Efficacy of atrazine and simazine applications over harvest residue in Queensland's subtropical softwood plantations

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Summary

This study investigated the efficacy of atrazine and simazine when spray technique, amount and timing of herbicide, and amount/arrangement of harvest residue were varied. Separate atrazine and simazine field trials were undertaken, soon after site-preparation, in second-rotation native hoop pine and exotic *Pinus* plantations, respectively, in south-eastern Queensland.

Spray patterns and atrazine recovery were determined when the herbicide was applied manually in a fan- or a sprinkle-spray pattern at a range of delivery rates. Herbicide recovery from soil and overlying residue was quantified following simulated rainfall events, ranging from 5 to 50 mm, over 1 m^2 plots with either nil, single- or double-residue cover. A separate trial assessed the effect of the timing of rainfall for periods between 10 and 30 days after herbicide application.

Under 'ideal' test conditions, the recovery of atrazine applied at 5 kg a.i. ha^{-1} from targets laid across the ground surface was 2.7, 4.7 and 4.5 (mean 4.0) kg ha^{-1} for the fan spray with delivery rates of 60, 120 and 240 L ha^{-1}, respectively, and 2.2, 2.8 and 2.7 (mean 2.6) kg ha^{-1} for the sprinkle spray with delivery rates of 30, 60 and 120 L ha^{-1}, respectively. The poorer recovery from the sprinkle spray was largely attributed to spray being delivered outside the target band width of 3 m.

When residue was retained on site, between 45% and 67% of recovered atrazine and between 27% and 52% of recovered simazine was intercepted by residue cover. Simulated rainfall events of up to 50 mm, and timing of 10 mm events up to 30 days after application, had little effect on the washing of intercepted herbicide from residue to the mineral soil.

Keywords: herbicides; weed control; crop residues; application methods; atrazine; simazine; *Pinus*; *Araucaria cunninghamii*; Queensland

Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-s-triazine) and simazine (2-chloro-4,6-bis-[ethylamino]-s-triazine) are important pre- and post-emergent residual herbicides. They are used to control fast-growing competitor weed species throughout the native and exotic softwood plantation estates of the Queensland Department of Primary Industries Forestry (QDPIF). Most of these estates are in south-eastern Queensland. The native hoop pine (*Araucaria cunninghamii*) plantations (45 000 ha) are within the coastal hinterland ranges on undulating to steep topography with well-drained, fine-textured soils which are highly fertile and relatively rich in organic carbon. The exotic *Pinus* (*P. elliottii*, *P. caribaea* var. *hondurensis* and their hybrid) plantations (150 000 ha) are primarily in coastal lowland areas where topography is flat to undulating (typically slopes <5%) and soils are coarse textured, infertile with little organic carbon, and subject to periodic waterlogging.

Because of differences between plantation species in specific herbicide tolerance, atrazine is used in hoop pine plantations and simazine in *Pinus* plantations. The herbicides are applied at rates up to 5 kg a.i. ha^{-1} (treated area) in bands (typically between 2.5 m and 3 m wide) along planting rows for the first 12 to 24 months of the rotation. The broad-scale rate is around 2.5 kg a.i. ha^{-1} because a significant proportion of the plantation area is not treated, being within the inter-row or in roading and watercourse protection zones. Across both plantation estates, herbicides are typically applied manually from a knapsack with either a fan- or sprinkle-spray unit, although some spraying from tractor-mounted units does occur. Recently the sprinkle spray has become popular because of operational efficiencies associated with a wider spray band (a single pass being required for a planting row) and the lower volume of mixture required per unit of land area. In contrast, the fan spray requires two passes on each row and a greater volume of mixture per unit of land area. To date, the selection of the optimum dosage for weed control has been based on empirical studies. However, environmental and economic constraints now make it necessary to minimise chemical usage. Therefore, quantitative studies have been undertaken, aimed at gaining a better understanding of the fate of applied herbicides.

Some anecdotal evidence from field observations in QDPIF plantations suggests that the efficacy of weed control by triazines has declined, and it has been proposed that harvest residues may be preventing direct contact between the herbicide and the mineral soil. Moreover, Bubb and Barnes (2000) reported that the recovery of atrazine in the mineral soil beneath harvest residues in a QDPIF hoop pine plantation, the day after application, was on average only 36% of the target rate. Similarly, studies in agriculture have reported between 15% and 80% of applied herbicide being intercepted by crop residues and associated vegetation (Sadeghi and Isensee 2001). However, whilst interception is an important process, it is also likely that more than one factor is contributing to the poor weed control. In particular, duration and effectiveness of control depends on the amount of chemical applied, the effectiveness of application, the soil type, antecedent soil moisture and particular weed species. The amount and timing of rainfall are also important factors (Shipitalo *et al*. 1990; Sorenson *et al*. 1991).

