

Reef Rescue Research & Development

Technical Report

Pesticides in the sugarcane industry:
an evaluation of improved management
practices and the use of new/alternative herbicides
RRRD037



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Pesticides in the sugarcane industry: an evaluation of improved management practices and the use of new/alternative herbicides

Project RRRD037 Pesticides in Sugar

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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 – Spot spray trials in Burdekin; Top Right – Rainfall Simulation experiments in Burdekin; Bottom Left – Banded herbicide application trials in the Burdekin Bottom Right – Pesticide degradation experiments. Images supplied by TropWater, James Cook University and Department of Natural Resources and Mines, Queensland.

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

Executive Summary

Few studies have quantified the water quality (and agronomic) benefits of improved management practices (e.g. spot spraying, hooded/shielded application) largely aimed at reducing the loss/use of 'residual herbicides' from sugarcane paddocks. In the Great Barrier Reef catchment area such work is critical to examine whether water quality targets in Reef Plan 2013 (i.e. a 60% reduction in pesticide loads to the Great Barrier Reef) are achievable under what are considered 'current best practice' or 'aspirational practices'. Another key consideration is the evaluation of the purported 'new/alternative' herbicides that have become available to the sugarcane industry as 'softer' alternatives to diuron and atrazine. In this study, a series of spot spray rainfall simulation trials were conducted across the Burdekin and Mackay Whitsunday regions to examine the potential of improved spray technology (i.e. spot spraying using weed seeking technology, banded/shielded spraying) to reduce the surface runoff losses of herbicides from the cane paddocks. The effectiveness of banded/shielded spray application was also examined on a commercial furrow-irrigated paddock in the Burdekin region. Finally, the data are used to examine the relative risk of the key herbicides (diuron, atrazine, ametryn, hexazinone, metribuzin, metolachlor, pendimethalin, isoxaflutole, imazapic, glyphosate, paraquat, 2,4-D, fluroxypyr) used in the sugarcane industry based on their relative toxicity and their runoff in the dissolved phase from paddocks.

The results show that the application of less herbicide on the paddock translated to a proportional reduction in the surface runoff losses of herbicides from the paddock. While this result was expected, it demonstrated that marked reductions in residual herbicide application could be made (without any detrimental impact on the industry) and that the current Reef Plan targets are achievable under best practice scenarios. The data also provide insights on how the different herbicides runoff from a paddock with the vast majority being lost in the dissolved phase. Exceptions such as pendimethalin and imazapic were predominately transported attached to particles, while glyphosate, 2,4-D and diuron all had some affinity ($\sim <20\%$) for the particulate phase. Hence, the herbicides with the affinity for particulates could be managed by controlling soil loss from the paddock, while management of the hydrology of the paddock (i.e. reducing the amount of water leaving the paddock) could reduce losses for the herbicides transported in the dissolved phase. Another trial examining the effectiveness of banded spraying in the Burdekin region was conducted to determine the reduction of PSII inhibitor herbicides (atrazine and diuron) where furrow irrigation was applied to the paddock. These results showed that for these irrigation systems diuron and atrazine loads leaving the paddock could be reduced by $\sim 90\%$. If this practice was widely adopted across the Burdekin region, the results suggest that freshwater ecosystems such as Barratta Creek would benefit greatly with concentrations maintained below ecosystem protection guidelines for most of the year (as opposed to concentrations being above guidelines for ~ 6 months).

The relative risk analysis suggests that, for the herbicides examined in the rainfall simulation trials, the alternative/new herbicides have a generally lower risk than diuron. However, trifloxysulfuron sodium (Krismat), s-metolachlor (Dual Gold, more toxic than metolachlor) and the metabolite of isoxaflutole (Balance) (DKN) need further analysis before we can have full confidence in these results. Additional Great Barrier Reef toxicity data would also help confirm our model. This preliminary analysis suggests that provided the residual herbicides

are applied with banded/shielded sprayers on the raised bed or hill (50 to 60% less than what would be applied as a broadcast application), residual herbicides can be adequately managed in the sugarcane industry with far less impact on the Great Barrier Reef.

