

# Reef Rescue Research & Development

Technical Report

Pesticide dynamics in the Great Barrier Reef  
catchment and lagoon: management practices  
(grazing, bananas and grain crops) and risk assessments:  
Tebuthiuron Management in Grazing Lands  
*RRRD038*



Craig M Thornton and Amanda E Elledge



# Pesticide Dynamics in the Great Barrier Reef Catchment and Lagoon: Management Practices (Grazing, Bananas and Grain Crops) and Risk Assessments (Project RRRD038)

## *Tebuthiuron Management in Grazing Lands*

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Cover photographs: Graslant tebuthiuron granular pellets (top left), paddock 512 days after aerial application of tebuthiuron (top right), paddock 793 days after aerial application of tebuthiuron (bottom left) and runoff event through flume (bottom right) are all sourced from the Brigalow Catchment Study photo archives, courtesy of the Department of Natural Resources and Mines.

This report is available from the Reef Rescue R&D website: <http://www.reefrescueresearch.com.au>

## Executive Summary

The Brigalow Belt Bioregion of Queensland has been extensively cleared for agriculture, with the majority of cleared areas being utilised for grazing (Thornton and Elledge 2013). If left uncontrolled, the proportion of woody species in grazed pastures increases over time, leading to a decrease in pasture productivity (Burrows 2002, Scanlan 2002). This productivity decline has negative implications for both the environment and the viability of grazing enterprises. In order to avert productivity decline, the regrowth of woody species in grazed pastures is typically controlled by either mechanical intervention, such as blade ploughing or stick raking, or by the use of herbicides, such as tebuthiuron (Partridge *et al.* 1994).

Under Objective 1 of Reef Plan 2009 (Department of the Premier and Cabinet 2009), tebuthiuron is one of the five priority herbicides identified as main pollutants in water entering the Great Barrier Reef lagoon. A literature review of tebuthiuron research in Australia found 12 published papers; six of which focused on end of system water quality loads and concentrations at the basin scale (>10,000 km<sup>2</sup>) with little focus on process understanding. Thus, this study sought to examine the movement of tebuthiuron in runoff at both the plot (1.7 m<sup>2</sup>) and paddock (12.7 ha) scales, in addition to movement in soil.

At the paddock scale, runoff 100 days after application showed high concentrations of tebuthiuron (mean 103 µg/L); however, the total lost in runoff was only 0.05% of the amount applied. Runoff was monitored up to 472 days after application with losses of applied tebuthiuron ranging between 0.05 and 0.45%. The highest loss was associated with the highest discharge runoff event. Comparison of individual event hydrographs showed that tebuthiuron concentrations declined exponentially with time. Furthermore, results indicated that tebuthiuron movement in runoff was in a dissolved form rather than being transported adsorbed to suspended sediments.

At the plot scale, maximum load of tebuthiuron in the soil from 0 to 5 cm deep occurred 28 days after application. This is likely due to the movement of tebuthiuron from trash into the soil following rainfall. Maximum loads in the soil from 5 to 20 cm deep occurred between 56 and 98 days after application. After 98 days tebuthiuron concentrations at all depths tended to decrease over time. Losses of tebuthiuron in runoff were greater from Vertosols than Sodosols.

This study has filled a significant knowledge gap about the behaviour of tebuthiuron at the plot and paddock scale, and provides data where none previously existed. The data also improves understanding of tebuthiuron behaviour from predominantly grazed catchments that discharge into the Great Barrier Reef lagoon. Limitations of this study are: (1) data were sourced solely from the Fitzroy Basin; (2) only Vertosol and Sodosol soil types were investigated; (3) investigation of persistence in soil was limited to particular profile depths and time intervals; and (4) runoff at the paddock scale was limited to 17 months data with only small runoff events immediately after application. These limitations could be easily addressed by replicating the plot components of this study on additional soil types in other

Great Barrier Reef catchments. Opportunities also exist for replicating the paddock scale work in additional catchments of the Brigalow Catchment Study.

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## Abbreviations

<b>a.i.</b>	Active Ingredient
<b>EMC</b>	Event Mean Concentration
<b>GBR</b>	Great Barrier Reef
<b>PQL</b>	Practical Quantitation Limit
<b>PSII</b>	Photosystem-II– a mode of action of certain herbicides

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## General Introduction

### ***Great Barrier Reef Water Quality***

The Great Barrier Reef (GBR) is the largest reef ecosystem in the world, and due to its outstanding beauty and high diversity of habitats and species, it was placed on the World Heritage List in 1981 (Great Barrier Reef Marine Park Authority 2010; United Nations Educational, Scientific and Cultural Organisation 2013). The GBR covers 348,000 km<sup>2</sup> along the north-eastern coast of Australia and there are five adjacent terrestrial regions that are a main source of pollutants: Wet Tropics, Burdekin, Mackay-Whitsundays, Fitzroy and Burnett-Mary (Great Barrier Reef Marine Park Authority 2010; Department of the Premier and Cabinet 2011; United Nations Educational, Scientific and Cultural Organisation 2013). These regions have undergone extensive anthropogenic modifications over the last 150 years which has led to increased pollutant loads of nutrients, sediments and pesticides (Department of the Premier and Cabinet 2009).

For example, it has been estimated that the mean annual load of photosystem-II (PSII) herbicides entering the GBR is 30,000 kg/yr. Anthropogenic activities can be attributed to 100% of this load, as no herbicides would have been present before European settlement (Kroon *et al.* 2012). Herbicides have the capacity to adversely impact non-target organisms, such as coral and seagrass (Department of the Premier and Cabinet 2011). However, the persistence of pesticides in tropical marine water is poorly understood (Brodie *et al.* 2001). Understanding pesticide dynamics is imperative so that appropriate management practices can be implemented to reduce non-target environmental impacts and ensure long-term health of the GBR (Devlin and Lewis 2011).

The Reef Water Quality Protection Plan, commonly referred to as Reef Plan, was enacted by the Australian and Queensland Governments in 2009 to reduce the risk of declining water quality entering the GBR (Department of the Premier and Cabinet 2009). Reef Plan identifies agriculture as the largest contributor to pollutant loads entering the GBR (Department of the Premier and Cabinet 2009) and sets targets for pollutant reductions. Thus, the Reef Rescue Research and Development Program, a component of Reef Plan, aims to improve understanding of the link between agricultural land management practices and environmental impacts on water quality for the grazing, sugarcane, horticulture and dairy sectors.

### ***Tebuthiuron and the Grazing Industry***

Five PSII herbicides are targeted in Reef Plan: ametryn, atrazine, diuron, hexazinone and tebuthiuron (Department of the Premier and Cabinet 2009). The first four are registered for use in sugarcane whereas tebuthiuron is registered for use in grazing (Lewis *et al.* 2007). Grazing in reef catchments accounts for 87% (27 MHa) of agricultural land use, which mainly occurs in the Burdekin (12 MHa) and Fitzroy (11 MHa) Basins (Australian Bureau of Statistics

2009). In Queensland, tebuthiuron is used to control regrowth of brigalow (*Acacia harpophylla*), tea tree (*Melaleuca spp.*) and other problem woody weeds on grazing lands (Figure 1) (Dow AgroSciences 2013a, b). It is applied to the soil in a granular pellet form which is then absorbed by plant roots and translocated to target sites in the stems and leaves (Camilleri *et al.* 1998; Tomlin 2000; Lewis *et al.* 2012).

Tebuthiuron has been detected in GBR flood plumes from the Wet Tropics, Burdekin, Mackay-Whitsunday and Fitzroy regions (Kennedy *et al.* 2012b). The highest concentration of tebuthiuron in plumes was detected in the Fitzroy Basin (0.014 µg/L), which was more than double the second highest maximum from the Burdekin Basin (0.006 µg/L) (Kennedy *et al.* 2012b). In addition, Kennedy *et al.* (2012a) reported tebuthiuron concentrations exceeding the 0.02 µg/L trigger value for 99% ecological protection at sites between 3 and 11 km from the mouth of the Burdekin River and up to 240 km from the mouth of the Fitzroy River. Thus, the large area of land that is grazed and the high concentration of tebuthiuron sourced from grazed reef catchments indicate the importance of understanding tebuthiuron dynamics in grazing systems.

