

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: Dissolved and particulate herbicide transport in central Great Barrier Reef catchments *RRRD038*



Bob Packett

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

Dissolved and particulate herbicide transport in central Great Barrier Reef catchments.

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Australian Government

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The Reef Rescue Research and Development Program (Reef Rescue R&D) was funded under the Australian Government's Caring for our Country program, and consisted of 18 projects. The Reef Rescue R&D is designed to improve our understanding of the link between land management practices and environmental impacts, and improve water quality across the Great Barrier Reef by informing on-ground projects to reduce the amounts of nutrients, pesticides and sediments reaching the Reef from agricultural lands.

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Cover photographs: Top Left – fresh water in a branch of the Mackenzie River (Fitzroy Basin) 2005; Top Right -: Cane spray rig Bundaberg, Bottom Left -Fitzroy River Barrage, Bottom Right -water quality sampling bottles Fitzroy River. Sourced from authors image collection.

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Executive Summary

Current best management practice in agriculture often involves reducing mechanical soil disturbance and increased use of chemicals to control weed growth. However, offsite transport of herbicides to the marine environment can impact on non-target species and ecosystems (Haynes et al. 2000; Jones et al 2003). In response to declining water quality in the Great Barrier Reef (GBR) lagoon the Reef Water Quality Protection Plan has been implemented (Reef Water Quality Protection Plan Secretariat, 2009). Major components of the plan are the GBR catchment event monitoring and modelling programs (Joo et al., 2012). The monitoring program does not currently differentiate between dissolved and particulate transport of herbicides and the modelling program is constrained by a lack of data for simulating exports of particulate bound fractions of herbicides to the reef lagoon.

A range of pesticides are used on agricultural lands in the Central Queensland region which includes the Fitzroy, Burdekin and Mackay Whitsunday, Great Barrier Reef catchments (Bainbridge et al., 2009a). The objectives of this project were to collect and analyse water runoff samples from agricultural lands at various scales to determine the percentage of herbicides transported in the dissolved and particulate phase. Sampling was undertaken at a range of scales from rainfall simulator plots (<3m²), farm, sub catchment and catchment (14,700,000 ha) scale. Water samples were collected during 2012 and 2013 specifically for partitioning analysis. Thirty six samples were collected from rain simulation trials on sugar cane plots in the Burdekin and Mackay Whitsunday catchments, and from rainfall simulation trials on grazing plots in the Fitzroy Catchment. Fifty eight runoff event samples were collected at farm, sub catchment and whole of catchment scales from cropping and grazing lands in the Fitzroy basin. Samples were analysed to determine the types of chemicals transported and the percentage of herbicide concentration being transported in the dissolved and particulate phase.

Results from rain simulation trials were in general agreement with data from the literature regarding mobility, a function of solubility and partitioning properties, for common herbicides. Those with low movement ratings tended to move off site with substantial percentages in the particulate phase, while those with high movement ratings were transported mainly in the dissolved phase. Catchment scale runoff events produced by natural rainfall resulted in minor particulate phase transport and major dissolved phase transport. The information gained will assist land managers to make informed decisions about the potential for offsite transport of different herbicide selections. The data produced by this study should also assist catchment modellers and model developers to more accurately represent the transport of herbicides from paddock scale through to the GBR lagoon. Future studies could investigate methods for collecting larger amounts of suspended sediments from flood waters for analysis. Filtering of larger (known) volumes of flood water would provide sufficient amounts of suspended sediments to help increase confidence in results from laboratory analysis. Further studies on half-lives and partitioning of chemicals in a range of soil types under controlled conditions are also suggested. This would allow for increased knowledge of *in-situ* partitioning of chemicals over time and the potential risk for runoff transport.

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Acronyms

DNRM	Department of Natural Resources and Mines
GBR	Great Barrier Reef
NRM	Natural Resource Management
RRRD	Reef Rescue Water Quality Research & Development Program

Abbreviations

EMC	Event Mean Concentration
LOR	Limit of Reporting
mg/L	milligrams per litre
PSII	Photo System two
Rainsim	Rainfall simulation
TSS	Total Suspended Solids
µg/L	micrograms per litre

Acknowledgements

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Introduction

In recent years pesticides (e.g. insecticides and herbicides) in catchment runoff have been identified as a threat to water quality in the Great Barrier Reef lagoon (Reef Water Quality Protection Plan Secretariat, 2009). Knowledge about the amount of herbicides exported to the Great Barrier Reef (GBR) lagoon is increasing from a concentration and total loads perspective (Brodie et al., 2012; Kennedy et al., 2012a; Lewis et al., 2012; Kapernick et al., 2007); however, the mechanisms involved in the transport of herbicides are not well understood (Davis et al., 2012; Brodie et al., 2009). While loads of herbicides can be calculated from monitoring data, modelling to simulate management change scenarios depends on appropriate parameterisation for dissolved and particulate fractions with relevant local data to increase confidence in model results.

Project Objectives

There is currently a need for data on the mechanisms involved in herbicide transport to inform catchment management and modelling projects. New hydrological models have recently been developed and implemented to simulate catchment exports of sediments, nutrients and photo system II herbicides (PSII) to the Great Barrier Reef lagoon. The current Source Catchments implementation for modelling reef catchments has the capacity to simulate dissolved and particulate constituents. Dissolved chemicals in runoff water will pass through a fine filter, whereas chemicals adsorbed to sediments and other substances will form the particulate proportion. To date, there has been a lack of data to adequately set model parameters for both dissolved and particulate forms of PSII herbicides.

A range of pesticides are used on agricultural lands in the Central Queensland region which includes the Fitzroy, Burdekin and Mackay Whitsunday, Great Barrier Reef catchments (Bainbridge et al., 2009a). The objectives of this project were to collect and analyse water runoff samples from agricultural lands at various scales to determine the percentage of herbicides (including PSII) transported in the dissolved and particulate phase. While the over-arching project objectives were to collect data for chemicals primarily used in the grazing and cropping industries, a collaborative opportunity arose to secure additional data from rainfall simulation studies on sugar cane productions sites. The data acquired will help inform catchment management and modelling projects about the proportion of a chemical being transported via the dissolved or particulate phase at various scales.

Methods

The rationale of this study was to collect water runoff samples containing representative concentrations of chemicals used in agriculture in central GBR catchments. The samples were then analysed for partitioning between the dissolved and particulate portions to determine the phase of transport for selected chemicals. Sample site locations and methods used are outlined in the following sections.

Study area

Runoff water samples for this study were collected from the Burdekin, Mackay Whitsunday and Fitzroy regions. Locations for primary sampling sites are shown in Figure 1 by yellow/black discs.

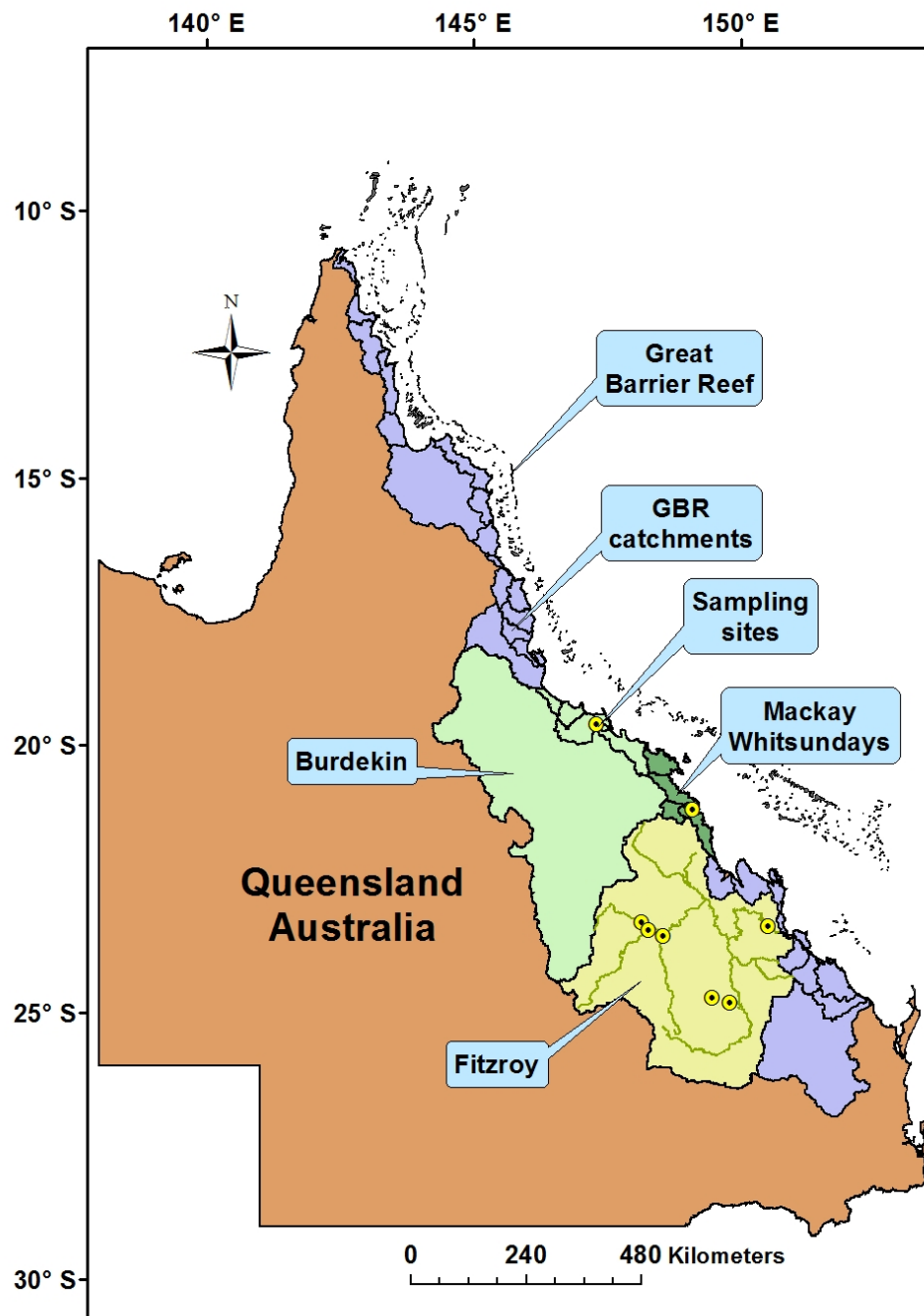


Figure 1: Great Barrier Reef catchments and project sampling sites in the Burdekin, Mackay Whitsunday and Fitzroy catchments marked with yellow and black circles.

