of soil that controls sorption behaviour of non-ionic pesticides and this can explain the wider range of K_d values of 0.55–18.7 mL/g for atrazine in the sandy soils of the Swan Coastal Plain (0.82–4.80% organic carbon) reported by Kookana *et al.* (2001) and the even wider range of K_d values of 0.24–24.9 mL/g for Australian soils (0.1–6.0% organic carbon) reported by Kookana *et al.* (1998). The K_d value of 28.4 mL/g found after 57 days is above these ranges. Nevertheless, it should be noted that the extractant to soil ratio of 10 : 1 in the laboratory determination of K_d values is far greater than would be found in soil in the field. This ratio inherently tends to overestimate short-

term sorption but underestimate longer term sorption and values determined in the laboratory may vary from the true average of K_d in the field by a factor of up to 2 (Wauchope *et al*. 2002).

Converting the K_d values to K_{OC} gave values of 146–223 mL/g from days 2 to 30. However, these values, and comparisons with those from other workers, should be interpreted with caution. Wauchope *et al*. (2002) noted that K_{OC} values are used universally as a measure of the relative potential mobility of pesticides in soils. However, they emphasise that the variability in the measurement of soil organic carbon and differences in methodology from different studies can lead to great differences in the values reported for particular pesticides.

The assumption that soil organic matter is the determinant of atrazine sorption for the clay soils of the Darling Downs is not evident from the relationship between K_d and organic carbon for the 12 soils of Walker *et al*. (1994) in fig. 6 of Kookana *et al*. (1998) where the role of clay in determining sorption was predominant. Nevertheless, in the present study, having a topsoil pH of 7.4–8.0, the atrazine, with a pK_a of 1.7 (Stevenson 1972), would not be expected to be ionised, so it would be retained by adsorption, not by ionic bonding.

Relationship between atrazine in soil and runoff

There was a strong correlation between the atrazine concentrations in the surface soil (0–0.05 m) and the atrazine concentrations in the runoff from the waterway and the contour bays (Fig. 7). This is the classic pattern for herbicides in runoff from watersheds found by Leonard (1990) and Leonard *et al*. (1979), who found runoff concentrations to be somewhat greater at higher soil concentrations, with an exponent of 1.2, which is similar to the exponent of 1.3 found in this study (Fig. 7). Leonard *et al*. (1979) found the relationship fitted the equation Y (µg/L) $= 50X^{1.2}$, compared with the multiplier of 25 in Fig. 7. The exponents >1 and the different multipliers may be explained by a consideration of distribution of atrazine with soil depth. In the study conducted by Leonard *et al*. (1979) atrazine measurements were made in the 0–0.01 m of soil, while in the present study the surface soil was defined as 0–0.05 m. In both studies the highest concentrations were found at the commencement of the experiment, soon after atrazine application, and over time a portion of the atrazine would move below the zone defined as the surface soil, as discussed by Leonard (1990), Simpson *et al*. (2001), and Silburn (2003).

Two days after atrazine application, the concentration of total atrazine at 0–0.05 m was 6.8 mg/kg (Fig. 3). Assuming a soil bulk density of 1.0 t/m^3 this translates to 3.4 kg/ha of atrazine, which is more than the 2.5 kg/ha application rate estimated originally. From the regression given in Fig. 7, $Y = 25X^{1.3}$, had runoff occurred on the day of application the concentration in runoff would have been 300 µg/L; however, at a soil concentration of 5 mg/kg, the runoff concentration would only have been 200 µg/L. The importance of the exponent in the relationship is apparent when we consider that while the over-application was 35%, the runoff concentration potential went up by 50%.

Atrazine leaching

The rapid dissipation of atrazine in the soil ensured that leaching of atrazine, even below 0.10 m, was minimal. This indicates a low risk of contaminating subsoil, and as such poses a low risk of groundwater contamination in this environment. Application of the atrazine was accompanied by light scarification resulting in 95% of the chemical remaining in the 0–0.05 m layer (Table 3). The initial rainfall of 80 mm to day 30 (Fig. 2) resulted in some movement to 0.10 m but even after 57 days, with an additional rainfall of 87 mm and runoff, only 5% of total atrazine was found at 0.20–0.30 m and thereafter it was not measured and only 2% was measured in the profile. Of the 33% measured as KCl-extractable atrazine after 2 days, the highest concentration at 0.05–0.10 m was 3.5% after 30 days. The transitory increases and then loss of the metabolites were minor and again were concentrated in the surface 0.10 m. Preliminary findings by Connolly *et al*. (2000) on this site were that atrazine remained concentrated at 0–0.05 m, was virtually undetectable below 0.20 m, and negligible residues were found after 4 months. The implied negligible leaching of atrazine is further supported by the suggestion of Briggs (1981) that even with high rainfall (250 mm), for soils with K_d values of 1 to 10 mL/g there will be little movement below 0.05 m, and this range encompasses values of 1.3–2.9 mL/g as found from days 2–30 in this study. Moreover, on a Redoxic Hydrosol and Red Ferrosol used for sugarcane (Simpson *et al*. 2001) and on a Sodosol for grain cropping (Hargreaves and Noble 1993), atrazine was rarely found below 0.30 m.

Total loss of atrazine in runoff

Wauchope (1978) considers that for the majority of pesticides, total losses are 0.5% or less of the amounts applied unless severe rainfall conditions occur within a fortnight of application and that pesticides with solubilities >10 mg/L are lost mainly in the water phase in runoff. This is supported by the present study with atrazine (solubility 33 mg/L) and total loss of about 0.4%.

Conclusions

Atrazine dissipated rapidly (half life 16–20 days) in the soil, reducing the potential for losses by both runoff and leaching. Minimal leaching of atrazine occurred from the surface soil with cropping on this Vertosol. Moreover, the uniform profile implies effective sorption much deeper than the surface, so there should be little expectation of leaching to groundwater. Runoff accounted for a loss of about 0.4% of applied atrazine, most of this being in solution, rather than sorbed to sediment. These conclusions are supported by the K_d values for the soil and K_p values for the runoff. However, the timing of the runoff after atrazine application is a crucial consideration and much higher losses in runoff are predicted if heavy rains fall soon after application of the herbicide. Therefore, every endeavour should be made to avoid atrazine application at a time when heavy rains are expected, as exemplified by the rapid loss of KCl-extractable atrazine after 30 days in this study.

A strong relationship was found between concentrations in the soil and in runoff. Minimising off-site movement of atrazine requires cultural practices that minimise the concentration in the soil surface (e.g. incorporation and avoiding over-application) and minimise the chances of runoff.

This study is one of few to follow the changes in KCl-extractable atrazine in the field and help account for the

subsequent ineffectiveness of the herbicide for weed control. The rapid dissipation of KCl-extractable atrazine is not accounted for by either runoff or leaching and is probably due to degradation. The K_d, K_{OC}, and K_p values for atrazine and DEA in this study fall within the ranges reported elsewhere in Australia and overseas. It was identified that field-measured K_d may provide a useful surrogate for K_p. Also the concentrations of total atrazine > KCl-extractable atrazine ≫ DEA > DIA follow the pattern expected from research elsewhere.

Acknowledgments

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