### **Current Knowledge Gap**

Despite the regular detection of tebuthiuron in the GBR, there is a paucity of information on how this herbicide behaves in the Australian environment. A Scopus ([www.scopus.com](http://www.scopus.com)) database search was conducted in July 2013 using the keywords 'tebuthiuron' and 'Australia' which resulted in only 12 journal papers. Six of these studies focused on freshwater and/or marine water quality at the reef catchment scale (Lewis *et al.* 2011; Kennedy *et al.* 2012a, b; Kroon *et al.* 2012; Lewis *et al.* 2012; Smith *et al.* 2012); five studies determined the impacts and toxicity of herbicides to a range of organisms, including plants, fish, algal, coral and seagrass (Lane *et al.* 1997; Jones and Kerswell 2003; van Dam *et al.* 2004; Bengtson Nash *et al.* 2005; Magnusson *et al.* 2010); and one study assessed the role of herbicides on sustainability and water quality of forest ecosystems (Neary and Michael 1996). Some of these studies focus on PSII herbicides as a group rather than quantifying the concentration and effects of tebuthiuron as an individual herbicide. Most of the papers, particularly those on GBR water quality, have monitored large areas with multiple land uses which mean that interpretation of tebuthiuron data from grazing is inferred rather than measured directly. Furthermore, the literature currently shows no Australian data on the movement of tebuthiuron in soil or runoff from grazed pastures at the paddock scale. Review of the international literature indicates that rainfall (Bovey *et al.* 1978; Scifres 1980) and soil organic matter and clay content (Chang and Stritzke 1977) are linked to tebuthiuron dynamics. The current lack of data relating to tebuthiuron movements in the Australian grazing landscape, including loss in runoff, is a distinct knowledge gap.



Figure 1: Temporal series of photographs from the Brigalow Catchment Study grass pasture that had aerial application of tebuthiuron in November 2011.

## ***Project Objectives***

The overarching goal of this project was to provide preliminary data from Australia on the persistence and movement of tebuthiuron in a grazing system. This was achieved by the completion of three main objectives:

- (1) Determine the persistence of tebuthiuron in Black and Grey Vertosols and Black and Brown Sodosols to a depth of 40 cm up to 314 days after application under natural rainfall conditions.
- (2) Compare tebuthiuron loads exported in runoff from different formulations (granular and dry flowable) and soil types (Vertosol and Sodosol) at the plot scale (1.7 m<sup>2</sup>) under simulated rainfall conditions.
- (3) Quantify tebuthiuron loads exported in runoff at the paddock scale (12.7 ha) under natural rainfall conditions.

## **Methods**

### ***Study Site***

Data were collected at the Brigalow Catchment Study site (24°48'S and 149°47'E) which is located near Theodore in central Queensland, Australia (Figure 2). Soils are predominantly Black and Grey Vertosols with a mean slope of 2.5%. The site was vegetated with brigalow scrub communities in its virgin state (Thornton and Elledge 2012). The region has a semi-arid, subtropical climate. Summers are wet with 70% of the annual mean rainfall of 720 mm falling between October and March, while winter rainfall is low (Thornton *et al.* 2010). Further site details are documented in other sources (Cowie *et al.* 2007; Thornton and Elledge 2013).

### ***Tebuthiuron Movement through the Soil Profile under Natural Rainfall***

The vertical movement of tebuthiuron on two soil types was investigated at the plot scale under natural rainfall conditions. The first soil type was an association of Black and Grey Vertosols, while the second soil type was an association of Black and Brown Sodosols. Each soil type was the subject of two separate investigations as described below.

As soil concentrations of tebuthiuron decrease with increased radial distance from the site where granular pellets are placed (Parry and Batterham 1999) there is a risk of bias in results due to the choice of sampling locations within the plot. To reduce this risk a dry flowable formulation (Spike® 80DF) (Dow AgroSciences 2013c) was used in lieu of the granular

product that is standard practice for commercial applications in Australia. Plots of 1.0 x 1.7 m were treated with 3000 g/ha of active ingredient (a.i.).

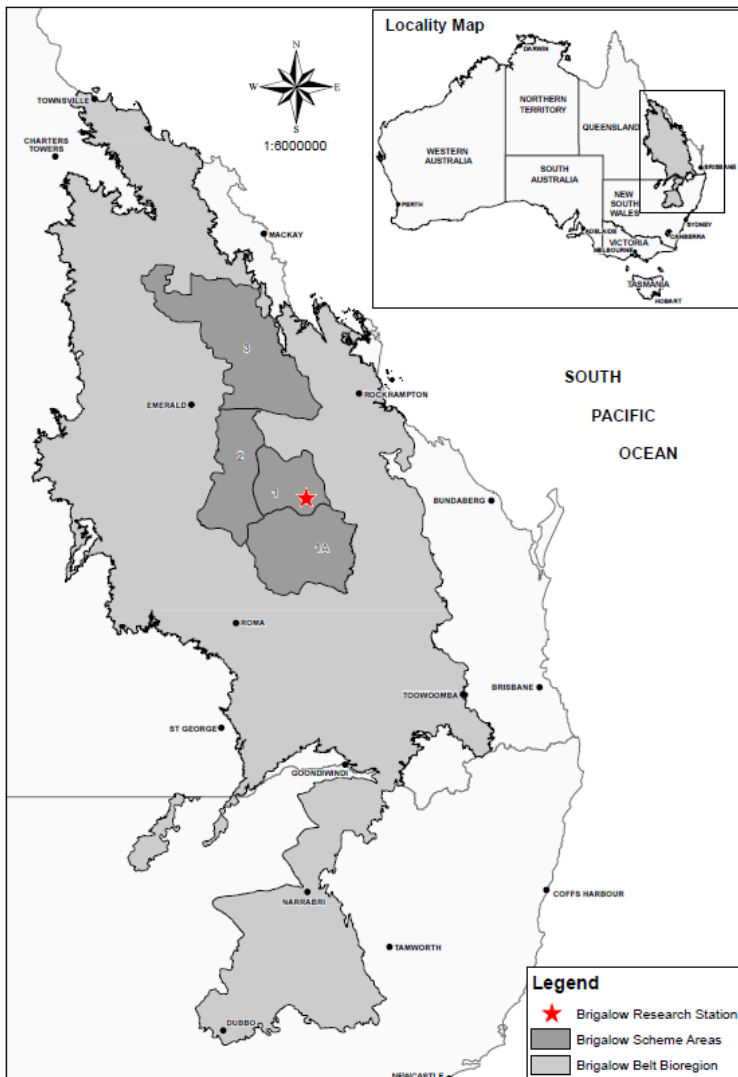


Figure 2: Brigalow Catchment Study site (star) located in the Fitzroy Basin within the Brigalow Belt Bioregion of central Queensland Australia.

The movement of tebuthiuron down the soil profile was determined by taking soil samples with a hydraulic coring rig. Six samples were taken randomly within a plot at each sampling interval. Each plot was used for only one sampling interval with no plot was sampled twice. Herbicide analyses by liquid chromatography mass spectrometry were completed by Queensland Health Forensic and Scientific Services in Coopers Plains, Queensland. Concentration of tebuthiuron in soil was converted into mass per sampling depth increment using measured soil bulk density. Dissipation was represented using a first-order equation and half-lives of tebuthiuron in soil to 40 cm calculated according to the method of Wauchope *et al.* (1992).

