

Tebuthiuron Movement via Leaching and Runoff from Grazed Vertisol and Alfisol Soils in the Brigalow Belt Bioregion of Central Queensland, Australia

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ABSTRACT: Tebuthiuron is one of five priority herbicides identified as a water pollutant entering the Great Barrier Reef. A review of tebuthiuron research in Australia found 13 papers, 6 of which focused on water quality at the basin scale (>10,000 km²) with little focus on process understanding. This study examined the movement of tebuthiuron in soil and runoff at the plot (1.7 m²) and small catchment (12.7 ha) scales. The greatest concentration and mass in soil occurred from 0 to 0.05 m depth 30–57 days after application. Concentrations at all depths tended to decrease after 55–104 days. Runoff at the small catchment scale contained high concentrations of tebuthiuron (average = 103 μg/L) 100 days after application, being 0.05% of the amount applied. Tebuthiuron concentrations in runoff declined over time with the majority of the chemical in the dissolved phase.

KEYWORDS: *tebuthiuron, leaching, runoff, soil, pesticide, herbicide, brigalow, Brigalow Catchment Study, grazing*

■ INTRODUCTION

In 2009, the Australian and Queensland governments enacted the Reef Water Quality Protection Plan to reduce the risk of declining water quality entering the Great Barrier Reef (GBR). Five photosystem II (PSII) herbicides are targeted in the Reef Plan: ametryn, atrazine, diuron, hexazinone, and tebuthiuron.¹ The first four are registered for use in sugar cane, whereas tebuthiuron is registered for use in grazing.² Tebuthiuron is a substituted urea herbicide, chemical name *N*-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-*N,N'*-dimethylurea and chemical formula C₉H₁₆N₄OS.³ Internationally, tebuthiuron is registered for use in grasslands and grazing systems in South Africa and the United States^{3,4} and in sugar cane in Brazil.^{5,6} It is not approved or known to be used in European countries.^{6,7} Granular tebuthiuron has been registered in Australia since the 1980s and is used to control regrowth of brigalow (*Acacia harpophylla*), tea tree (*Melaleuca* spp.), and other problem woody weeds on grazing lands in Queensland.^{8–10}

Tebuthiuron has been detected in GBR flood plumes from the Wet Tropics, Burdekin, Mackay-Whitsunday, and Fitzroy catchments. The greatest concentrations of tebuthiuron found in flood plumes were 0.014 μg/L from the Fitzroy basin and 0.006 μg/L from the Burdekin basin.¹¹ Kennedy et al.¹² reported tebuthiuron concentrations exceeding the ANZECC trigger value of 0.02 μg/L for 99% ecological protection at sites 3–11 km from the mouth of the Burdekin River and up to 240 km from the mouth of the Fitzroy River. Despite regular detections of tebuthiuron in the catchments of the GBR, there is a paucity of information on how this herbicide behaves in soil and water in the Australian environment. A literature review using “tebuthiuron” and “Australia” in 2015 found 13 journal papers. Six of these studies focused on freshwater and/or marine water quality at the reef catchment scale;^{11–16} five studies determined the impacts and toxicity of herbicides to a range of organisms, including plants, fish, algal, coral, and seagrass;^{17–21} one study assessed the role of herbicides on

sustainability and water quality of forest ecosystems;²² and another study considered the use of chemically reactive barriers for the treatment of runoff and drainage containing herbicides.²³ 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 relating to water quality, have monitored large areas containing multiple land uses with interpretation of tebuthiuron data from grazing inferred rather than measured directly. Furthermore, the literature review found no Australian data relevant to the movement of tebuthiuron in soil or in runoff from grazed pastures at the small catchment scale. Review of the international literature indicates that rainfall and soil organic matter and clay contents are linked to tebuthiuron dynamics.^{24–26} The current lack of data relating to tebuthiuron movements in the Australian grazing landscape, including loss in runoff, is a knowledge gap.

The objective of this study was to better understand the persistence and movement of tebuthiuron in grazing systems in GBR catchments by investigating (1) the persistence of tebuthiuron in Vertisol and Alfisol soils under natural rainfall conditions, (2) the movement of granular and dry flowable tebuthiuron in runoff from both soil types at the plot scale (1.7 m²) under simulated rainfall conditions, and (3) the movement of granular tebuthiuron in runoff at the small catchment scale (12.7 ha) under natural rainfall conditions.

■ MATERIALS AND METHODS

Site Description. This research was conducted at the Brigalow Catchment Study (BCS), which is a long-term (50 years) paired

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calibrated catchment study located in the Dawson subcatchment of the Fitzroy basin, central Queensland, Australia (24°48'29" S, 149°47'50" E using the Geodetic Datum Australia²⁷). An overview of the BCS is presented in Cowie et al.,²⁸ rainfall and runoff results are presented in Thornton et al.²⁹ and Thornton and Yu,³⁰ agronomic and soil fertility results are presented in Radford et al.,³¹ and the deep drainage component of the water balance is presented in Silburn et al.³² The region has a semiarid, subtropical climate. Annual average rainfall (October–September) from 1965 to 2014 was 661 mm. Summers are wet with 70% of the annual rainfall falling between October and March, whereas winter rainfall is low.³³

Soil Descriptions. The soils of the BCS are predominantly Vertisols and Alfisols with an average slope of 2.5%. In its virgin state the site was vegetated with brigalow scrub vegetation communities.³⁴ Tebuthiuron persistence in soil and its movement under simulated rainfall were investigated on two soil types, a Sodic Calcicusterts Vertisol (Vertisol) and a Typic Natrustalfs Alfisol (Alfisol). The small catchment area of the natural rainfall study was 58% Vertisols and 42% Alfisols. In their virgin state, the Vertisols had an acid reaction trend with clay content increasing from 36% in the surface soil to 54% at 1.8 m.³⁵ In contrast, the Alfisols had an alkaline reaction trend with clay content of 18% in the surface soil, 31% at 0.2–0.3 m, and then decreasing with depth.³⁵ The physiochemical characteristics of the Vertisols and Alfisols at this site are given in Table 1.