The samples taken from the lower Burdekin and Mackay Whitsunday regions were from collaborative rain simulations studies aimed at improved management practices for

chemicals used in the cane industry (Lewis et al., 2013). Samples collected in the Fitzroy catchment (Figure 2) were primarily for partitioning of chemicals used in the cropping and grazing industries.

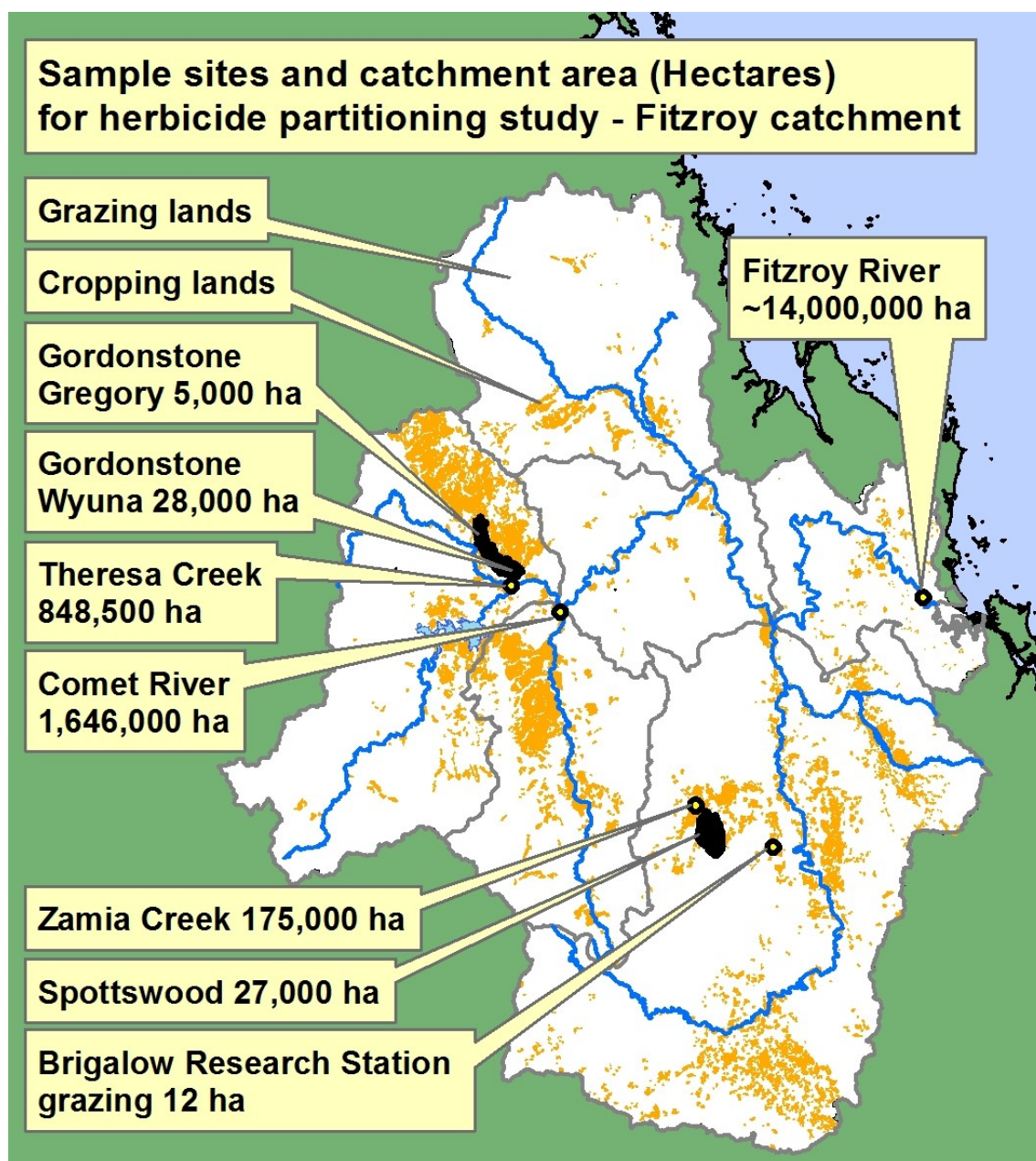


Figure 2: Locations and approximate catchment areas for sampling sites in the Fitzroy Basin, grey lines indicate major sub catchment boundaries while blue lines indicate major rivers and creeks, dominant land use for grazing and cropping are shown in white and orange backgrounds respectively.

A summary of primary land use, dominant soil types and area for each site is given in Table 1 in order of increasing scale. Two additional rain simulation (Rainsim) sites (Banana and Sunnyholt) in the Fitzroy catchment are omitted from the table, a small number of tebuthiuron results from these sites are reported in the results section.

Table 1: Sampling locations, number of water samples, primary land uses, major soils types and approximate areas of catchment upstream of sampling site (Rainsim = Rain simulator runoff).

GBR catchment (sub-catchment)	Sampling site	Primary land use	Dominant Soil types	~ Area	Number of samples
Mackay Whitsundays Burdekin	~ 15km SW of Mackay ~ 10km SW of Ayr	Sugar cane (Rainsim) Sugar cane (Rainsim)	Sodosol Kandosol	2.3 (m ²) 2.3 (m ²)	18 18
Fitzroy (Dawson River)	Brigalow Research Station	Grazing	Vertosol Sodosol	12 (ha)	12
Fitzroy (Nogoa River)	Gordonstone Creek at Gregory	Dryland cropping	Vertosol	5,000 (ha)	2
Fitzroy (Dawson River)	Spotswood Creek	Grazing/Cropping	Vertosol Chromosol	27,000 (ha)	2
Fitzroy (Nogoa River)	Gordonstone Creek at Wyuna	Cropping/Grazing	Vertosol	28,000 (ha)	6
Fitzroy (Dawson River)	Zamia Creek at Dawson Hwy	Grazing/Cropping	Vertosol Chromosol	175,000 (ha)	2
Fitzroy (Theresa Ck)	Theresa Creek outlet	Grazing/Cropping	Vertosol	848,500 (ha)	8
Fitzroy (Comet river)	Comet River outlet	Grazing/Cropping	Vertosol Kandosol	1,646,000 (ha)	8
Fitzroy	Fitzroy River outlet	Grazing/Cropping	Mixture of all above	14,700,000 (ha)	18

Collection methods

Water samples from rain simulation experiments were collected during runoff at regular timed intervals to form a single composite sample. Paired samples (two samples taken one after the other) from Brigalow Research Station runoff were collected via runoff flumes and an auto sampler. All other samples were grab samples collected manually in duplicate from creeks and rivers ~200mm below the water surface, where “paired samples” means two samples collected at the same time. All water samples were collected in 1 or 2L glass containers with teflon lid liners prepared specifically for agricultural chemical analysis. Samples were stored at 4 °C before and during transport to laboratories for analysis. In addition to the 1-2L samples collected from the Fitzroy River at Rockhampton two 5L (bulk) samples were collected and sent to the laboratory for spiking with environmentally relevant concentrations of a range of commonly used herbicides. The spiked samples were then analysed for total and dissolved partitioning.

Analytical methods

Water sample chemical analysis was conducted via various versions of liquid chromatography mass spectrometry (LCMS) depending on the chemical type. Samples collected from the rain simulation studies were analysed at ACS laboratories in Kensington, Victoria, Australia, while all other samples were analysed by Queensland Health Forensic and

Scientific Services, Coopers Plains, Queensland, Australia. Methods for the rain simulation samples involved filtering total water samples through a 0.45 µm glass fibre filter to separate the fraction of chemicals in solution from the fraction adsorbed to suspended sediment particles. Solvent extraction and chemical analysis was then carried out on the particulate and dissolved fractions independently. The percentage of dissolved and particulate concentrations for a chemical was then calculated after summing the two values to arrive at a total sample concentration. For all other sample analysis, two (paired) samples were used, where an unfiltered and a filtered sample both underwent solvent extraction methods. The particulate bound fraction was inferred from the difference between results from the total sample and the dissolved sample fractions.