The systems of residue retention currently used by QDPIF have been evolving over the past 5–6 y and have generally replaced the traditional methods of 'push and burn' and 'broadcast burn'. In the steep hoop pine plantations, site preparation consists of forming planting lanes (single lanes 5 m wide or multiple lanes 15 m wide) by raking large harvest debris (>10 cm diameter) into continuous windrows along the contour. Either an excavator-mounted rake head or a 'dozer with a wide-tine stick-rake blade is used. The smaller logging debris and forest litter is left relatively undisturbed as *in situ* ground cover, and the windrows are left to decompose (Costantini *et al*. 1997). In the *Pinus* plantations, planting lanes are established by cultivating directly through the *in situ* harvest debris. A consequence of these new systems is that the amount of residue varies depending on the method of harvesting (e.g. roadside versus at-stump processing) and the technique used for site preparation (strip, continuous or intermittent mounding). The retention of residue is paramount to long-term maintenance of site fertility, not only as a major nutrient sink, but also through improvement of key physical, chemical and biological soil processes, and erosion mitigation. However, the residue cover remaining after site preparation can have high spatial variability. For instance, Bubb *et al*. (2000, 2002) found a significant degree of disturbance and redistribution of residue in both plantation estates following harvest and site preparation.

To date there has been little reported quantitative research on the efficacy of atrazine and simazine in Queensland's subtropical forest plantations in respect of spray techniques, and the interaction between systems of residue retention and the amount and timing of rainfall following application. The objectives of this study were to: (i) quantify the recovery of atrazine applied by fan- and sprinkle-spray techniques; and (ii) assess the effects of the amount and timing of rainfall following application on herbicide interception by harvest residues.

Materials and methods

Study location

The study was conducted at two sites which had been recently clearfelled and subsequently prepared for a second rotation (2R), namely: (i) a hoop pine plantation at Imbil situated at 26°29'S 152°40'E; and (ii) a *Pinus* plantation at Toolara situated at 26°02'S 152°52'E.

The Imbil site is a relatively level area on a ridge with a north-eastern aspect, an altitude of 200 m a.s.l., and a slope of about 5%. The soil is classified as a Xanthozem (after Stace *et al*. 1968) with a clay loam A horizon to 50 cm, overlying a light clay B1 horizon to 110 cm. Saturated hydraulic conductivity (Ksat) was determined by the well permeameter method of Reynolds (1993) at the surface, and 20 and 70 cm depths. The mean values, 420, 40 and 20 mm h^{-1}, respectively, indicate a highly permeable soil typical of the study area.

The Toolara site is relatively level with a northerly aspect and altitude of about 50 m a.s.l. The soil is characterised as a Grey Podzolic with a clayey sand A horizon to 30 cm and a fine sandy clay B horizon to 100 cm. The mean Ksat values determined at the soil surface, 20 and 70 cm depths were 53, 6 and 17 mm h^{-1} respectively.

Design

The study assessed (i) the spray pattern and atrazine recovery for two routinely-used application techniques (i.e. fan and sprinkle sprays); (ii) the effect on herbicide recovery of interaction between residue cover and amount of rainfall; and (iii) the effect of the timing of rainfall on herbicide recovery.

(i) Spray techniques

The design for this component of the study consisted of two application techniques ('fan' spray and 'sprinkle' spray), three delivery rates (60, 120 and 240 L ha^{-1} for the fan spray and 30, 60 and 120 L ha^{-1} for the sprinkle spray) and three replicates. The fan spray had a 'Turbo Teejet TT110-05' nozzle, and the sprinkle spray a 'Dan microsprinkler 8855' nozzle. Both techniques used a knapsack with 1 bar pressure output which delivered about 1.1 L min^{-1}.

First, a series of test runs determined the height above ground at which the spray nozzle should be held to provide the required band width. Then the trial was conducted along a level gravelled road during a period of fine weather and minimal wind. Each treatment run was assessed over a path 10 m long with a spray-band width of 3 m. The fan spray was applied as two contiguous bands 1.5 m wide, and the sprinkle spray in a single 3 m band. The low rates for both techniques (60 and 30 L ha^{-1} for the fan and sprinkle sprays, respectively) were applied at a walking speed of 2 m s^{-1}. The mid- and high rates were applied at the standard 1 m s^{-1}, the high rate being a second application of the mid-rate. The atrazine mixture for each treatment was calibrated to deliver a rate of 5 kg a.i. ha^{-1}.