Movement in Soil under Natural Rainfall. The vertical movement of tebuthiuron was monitored in a Vertisol and an Alfisol under natural rainfall. On each soil type a row of 1.0 × 1.7 m adjacent unbounded plots was established. Graslan (200 g active ingredient (ai)/kg) is a tebuthiuron product registered for commercial application in Australia;¹⁰ however, as soil concentrations of tebuthiuron decrease with distance from the site where granular pellets are placed, results can be biased by the choice of sampling locations within a plot.³⁶ To account for this sampling challenge, Spike 80DF (800 g ai/kg),³⁷ a dry flowable formulation of tebuthiuron, was applied to the plots at a rate of 3000 g/ha of ai instead of the granular product. Spike 80DF is not registered for commercial application in Australia but was approved for experimental use under a small-scale trial permit. Each plot was used for only one sampling interval with no plot sampled twice. Six soil cores were taken randomly from each plot using a hydraulic coring rig. Each core was divided into depth increments of 0–0.025, 0.025–0.05, and 0.05–0.1 m and then 0.1 m increments until a maximum of 0.4 m before the cores were combined to make a composite sample for analysis. Tebuthiuron concentration was determined by liquid chromatography–mass spectrometry (LC-MS/MS) method KEP14D.³⁸ In this method, the soil was shaken with acetone using a tabletop shaker for approximately 12 h. The herbicide was then extracted using a QuEChERS procedure. The final extract was analyzed by LC-MS/MS. The limits of detection, quantification, and reporting for this method are 0.2, 0.5, and 1 µg/kg, respectively. The concentration of tebuthiuron in soil was converted into mass per sampling depth using measured soil bulk density. Dissipation of tebuthiuron was represented using a first-order equation.³⁹ Half-lives of tebuthiuron in soil to 0.4 m were calculated by taking the natural log of soil tebuthiuron concentration at each sampling time, fitting a linear regression to the data, and then estimating the half-life by dividing the natural log of 0.5 by the slope of the regression line.

Sampling commenced in October 2011 with soil samples taken at 57, 104, 197, and 314 days after tebuthiuron application. This sampling strategy was chosen based on half-lives of 1–2 years reported in the literature.^{3,40,41} Sampling was repeated in October 2012 with soil samples taken at 1, 16, 30, 55, and 104 days after tebuthiuron application. More intensive sampling was conducted to obtain data at shorter time intervals, particularly within the first 50 days after tebuthiuron application, to more accurately reflect the half-lives observed in the first sampling.

Movement in Runoff at the Plot Scale under Simulated Rainfall. Simulated rainfall was used to investigate tebuthiuron concentrations in runoff from a Vertisol and an Alfisol. In October 2011, six plots 1.0 × 1.7 m on each soil type were treated with

3000 g ai/ha of tebuthiuron, three with granular tebuthiuron (Graslan) (200 g ai/kg) and three with dry flowable tebuthiuron (Spike 80DF) (800 g ai/kg). Tebuthiuron was applied to the plots immediately before simulated rainfall. Rainfall was then applied to each plot at a target intensity of 80 mm/h. Once runoff commenced, rainfall continued on the plot for a further 30 min, during which time 1 L runoff samples were collected at 5 min intervals (0, 5, 10, 15, 20, 25, and 30 min) for the determination of runoff rate. Within each 5 min interval, runoff was sampled for a set time to generate one 0.75 L composite flow weighted-average sample for the determination of tebuthiuron concentration. Samples of the water used to simulate rainfall were also analyzed for tebuthiuron to allow the calculation of a corrected runoff result if necessary.

Details on the rainfall simulation setup are given in Thornton and Elledge.³⁴ Each plot was encapsulated by a three-sided sheet metal edge (0.15 m high) placed approximately 0.05–0.07 m into the ground to achieve a hydraulic barrier. The short, downslope side of the plot had a separate metal plot end with a trough and spout for collecting runoff; the plot end was pushed into the ground until the top edge was level with the soil surface. The rainfall simulator used was in an A-frame configuration. Three downward-facing oscillating nozzles delivered a flat spray pattern of water across the plot with a fan angle of 80°. A metal shroud positioned below each nozzle limited the lateral and longitudinal spray delivery and also collected excess water, which was returned to the pump delivery unit for recycling. The assembly was adjusted at each plot for adequate magnitude of nozzle sweep and symmetry of sweep relative to the simulator frame. Total runoff was calculated by a linear interpolation of the runoff rate of the seven 1 L samples integrated for the duration of the event using Water Quality Analyzer v2.1.2.4.⁴² Tebuthiuron concentration was determined by liquid chromatography–mass spectrometry (LC-MS) method QJS 29937.³⁸ In this method an aliquot of water sample is extracted on a solid phase extraction cartridge prior to determination of herbicides by LC-MS/MS. The limits of detection, quantification, and reporting for this method are 0.003, 0.01, and 0.01 µg/kg, respectively. Tebuthiuron loads in runoff were then calculated as follows:

$$\text{load (g ai/ha)} = \left[\frac{[\text{concn in runoff } (\mu\text{g/L}) \times \text{runoff vol (L)}] / 1000}{\text{plot length (m)} \times \text{plot width (m)}} \right] \times 10000 / 1000$$

Comparison of tebuthiuron load losses for the two formulations was made for each soil type using analysis of variance in Genstat v14.1.⁴³ The replicate and residual variances for soil types were then compared, determining that it was appropriate to pool variances and, thus, allowing soil types to be compared.

Movement in Runoff at the Small Catchment Scale under Natural Rainfall. Tebuthiuron movement in runoff was investigated at the small catchment scale (12.7 ha) in a buffel grass pasture (*Cenchrus ciliaris* cv. Biloela) under natural rainfall conditions. Pasture cover is consistently >80%. There had been no control of regrowth vegetation since clearing in 1982. Granular tebuthiuron (Graslan Aerial 200 g ai/kg) was applied by plane on November 15, 2011, by Dow AgroSciences at a rate of 12.5 kg/ha (2.5 kg ai/ha), reflecting commercial practice.^{10,44} The catchment was instrumented to measure runoff using a 1.2 m steel HL flume with a 3.9 × 6.1 m concrete approach box. Water height through the flume was recorded using a mechanical float recorder. Rainfall was recorded at the head of the catchment.²⁹ A runoff event was defined as the period when water was flowing through the flume. Event-based water quality samples were collected by automated samplers between November 2011 and January 2015 with a maximum of 12 samples per an event. Samples were collected every 0.1 m change in absolute flow height. Tebuthiuron concentration was determined by LC-MS method QJS 29937 (as for the plot scale analysis), whereas total suspended solids was determined by gravimetric quantification of solids in water method 18211.³⁸ In this method a well-mixed sample is filtered through a predried and preweighed glass fiber filter. The residue on the filter is washed to remove soluble salts and then dried to a constant