A number of filtered water samples reported a slightly higher concentration than the total water concentration for a chemical, particularly for samples taken from the Fitzroy River at Rockhampton when herbicide concentrations were close to the limit of reporting (LOR) and Total Suspended Solid (TSS) concentrations were low. The laboratory methods error range for low concentration analysis accounts for these discrepancies. A recent study for flood water chemical partitioning in the Burdekin catchment found similar results for some samples with very low concentrations also via LCMS (Davis, et al., 2012). Where filtered analysis results were reported at higher concentrations than the total sample concentration, the overall result is reported here as 100% dissolved phase for a chemical.

Results

Results are presented according to the scale of the runoff catchment area, starting with rain simulation plots (<3m²) through to large scale sub catchment and whole of catchment scales (~14,700,000 ha). All analysis results are given as a percentage of chemical in dissolved and particulate fractions. Where no particulate fraction is given the results are for 100% dissolved phase transport. Partitioning study results for soil-water mixtures are normally reported as a partition coefficient, K_d , (partition between the solid and aqueous phase) where K_d = concentration on sediment / concentration in water, and/or the soil organic carbon coefficient, K_{oc} , where $K_{oc} = K_d / F_{oc}$, where F_{oc} is the fraction of organic carbon in soil (Wauchope, et al., 2002). This study deals with partitioning of chemicals in runoff waters and will only report on dissolved and particulate percentages of a chemical in a collected total water and suspended sediment sample instead of partition coefficients.

Rain simulation sample results (bare sugar cane plots)

Rain simulation studies at sites in the Burdekin and Mackay Whitsunday catchments on bare sugar cane plots were conducted during September 2012. These studies were concerned with application and runoff (1 to 2 days after application) of various chemicals (at same application rates) under simulated rain conditions. Herbicide event mean concentrations (EMC) and dissolved and particulate partitioning results for Burdekin bare cane Rainsim plots are given in Figures 3 and 4.

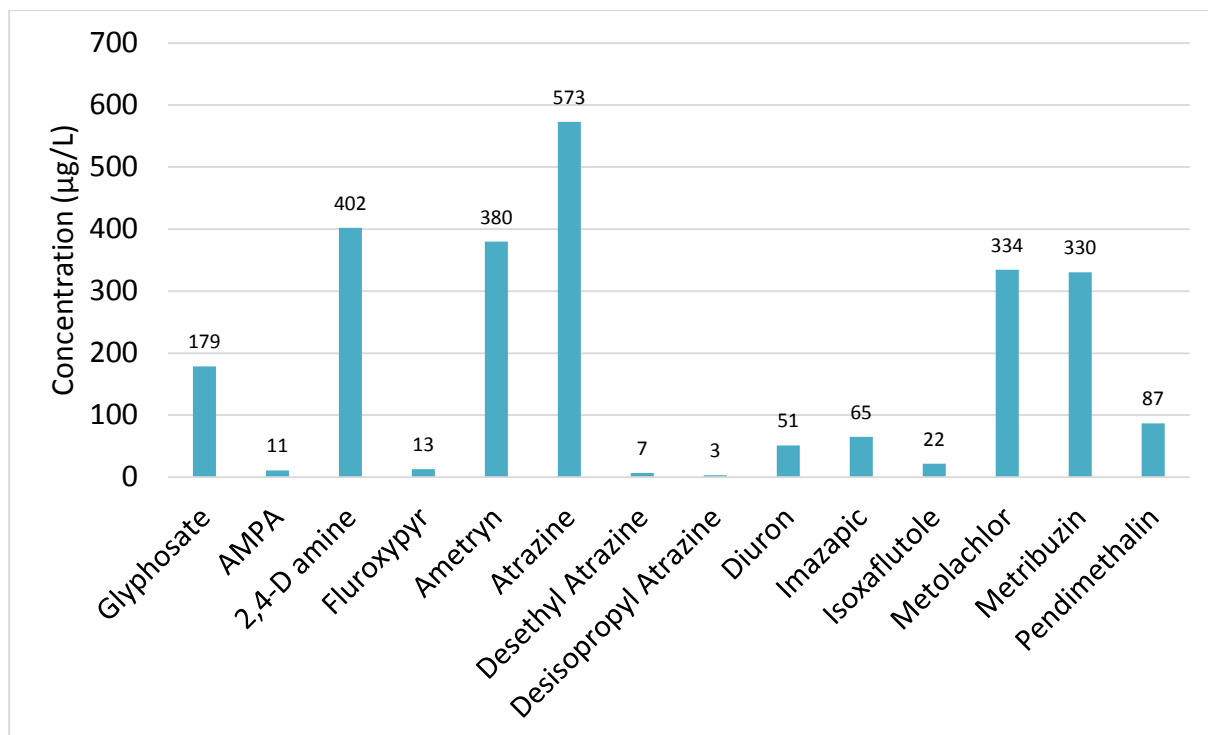


Figure 3: Event mean concentrations for chemicals detected during runoff from bare cane plots in the Burdekin catchment n = 18.

It can be seen that the mean concentration of chemicals in runoff water varied. Average atrazine concentrations in runoff (Figure 3) were the highest of all chemicals applied.

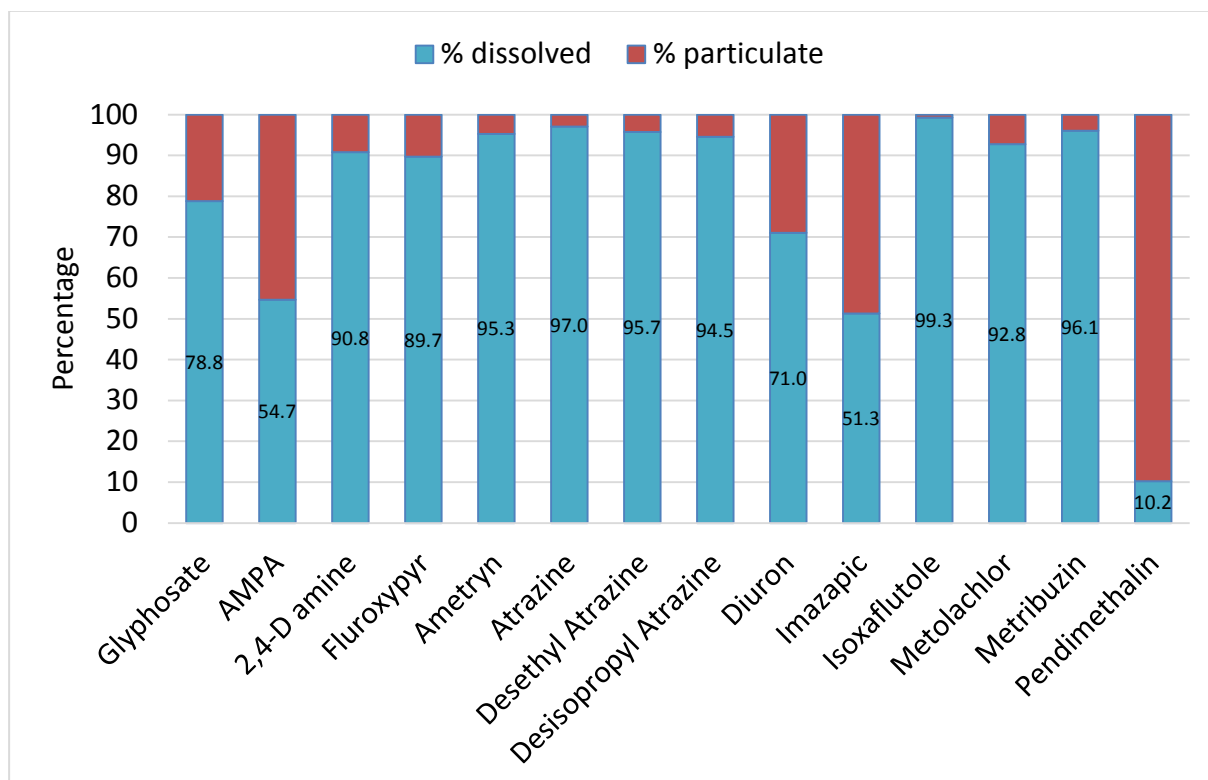


Figure 4: Event mean dissolved and particulate percentages for chemicals detected during runoff from bare cane plots in the Burdekin catchment n = 18.

Nine of the fourteen herbicides had over 90% of the chemical in the dissolved phase in runoff (figure 4). Apart from isoxaflutole, atrazine had the highest percentage of dissolved phase runoff compared to other chemicals, while pendimethalin ran off mainly in the particulate phase (Figure 4). Pendimethalin was the only herbicide with >50% of the compound in the particulate rather than dissolved phase. Imazapic and AMPA, the degradation product of glyphosate, showed close to 50% bound to particles in runoff.

Results of runoff from Rainsim bare cane plots in the Mackay Whitsunday are given in Figures 5 and 6 below.