The spray pattern for each treatment was assessed using commercially-available water-sensitive cards (7.5 cm × 2.5 cm) placed on three randomly-selected transects across a run; ten cards were placed evenly on each transect across the path of the 3 m spray band. Following treatment, the cards were collected and photographed. Atrazine recovery was quantified separately by using cardboard-backed alfoil targets (10 cm × 10 cm) placed across the spray path, as above. This trial was not repeated for simazine as its spray pattern was assumed to be similar to that of atrazine.

(ii) Interaction between amount of residue cover and amount of rainfall

The design for this component of the study was based on three levels of residue cover (nil, single and double), four rainfall amounts (5, 10, 20 and 50 mm), and three replications. Plot size was 1 m^2 surrounded by a minimum 1 m buffer width, all treatments being allocated randomly. Residue was removed from the bare plots and transferred to the double-residue plots, whilst undisturbed plots were used as single residue. There was a degree of variability in the residue mass across the single- and double-residue treatment plots. In the hoop pine plantation the masses typically ranged from 45 to 80 t ha^{-1} and 90 to 160 t ha^{-1}, respectively; across the *Pinus* plantation, masses ranged from 20 to 35 t ha^{-1} and 50 to 70 t ha^{-1}, respectively.

In line with manufacturer's guidelines and QDPIF best management practice (BMP), atrazine and simazine were applied when moderate antecedent soil moisture was present at the respective sites. Plots were treated at rates equivalent to 5 kg a.i. ha^{-1} with a mixture delivery rate of 120 L ha^{-1} using the fan-spray method.

Rainfall was applied with a simulator at a high intensity of 50–150 mm h^{-1}; the intensity was adjusted for individual plots to immediately below that which would cause surface runoff. A plastic skirt around the rainfall simulator prevented drift to adjacent plots. High-intensity rainfall was used to ensure that rainfall was applied to all plots on the same day as the herbicide application.

Immediately following the simulated rainfall, the residue (where present) was removed from the plot, weighed and sub-sampled separately for later determination of moisture content and herbicide concentration. Subsequently, three replicate soil core samples were taken and bulked for similar analysis. Soil sampling was limited to a depth of 10 cm as it was assumed this was the primary region of the profile where germination and development of weed species occurs. To calculate herbicide recovery from soil in terms of kg ha^{-1}, soil bulk density (at 0 to 10 cm depth) was determined from five replicate soil cores taken from five soil pits at each site.

(iii) Interaction with rainfall timing

The third component of the study consisted of two levels of residue cover (nil and single), and three rainfall timings (10, 20 and 30 days after application) of a 10 mm rainfall event, and three replicates. Plot size, layout, residue treatments and allocation of treatments were as outlined above. The trial area was covered by a clear plastic structure to exclude natural rainfall yet allow transmission of direct sunlight along with relatively unimpeded air circulation. Atrazine and simazine were applied, and residue cover and soil sampled, in the same manner as outlined above.

Triazine concentration in water samples (to determine the concentrations in spray mixtures) was determined by high performance liquid chromatography (HPLC) using the method of Reupert *et al*. (1990). Soil samples were assayed by an initial extraction with acetonitrile, followed by a cleanup with acetone and SPE C18 cartridge; the extracts were analysed by HPLC using a method adapted from Moreau and Mouvet (1997). A similar extraction and cleanup procedure was used for ground litter samples; extracts were analysed by gas chromatography using a nitrogen–phosphorus detector and methods adapted from Walker and Blacklow (1994).

Results and discussion

(i) Spray techniques

Atrazine recovery (mean) from targets ranged from 2.7 to 4.7 kg ha^{-1} (54% and 94% of the target rate) for the fan spray and from 2.2 to 2.8 kg ha^{-1} (44% and 54% of the target rate) for the sprinkle spray (Table 1). With the exception of the Fan 60 (fan application at 60 L ha^{-1}), the recovery from the fan spray was consistently higher (about 60%) than from the sprinkle spray. The Fan 60 treatment was repeated with no observed changes to the results presented.