Contents

Executive Summary	i
Contents.....	iii
List of Figures	iv
List of Tables	iv
Acknowledgements.....	vi
Introduction	1
Project Objectives	2
Methods.....	2
Rainfall simulation trials	2
Banded/shielded spraying furrow irrigation trial	5
New/alternative products	6
Results.....	8
Rainfall simulation trials	8
Herbicide relative risk to the Great Barrier Reef	13
Banded/shielded spraying furrow irrigation trial	15
Discussion.....	18
Herbicide information gaps	20
Conclusions	23
Future Directions	23
References	25
Appendix 1: Publications	28

List of Figures

Figure 1. Rainfall simulation trials were carried out in the Burdekin and Mackay Whitsunday regions to examine the runoff of the key and emerging products used in the sugarcane industry.	4
Figure 2. The banded/shielded sprayer in action. Atrazine, diuron, paraquat and 2,4-D were applied on the raised beds and glyphosate and 2,4-D were applied in the inter-rows/furrows. Flows off the paddock were measured in V-notch weirs or the time it took to fill a 20 L bucket.	5
Figure 3. Spot spray trials of the established and emerging (and one metabolite of atrazine) herbicides used in the sugarcane industry with runoff either dissolved in water or attached to sediment (Burdekin 2012 trial).	9
Figure 4. Rainfall simulation 2012 trials in the Burdekin Region suggest that the new/alternative herbicides generally runoff the same as the PSII herbicides in current widespread use with the exception of pendimethalin, which had much lower loss rates.	12
Figure 5. Results from the rainfall simulation 2012 trials in the Mackay Whitsunday Region. The left bar for each herbicide represents the runoff concentration to spray rate ratio of the total sample while the right bar represents the ratio of the filtered (i.e. dissolved herbicide) sample.	12
Figure 6. Example of the flow data from Bay 1 derived from the V-notch weir crate that had been calibrated prior to the field experiment and from the manual measurements made using volumes of water collected in the bucket at designated times throughout the irrigation event.	16
Figure 7. Concentrations of atrazine (A), diuron (B) and 2,4-D (C) in the trial. For atrazine and diuron there was a significant difference in the concentrations between the conventional (broadcast) application and the banded/shielded sprayer while 2,4-D displayed no significant difference.	17
Figure 8. The WeedSeeker technology has been applied in the Mackay Whitsunday region and can reduce application of some herbicides by up to 80% (from http://reefcatchments.com.au/files/2013/02/WeedSeekerSm1.pdf).	19

List of Tables

Table 1. Summary site farming system and soil type characteristics of RR R&D Rainfall simulation sites. (Rainfall simulation sites herbicide runoff was compared in collaboration with Sugar Research Australia and NCEA-USQ).	3
Table 2. Pesticide products applied in rainfall simulation trials for 100% application treatments. Selected physical chemical properties are provided.	4
Table 3. Regression analysis results for the loss of herbicides in runoff relative to the percent of the field to which herbicides were applied.	11
Table 4. Mean EMC (dissolved phase) measured in rainfall simulation studies (at 2 days after application) combined with the relative toxicity score (see Table 5) to provide an assessment of the relative risk of offsite transport for commonly applied herbicides in the sugarcane industry. N/A – Event mean concentrations not available.	13
Table 5. Relative potencies for herbicides based on EC ₅₀ values for population growth or abundance endpoints (h-REP) with respect to the reference herbicide diuron (REP=1).	14
Table 6. Predicted EMCs (dissolved phase) and relative risk if rainfall occurred 30 days after application based on the mean soil half-life data reported in Shaw et al. (2013).	15

Acronyms

DSEWPac	Department of Sustainability, Environment, Water, Population and Community
GBR	Great Barrier Reef
GBRMPA	Great Barrier Reef Marine Park Authority
NRM	Natural Resource Management
QDAFF	Queensland Department of Agriculture, Fisheries and Forestry
RRRC	Reef and Rainforest Research Centre Limited
RRRD	Reef Rescue Research & Development
RWQPP	Reef Water Quality Protection Plan
LC MSMS	Liquid chromatography mass spectrometry mass spectrometry
EC₅₀	The concentration that induces a toxic response halfway between the baseline and maximum after a specified exposure time.
EMC	Event mean concentration

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Introduction

The offsite loss of pesticides from agricultural, urban and industrial lands via surface runoff or deep drainage has been known to contaminate water supplies around the globe and potentially reach concentrations that impact upon town drinking water and freshwater and marine ecosystems (e.g. Geiger et al., 2010; Loos et al., 2010; Schafer et al., 2011). This contamination has also been observed in the catchments and lagoon of the Great Barrier Reef and occasionally concentrations of photosystem II inhibiting (PSII) herbicides have exceeded water quality guidelines for ecological protection (Lewis et al., 2009, 2012; Davis et al., 2012, 2013; Smith et al., 2012); these herbicides are predominantly sourced to agriculture. In this regard, improved pesticide management in agricultural lands is required to reduce pesticide losses to a level needed to protect these ecosystems.