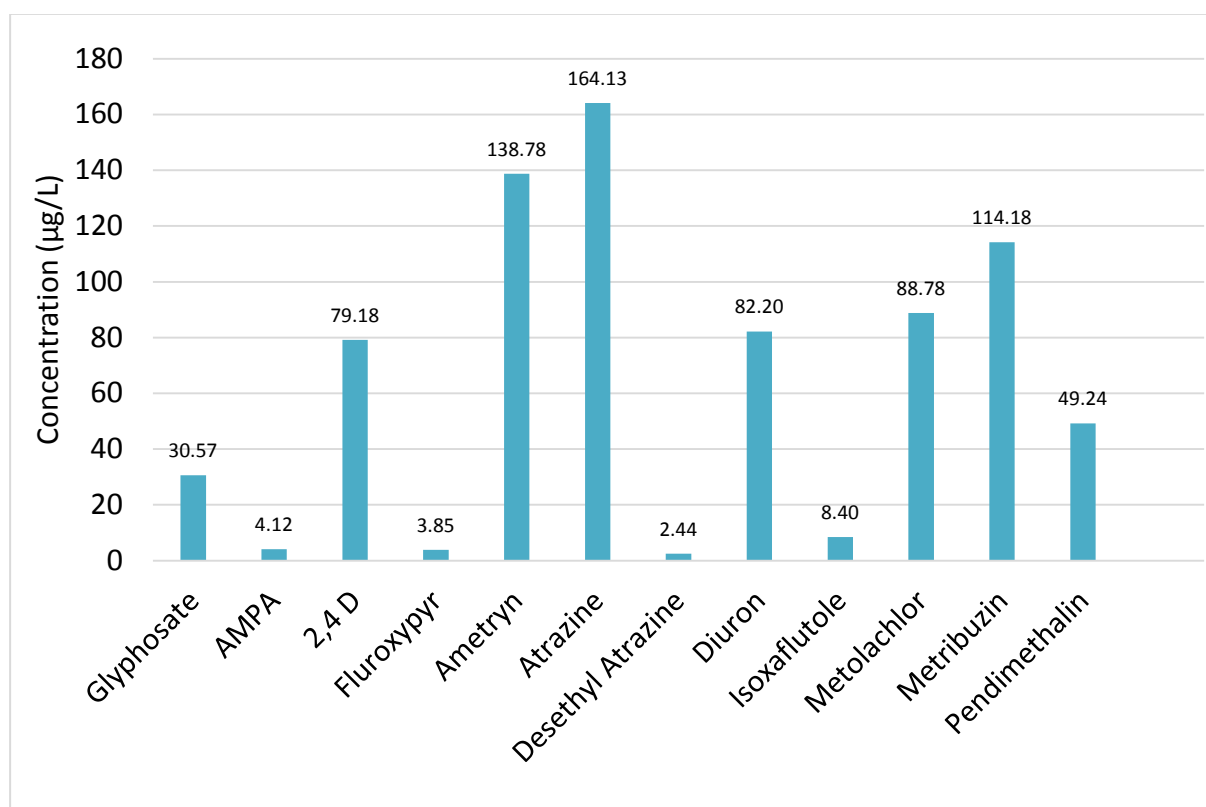


Figure 5: Event mean concentrations for chemicals detected during runoff from bare cane plots in the Mackay Whitsunday catchment n = 18.

Atrazine EMC's for the Mackay Whitsunday Rainsim trials were higher than other chemicals (Figure 5) and the patterns of variability in concentrations for most chemicals are similar to those for the Burdekin Rainsim results. Overall, the Mackay Whitsunday maximum concentrations were substantially lower than those for the Burdekin results. Diuron concentrations are an exception with relatively higher runoff values compared to the Burdekin results.

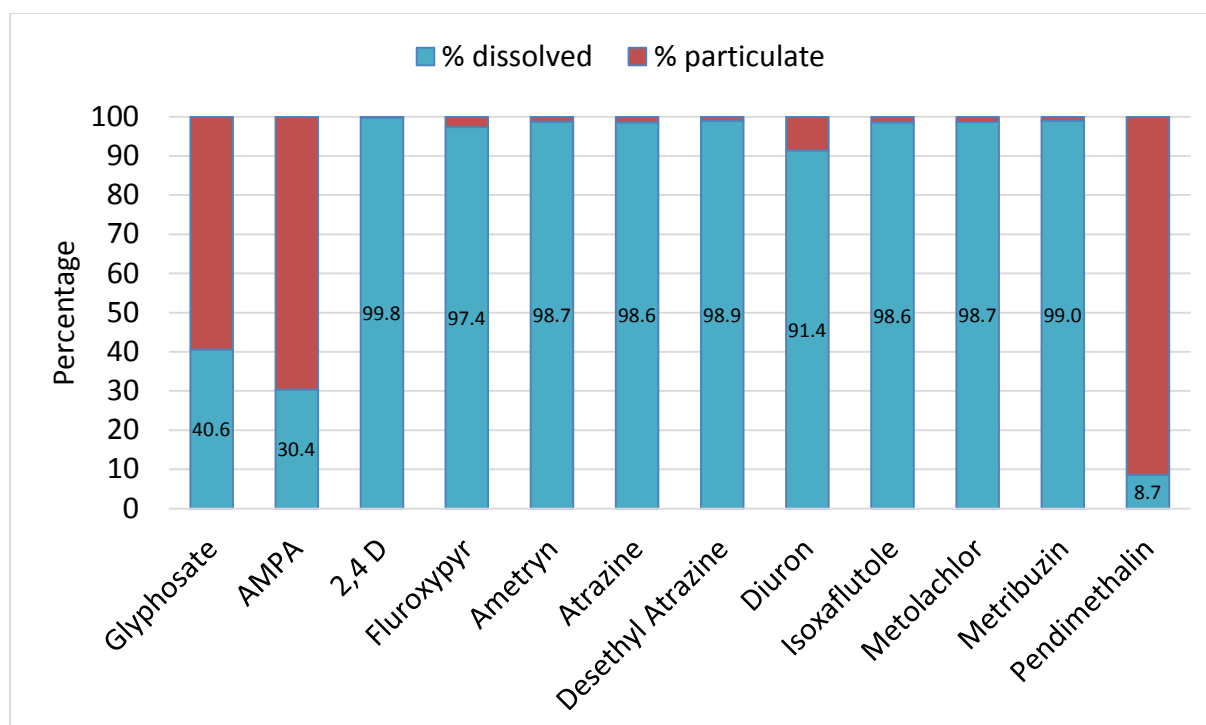


Figure 6: Event mean dissolved and particulate percentages for chemicals detected during runoff from bare cane plots in the Mackay Whitsunday catchment n = 18.

The percentages of dissolved glyphosate were much lower for the Mackay Whitsunday (Figure 6) Rainsim runoff results than the Burdekin results (Figure 4). However, similar to the results for the Burdekin, most herbicides had >90% of compound in dissolved fraction and pendimethalin was mostly in the particulate bound phase in runoff.

Additional rain simulation run off data (grazing land use)

A number of samples were collected during rain simulation study plots (<3m²) at 70 to 80 mm/hr rainfall rates on grazing lands in the Banana region (Dawson River sub catchment) and near Sunnyholt in the Acadia Valley (Comet River sub catchment) during July 2012. Tebuthiuron was the only chemical analysed for dissolved and particulate partitioning 1 to 2 days after granular chemical application. Results for paired samples from each site are shown in Table 2 with 100% of tebuthiuron samples being in the dissolved form.

Table 2: Summary of Rain simulation samples collected from grazing lands in the Comet and Dawson River catchments, where n = 2 sets of paired samples for each site with 100% dissolved tebuthiuron runoff.

Site	Land use	Sub catchment	Runoff type	TSS (mg/L) mean	Tebuthiuron (µg/L) mean
Banana	Grazing	Dawson River	Rain simulation	500	5600
Sunnyholt	Grazing	Comet River	Rain Simulation	590	4850

While the average suspended sediment concentrations in runoff were relatively high (500 to 590 mg/L) the tebuthiuron was totally in the dissolved phase when it left the Rainsim plots.

Catchment runoff results

The following results are from samples taken at various catchment scales from natural rainfall during 2012 and 2013. The Brigalow Research Station results are from runoff collected at farm scale (12 ha) via channeled runoff and automatic sampling equipment. Details on the background of the site, chemical application, soils and cover condition are covered in a companion report in this series (Thornton and Elledge, 2013). All other catchment results are from natural rainfall on larger scale sub catchments via manual sample collection.

Brigalow Research Station – Tebuthiuron partitioning

Results from runoff samples collected at the Brigalow Research Station ~100 days after aerial application of granular tebuthiuron to grazing trial sites are given below in Figures 7 and 8.

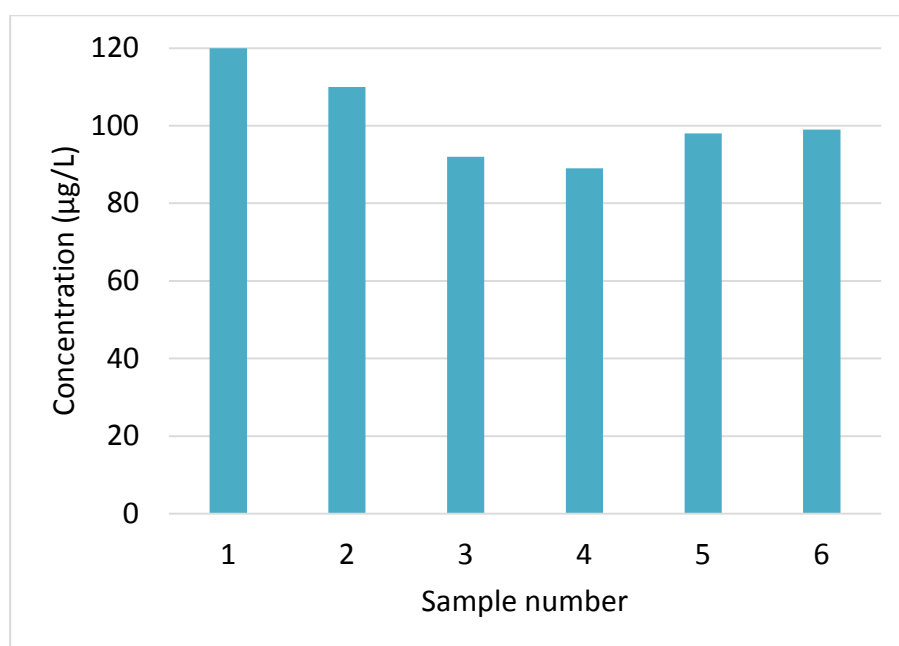


Figure 7: Event mean concentrations for tebuthiuron in runoff from the Brigalow Research Station catchment during February 2012, n = 6.