### First Investigation

The first investigation was conducted on soils vegetated with buffel grass (*Cenchrus ciliaris* cv. Biloela). Based on international literature showing half-lives of tebuthiuron exceeding



360 days in soil (Elanco 1988; Bicalho *et al.* 2010), the first investigation sampled soil at 57, 104, 197 and 314 days after tebuthiuron application on 5 October 2011. Soil in the first two sampling intervals was sampled at 0 to 2.5 cm, 2.5 to 5 cm, 5 to 10 cm and then 10 cm increments thereafter to 30 cm; day 197 sampled to 40 cm; and day 314 sampled to a depth of 100 cm. The smaller depths originally sampled were based on an assumption that there would be limited movement of tebuthiuron in the soil. The results showed that this assumption was incorrect; however, long delays for laboratory results meant that the experimental design could not be adapted. Rainfall occurred between all sampling intervals and the cumulative total was 710 mm over the investigation period (Table 1).

**Table 1: Cumulative rainfall since tebuthiuron applied on 5 October 2011 and total rainfall between sampling intervals for the first investigation.**

Days Since Application	Date	Cumulative Rainfall Since Application (mm)
57	01/12/2011	84.7
104	17/01/2012	228.2
197	19/04/2012	517.2
314	14/08/2012	709.7

### Second Investigation

The second investigation was conducted on soils vegetated with butterfly pea (*Clitoria ternatea* cv. Milgarra) and Rhodes grass (*Chloris gayana* cv. Callide). More intensive sampling was conducted to obtain data at greater soil depths and shorter time intervals, particularly within the first 50 days after tebuthiuron application. Tebuthiuron is not normally applied to butterfly pea in a commercial operation, as it is typically used as a ley pasture in cropping systems. However, this site was selected due to its close proximity to the first investigation site and similar soil types. Soil was sampled at 1, 3, 7, 16, 21, 30, 55, 70 and 104 days after tebuthiuron application on 2 October 2012. The first two sampling intervals were sampled at 0 to 2.5 cm, 2.5 to 5 cm, 5 to 10 cm and then 10 cm increments thereafter to 30 cm; day 7 and 16 sampled to 50 cm; day 21 and 30 sampled to 80 cm; and day 55, 70 and 104 sampled to 100 cm. Tebuthiuron persistence in soil is associated with rainfall (Helbert 1990); thus, only sampling intervals that were separated in time by rainfall were used in analyses after day 1 (Table 2). This reduced the dataset to 1, 16, 30, 55 and 104 days after tebuthiuron application. Cumulative total rainfall over the second investigation period was 174.5 mm.

**Table 2: Cumulative rainfall since tebuthiuron applied on 2 October 2012 and total rainfall between sampling intervals for the second investigation. \* indicates data used in results.**

Days Since Application	Date	Cumulative Rainfall Since Application (mm)
1 *	03/10/2012	0.0
3	05/10/2012	0.0
7	09/10/2012	0.0
16 *	18/10/2012	26.0
21	23/10/2012	26.0
30 *	01/11/2012	53.0
55 *	26/11/2012	165.0
70	11/12/2012	165.0
104 *	14/01/2013	174.5

Despite some soil samples being collected to depths of 100 cm within both the first and second investigations, only results to a depth of 40 cm were presented in this report for three main reasons: (1) no or very low concentrations of tebuthiuron were detected at the lower depths; (2) multiple samples at depth were difficult to obtain, particularly from Sodosols; and (3) sampling error was likely to exceed treatment effect due to the earlier two points.

### ***Tebuthiuron Movement in Runoff at the Plot Scale under Simulated Rainfall***

Simulated rainfall was used to investigate tebuthiuron concentrations in runoff from a Black Vertosol and a Black Sodosol. This study was conducted in buffel grass pasture at the Brigalow Catchment Study site during October 2011. Six plots 1.0 x 1.7 m were established on each soil type and treated with 3000 g a.i./ha of tebuthiuron; three were treated with granular tebuthiuron (Graslan™) (200 g a.i./kg) (Dow AgroSciences 2013b) and the other three with dry flowable tebuthiuron (Spike® 80DF) (800 g a.i./kg) (Dow AgroSciences 2013c). Thus, there were three plots by two tebuthiuron formulation treatments by two soil types.

A standard Paddock to Reef Program storm event was applied to all plots with simulated rainfall applied at intensities between 59 and 81 mm/hr. Rainfall events had an average recurrence interval between 2 and 5 years and an annual exceedance probability between 18 and 39%. Dunkerley (2008) reviewed 40 rainfall simulation studies and found that intensities typically ranged between 60 and 100 mm/hr, which more closely resemble extreme weather events rather than natural rainfall events. Further details on the rainfall simulation setup are documented in Thornton and Elledge (2013).

Tebuthiuron was applied to the plots immediately before simulated rainfall. Rainfall was then applied to wet each plot until runoff commenced. Rainfall continued on the plot for a further 30 minutes, during which time discrete one litre runoff samples were collected at five minute intervals (0, 5, 10, 15, 20, 25 and 30 min) for the later determination of discharge volume using Water Quality Analyser (WQA) (version 2.1.2.4; www.ewater.com.au). Within each interval runoff was also sampled for a set time to generate one 750 ml composite flow weighted average sample from the event for determination of tebuthiuron loss (discharge volume x sample concentration). Samples of source water were also analysed for tebuthiuron to allow the calculation of a corrected runoff tebuthiuron loss. Herbicide analyses by liquid chromatography mass spectrometry were completed by the Queensland Health Forensic and Scientific Services in Coopers Plains, Queensland; and a quality assurance and control criteria was later applied to all laboratory results (Table 3). The data from this study were collected in collaboration with the Paddock to Reef rainfall simulation project (Cowie *et al.* 2013; Thornton *et al.* 2013) (Appendix 1).

Tebuthiuron loads lost in runoff, on a g a.i./ha basis, were then calculated by:

$$\left[ \frac{[\text{Corrected Runoff Result } (\mu\text{g/L}) * \text{Runoff Volume (L)}] / 1,000}{\text{Plot Length (m)} * \text{Plot Width (m)}} \right] * 10,000 / 1,000$$

**Table 3: Quality assurance and control criteria applied to the tebuthiuron results. Good = sample quality ok and data used in analyses, PQL = practical quantitation limit, and blank = missing data or data not used in analyses.**

<b>Runoff Water Sample (A)</b>	<b>Source Water Sample (B)</b>	<b>Corrected Runoff Result (C)</b>
Good	Good	A - B
Good	< PQL	Good
Good	Blank	Good
Good	> A	Blank
Good	= A	Blank
< PQL	< PQL	Blank
< PQL	Blank	Blank
< PQL	> A	Blank
< PQL	Good	Blank
Blank	< PQL	Blank
Blank	Blank	Blank
Blank	> A	Blank
Blank	Good	Blank

Comparison of tebuthiuron load losses between formulations was made separately for each soil type using analysis of variance in GenStat (version 14.2; www.vsni.co.uk). The replicate and residual variances for soil types were then compared to determine if it was appropriate to pool variances; thus, allowing soil types to be compared.

### ***Tebuthiuron Movement in Runoff at the Paddock Scale under Natural Rainfall***

Tebuthiuron movement in runoff was investigated at the paddock scale (12.7 ha) under natural rainfall conditions. The study was conducted in buffel grass pasture at the Brigalow Catchment Study site. Pasture cover is consistently greater than 80%, and soils are 58% cracking and non-cracking Black and Grey Vertosols and Black and Grey Dermosols, and 42% Black and Brown Sodosols. There had been no control of regrowth vegetation since clearing in 1982. Aerial application of granular tebuthiuron (Graslan™ Aerial 200 g a.i./kg) (Dow AgroSciences 2013a) was undertaken on 15 November 2011 by Dow AgroSciences at a rate of 12.5 kg/ha (2.5 kg a.i./ha), reflecting a commercial application for this paddock.