A low recovery from the fan spray at high walking speeds (i.e. 2 m s^{-1}) has been noted in previous screening trials (unpublished data), but reasons for this poor performance have not been fully investigated. Recoveries were similar at fan-spray delivery rates of 120 and 240 L ha^{-1}, a result mirrored by visual assessment of water-sensitive cards (Fig. 1). This suggests that a delivery rate of 120 L ha^{-1} would be more suitable for field operations because of the lower mass of mixture required to be carried manually across the general plantation area.

The poor recovery from the sprinkle spray can be largely attributed to a significant amount of spray being delivered outside the target band as indicated by water-sensitive paper placed outside the designated 3 m band (data not presented). It was also noted that any upward movement of the relatively long (3 m) boom increased the amount of spray delivered to the non-target region. Given that this trial was conducted on flat open terrain, these results are likely to represent a 'best case scenario'; typical field conditions often require operators to traverse much rougher terrain. Past screening work in QDPIF plantations directed to identifying optimal lethal dosage of herbicide was based on fan-spray techniques. Despite the operational efficiencies associated with the sprinkle spray, it is likely to deliver a sub-optimal dose to the

Table 1. Atrazine recovered from alfoil targets following application at 5 kg a.i. ha^{-1} to a level surface under fine weather conditions and minimal wind. Standard deviations are shown in parentheses.

Spray nozzle and delivery rate (L ha^{-1})	Atrazine recovery from target (kg a.i. ha^{-1})
Fan 60	2.7 (1.0)
Fan 120	4.7 (0.2)
Fan 240	4.5 (0.8)
Mean	4.0
Sprinkle 30	2.2 (0.8)
Sprinkle 60	2.8 (0.5)
Sprinkle 120	2.7 (0.5)
Mean	2.6

a.i. = active ingredient

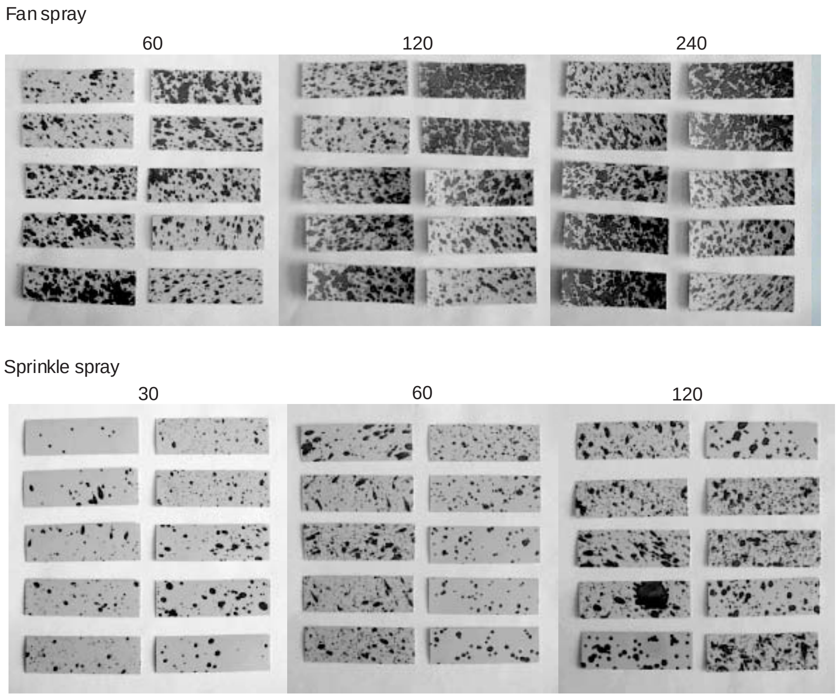

Figure 1. Spray distribution on water-sensitive paper from fan and sprinkle sprays at varying mixture delivery rates (30 to 120 L ha $^{-1}$)

target area, and to cause wastage when spray is directed to the non-target inter-row area. Consequently, the adoption of the sprinkle-spray technique in recent years without sufficient quantitative testing has probably contributed to reduced triazine efficacy in both plantation estates.