It can be seen from Figure 7 that tebuthiuron concentrations were much lower compared to the previous results for the Banana and Sunnyholt Rainsim runoff values which were collected 1 day after application.

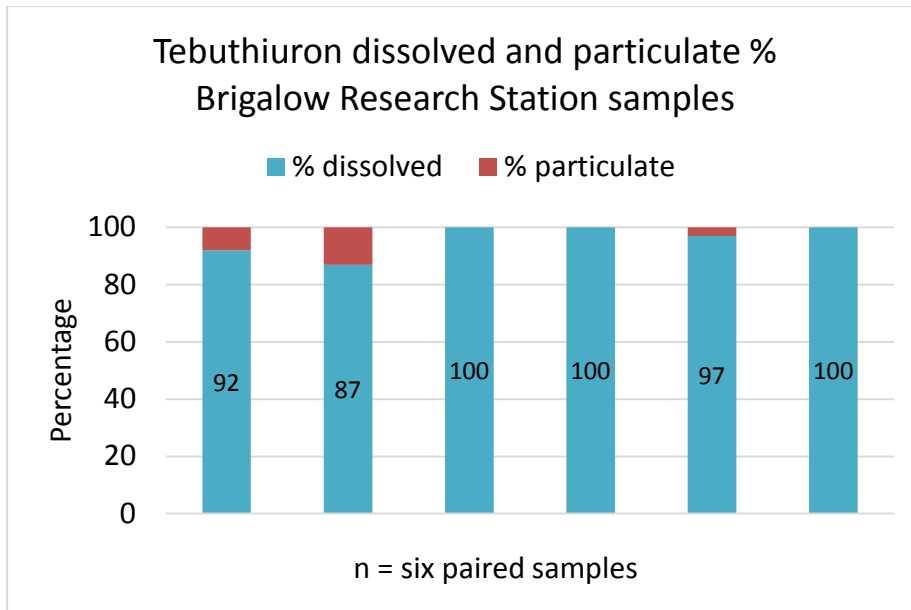


Figure 8: Dissolved and particulate percentages for tebuthiuron in runoff from the Brigalow Research Station catchment during February 2012, n = 6.

It can be seen from Figure 8 that the majority of tebuthiuron leaving the catchment was in the dissolved phase. Concentrations for TSS in the samples ranged from 38 to 266 mg/L with a mean concentration of 152 mg/L (n = 6 paired samples).

Gordonstone Creek events January and February 2012

Results from samples collected at sites on Gordonstone Creek (Nogoa River catchment) are given in Figures 9 and 10 below.

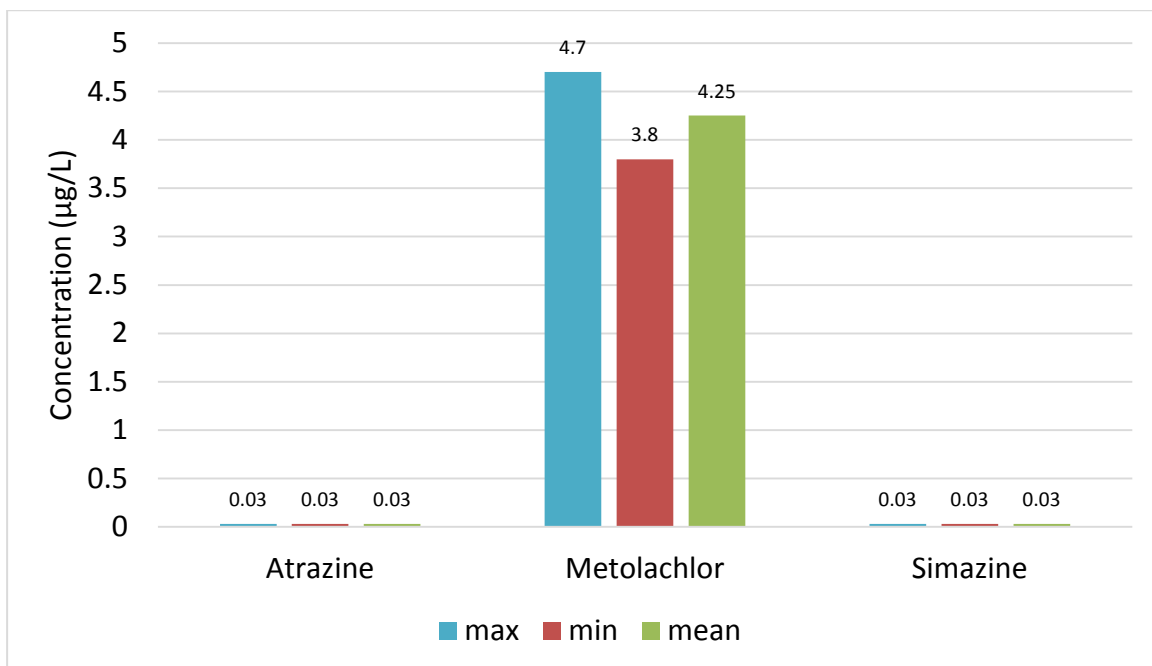


Figure 9: Range of concentrations for chemicals detected in runoff from Gordonstone Creek at Gregory site during January 2012, n = 6 paired samples.

Only three herbicides were detected at the Gregory site; atrazine, metolachlor and simazine. Of these herbicides the highest concentrations observed were for metolachlor.

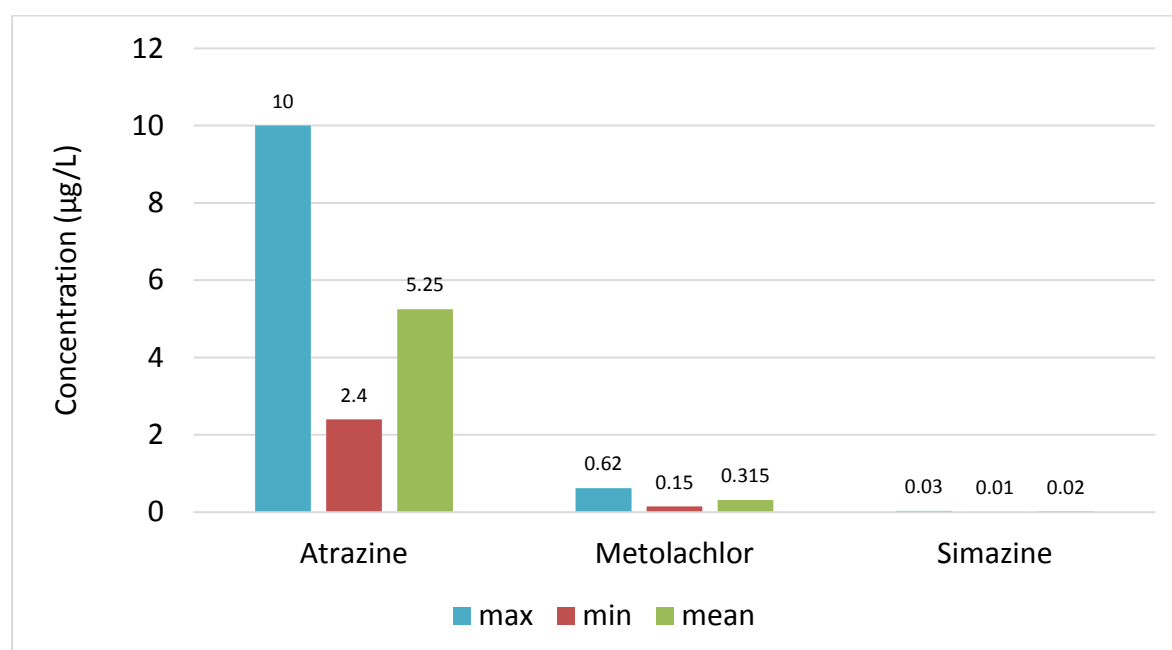


Figure 10: Range of concentrations for chemicals detected in samples from Gordonstone Creek at Wyuna site during January 2012, n = 6 paired samples.

Suspended sediment concentrations for the two sites ranged from 668 to 1300 mg/L. Only three of the six samples exhibited partitioning (Table 3) the remainder was all in the dissolved phase.

Table 3: Summary of samples from Gordonstone catchment with a percentage of chemical in dissolved and particulate fractions (n= 6 paired samples)

Gordonstone Creek catchment site	Chemical	Total concentration (µg/L)	% in dissolved phase
Wyuna	Simazine	0.03	67
Wyuna	Desethyl atrazine	0.68	96
Wyuna	Desethyl atrazine	0.61	90

Note that the concentrations for simazine are close to the analytical Limit of Reporting (LOR) of 0.01 µg/L for this chemical.

Zamia and Spottswood Creeks event February 2012

Two sets of paired samples were collected from Zamia and Spottswood Creeks during a flow event on 16/02/2012. TSS concentration for the Spottswood samples were 333 mg/L. Only two chemicals were detected at these neighboring catchments with tebuthiuron concentrations higher than those of atrazine at both sites as shown in Figure 11.