The paddock was instrumented to measure runoff using a 1.2 m steel HL flume with a 3.9 x 6.1 m concrete approach box. Water heights through the flume were recorded using a mechanical float recorder. Rainfall was recorded adjacent to each flume and at the head of the paddock (Thornton *et al.* 2007). A runoff event was defined as commencing when stage height exceeded zero and finished when it returned to zero. Event based water quality samples were collected by automated samplers between November 2011 and March 2013 up to a maximum of 12 discrete samples per an event. Herbicide analyses by liquid chromatography mass spectrometry and total suspended sediment analyses by gravimetric quantification of solids in water were completed by Queensland Health Forensic and Scientific Services in Coopers Plains, Queensland. Load and Event Mean Concentration (EMC) for each event are presented. Further details on instrumentation and load calculations are

documented in Thornton and Elledge (2013). Statistical analyses were undertaken using the linear regression and standard curves tools in GenStat (version 14.2; www.vsni.co.uk).

### **Scaling Tebuthiuron Loads in Runoff from the Paddock to the Fitzroy Basin**

Paddock scale results from this study can be used to calculate potential tebuthiuron loads sourced from the Fitzroy Basin in the GBR lagoon based on a simple scaling equation:

$$\text{Tebuthiuron load (t)} = \frac{\left[ (A \times GA \times GA_T) \times \left( \frac{R \times C}{100} \right) \right] \times (EMC \times 10^6)}{1 \times 10^{12}}$$

Where,

*A* = Area of the Fitzroy Basin (ha).

*GA* = % of the Fitzroy Basin that is grazed.

*GA<sub>T</sub>* = % of *GA* that is treated with tebuthiuron in a given year.

*R* = Annual rainfall (mm).

*C* = Coefficient of runoff (amount of rainfall that becomes runoff) (%).

*EMC* = Event mean concentration of tebuthiuron in runoff (µg/L).

Values for populating the equation can be readily obtained from the literature. *A* is equal to 14,200,000 ha (Carroll *et al.* 2010; Packett *et al.* 2009). *GA* can be conservatively estimated at 80% (Carroll *et al.* 2010; Packett *et al.* 2009). *GA<sub>T</sub>* can be estimated based on historical observations of land clearing behaviour. Traditionally, blade ploughing for regrowth control was undertaken at intervals ranging from 5 to 20 years (Graham *et al.* 1991), so an average of 10 years can be assumed. If it is assumed that regrowth control is staged, 10% of a property could be treated per year so that over a 10 year period, the entire property would have received treatment. If 100% of blade ploughing is replaced by tebuthiuron, *GA<sub>T</sub>* is estimated at 10%, however a range of scenarios were considered. *R* can be conservatively estimated at 500 mm, which is equal to the mean rainfall in the far west of the basin (Department of Natural Resources and Mines 2013; Packett *et al.* 2009). *C* can be estimated at 10% (Thornton *et al.* 2007). *EMC* can be estimated using the results of this study. This approach does not allow for breakdown or other in-stream processes. However, these losses are expected to be minimal as the literature clearly indicates that tebuthiuron is highly soluble and very stable in water (United States Environmental Protection Authority 1994).

## **Results**

### **Tebuthiuron Movement through the Soil Profile under Natural Rainfall**

During the first investigation, tebuthiuron in the Vertosol showed a trend of declining mass over time at all depths measured up to 40 cm (Figure 3A). The only exception to this trend was some redistribution of tebuthiuron between 10 and 30 cm at 314 days after application. In the Sodosol, redistribution of tebuthiuron across soil depths and time was observed

(Figure 3B). Nonetheless, tebuthiuron mass declined over time at the 0 to 2.5 cm depth, and a temporal decline also occurred between 10 and 40 cm depths from day 104. The half-life of tebuthiuron to a depth of 40 cm was 67 days in the Vertosol and 101 days in the Sodosol.

During the second investigation, the highest mass of tebuthiuron in the 0 to 5 cm depths was at day 30 for both the Vertosol and Sodosol soils. Trends of tebuthiuron movement below this depth in the Vertosol are difficult to interpret, as sampling error probably exceeds loss via breakdown and redistribution at less than the 50 day time step (Figure 4A). Mass of tebuthiuron in the 5 to 20 cm depths was highest at day 56 in the Sodosol (Figure 4B); however, at lower depths the same issue as the Vertosol applies. Samples 20 to 40 cm deep in the Vertosol were taken, but no tebuthiuron was detected. In contrast, samples at the same depth from the Sodosol were not taken due to difficulty obtaining samples at those depths. The half-life of tebuthiuron to a depth of 40 cm was 181 days in the Sodosol. High variability of tebuthiuron loads over time in the Vertosol did not allow for half-life calculation.

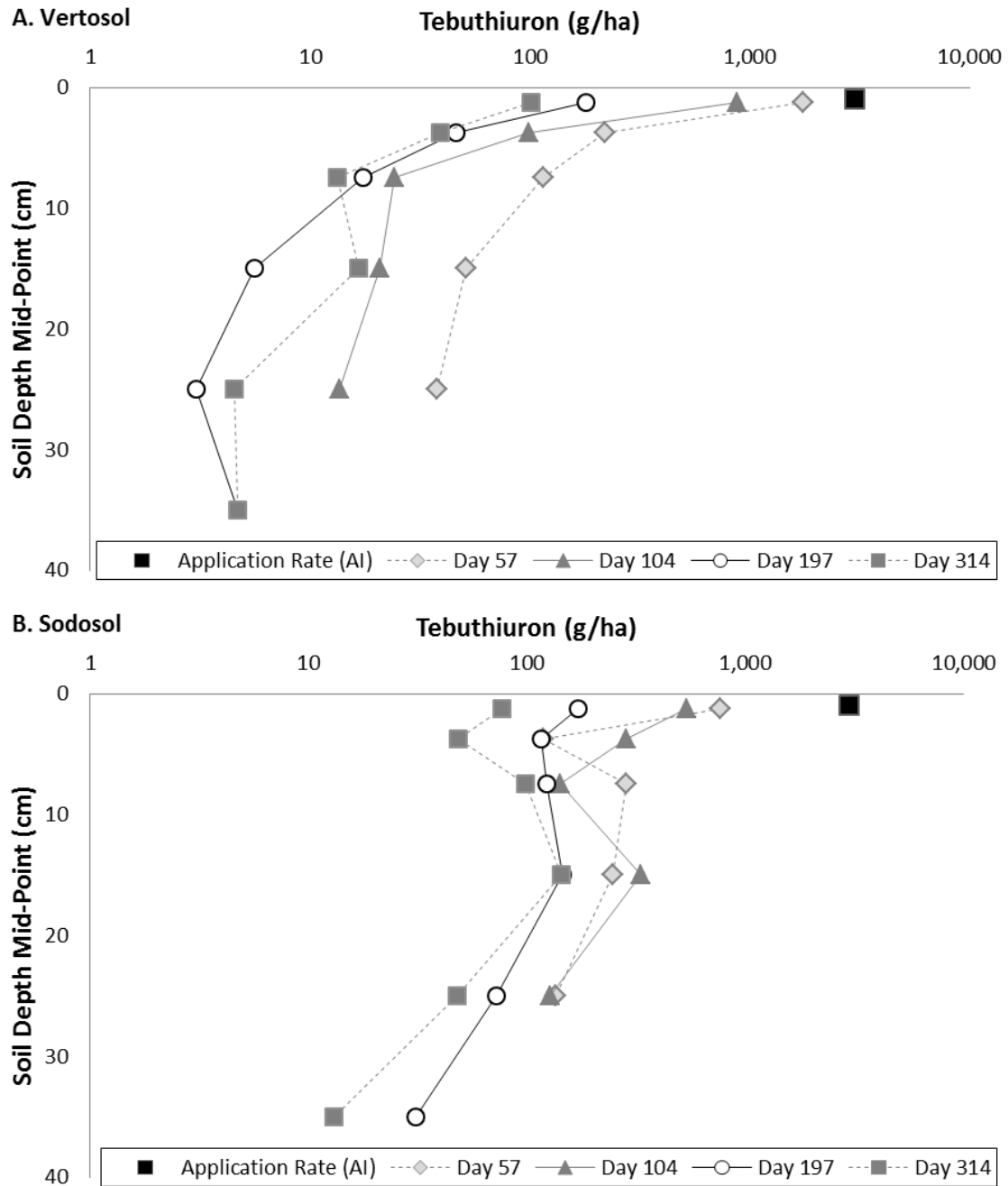


Figure 3: Tebuthiuron mass (g/ha) in the 0 to 40 cm profile of Vertosol (A) and Sodosol (B) soil at 57, 104, 197 and 314 days after application to the soil surface. Tebuthiuron was applied at a rate of 3,000 g a.i./ha.