The establishment of the Reef Water Quality Protection Plan (RWQPP: Queensland Department of the Premier and Cabinet, 2003, 2009, 2013) in 2003 (with updates in 2009 and 2013) aims to halt and reverse the decline of water quality entering the Great Barrier Reef (GBR) with a particular focus on the runoff of sediments, nutrients and pesticides (largely PSII inhibiting herbicides) from the adjacent catchments. The identification of sugarcane as a major contributor to pesticide pollution in the GBR led in large part to the RWQPP (2009) introducing targets to reduce end-of-catchment pesticide loads of diuron, atrazine, hexazinone, ametryn and tebuthiuron by a minimum of 50% (2009 to achieve by 2013) and 60% (2013 to achieve by 2018) (Queensland Department of the Premier and Cabinet, 2009, 2013). To help achieve these targets the Queensland Government introduced a package of legislation, extension and research in 2010 known as the Reef Water Quality Program, which included restrictions on the use of diuron, atrazine, hexazinone and ametryn (regulated PSII pesticides) on sugarcane, on properties in the Wet Tropics, Burdekin Dry Tropics and Mackay Whitsunday catchments. However, upon the announcement of the targets set for the 2009 RWQPP, it was largely unclear on what was required by the agricultural industries of the GBR in order to achieve these targets.

During this time, the Federal Government invested in the Reef Rescue (RR) Research and Development Program to quantify the water quality benefits of improved herbicide management practices in sugarcane, banana and grazing lands. Innovative techniques based around precision application of pesticides (spot spraying (mimicking the 'Weedseeker® technology'), banded/shielded spraying) and the application of new/alternative products to the regulated PSII suite have all been recently promoted within the sugarcane industry to reduce pesticide runoff from paddocks. The purported benefits of these promoted 'A class' practices to reduce the amount of pesticide runoff are, however, largely unquantified. These links are critical in the management of application rates of certain pesticides in the GBR catchments and to inform/validate modelling within the RR Water Quality (WQ) grants and monitoring and evaluation (M&E) components. While some pesticides have higher runoff potential than others due to their individual physicochemical properties (e.g. half-life, solubility), quantification of the relative propensity for traditional and emerging alternative chemicals to wash-off paddocks remains scant. Better quantification of the likelihood of individual pesticide chemicals (both traditional and emerging) to move off-site under farming systems in the Queensland sugarcane industry is also required to better parameterise/validate predictive models such as How Leaky? that currently underpin

paddock up-scaling and catchment load calculations under the Paddock to Reef Integrated Monitoring, Modeling and Reporting program (Carroll et al. 2010).

Knowledge of the likely environmental fate and off-site ecological effects of the alternative herbicides in GBR sugarcane catchments is also currently scarce. A variety of inherent physicochemical and toxicological characteristics all affect the likely environmental risk posed by pesticides (Simpson et al., 2001). Many of these herbicides, particularly those likely to fill a similar weed suppression role to the regulated PSII herbicides, share similar physicochemical profiles to the more traditional PSII herbicides currently regarded as environmentally problematic. In some cases, herbicides such as metribuzin, s-metolachlor, trifloxysulfuron sodium and pendimethalin actually have higher toxicities to particular aquatic primary producers, at least in freshwater situations. There has, however, until this point, been surprisingly little structured assessment of the comparative potential environmental effects of broad-scale sugarcane industry changes from traditional PSII products to this alternative suite of herbicides.

Recent modelling has suggested that >90% of the current annual PSII inhibitor herbicide load of approximately 17,000 kg delivered to the GBR is derived from sugarcane lands (Kroon et al., 2013). Hence if the new technologies could reduce paddock losses by ~60% then the RWQPP targets could be achieved. This report examines the reductions in herbicide runoff from paddocks under the adoption of spot spray technology, banded/shield spraying and the application of new/alternative herbicide products in the sugarcane industry. We also examine the runoff and the relative toxicities of the new/alternative herbicides in comparison to the existing herbicides used in the sugarcane industry. This project broadly aligns with all five of the Reef Rescue research priorities but is specifically aligned to both the *“land management practices that improve water quality outcomes in the sugarcane, grazing, horticulture and dairy sectors”* and *“the impact of pesticides on water quality in the GBR”* key priorities.