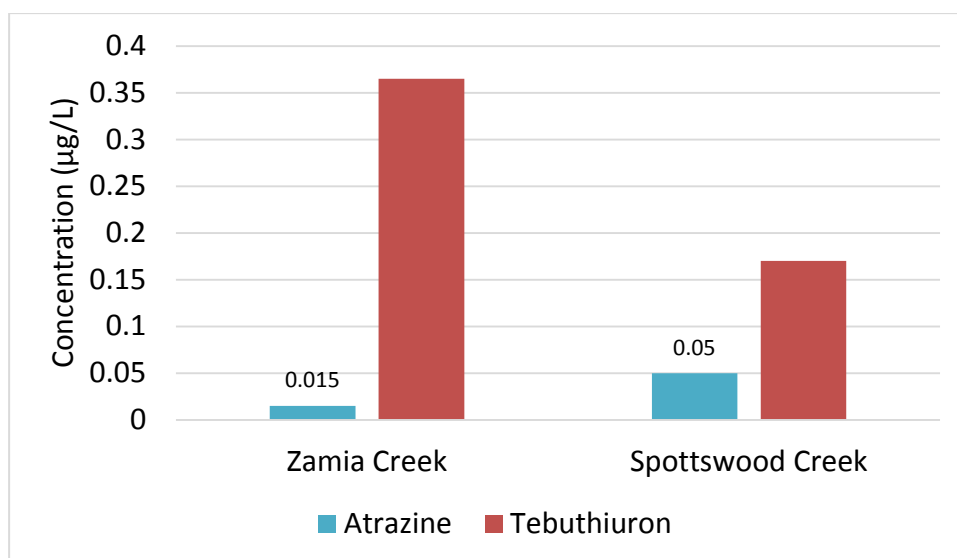


Figure 11: Concentration of atrazine and tebuthiuron in flows at sites on Zamia and Spottswood creeks during February 2012, n = 2 paired samples for each site.

Both atrazine and tebuthiuron concentrations were 100% dissolved for all samples at both Zamia and Spottswood Creek sampling sites.

Theresa Creek events February 2012

Six chemicals were detected in eight paired samples collected from Theresa Creek (at Gregory Highway) during flow events in February 2012. The ranges of concentrations are given in Figure 12 below. Four minor flow peaks occurred at this site between 01/02/2012 and 26/02/2012. Two sets of samples were collected from each event and analysed for dissolved and particulate partitioning.

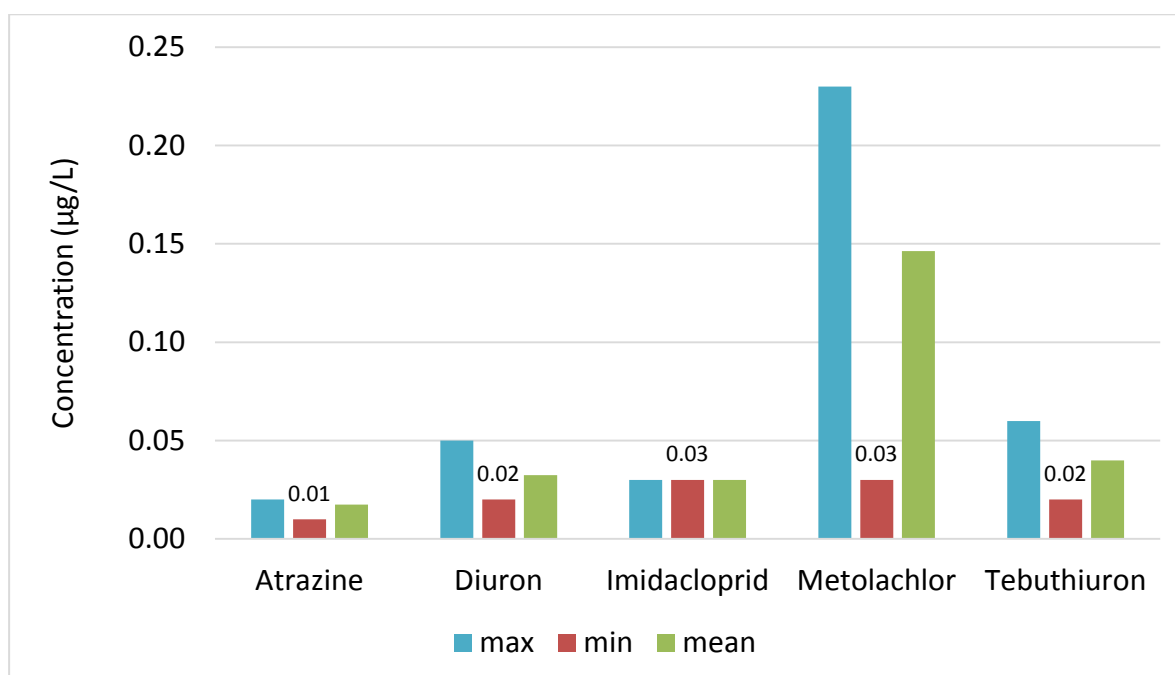


Figure 12: Range of concentrations for chemicals detected in samples from Theresa Creek at Gregory Highway site during February 2012 events, n = 8 paired samples.

One sample set analysed had an 80% dissolved and 20% particulate partitioning value for the chemical diuron. TSS concentration for this sample was 1380 mg/L for an event on 24/02/2012, while the average TSS concentration for the 4 minor events over the sampling period was 508 mg/L. All other chemical detections were in the 100% dissolved phase.

Comet River events February 2012

A number of herbicides were detected in samples collected from the Comet River (at Comet Weir) during minor flood events from 01/02/2012 to 24/02/2012. TSS concentrations for these events ranged from 146 to 679 mg/L with an average of 334 mg/L. The concentration range of detected chemicals is shown in Figure 13 below.

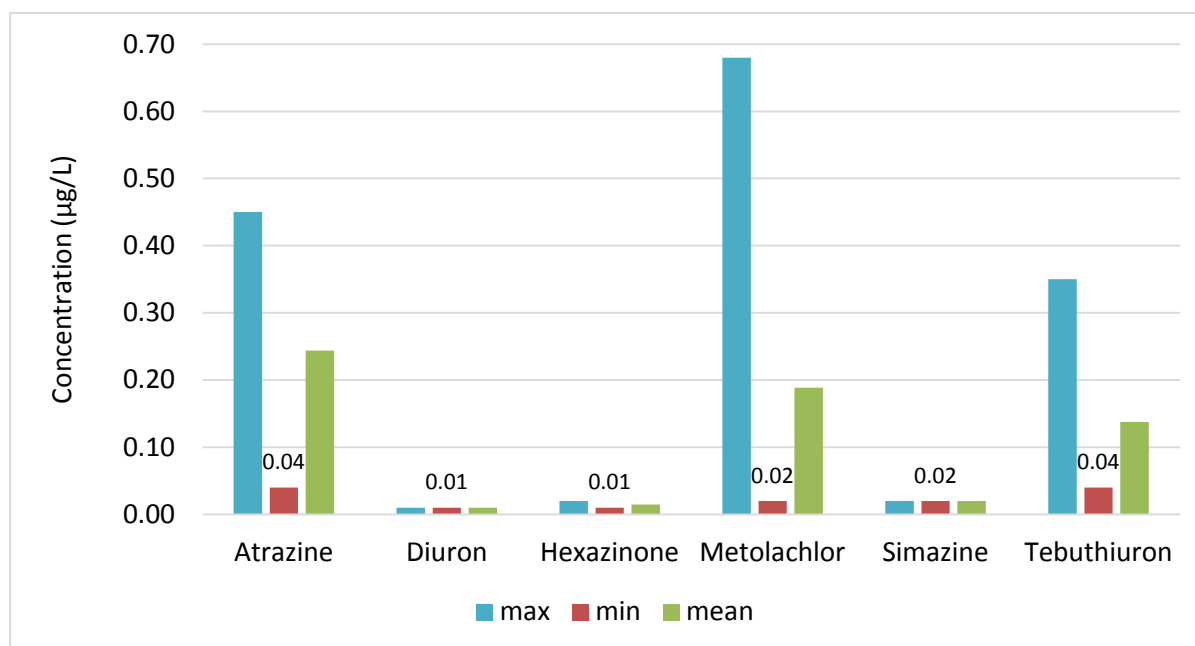


Figure 13: Range of concentrations for chemicals detected in samples from Comet River at Comet weir during February 2012 events, n = 8 paired samples.

It can be seen from Figure 13 that metolachlor had the highest maximum concentration and atrazine the highest averaged concentration during the four minor flood events. Note that diuron, hexazinone and simazine are close to the Limit of Reporting (LOR) of 0.01 µg/L for these chemicals. All herbicides were in the 100% dissolved phase for these events.

Fitzroy River events 2012 and 2013

During the 2012 wet season a number of herbicides were detected in samples collected from the Fitzroy River at Rockhampton. The highest number of detections were for atrazine, diuron, metolachlor, simazine and tebuthiuron. Other chemicals were detected either sporadically or in isolation and at low concentrations and are not reported here. The pattern of chemical detections and concentrations is considered typical for this site compared to historical data (Packett, et al., 2009). Of the 34 water samples analysed for pesticides residues 14 were analysed for dissolved / particulate fractions. The range of concentrations of primary herbicides detected are given in Figure 14 below.