(ii) Interaction between amount of residue cover and amount of rainfall

Across the nil-residue plots at the Imbil hoop pine plantation, the recovery of atrazine from the soil (top 10 cm) ranged between 2.0 and 3.1 (mean 2.7) kg ha^{-1} (Table 2). Less atrazine was recovered from the soil beneath residue plots: 0.4 to 1.5 (mean 0.9) kg ha^{-1}. There were similar findings at Toolara; the recovery of simazine from soil in the nil-residue plots was between 3.4 and 4.3 (mean 3.9) kg ha^{-1}, and from the soil (top 10 cm) beneath residue plots, between 0.9 and 2.0 (mean 1.4) kg ha^{-1} was recovered (Table 3). The difference between the target application rate (i.e. 5.0 kg ha^{-1}) and the actual herbicide recovered from the nil-residue plots at both sites was probably due to wind or directional drift away from the target area. Leaching may also have contributed to the differences, because the soil, which was saturated, has a relatively high saturated hydraulic conductivity.

In the hoop pine plantation the combined total atrazine recovered from soil and residue cover ranged from 1.7 to 2.6 (mean 2.0) kg ha^{-1} on single-residue plots and from 1.2 to 2.9 (mean 2.1) kg ha^{-1} on double-residue plots. Similarly in the *Pinus* plantation, the combined total simazine for single- and double-residue plots ranged from 1.5 to 2.7 (mean 2.2) kg ha^{-1}, and from 2.0 to 3.1 (mean 2.5) kg ha^{-1}, respectively. Irrespective of the amount of rainfall, the amount of atrazine intercepted by hoop pine harvest debris as a percentage of the total recovered from the soil+residue system for single- and double-residue treatments averaged 45% for single-residue and 67% for double-residue treatments. Similarly, simazine intercepted by *Pinus* harvest residue in single- and double-residue treatments was on average 27% and 52% respectively of the total recovered from the soil+residue system. These findings are similar to those widely reported in agricultural studies where overlying crop residue intercepts between 15% and 80% of applied atrazine in zero-tillage systems (Isensee *et al*. 1998; Sadeghi and Isensee 2001).

Table 2. Recovery of atrazine (kg ha^{-1}) from hoop pine residue cover and soil following simulated rainfall events ranging between 5 and 50 mm. Standard deviations are shown in parentheses.

Residue treatment and source of recovered herbicide	Amount of simulated rainfall (mm)				Mean — all rainfall
	5	10	20	50	
Nil residue					
Cover	Nil	Nil	Nil	Nil	Nil
Soil	2.8 (1.6)	2.0 (1.1)	3.0 (0.6)	3.1 (0.5)	2.7
Total	2.8	2.0	3.0	3.1	2.7
Single residue					
Cover	1.0 (0.6)	0.7 (0.4)	0.7 (0.7)	1.1 (1.1)	0.9
Soil	0.8 (0.3)	1.4 (0.8)	0.9 (0.5)	1.5 (1.0)	1.1
Total	1.8	2.1	1.7	2.6	2.0
Double residue					
Cover	0.9 (1.0)	1.2 (0.7)	2.3 (1.0)	1.3 (0.7)	1.4
Soil	0.4 (0.2)	0.5 (0.3)	0.6 (0.5)	1.3 (0.6)	0.7
Total	1.2	1.7	2.9	2.6	2.1

Table 3. Recovery of simazine (kg ha^{-1}) from *Pinus* residue cover and soil following simulated rainfall events ranging between 5 and 50 mm. Standard deviations are shown in parentheses.

Residue treatment and source of recovered herbicide	Amount of simulated rainfall (mm)				Mean — all rainfall
	5	10	20	50	
Nil residue					
Cover	Nil	Nil	Nil	Nil	Nil
Soil	3.5 (0.7)	4.3 (0.7)	3.4 (0.8)	4.2 (1.2)	3.9
Total	3.5	4.3	3.4	4.2	3.9
Single residue					
Cover	0.7 (0.2)	0.4 (0.0)	0.5 (0.3)	0.9 (0.2)	0.6
Soil	2.0 (0.7)	1.7 (0.7)	1.0 (0.5)	1.6 (0.1)	1.6
Total	2.7	2.1	1.5	2.5	2.2
Double residue					
Cover	1.6 (0.5)	1.7 (1.0)	1.0 (0.1)	0.9 (0.3)	1.3
Soil	1.5 (0.8)	0.9 (0.1)	1.3 (0.8)	1.1 (0.2)	1.2
Total	3.1	2.6	2.3	2.0	2.5

Regression analysis shows a significant linear relationship between the amount of rainfall (mm) and the amount of atrazine recovered (kg ha^{-1}) from the soil, but the slope of the relationship is relatively small, being 0.01 ($R^2 = 0.41$, $p < 0.05$) and 0.02 ($R^2 = 0.99$, $p < 0.05$) for single- and double-residue treatments respectively. These relationships represent a 0.1 to 0.2 kg ha^{-1} increase in atrazine recovery from the soil for each additional 10 mm of rainfall. In comparison, there was no significant relationship between the amount of rainfall and simazine recovery.