Project Objectives

- (1) Quantify the water quality benefits of improved herbicide application management practices in the sugarcane industry
- (2) Examine the relative run-off water quality benefits (if any) of the emerging/alternative herbicides available to the sugarcane industry compared to traditionally used PSII herbicides.

Methods

Rainfall simulation trials

A series of rainfall simulation trials across the Burdekin and Mackay Whitsunday regions (Table 1) were undertaken to directly compare the runoff behaviour of the new/alternative herbicides (fluroxypyr, imazapic, isoxaflutole, metribuzin, metolachlor, pendimethalin) with the herbicides that are widely used in the sugarcane industry (diuron, atrazine, hexazinone, ametryn, 2,4-D, glyphosate). Further, the work was designed to establish a relationship between the area of herbicide application on the paddock and the herbicide lost from the paddock. For example, the WeedSeeker® technology can reduce herbicide application to a

paddock by up to 80% (Reef Rescue case study document: WeedSeeker® <http://reefcatchments.com.au/files/2013/02/WeedSeekerSm1.pdf>) while the banded/shielded spraying reduces the amount of ‘residual herbicides’ applied (i.e. atrazine, diuron) by 50% to 60% (Masters et al., 2013; Oliver et al., 2014).

Table 1. Summary site farming system and soil type characteristics of RR R&D Rainfall simulation sites. (Rainfall simulation sites herbicide runoff was compared in collaboration with Sugar Research Australia and NCEA-USQ).

District	Year	Surface condition	Soil classification	Texture 0-10cm
Burdekin	2012	Bare, plant cane	Vertosol	clay loam
Mackay	2012	Bare, plant cane	Soloth	sandy clay loam

Both Mackay and Burdekin trials were conducted soon after planting and had no cane trash cover. Rainfall was applied for 40 minutes at approximately 70 mm.hr⁻¹ in the Burdekin trial; this rate constitutes roughly a 1 in 10 year event in the lower Burdekin region. Rainfall was applied for 80 minutes at approximately 80 mm.hr⁻¹ in the Mackay trial because the sandier soil had higher infiltration rates; this rate constitutes roughly a 1 in 5 year event in the Mackay Whitsunday region. Runoff volume was measured every few minutes, water samples were taken for sediment concentration and a composite water sample was taken for herbicide analysis in clean 1 L amber glass bottles.

To apply spot spray application treatments, a grid was laid in the furrow or paddock inter-row and the squares were sprayed (see Figure 1) with three different herbicide formulations, which were designed around their specific mode of action (to minimise impacts on soil microbial communities) and usage in the sugarcane industry (i.e. as knockdown/contact herbicides or as residual herbicides). These formulations included “SRDC mix” of glyphosate, fluroxypyr and 2,4-D; “DERM 1 mix” of atrazine, ametryn, diuron, isoxaflutole and metribuzin; and “DERM 2 mix” of atrazine, ametryn, metolachlor, imazapic and pendimethalin (for a list of products and spray rates used in the study see Table 2). The areas sprayed with the different herbicide formulations were 20%, 50%, 70% and 100% and each grid was done in duplicate or triplicate (Figure 1). Two days following the spraying, the simulated rainfall was applied to each plot (Figure 1) and the runoff was sampled from each furrow as a ‘flow weighted’ (i.e. the volume of water sampled was proportional to the volume of runoff from the paddock at each sampled time point) composite sample for analysis of water and sediment concentrations. We note that the 2 days following spraying likely represents a “worse-case” scenario where herbicide concentrations in runoff will be the highest. However, the results from this scenario also allow us to model the likely runoff concentrations following a longer period after spraying by using the soil half-life data reported in Shaw et al. (2013).

Sediment and water in runoff samples were separated and analysed for herbicides separately. Briefly, the total water samples were filtered through a 0.45 µm glass fibre filter to separate the fraction of herbicides 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. This allowed sediment:water partition coefficients to be calculated, and so determine whether the herbicides were running off paddocks in dissolved form or bound to particulate matter.



Figure 1. Rainfall simulation trials were carried out in the Burdekin and Mackay Whitsunday regions to examine the runoff of the key and emerging products used in the sugarcane industry.