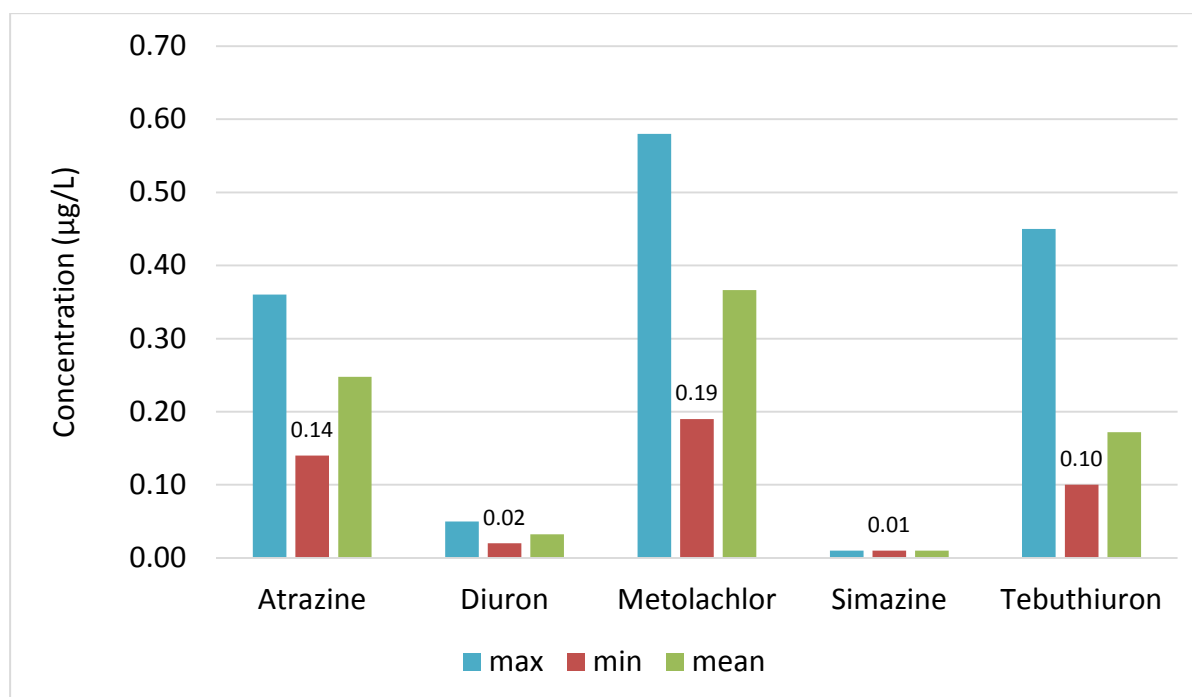


Figure 14: Concentration range for herbicide detections in the Fitzroy River at Rockhampton during February 2012 (n = 14 except for Simazine where n = 11).

It can be seen from Figure 14 that the highest maximum and average concentrations were for metolachlor. Historically, atrazine and tebuthiuron have usually shared the maximum concentration range, however, metolachlor is gradually exceeding both these chemicals in both concentration and number of detections during events at this site.

Concentrations of TSS for the samples ranged from 320 to 1270 mg/L with an average of 745 mg/L. Two paired sample sets returned a particulate partitioning result for the February event, namely 82 and 47% dissolved tebuthiuron for samples collected on 06 and 07/02/2012 respectively. The 47% dissolved value was treated as an outlier. The 2012 wet season was a relatively long one in historical terms with minor floods occurring to the end of April 2012, however, partitioning samples were primarily collected and analysed for the February floods (first flush). There were also minor winter floods during June and July 2012, partitioning samples collected for these flows were not analysed due to very low TSS concentrations. From a loads perspective, a summary of calculated herbicide loads exported from the Fitzroy River to the GBR lagoon for the February to May 2012 period is given in Table 4.

Table 4: Summary of herbicide loads exported from the Fitzroy River for February to May period 2012

Fitzroy River	Start Date	End Date	Event flow volume (ML)	Herbicide detected	Event Load (kg)	Event Mean Concentration (µg/L)
Rockhampton	29/01/2012	29/04/2012	6,360,914	Atrazine	741	0.12
				Diuron	34	0.01
				Metolachlor	531	0.08
				Tebuthiuron	829	0.13

It can be seen from Table 4 that the largest calculated load was for tebuthiuron closely followed by atrazine. Pesticides analysis for the Fitzroy River site at Rockhampton is usually limited to a small group of frequently detected herbicides. Detections of insecticides and less common herbicides are rare at this site and are normally confined to isolated low concentrations. As an example, glyphosate analysis (via specialised methods) is rarely requested as no detections have been reported for this site.

Roche Creek – glyphosate transport case study

In regards to the rain simulation partitioning results for glyphosate reported at the start of this section, it is worth re-calling results for a minor case study (previously unpublished) involving a substantial accidental spill of glyphosate in the upper Dawson River catchment. The data is included to show what may happen when relatively high concentrations of this chemical enter a stream network during high flow conditions.

Samples were collected at two sites in the upper Dawson River catchment after an accidental spill of an unconfirmed volume of glyphosate on the 17th February 2010. A traffic incident near a crossing over Roche Creek resulted in a number of broken chemical containers and the contents were spilt onto the road-side. A reported 1,000 to 2,000 litres (unconfirmed) of glyphosate was spilt, and although emergency work contained the spill, and a portion of the chemical was recovered, heavy rainfall that night washed the remainder into Roche Creek and eventually into Juandah Creek and the Dawson River.

A summary of concentrations of glyphosate and AMPA (the breakdown product of glyphosate) in samples collected at Taroom, ~83 km downstream of the spill site, is given in Table 5 along with tebuthiuron concentrations (as a reference chemical).

Table 5: Summary of Glyphosate and Tebuthiuron concentrations in Dawson River (Fitzroy Basin) minor flood during February 2010 after an accidental chemical spill near Roche Creek (Juandah Creek catchment).

Site	Date	Distance down stream from spill site	Glyphosate (µg/L)	AMPA (µg/L)	Tebuthiuron (µg/L)
Roche Creek	17/02/2010	0 km - Spill site	No data	No data	No data
Juandah Creek		~ 20 km	No data	No data	No data
Taroom	18/02/2010	~ 83 km	4.1	1.5	0.02
(Dawson River)	19/02/2010		4.7	1.2	0.02
	20/02/2010		9.0	5.5	0.09
	23/02/2010		<0.5	<0.5	0.01
	02/03/2010		<0.5	<0.5	0.06
	05/03/2010		<0.5	<0.5	0.05
Theodore	18/02/2010	~ 237 km	<0.5	<0.5	0.12
(Dawson River)	20/02/2010		<0.5	<0.5	0.18
	22/02/2010		<0.5	<0.5	0.24
	24/02/2010		<0.5	<0.5	0.11
	27/02/2010		<0.5	<0.5	0.12

It can be seen from Table 5 that glyphosate at substantial concentrations had reached the Dawson River at Taroom, however, samples taken down stream at Theodore on the Dawson River returned no detectable concentrations of either glyphosate or AMPA. There had also been wide spread rain leading up to the medium flood at Taroom and the Juandah Creek waters were mixing with other flood waters from the upper Dawson system. Tebuthiuron concentrations in the Dawson system during the event, based on historical data, were relatively normal and the data for this chemical is included to put the glyphosate detections into perspective.

In summary, a load calculation for the period 18/02/2010 to 20/02/2010 resulted in an estimated 600 kg of glyphosate (EMC = 4.86 µg/L) and 273 kg of AMPA (EMC = 2.21 µg/L) flowing past the Taroom site, with no detectable concentrations passing the Theodore site.

Discussion

In general, substantial partitioning to the sediment fraction was mainly observed at plot to paddock scale for most herbicides. The following comparisons that are made between site results are meant to highlight the differences or similarities in partitioning of chemicals in runoff water at different scales. Nearly all of the samples taken from the Burdekin and Mackay region rain simulation trials on bare cane plots had detectable levels of partitioning between the dissolved and particulate phases for most chemicals. The rain simulation results for tebuthiuron applications on grazing land in the Banana (Dawson River valley) and Sunnyholt (Comet River valley) regions returned nil partitioning values. In comparison, of the ~67 samples collected from natural runoff in the Fitzroy catchment at various scales, only 10 results (Table 6) indicated some partitioning between the dissolved and particulate transport phase.

Table 6: Summary of herbicide detections in runoff water (other than rain simulation studies) where a percentage of chemical was transported in the particulate phase. (Note: a result of 47% dissolved phase tebuthiuron (0.14 µg/L) for 07/02/2012 in Fitzroy River flows is omitted from Table due to low confidence in the value)

Site	Date	Chemical	% Dissolved phase	Concentration (µg/L)
Brigalow Research Station	23/02/2012	Tebuthiuron	92	120.00
Brigalow Research Station	23/02/2012	Tebuthiuron	87	110.00
Brigalow Research Station	23/02/2012	Tebuthiuron	97	95.00
Gordonstone at Wyuna	17/02/2012	Simazine	67	0.03
Gordonstone at Wyuna	23/02/2012	Desethyl Atrazine	96	0.68
Gordonstone at Wyuna	24/02/2012	Desethyl Atrazine	90	0.61
Theresa Creek outlet	24/02/2012	Diuron	80	0.05
Fitzroy at Rockhampton	06/02/2012	Tebuthiuron	82	0.14
Fitzroy at Rockhampton	14/03/2013	Metolachlor	86	0.07
Bulk sample spiked	10/02/2012	Bromacil	86	0.06

The sites in Table 6 are arranged in increasing scale (area) from paddock scale at top of the list to whole of catchment at bottom of list. The summarised results in Table 6 suggest that partitioning between dissolved and particulate fractions occurs more often and at higher concentrations closer to the source of application (Brigalow, Gordonstone) compared to

downstream sampling sites (Fitzroy River outlet). The following sections discuss results from a scale perspective starting with the small area rain simulation sites through to whole of catchment scale for the Fitzroy Basin.