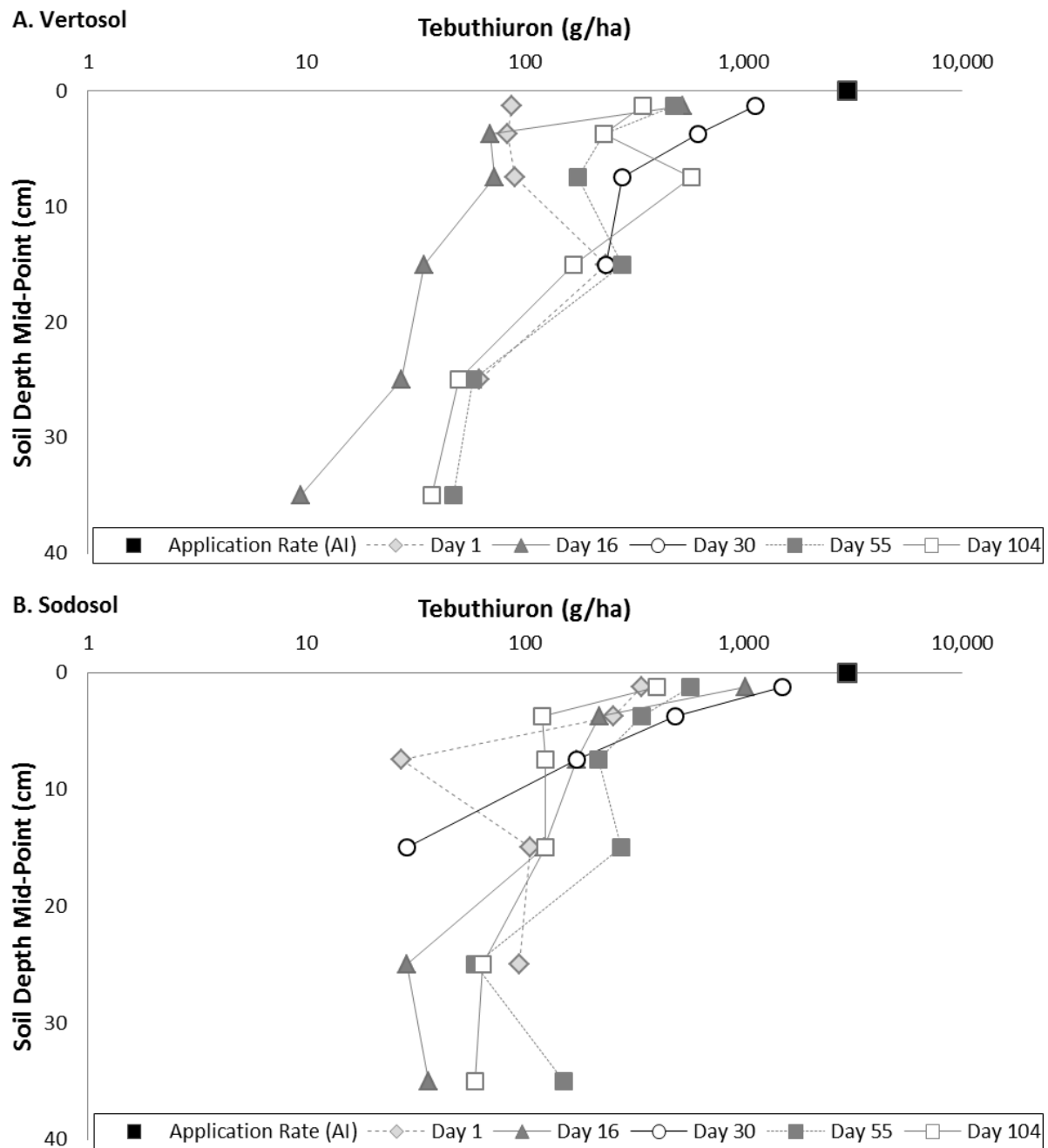


Figure 4: Tebuthiuron mass (g/ha) in the 0 to 40 cm profile of Vertosol (A) and Sodosol (B) soil at 1, 16, 30, 55 and 104 days after application to the soil surface. Tebuthiuron was applied at a rate of 3,000 g a.i./ha.

### ***Tebuthiuron Movement in Runoff at the Plot Scale under Simulated Rainfall***

More granular tebuthiuron was lost from Vertosols than dry flowable tebuthiuron ( $P < 0.05$ ); however, there was no difference in the amounts of each formulation lost from Sodosols (Figures 5 and 6). Irrespective of formulation, there was a trend for greater tebuthiuron loss from Vertosol compared to Sodosol soil ( $P < 0.10$ ).

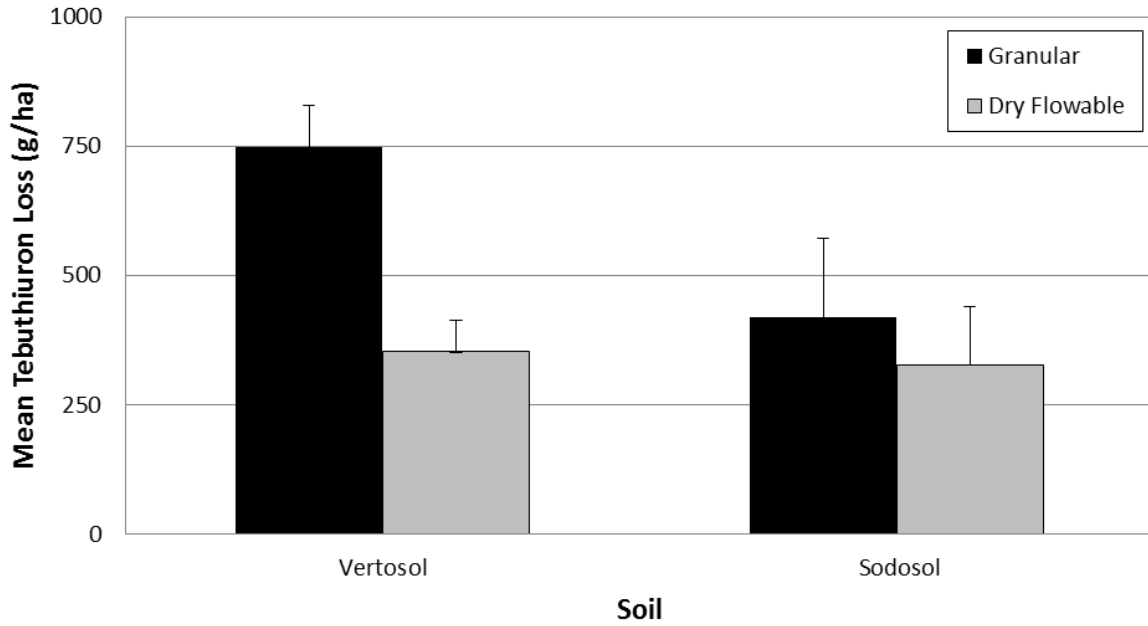


Figure 5: Mean (and standard error) tebuthiuron load (g/ha) exported in runoff from Vertosol and Sodosol soils under simulated rainfall conditions immediately after application. Tebuthiuron was applied at a rate of 3,000 g a.i./ha.