Table 1. Average Physiochemical Values for a Vertisol and Alfisol in Their Virgin State (After Cowie et al.²⁸)

depth (m)	pH	EC ^a (dS/m)	Cl ^b (μg/g)	OC ^c (%)	P ^d (NaHCO ₃) (μg/g)	NO ₃ -N ^e (KCl) (μg/g)	TKN ^f (%)	TP ^g (%)	TK ^h (%)	TS ⁱ (%)	exchangeable					day (%)
											Ca ²⁺ (cmol/kg)	Mg ²⁺ (cmol/kg)	Na ⁺ (cmol/kg)	K ⁺ (cmol/kg)	CEC (cmol/kg)	
Vertisol Soil																
0.0–0.1	6.56	0.16	75	1.58	12	2.7	0.16	0.03	0.15	0.03	12	11.1	1.4	0.4	36	
0.1–0.2	7.54	0.48	450	0.95	8	1.2	0.11	0.04	0.15	0.02	12	14.6	3.2	0.2	40	
0.2–0.3	8.14	0.68	730	0.52	4	0.5	0.06	0.02	0.14	0.02	10.0	15.4	4.1	0.2	44	
0.5–0.6	5.70	0.77	1040		3	0.2	0.01	0.01	0.14	0.01	5.9	14.6	4.6	0.2	45	
0.8–0.9	4.76	0.83	1145		1	0.2	0.01	0.01	0.14	0.01	4.1	13.7	4.9	0.1	46	
1.1–1.2	4.64	0.83	1170		1	0.2	0.01	0.01	0.14	0	3.4	13.4	5.4	0.1	46	
1.4–1.5	4.52	0.92	1320		2	0.1	0.01	0.01	0.14	0	3.4	15.0	6.6	0.2	50	
1.7–1.8	4.48	0.98	1385		2	0.1	0.01	0.01	0.15	0	3.3	15.7	6.9	0.3	54	
Alfisol Soil																
0.0–0.1	6.80	0.10	20	2.09	8	4	0.18	0.03	1.05	0.02	9.5	4.1	0.3	0.5	18	
0.1–0.2	7.16	0.17	130	0.73	4	1.1	0.08	0.02	0.84	0.01	6.4	9.2	2.3	0.2	31	
0.2–0.3	7.52	0.22	220	0.58	3	0.5	0.06	0.01	0.88	0.01	5.6	9.3	2.9	0.1	28	
0.5–0.6	8.83	0.40	400			0.2					6.3	9.9	4.7	0.2		
0.8–0.9	9.20	0.47	470			0.2					2.8	6.8	4.1	0.1		

^aElectrical conductivity. ^bChloride. ^cOrganic carbon (Walkley and Black). ^dBicarbonate-extractable phosphorus (Colwell). ^ePotassium chloride-extractable nitrate-nitrogen. ^fTotal Kjeldahl nitrogen. ^gTotal by X-ray fluorescence.

weight at 105 ± 2 °C. The increase in weight represents the total suspended solids. The limit of reporting for this method is 2 mg/L.

Event-based tebuthiuron load and event mean concentration (EMC) for each event are presented. Event loads were calculated by dividing the hydrograph into sampling intervals, multiplying the discharge in each interval by the sample concentration, and summing the loads over all of the intervals. The intervals were defined as the start of flow to the midpoint of sample one and sample two, the midpoint of sample one and sample two to the midpoint of sample two and sample three, and so on. Event-based EMC was calculated by dividing total event load by total event flow. Regressions were undertaken using Genstat v14.1.⁴³

Comparing Tebuthiuron Movement from Simulated and Natural Rain Studies. To explore if the data collected using rainfall simulation is representative of tebuthiuron movement under natural rainfall, the small catchment scale data were combined with the plot scale rainfall simulation data for analysis. The EMC of each plot from the rainfall simulation trial was treated as a separate “event”. Additionally, data from related plot scale rainfall simulation studies described by Cowie et al.⁴⁵ in the Wet Tropics, Burdekin, Fitzroy, and Burnett-Mary basins were included, with average tebuthiuron concentration in runoff calculated for each of the study sites, irrespective of tebuthiuron formulation or plot treatments. A time series of data from the various studies was combined to explore tebuthiuron movement in runoff relative to time after application.

RESULTS

Movement in Soil under Natural Rainfall. A total of 174 mm of rain fell during the 104 days of the short sampling interval study, with rainfall occurring between all sampling intervals. The greatest concentration of tebuthiuron from 0 to 0.05 m was measured 30 days after application for both soils (Figure 1). The greatest concentration from 0.05 to 0.4 m was measured 104 days after application in the Vertisol and 55 days in the Alfisol (Figure 1). The greatest mass of tebuthiuron from 0 to 0.4 m in both soils was also measured on day 30 (Figure 2). After 30 days, the mass of tebuthiuron from 0 to 0.4 m tended to decline over time in both soils (Figure 2).

A total of 710 mm of rain fell during the long sampling interval study, again with rainfall occurring between all sampling intervals. The greatest concentration of tebuthiuron from 0 to 0.05 m was measured 57 days after application for both soils. Tebuthiuron concentration tended to decline with time and depth in both soils (Figure 3). Tebuthiuron mass from 0 to 0.4 m declined over time in both soils (Figure 4). The change in tebuthiuron mass to 0.4 m equated to a half-life of 71 days in the Vertisol and 129 days in the Alfisol.

Movement in Runoff at the Plot Scale under Simulated Rainfall. Although the target intensity of simulated rainfall was 80 mm/h, actual intensities varied between 59 and 81 mm/h. When simulated rainfall was applied immediately after tebuthiuron application to Vertisols, 748 g/ha of granular formulation was lost in runoff (25% of applied tebuthiuron), significantly more than the 352 g/ha of dry flowable formulation lost in runoff (12% of applied tebuthiuron) ($P < 0.05$) (Figure 5). Average tebuthiuron loss in runoff from Alfisols was 373 g/ha (12.5% of applied tebuthiuron) with no significant difference in runoff loss due to formulation (Figure 5). Runoff from Vertisols averaged 123% of runoff from Alfisols, whereas tebuthiuron concentration in runoff was 125%, hence a significant trend for greater tebuthiuron loss from Vertisols compared to Alfisols ($P < 0.10$).