Rain simulation scale

Overall, the rain simulation results suggest substantial partitioning of certain herbicides between the dissolved and particulate phase, particularly at plot scale soon after application. For example, the percent partitioning of pendimethalin, glyphosate, AMPA and diuron in runoff from bare cane plots at the Burdekin and Mackay sites were relatively similar. The dissolved phase transport for pendimethalin was 10.2 and 8.7% respectively, even though runoff concentrations were much higher at the Burdekin site. There was also substantial partitioning between the dissolved (51%) and particulate fractions for imazapic at the Burdekin site.

In general the partitioning characteristics for individual chemicals agreed with those in the literature (NPIC, 2013), where glyphosate and pendimethalin are considered to have a low movement (off site transport) rating. The offsite movement ratings (similar to mobility ratings) are dependent on compound solubility and sorption coefficients. A summary of movement ratings for selected chemicals is given in Table 7 where glyphosate and atrazine have extremely low and high movement ratings respectively.

Table 7: Movement ratings, and collated characteristics for selected herbicides, adapted from the Oregon State University / U.S. EPA pesticide properties database (NPIC, 2013).

Common name	Herbicide movement rating	Half-life in soil (days)	Water solubility 22 to 25 C° (mg/L)	Sorption coefficient (soil K _{oc})
Glyphosate	Extremely low	47	900,000	24,000
Pendimethalin	Very low	90	0.275	5,000
Diuron	Moderate	90	42	480
2,4-D dimethylamine	Moderate	10	796,000	20
Metolachlor	High	90	530	200
Simazine	High	60	6.2	130
Atrazine	High	60	33	100
Metribuzin	High	40	1,220	60
Tebuthiuron	Very high	360	2,500	80
Hexazinone	Very High	90	33,000	54

Given that the runoff data from the bare cane plots are an average of multiple samples collected during controlled rain simulation trials, relatively high confidence is given towards the results. The results of the rain simulation trials on grazing lands (Banana and Sunnyholt) for tebuthiuron transport were also in close agreement with the value in Table 7, where the chemical has a very high movement rating. Even though the mean concentrations in runoff were relatively high at these sites (5600 and 4850 µg/L) and TSS mean concentrations ranged from 500 to 590 mg/L, the tebuthiuron appeared to be running off totally in the dissolved phase.

Farm and sub catchment scale

In contrast to the findings above, half of the samples collected in runoff from the Brigalow Research Station ~100 days after aerial application of tebuthiuron showed some degree of partitioning with a maximum particulate fraction of 13% for one sample. Average tebuthiuron concentrations (~100 µg/L) were low compared to the rain simulation values mentioned above, but relatively high compared to historical values for tebuthiuron in major creeks and rivers in the Fitzroy basin. Also, the TSS concentrations were quite low with an EMC of 105 mg/L and poor relationships were observed between TSS and tebuthiuron concentrations for individual sample results via linear regression analysis. The data suggests that the majority of tebuthiuron was leaving the catchment in the dissolved phase, with minor amounts bound to particulates. Residence time in the soil may explain why some of the chemical is bound to particulates as compared to the totally dissolve phase transport seen in the rain simulation trials where the applications were a day or two prior to runoff.

Dryland cropping is a major land use in the Gordonstone Creek catchment and the range of herbicides detected in runoff at the Gregory and Wyuna sites during January and February 2012 reflects this. Metolachlor and low concentrations of atrazine and simazine were detected in samples from the Gregory site, with no partitioning observed. Higher concentrations of atrazine and low concentrations of metolachlor and simazine were detected in runoff samples from the Wyuna site with two samples exhibiting partitioning for desethyl atrazine and one for simazine. The partitioning result of 67% dissolved for simazine seems questionable considering the chemical has a high movement rating (Table 7).

Theresa Creek is a major sub catchment of the Fitzroy basin with grazing and dry land cropping as the major land uses. The types of herbicides detected in flows during February 2012 include chemicals related to cropping and grazing with numerous detections of atrazine, diuron, metolachlor and tebuthiuron. A single result of 20% in the particulate phase for diuron was the only runoff sample with partitioning observed. Relatively high TSS concentrations (1380 mg/L) suggest that the partitioning result could be valid, however the diuron concentrations for these events were relatively low (0.05 µg/L maximum) and should be treated with caution.

The relatively low concentrations of atrazine and tebuthiuron observed in samples collected from Zamia and Spotswood Creeks in the Dawson River sub catchment during February 2012 are considered fairly typical for the area given the small proportion of cropping in the catchment. Grazing is the major land use in the region, with some areas of cropping and this is reflected in the chemicals detected in runoff samples with 100% transported in the dissolved phase.

Samples collected from the Comet River outlet during February 2012 returned detections of a range of chemicals associated with cropping along with tebuthiuron which is applied in grazing situations. The highest maximum concentrations detected were for metolachlor (~0.7 µg/L) followed by atrazine (~0.45 µg/L) and tebuthiuron (~0.35 µg/L) with low concentrations of diuron, hexazinone and simazine. All chemicals appeared to be transported in the dissolved phase despite relatively high TSS concentrations for some of the events (TSS mean of 334 mg/L).

The data for the Roche Creek glyphosate spill is primarily included in the results section to illustrate the possible fate of this chemical in streams at high concentrations over a short time span. While the results do not directly add to the partitioning study at hand, they do suggest that glyphosate can be transported in flood waters and may become adsorbed to suspended sediments and particles under high flow conditions. The chemical appeared to be lost from the system over a short distance and time period relative to the transport of other chemicals in the Fitzroy River basin. These results seem consistent with the plot scale rain simulation data for glyphosate which suggested the chemical has a very low movement rating. No TSS data was secured for this event, but tebuthiuron (and atrazine, not reported here) concentrations in the samples indicate that, apart from the spill, the event was a fairly typical one in regards to herbicide type and concentrations for the region.

Whole of catchment scale

A range of herbicides were detected in samples collected from the Fitzroy River at Rockhampton during the extended 2012 wet season. Only one sample exhibited partitioning for tebuthiuron with 82% of the chemical in the dissolved phase, while another result at 47% dissolved was treated as an outlier and not included in the results. Sampling in March 2012 returned one metolachlor partitioning value of 86%. All other samples analysed for chemical partitioning between the dissolved and particulate fractions (14 in total) returned results indicating that transport was in the 100% dissolved phase. TSS concentrations for the series of events were relatively low; however, there were maximum concentration values of 1270 mg/L indicating that fine sediment was available for chemical sorption. EMC values for the 2012 wet season were relatively low, but well above LOR concentrations (0.01 µg/L) for atrazine, metolachlor and tebuthiuron at 0.12, 0.08 and 0.13 µg/L respectively. Diuron and simazine concentrations were low and closer to the LOR values for these chemicals.

Benefits and application

The results of this study suggest that the majority of herbicides commonly detected in flood waters are transported from the Fitzroy catchment to the GBR lagoon are in the dissolved phase. As catchment area decreases, there appears to be a greater possibility for a fraction of a given chemical to be transported in the particulate form, however, even at sub catchment scale, nearly all of the total herbicide load is dissolved. Results indicate that it is only at the smaller (in area) farm (Brigalow Research Station) and plot (Rainsim) scales where substantial partitioning of chemicals is detected in runoff.

A primary and immediate benefit of these findings will be to help inform the current Source Catchment modelling of PSII herbicide export to the GBR lagoon. Greater confidence can now be placed in setting model partitioning parameters for dissolved and particulate transport of herbicides from the Fitzroy catchment. In addition, the data from rain simulations on bare cane plots in the Burdekin and Mackay Whitsunday catchments will provide useful information in relation to management changes and model scenarios aimed at reducing off farm transport of chemicals.

Conclusions

The results of this study suggest that herbicides commonly detected in flood waters exported from central GBR catchments, such as atrazine and metolachlor, are transported primarily in the dissolved phase. Even at plot scale and at high pesticide and sediment concentrations, these chemicals exhibit limited partitioning between dissolved and particulate fractions in runoff. Tebuthiuron transport in the Fitzroy catchment is also mainly via dissolved phase, and as the catchment area is increased all three chemicals are found at close to 100% dissolved fractions in flood waters. Modellers, model developers and natural resource managers can, with increased confidence, implement parameters and scenarios which simulate predominantly dissolved phase transport for priority PSII herbicides based on the findings of this study.

Future Directions

It is apparent from this study that alternative field and laboratory methods are needed to reliably determine chemical partitioning in floodwaters when TSS concentrations are low, and chemical concentrations approach the LOR for a herbicide. One approach to address this could be to filter substantial volumes of water in the field to obtain a greater mass of suspended sediment for analysis. Limited detections of partitioning in the particulate phase for diuron may need more investigation. The methods outlined above may assist in determining if low levels of diuron (in particular) are being exported in the particulate phase. Further studies on half-lives and partitioning of chemicals in a range of soil types under controlled conditions are also suggested. This would allow for increased knowledge of *in-situ* partitioning of chemicals over time and the potential risk for runoff transport.

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