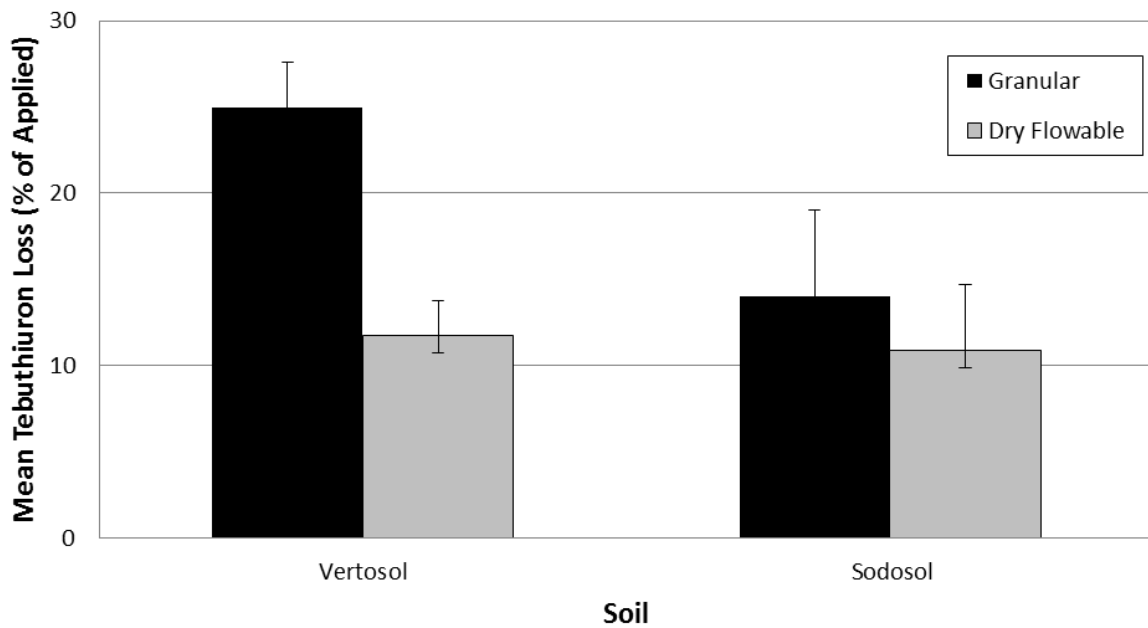


Figure 6: Mean (and standard error) tebuthiuron load, as a percentage of the applied rate, exported in runoff from Vertosol and Sodosol soils under simulated rainfall conditions immediately after application.

### ***Tebuthiuron Movement in Runoff at the Paddock Scale under Natural Rainfall***

Tebuthiuron samples were collected from five runoff events ranging from 100 to 472 days after application (Table 4). EMC of tebuthiuron showed a trend of exponential decay with the greatest decline between the first two events; 100 and 224 days after application (Figure 7). Cumulative rainfall had a strong negative exponential correlation with tebuthiuron EMC ( $R^2 = 0.99, P= 0.002$ ). At 472 days after application, a total of 1239 mm of rainfall had



occurred and a total of 1.03% of the applied tebuthiuron had been exported in runoff (Table 4). Tebuthiuron loss during each event was less than 0.45% of the total applied to the paddock. Cumulative loss of tebuthiuron showed a linear increase over time (Figure 8). Loss was also strongly correlated with cumulative rainfall ( $R^2 = 0.73$ ,  $P = 0.003$ ). No relationship was detected between tebuthiuron EMC and total suspended sediment EMC (Figure 9).

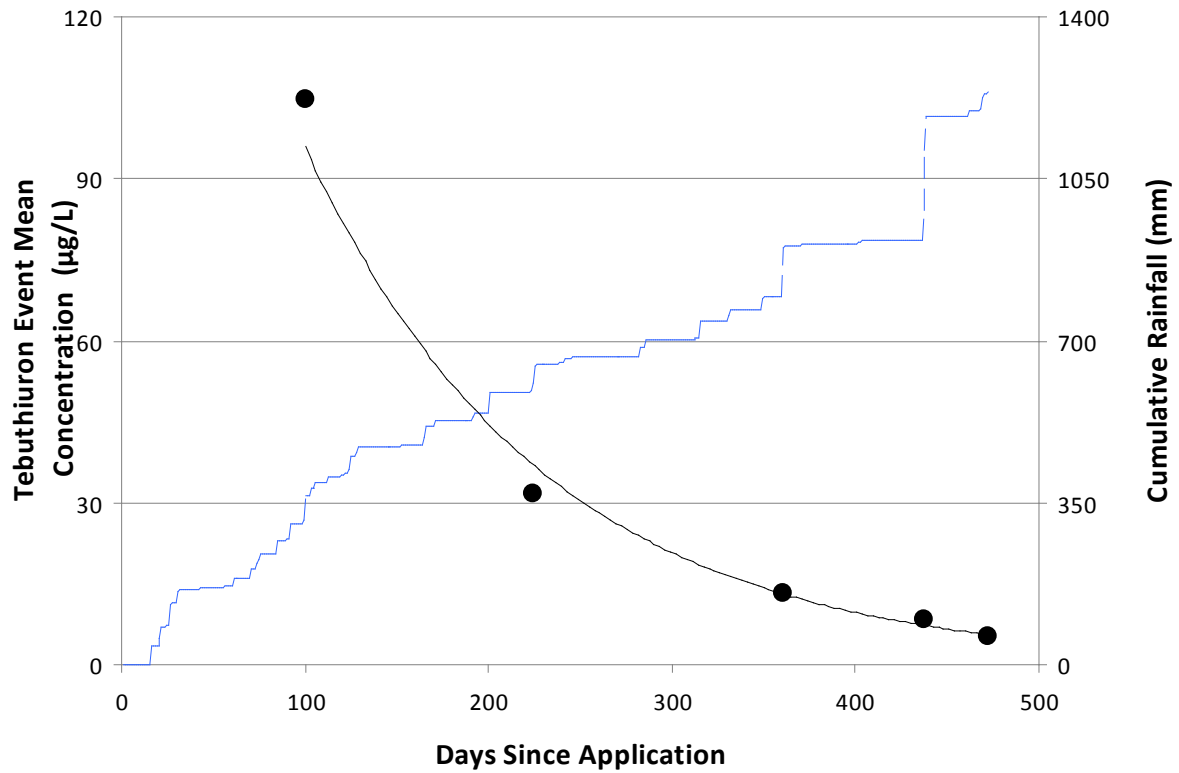


Figure 7: Event mean concentration (EMC) of tebuthiuron (points) in runoff at the paddock scale up to 472 days after aerial application to the soil surface and cumulative total rainfall (dashed line) since tebuthiuron application. Exponential curve (solid line)  $R^2=0.9905$ .

**Table 4: Event based loads and EMCs of tebuthiuron and total suspended sediment in runoff at the paddock scale under natural rainfall conditions. Tebuthiuron was applied on 15 November 2011 at a rate of 12.5 kg/ha (200 g a.i./kg).**

Runoff Event Date	Days Since Tebuthiuron Application	Cumulative Rainfall Since Tebuthiuron Application (mm)	Total Discharge (mm)	Number of Samples	Tebuthiuron			Total Suspended Sediments	
					Event Total Load (g/ha)	EMC ( $\mu\text{g/L}$ )	Loss (% of Applied)	Event Total Load (g/ha)	EMC ( $\mu\text{g/L}$ )
23/02/12	100	360	1.2	6	1.3	104.6	0.05	1.3	105.2
26/06/12	224	615	17.0	5	5.4	31.6	0.22	14.4	84.8
10/11/12	361	829	47.6	11	6.4	13.4	0.25	71.2	149.6
25/01/13	437	1006	138.1	2	11.3	8.2	0.45	-	-
01/03/13	472	1239	25.7	11	1.3	5.2	0.05	57.2	222.7