Movement in Runoff at the Small Catchment Scale under Natural Rainfall. Tebuthiuron samples were collected from 10 runoff events ranging from 100 to 1170 days after

application (Table 2). These events accounted for >90% of the runoff events with >1 mm of runoff that occurred in this period with the sampling pattern reflecting the seasonality of rainfall and runoff in this climate. Tebuthiuron EMC declined exponentially with time (eq 1, $R^2 = 0.998$, $P < 0.001$), rainfall (eq 2, $R^2 = 0.999$, $P < 0.001$), and runoff (eq 3, $R^2 = 0.985$, $P < 0.001$) since application.

$$\text{EMC (mg/L)} = 2.556 + 265.4 \times 0.99^x \text{ (time in days)} \quad (1)$$

$$\text{EMC (mg/L)} = 2.482 + 573.3 \times 0.995^x \text{ (rainfall in mm)} \quad (2)$$

$$\text{EMC (mg/L)} = 4.54 + 109.49 \times 0.289^x \text{ (runoff in mm)} \quad (3)$$

The greatest decline occurred between the first two events, 100 and 224 days after application (Figure 6). The concentration of tebuthiuron in individual runoff samples within an event showed little variation; thus, event EMC was almost identical to the average of the individual sample concentrations. At 1170 days after application, a total of 2426 mm of rainfall and 274 mm of runoff had occurred, and a total of 1.07% of the applied tebuthiuron had been exported in runoff (Table 2). Tebuthiuron loss during each event was <0.45% of the total applied to the catchment. No relationship was detected between tebuthiuron concentration and the total suspended solids concentration of individual runoff samples ($P = 0.57$) (Figure 7).

Comparing Tebuthiuron Movement from Simulated and Natural Rain Studies. The combined data set of tebuthiuron EMCs in runoff from the small catchment scale under natural rainfall (section above) and tebuthiuron EMCs in runoff from 13 simulated rainfall studies at the plot scale (data presented under Movement in Runoff at the Plot Scale under Simulated Rainfall combined with the data of Cowie et al.⁴⁵) showed an exponential decline over time since application (eq 4, $R^2 = 0.776$, $P < 0.001$) (Figure 8). The shortest time between tebuthiuron application and runoff was 5 min (the rainfall simulation studies), whereas the longest was 1170 days (the small catchment scale study). However, the relationship developed at the small catchment scale substantially underestimated EMCs from the combined data set prior to 30 days after application. When the time series of data was limited to events occurring >30 days after tebuthiuron application, a significant exponential decline over time was found (eq 5, $R^2 = 0.916$, $P < 0.001$).

$$\text{EMC (mg/L)} = 3.08 + 2349 \times 0.9432^x \text{ (time in days)} \quad (4)$$

$$\text{EMC (mg/L)} = 4.32 + 314.94 \times 0.9849^x \text{ (time in days)} \quad (5)$$

DISCUSSION

Tebuthiuron was found to be mobile to depths of 0.4 m in both Vertisols and Alfisols. The greatest concentrations and greatest mass of tebuthiuron in both soils was measured 30–57 days after application to the soil surface. Movement down the soil profile is consistent with international literature, which has reported tebuthiuron at depths of 0.15–0.6 m.^{3,5,24,46} Movement of tebuthiuron to 1.8 m has been found in soil composed of 92% sand.³ Emmerich et al.⁴⁷ 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 1.8 m in soil with an extremely high sand content. In contrast, Matallo et al.⁴⁸

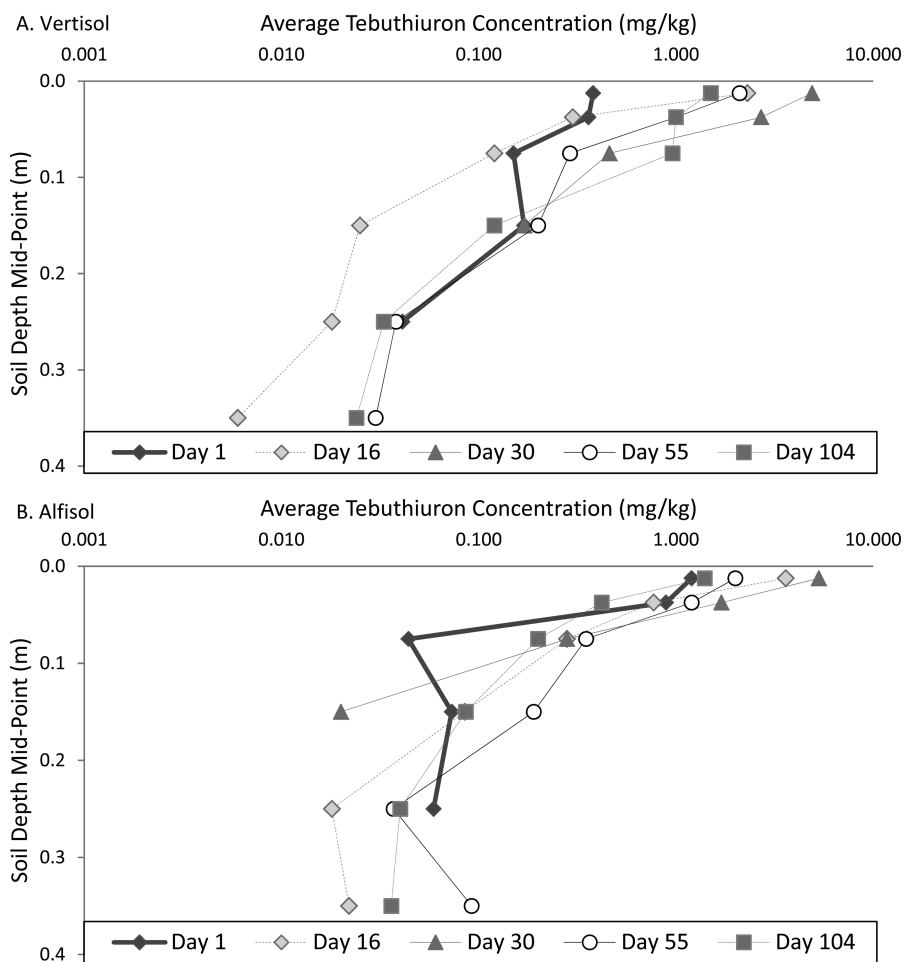


Figure 1. Tebuthiuron concentration (mg/kg) in the 0–0.4 m profile of the Vertisol (A) and Alfisol (B) at 1, 16, 30, 55, and 104 days after application to the soil surface. Tebuthiuron was applied at a rate of 3000 g ai/ha.