These results suggest that rainfall events of up to 50 mm wash little atrazine or simazine from harvest residues at either plantation estate. This was quite unexpected, given results from similar studies in agriculture where, for instance, up to 50% of herbicide can be washed from residues by the first 10 mm of rain (Mickelson *et al*. 2001). The type of plant material can also play an important role: atrazine has been found to be more readily washed from aged crop residues than from living or fresh residues (Sigua *et al*. 1993; Isensee *et al*. 1998). Whilst it is evident that interception can play an important role in reduced efficacy of herbicide application, the processes by which forest harvest residues prevent atrazine and simazine from being transported to soil require more research. Indeed such research may also help to identify an adjuvant that may reduce the effects of interception by residue.

(iii) Interaction with the timing of rainfall

Following 10 mm rainfall events at 10, 20 and 30 days after application, the average amount of atrazine washed from hoop pine residue to the soil was 1.1, 0.3 and 0.7 kg ha^{-1}. Recoveries from the soil on plots with nil residue were 3.0, 1.6 and 1.6 kg ha^{-1} (Table 4). Similarly, the amounts of simazine recovered from the soil beneath *Pinus* residue were 1.2, 1.2 and 0.5 kg ha^{-1} at 10, 20 and 30 days after application respectively compared with 3.1, 2.9 and 2.0 kg ha^{-1} respectively, for the nil-residue plots (Table 5). Interestingly, the amount of atrazine

Table 4. Trends in atrazine recovered (kg ha^{-1}) from hoop pine residue cover and soil following a simulated 10 mm rainfall event at 10, 20 and 30 days after herbicide application. Standard deviations are shown in parentheses.

Residue treatment and source of recovered herbicide	Interval between herbicide application and simulated rainfall event (days)		
	10	20	30
Nil residue			
Soil	3.0 (1.1)	1.6 (0.4)	1.6 (0.8)
Single residue			
Cover	0.6 (0.2)	1.0 (0.2)	1.5 (0.1)
Soil	1.1 (0.5)	0.3 (0.1)	0.7 (0.1)
Total	1.7	1.3	2.2

Table 5. Trends in simazine recovered (kg ha^{-1}) from *Pinus* residue and soil following a simulated 10 mm rainfall event at 10, 20 and 30 days after application. Standard deviations are shown in parentheses.

Residue treatment and source of recovered herbicide	Interval between herbicide application and simulated rainfall event (days)		
	10	20	30
Nil residue			
Soil	3.1 (0.6)	2.9 (0.5)	2.0 (0.5)
Single residue			
Cover	1.7 (0.8)	2.1 (0.2)	1.7 (0.2)
Soil	1.2 (0.6)	1.2 (0.4)	0.5 (0.5)
Total	2.9	3.3	2.2

intercepted by hoop pine residue increased with time (from 0.6 to 1.5 kg ha^{-1}), suggesting some sort of 'sponge' effect, whereas the amount of simazine intercepted by *Pinus* residue remained relatively constant (mean 1.8 kg ha^{-1}). This suggests that both herbicides are being stored in the residue for periods of at least 30 days after application, thus contributing to a reduced efficacy during this period. As demonstrated in the previous section there was little 'washing' effect from the rainfall, and this would seem to hold for the data presented for periods up to at least 30 days after application. Whether these herbicides are washed by subsequent rainfall or released by some other process is not known and warrants further investigation, including whether they play a role in controlling target weed species.

On the basis of first-order kinetics, the half-life of atrazine and simazine in soil with nil residue was 18 and 34 days respectively during autumn. This relatively short persistence compares favourably with that reported by Bubb and Barnes (2000) and Bubb (2001) from leaching studies at Imbil and Toolara, where the average half-life over summer–winter seasons was 12 and 13 days for atrazine and simazine respectively.

Conclusions

In comparison to the fan spray, the sprinkle spray is considerably less effective at meeting target dosage rates. Interception of both atrazine and simazine by forest harvest residue accounts for a significant proportion of the applied herbicide irrespective of the amount of rainfall (up to 50 mm) and its timing up to 30 days after application. It is likely that the poor performance of the sprinkle spray and interception of spray by residue are both contributing to reduced efficacy of these herbicides.

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