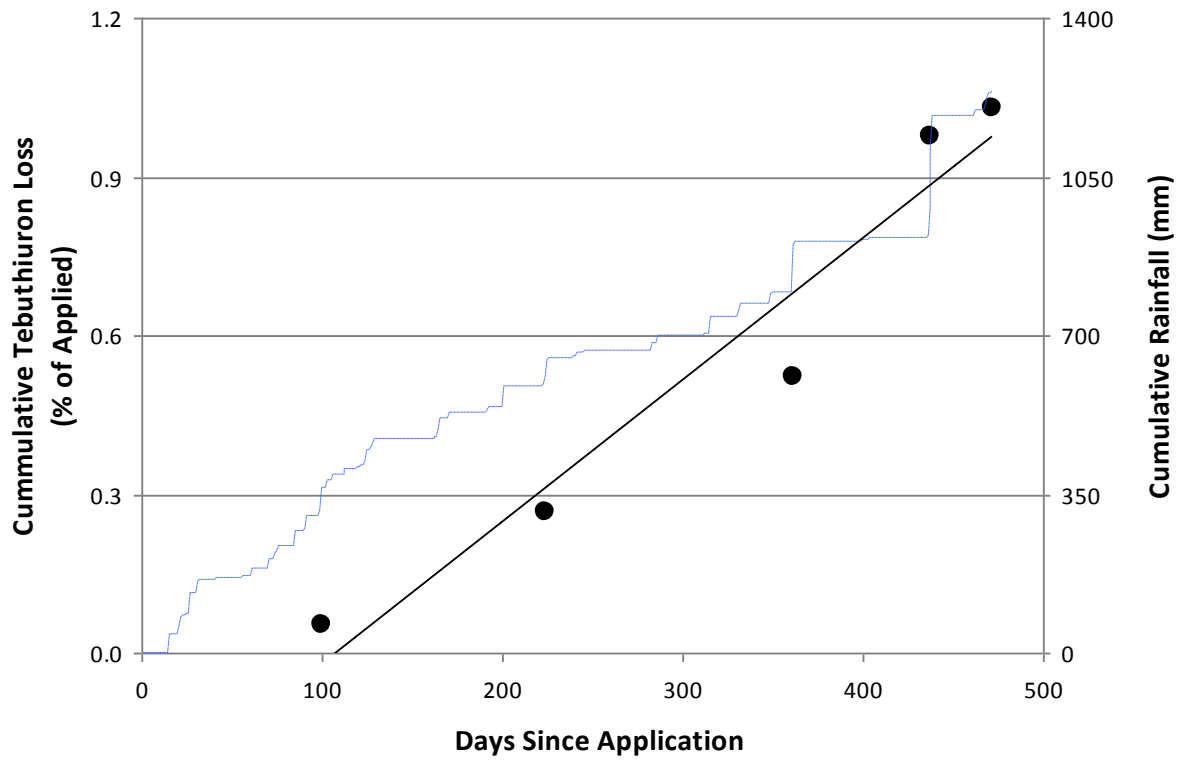


Figure 8: Cumulative loss of tebuthiuron (points) in runoff at the paddock scale up to 472 days after aerial application to the soil surface and cumulative total rainfall (dashed line) since tebuthiuron application. Linear curve (solid line)  $R^2=0.9415$ .

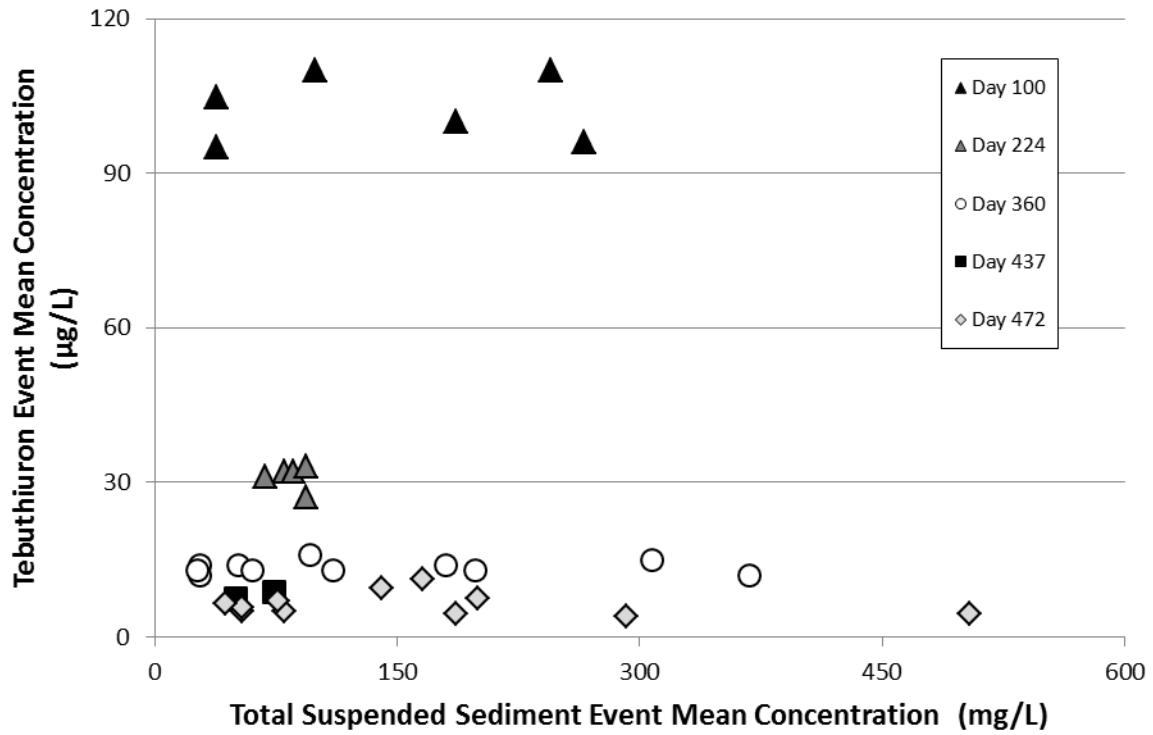


Figure 9: Relationship between event mean concentration of tebuthiuron and total suspended sediment in runoff at the paddock scale up to 472 days after aerial application to the soil surface. Exponential curve (all data points)  $R^2=0.0108$ .

### ***Scaling Tebuthiuron Loads in Runoff from the Paddock to the Fitzroy Basin***

Table 5 shows the results of scaling the paddock data from this study to the whole of the Fitzroy Basin. The scaling equation was populated using fixed values of  $A=14,200,000$  ha,  $GA=80\%$ ,  $R=500$  mm,  $C=10\%$  and  $EMC=13$   $\mu\text{g/L}$ . This study reported an EMC of 13  $\mu\text{g/L}$  one year after tebuthiuron application (Table 4), and is assumed to represent the best case EMC for areas treated in the previous year. A range of  $GA_T$  scenarios were considered ranging from 0.5 to 10%.

**Table 5: Estimated loads of tebuthiuron lost from the Fitzroy Basin based on extrapolation of paddock scale results.**

<b>Area of Fitzroy Basin Treated (ha)</b>	<b>Area of Fitzroy Basin Treated (%)</b>	<b>Total Load in Fitzroy Basin (t)</b>
56,800	0.5%	0.37
113,600	1%	0.74
340,800	3%	2.22
568,000	5%	3.69
1,136,000	10%	7.38

## **Discussion**

Tebuthiuron field half-lives in soil from this study were two to six months, which is considerably shorter than the one to two year half-lives reported in the international literature (Worthington 1983; United States Environmental Protection Authority 1994; Weed Science Society of America 1994). These half-lives simply account for volumetric change in tebuthiuron in the soil profile irrespective of the change being attributed to breakdown, movement or uptake by vegetation. In this study, tebuthiuron was also found to be highly mobile to depths of 40 cm in both Vertosols and Sodosols. This is consistent with international literature which has reported tebuthiuron at depths 15 to 30 cm down the soil profile with smaller quantities detected up to 60 cm (United States Environmental Protection Authority 1994). On Vertosols, similar to this study, Bovey *et al.* (1978) also found tebuthiuron at depths between 46 and 61 cm. Movement of tebuthiuron to 180 cm has been found in soil composed of 92% sand (United States Environmental Protection Authority 1994).