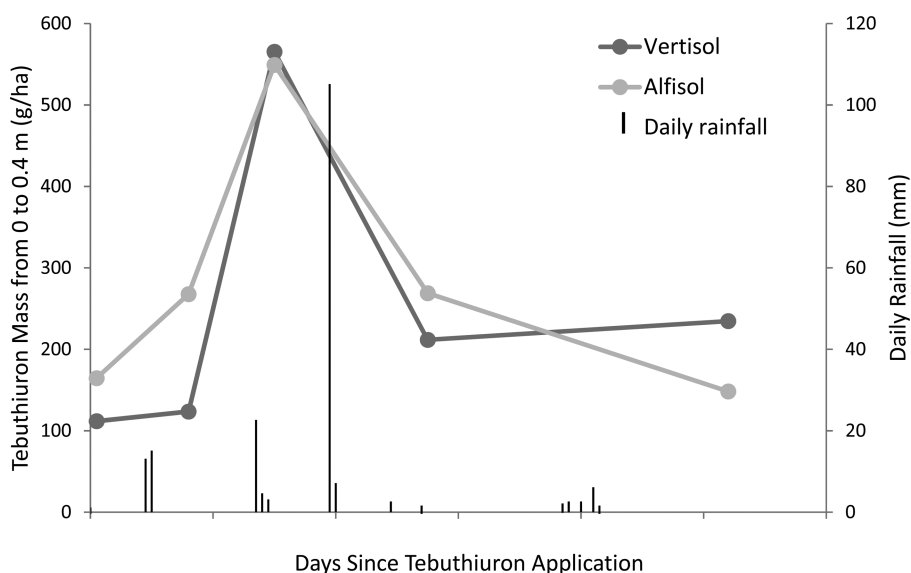


Figure 2. Tebuthiuron mass (g/ha) in the 0–0.4 m profile of the Vertisol and Alfisol at 1, 16, 30, 55, and 104 days after application to the soil surface. Tebuthiuron was applied at a rate of 3000 g ai/ha.

noted that tebuthiuron was poorly sorbed to soil but, similar to the results of Emmerich et al.,⁴⁷ found less leaching from clayey soil than from sandy soil. Given that tebuthiuron is highly soluble in water, its movement to depth in soil is likely a

function of soil water-holding capacity and hydraulic conductivity, both of which are heavily influenced by clay and organic matter content.^{3,36,49} This is supported by the redistribution of tebuthiuron in the soil profile after rainfall,

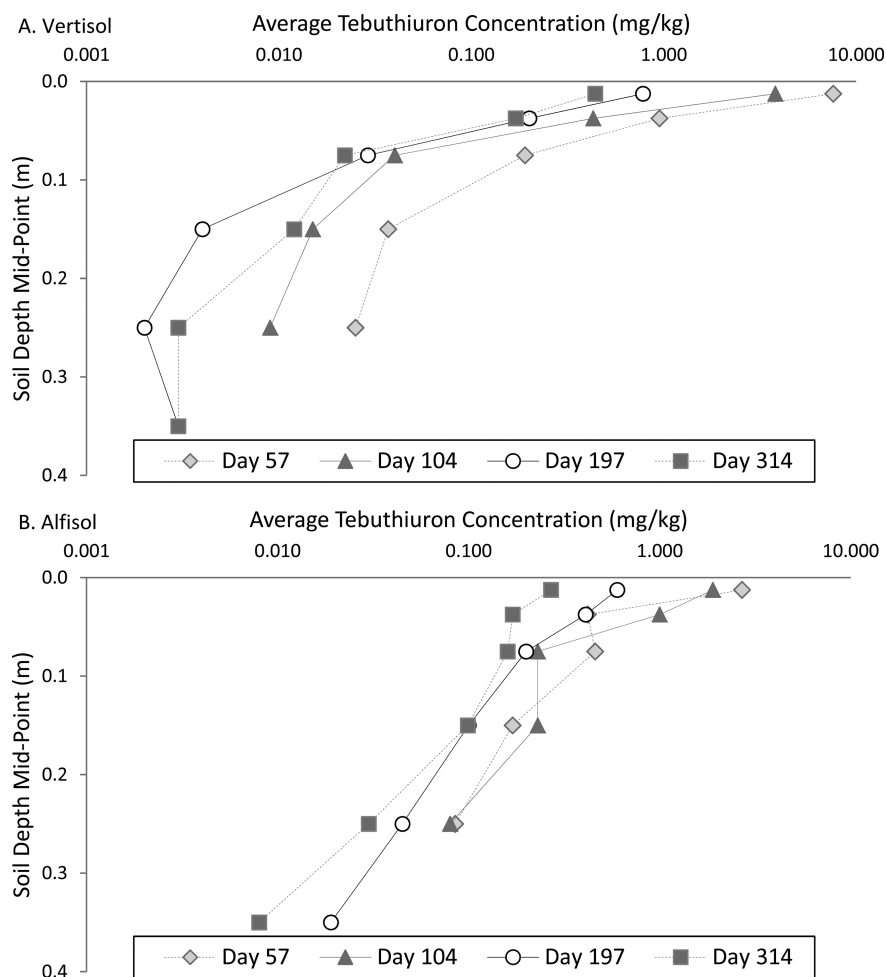


Figure 3. Tebuthiuron concentration (mg/kg) in the 0–0.4 m profile of the Vertisol (A) and Alfisol (B) at 57, 104, 197, and 314 days after application to the soil surface. Tebuthiuron was applied at a rate of 3000 g ai/ha.

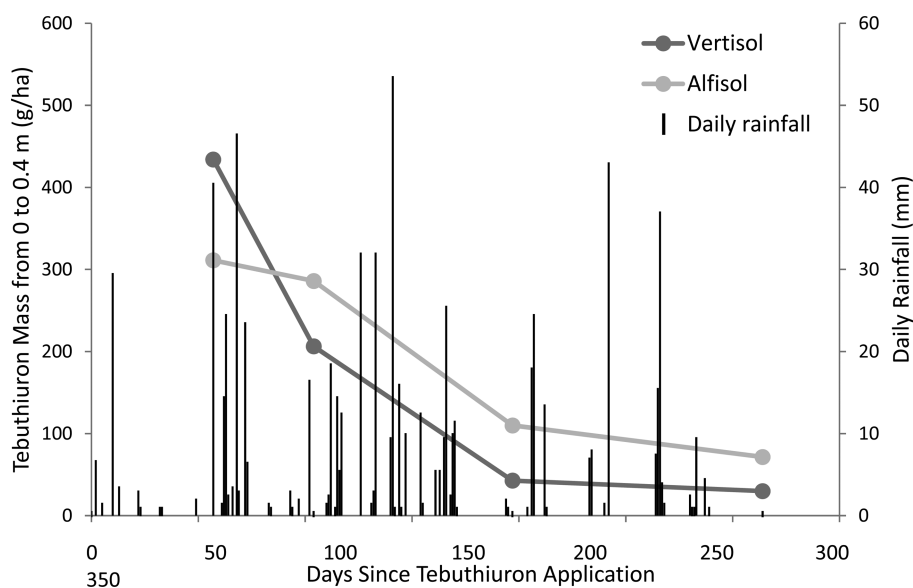


Figure 4. Tebuthiuron mass (g/ha) in the 0–0.4 m profile of the Vertisol and Alfisol at 57, 104, 197, and 314 days after application to the soil surface. Tebuthiuron was applied at a rate of 3000 g ai/ha.

which was observed in this study and was earlier noted by Parry and Batterham,³⁶ and by the observation that the pattern

of tebuthiuron redistribution differed between the two soils, which have differing clay and organic matter contents.

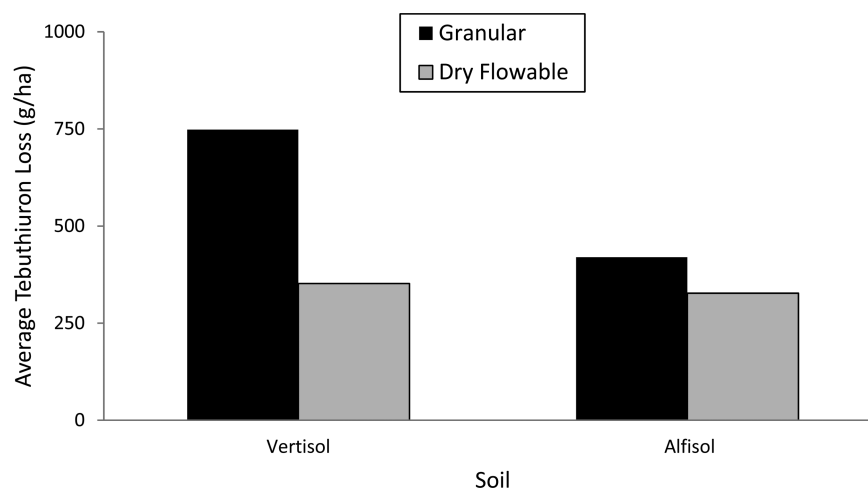


Figure 5. Average tebuthiuron loss (g/ha) in runoff from Vertisol and Alfisol soils under simulated rainfall immediately after application. Tebuthiuron was applied at a rate of 3000 g ai/ha.

Table 2. Event-Based Loads and Concentrations of Tebuthiuron and Total Suspended Solids in Runoff at the Small Catchment Scale under Natural Rainfall Conditions^a

runoff event date	days since tebuthiuron application	cumulative rainfall since tebuthiuron application (mm)	total event discharge (mm)	no. of samples	tebuthiuron				total suspended solids	
					event load (g/ha)	av sample concn ($\mu\text{g/L}$)	event EMC ($\mu\text{g/L}$)	loss (% of applied)	event load (kg/ha)	event EMC (mg/L)
Feb 23, 2012	100	360	1.2	6	1.29	102.6	104.6	0.051	1.3	105.2
June 26, 2012	224	615	17.0	5	5.39	31.0	31.6	0.215	14.4	84.8
Nov 10, 2012	360	829	47.6	11	6.37	13.5	13.4	0.255	71.2	149.6
Jan 25, 2103	437	1006	138.1	2	11.30	8.0	8.2	0.450		
March 1, 2013	472	1239	25.7	11	1.30	6.0	5.2	0.050	57.2	222.7
Nov 23, 2013	739	1581	21.1	12	0.67	3.0	3.2	0.027	40.5	191.8
Dec 12, 2013	758	1680	10.4	4	0.26	3.0	2.5	0.011	170.8	1640.3
March 31, 2014	867	1994	0.2	3	0.01	2.8	2.8	0.000	0.5	
Dec 17, 2014	1128	2253	5.0	3	0.08	1.5	1.5	0.003	9.4	
Jan 28, 2015	1170	2426	7.7	3	0.08	1.0	1.0	0.003	7.6	99.5
total	1170	2426	274.1		26.7			1.1	372.9	
av			27.4		2.7	17.3	17.4	0.1	41.4	356.3

^aTebuthiuron was applied on Nov 15, 2011, at a rate of 12.5 kg/ha (200 g ai/kg).

Redistribution of tebuthiuron by rainfall is also likely responsible for two of the tebuthiuron dynamics observed in soil. First, the maximum concentration of tebuthiuron in the soil at 0–0.05 m occurred at day 30 rather than at day 1 in the short sampling interval study and, second, the concentrations of tebuthiuron fluctuated at depth in both studies. These dynamics are attributed to the interception of dry flowable tebuthiuron by plant residues during application and its subsequent wash-off and hence delayed transport into the soil profile. Herbicide interception by trash and subsequent wash-off into soil is a well-documented process with significant amounts of herbicide able to be intercepted.^{50,51} It is likely that this behavior was absent from the long sampling interval study as the wash-off process had already occurred with the 85 mm of rainfall prior to the first sampling. This is supported by the apparent completion of the wash-off process in the short sampling interval study with the 53 mm of rainfall that occurred prior to the maximum soil concentration at 0–0.05 m.