Emmerich *et al.* (1984) reported that tebuthiuron adsorbed to clay and organic matter in soil, and that movement decreased as clay and organic matter content increased. This may explain the movement of tebuthiuron to 180 cm in soil with an extremely high sand content. However, given that tebuthiuron is highly soluble in water (Parry and Batterham 1999; United States Environmental Protection Authority 1994), its movement to depth in soil is more likely a function of soil water holding capacity and hydraulic conductivity; both of which are heavily influenced by clay and organic matter content. This is supported by the redistribution of tebuthiuron in the soil profile after rainfall, which was observed in this study and earlier noted by Parry and Batterham (1999).

Rainfall simulation at the plot scale showed a greater loss of tebuthiuron in runoff from Vertosols compared with Sodosols. This is consistent with the theory that tebuthiuron movement is a function of soil water holding capacity and hydraulic conductivity. Infiltration on Vertosols is expected to be lower than that of Sodosols due to higher clay content, which results in a shorter time to runoff and an increase in runoff volume (Thornton *et al.* 2007; Thornton 2012). A greater proportion of rainfall onto Vertosols interacts with highly soluble tebuthiuron that has not leached deeper into the soil prior to runoff, resulting in greater losses than from Sodosols.

Although there are conflicting publications on whether tebuthiuron is transported in a dissolved phase in water (Brodie *et al.* 2012) or adsorbed to soil particles (Parry and Batterham 1999) which are then lost from the paddock via erosion processes, the weak relationship observed between tebuthiuron and total suspended solids in this study indicate that the movement of tebuthiuron in runoff at the paddock scale is occurring in the dissolved phase. This is consistent with the United States Environmental Protection Authority (1994) who state that the principle route of dissipation is mobilisation in water, which includes loss by solubilisation in runoff.

Whilst it is expected that tebuthiuron lost in runoff would exhibit a first order decay pattern (Cook *et al.* in press), no reference to tebuthiuron decay could be found in the literature under natural rainfall conditions at the paddock scale. This study appears to be the first to demonstrate this pattern. A simulated rainfall experiment on Vertosols in the Burdekin Basin reported a tebuthiuron concentration of 157 µg/L in runoff 32 days after application (Cowie *et al.* 2013). This data point shows a good fit when plotted on the decay curve of Figure 7. This provides further evidence of the behaviour of tebuthiuron in runoff at the plot and paddock scales.

Tebuthiuron loads entering the GBR from the Fitzroy Basin were estimated to be 6,000 kg over the 2010/2011 wet season (Warne, M. *pers. comm.* 2012 Department of Science, Information Technology, Innovation and the Arts). Despite the Fitzroy Basin being predominantly grazing with probably the largest area of tebuthiuron application of all reef catchments (Lewis *et al.* 2011), this value was originally considered with caution. However, a simple desktop extrapolation of paddock scale data from this study showed that loads of these magnitudes are realistic. The 2010/2011 end of catchment load for the Fitzroy Basin could have been achieved if between 5 and 10% of the catchment had tebuthiuron applied. Alternatively, the same load may also be possible with higher tebuthiuron concentrations in runoff from a smaller area of application.

It has been suggested that 0.5% of water soluble, soil applied herbicides will be lost in runoff (Wauchope 1978). Given that tebuthiuron losses at the paddock scale averaged 0.2% of the amount applied in this study, it is unlikely that there is scope for minimising loss through application or formulation technology. Despite the relatively small losses compared to application amounts, high solubility and low adsorption to soil can result in detectable levels of tebuthiuron downstream (Wauchope 1978). Strategies to minimise the risk of tebuthiuron loss in runoff are already in place under Queensland legislation, which currently does not permit broad-scale applications between November 1 and March 31 to minimise runoff losses during the high rainfall months.

Currently, recommendations for tebuthiuron management in grazing lands to minimize water quality impacts are based on the ANZECC and ARMCANZ (2000) water quality guidelines. The ANZECC and ARMCANZ (2000) guideline value for tebuthiuron concentrations at which 99% of species are protected has been adopted in the Great Barrier Reef Marine Park Authority Water Quality Guidelines for the Great Barrier Reef Marine Park (Great Barrier Reef Marine Park Authority 2010). As stated in the guidelines, the trigger value for tebuthiuron is considered to have low reliability. Lewis *et al.* (2012) state that under this guideline, tebuthiuron usage in the Fitzroy Basin would require immediate management action. In contrast, photosystem inhibition data suggest it is of much lower concern than other PSII herbicides used in the GBR, suggesting that additional toxicity data are required to provide further direction on the management of this herbicide (Lewis *et al.* 2012). The current study supports the need for further ecotoxicology data given that tebuthiuron EMC in runoff at the paddock scale was 5.2 µg/L 472 days after application. This exceeds the current freshwater guideline of 0.02 µg/L (ANZECC and ARMCANZ 2000) by a factor of 260, indicating that 260 ML of receiving water would be required to dilute 1 ML of runoff containing 5.2 µg/L of tebuthiuron to a concentration of 0.02 µg/L.

### **Future Directions**

Despite this research being some of the first empirical data on tebuthiuron movement in soil and runoff from grazing lands in Australia, there were four main limitations: (1) data was sourced solely from the Fitzroy Basin; (2) only Vertosol and Sodosol soil types were investigated; (3) investigation of persistence in soil was limited to particular profile depths and time intervals; and (4) runoff at the paddock scale was limited to 17 months data with only small runoff events immediately after application, raising the questions of what losses of tebuthiuron would have occurred if runoff had occurred with the first 100 days after application and what is the long-term average loss. Thus, there is scope for more research to further understand the persistence and movement of tebuthiuron in Queensland's grazing landscapes. Opportunities exist to replicate the plot scale investigations on additional soil types in other reef catchments, and also to continue monitoring of water quality at the paddock scale.

One of the key priorities for reducing the risk from pollutants to the GBR is the reduction of pesticide losses from grazing lands in the Fitzroy Basin (Waterhouse *et al.* 2012). Further research on this topic can be cost effectively investigated at the Brigalow Catchment Study, and there are three main benefits to the inclusion of this site in future projects: (1) avoiding expenditure on the development of new sites; (2) getting research activities on-ground in a short time period, as management practice treatments are already imposed and monitoring equipment is installed; and (3) the experimental design can be tailored to meet a specific research need and can be adaptively managed. Furthermore, the Brigalow Catchment Study is an ideal site to represent the broader grazing landscape, as it is located in the Fitzroy Basin which is not only Queensland's largest reef catchment (Australian Bureau of Statistics 2009), but also the reef catchment with the greatest number of cattle (Heather and Clouston 2006).

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## Appendix 1: Publications

There are two publications that have resulted from this project:

- (1) COWIE, B., DAVISON, L., TANG, W., THORNTON, C. and ELLEDGE, A., 2013. Appendix 16. Runoff tebuthiuron loss from 57 grazing plots with simulated rainfall. In: B. COWIE, L. DAVISON, W. TANG, G. MCDONALD, D. SOUTHWOOD and M. PIERCE, eds, Final report: Paddock to Reef: Paddock Scale Monitoring and Modelling - Rainfall Simulation Program 2010 – 2013. Queensland: Department of Natural Resources and Mines.
- (2) THORNTON, C., COWIE, B., DAVISON, L., ELLEDGE, A. and TANG, W., 2013. Appendix 13. Impact of tebuthiuron formulation on runoff loss. In: B. COWIE, L. DAVISON, W. TANG, G. MCDONALD, D. SOUTHWOOD and M. PIERCE, eds, Final report: Paddock to Reef: Paddock Scale Monitoring and Modelling - Rainfall Simulation Program 2010 – 2013. Queensland: Department of Natural Resources and Mines.