Tebuthiuron half-lives in soil from this study were 71 and 129 days. This is considerably shorter than the 1–2 year half-lives reported in the United States, but not as short as the

16–20 days found in Brazil.^{3,5,40,41} The half-lives from this study account for mass change of tebuthiuron in the soil profile irrespective of the change being attributed to breakdown, movement, or uptake by vegetation.

Simulated rainfall at the plot scale showed a greater loss of tebuthiuron in runoff from Vertisols compared with Alfisols. This is consistent with the theory that tebuthiuron movement is a function of soil water-holding capacity and hydraulic conductivity. Infiltration on Vertisols is expected to be lower than that of Alfisols due to higher clay content, which results in a shorter time to runoff and an increase in runoff volume.^{29,52} A greater proportion of rainfall onto Vertisols interacts with highly soluble tebuthiuron that has not leached deeper into the soil prior to runoff, resulting in greater losses than from Alfisols.

The literature shows that pesticide decay after application generally exhibits a first-order decay pattern; however, no reference to the pattern of tebuthiuron decay in runoff over time could be found in the literature under natural rainfall conditions at the small catchment scale.⁵³ This study appears to be the first to demonstrate this pattern. A common trend of an exponential decline in tebuthiuron EMC over time when

undertaking combined analysis of small catchment scale and simulated rainfall data from this study gives confidence that the data obtained using simulated rainfall reflect those collected under natural conditions. Silburn and Kennedy⁵⁴ presented the same conclusion when considering the suitability of simulated rainfall for pesticide research. Analysis of other simulated rainfall data from the Wet Tropics, Burdekin, Fitzroy, and Burnett-Mary basins with results obtained in this study also gives confidence that the exponential trend of declining tebuthiuron EMC over time is not just site-specific, but rather that it is indicative of the behavior of tebuthiuron in the broader landscape.

It is clear that tebuthiuron concentrations in both soil and runoff are a function of time and rainfall since application; however, as this study did not consider the decay of tebuthiuron in the absence of rainfall, it is difficult to separate the effect of each driver. Despite this limitation, the drivers can be inferred from the behavior of tebuthiuron in soil at the plot scale and in runoff at both the plot and small catchment scale. It is likely that time since application is the greater driver of the exponential decay of tebuthiuron EMC in runoff given that cumulative rainfall tends to be linear. This is supported by the combined analysis of this study with the simulated rainfall studies of Cowie et al.,⁴⁵ which showed good correlation of EMC with time when runoff occurred >30 days after tebuthiuron application. The first 30 days after application, when EMC in runoff was not well correlated with time since application, corresponds to the timing of peak soil tebuthiuron concentration in the surface layer and the greatest total mass in the profile for both soil sampling regimens. If time since application was the key driver in the first 30 days since application, it would be expected that the mass of tebuthiuron in soil at day 55 would have been similar for both samplings. This was not the case, with greater mass at day 55 in the long sampling interval study for both soils. Rainfall to day 55 during the long sampling interval study was 85 mm, only 51% of the 165 mm of rainfall to day 55 in the short sampling interval study. This suggests that rainfall rather than time is the main driver of tebuthiuron mass in soil for at least the first 8 weeks after application. From day 55 to day 104, rainfall in the long sampling interval study was 143 mm, whereas rainfall in the short sampling interval study was 9 mm. Despite the marked difference in rainfall totals during this 50 day period, a clearly proportional response in tebuthiuron mass was not found for either sampling. This suggests that rainfall is no longer the key driver of tebuthiuron mass in soil after about 55 days.

There are conflicting opinions on whether tebuthiuron is transported in dissolved phase in water or adsorbed to soil particles that are then lost from the catchment via erosion processes.^{36,55} The lack of relationship observed between tebuthiuron and total suspended solids in this study indicates that the movement of tebuthiuron in runoff at the small catchment scale is occurring in a dissolved phase. This is consistent with the U.S. Environmental Protection Agency, which stated that the principal route of dissipation is mobilization in water, which includes loss by solubilization in runoff.³ The lack of variability in tebuthiuron concentrations in runoff samples within an event suggests that high-frequency sampling may not be necessary to gain an accurate measure of tebuthiuron concentration in runoff.

It has been suggested that 0.5% of water-soluble, soil-applied herbicides will be lost in runoff.⁵⁶ The maximum tebuthiuron loss for an event at the small catchment scale in this study is

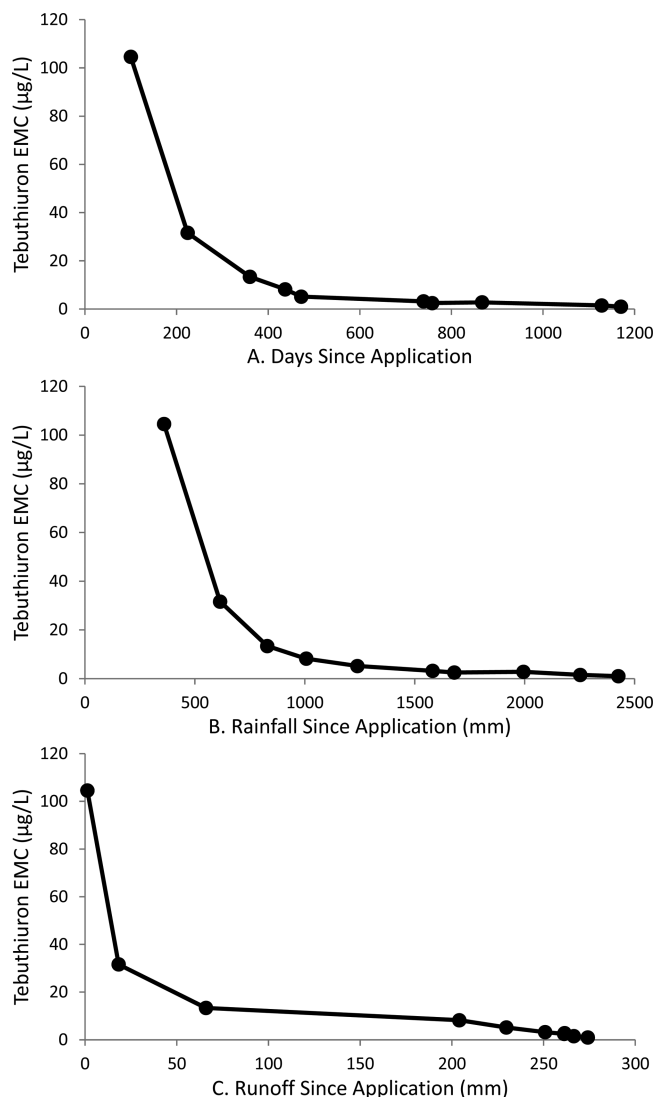


Figure 6. Event mean concentration (EMC) of tebuthiuron in runoff at the small catchment scale up to 1170 days (A), 2426 mm of rainfall (B), and 274 mm of runoff (C) following aerial application of 2500 g ai/ha of tebuthiuron to the soil surface.

similar to this figure, being 0.45% and averaging 0.1% of the amount applied. Despite the relatively small losses compared to application amounts, high solubility and low adsorption to soil can result in detectable levels of tebuthiuron downstream.⁵⁶ Strategies to minimize 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 minimize losses in runoff during the high-rainfall months.

Recommendations for tebuthiuron management in grazing lands to minimize water quality impacts should be based on the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ) water quality guidelines.⁵⁷ The ANZECC and ARMCANZ freshwater guideline value for tebuthiuron concentrations at which 99% of species are protected is 0.02 µg/L. This value has also been adopted in the Great Barrier Reef Marine Park Authority Water Quality Guidelines for protection of the Great Barrier Reef.^{57,58} However, the trigger value for tebuthiuron is considered to have low reliability. Lewis et al. state that if using the 0.02 µg/L

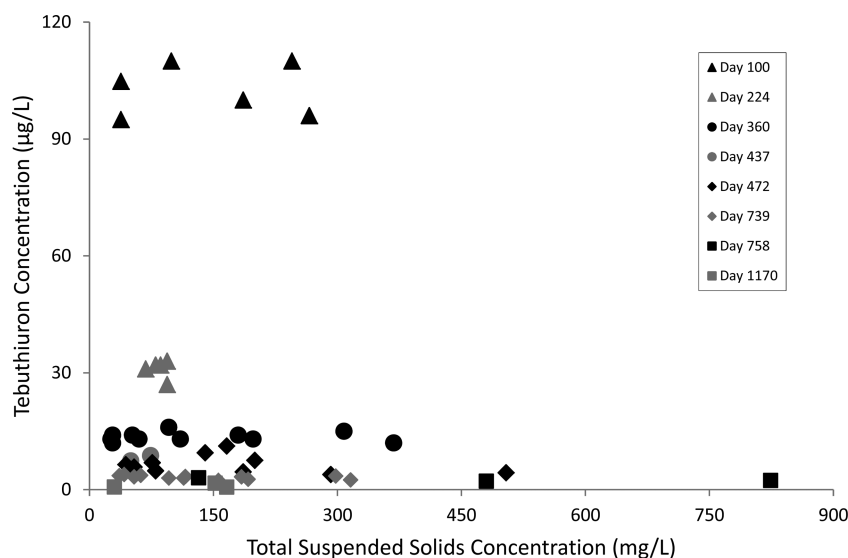


Figure 7. Comparison of total suspended sediment and tebuthiuron concentrations in individual runoff samples at the small catchment scale up to 1170 days after aerial application of tebuthiuron to the soil surface.

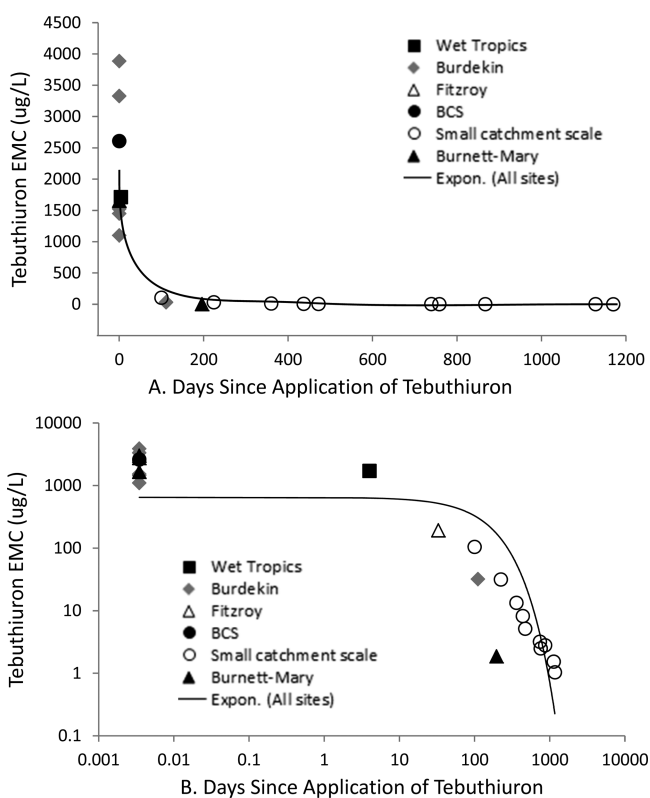


Figure 8. Linear (A) and logarithmic (B) plots of tebuthiuron event mean concentration in runoff from the small catchment scale and in runoff from 13 simulated rainfall studies across five catchments. Note the fitted line is an exponential.

guideline, tebuthiuron use in the Fitzroy basin would require immediate management action.¹³ In contrast, photosystem inhibition data indicate that tebuthiuron 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.¹³ This study supports the need for further ecotoxicology data given that tebuthiuron EMC in runoff at the small catchment scale was

5.2 µg/L 472 days after application. This exceeds the current freshwater guideline of 0.02 µg/L 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.⁵⁷

Recent synthesis of pesticide research in Great Barrier Reef catchments has clearly shown that ecosystems are simultaneously exposed to multiple pesticides with toxicity effects that may be additive, synergistic, or antagonistic.⁵⁹ Simultaneous exposure is less applicable in upland catchments where grazing is the predominant, if not the sole, land use and where tebuthiuron is the most commonly used PSII herbicide. However, the risk of simultaneous exposure increases in the downstream transition from upland single land use catchments to multiple land use catchments and the marine environment. The stability of tebuthiuron in saltwater results in long residence times, which increase the risk of simultaneous exposure.⁶⁰

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