The samples were analysed at the ACS laboratories Australia, Kensington, Victoria. Glyphosate and metabolite (or degradation product) AMPA were analysed using LC MSMS, method number ACS-AM-TM-029; fluroxypyr and 2,4-D were analysed using LC MSMS, method number ACS-AM-TM-201.1 (for 'acid herbicides') and; diuron (and metabolites DCPU and DCPMU), atrazine (and metabolites desethyl atrazine and desisopropyl atrazine), ametryn, isoxaflutole, metribuzin, metolachlor, imazapic and pendimethalin using LC MSMS, method number ACS-AM-TM-201 (for non-acid herbicides).

Table 2. Pesticide products applied in rainfall simulation trials for 100% application treatments. Selected physical chemical properties are provided.

Active Ingredient	Product Name (A.I. g/kg or g/L)	Application Rate (L/ha) (g.a.i./ha)		$T_{1/2}$ Soil ^a (days)	Koc ^{a,b} (ml/g)
Diuron	Diurex (900)	1.5/0.5 ^c	1350/450 ^c	39 ^b	1067
Atrazine	Gesapax Combi (250)	8	2000	29	100
Ametryn	Gesapax Combi (250)	8	2000	37	316
Metribuzin	Soccor (750)	2	1500	19	38
S-metolachlor	Dual Gold (960)	1.8	1728	21	226.1 ^d
Pendimethalin	Stomp Xtra (455)	3.3	1500	90	15744
Imazapic	Flame (240)	0.4	96	232	137
Isoxaflutole	Balance (750)	0.2	150	14	145
Fluroxypyr	Comet (400)	0.65	260	51	68
Glyphosate	Roundup Attack (570)	4.7	2680	12	21699
2,4-D	Amicide Advance (700)	3.1	2170	10	88.4

^a Pesticides Properties Database (PPDB), University of Hertfordshire.

^b Soil organic carbon partitioning factor (linear).

^c Mackay/Burdekin application rates

^d Freundlich Koc, rather than linear

Banded/shielded spraying furrow irrigation trial

A furrow irrigation trial was completed in the Burdekin Region to evaluate the effectiveness of the banded/shielded spraying technology in reducing runoff loads of herbicides from cane paddocks. Banded spraying restricts the application of the more mobile or environmentally problematic herbicides, (such as atrazine and diuron) only to the raised beds of the paddock (banded application), and replace their application in furrows with alternative herbicides that have relatively shorter half-lives and/or are less soluble in water. The outcomes of this work have been published in *Science of the Total Environment* and for further details of this work the reader is referred to that publication (Oliver et al., 2014). Briefly, the experiment was conducted on a commercial sugarcane farm in the Mulgrave district of the Burdekin-Haughton Water Supply Scheme region near Clare. Water for irrigation was supplied from the Burdekin Falls Dam and this grower recycled his irrigation water by capturing drainage water from irrigation in on-farm storage pits. At this site the soil texture was clay loam throughout the profile and the site had been laser levelled prior to the raised bed formation. The treatments were a conventional broadcast application of herbicides across the beds and furrows from boom sprayers (Conventional) and a banded application using a shielded sprayer (Banded) where certain herbicides (2,4-D and glyphosate) were applied to furrows only and other herbicides (diuron, atrazine, 2,4-D and paraquat) to raised beds only. The herbicides studied were chosen because they are commonly used in sugarcane production in the Burdekin region. Two herbicide treatments were applied in duplicate on November 24, 2012 to designated blocks. In this study, each block consisted of 6 furrows and 6 raised beds (910 m long x 9.12 m wide), giving a total treatment area of 0.83 ha. The shields were 900 mm wide and the over top sprays were 620 mm wide. Photos of the field application are shown in Figure. 2.



Figure 2. The banded/shielded sprayer in action. Atrazine, diuron, paraquat and 2,4-D were applied on the raised beds and glyphosate and 2,4-D were applied in the inter-rows/furrows. Flows off the paddock were measured in V-notch weirs or the time it took to fill a 20 L bucket.

Usually water is applied to the paddock 2-3 days post-herbicide application for approximately 12 hours with excess water running off the end of the field into drains and from there into nearby creeks and rivers. On-farm storage pits to collect runoff are common in the region (including this study's farm), but the proportion of runoff that can be stored varies with pit size (Thorburn et al., 2011). The bays (i.e. a collection of six rows and six

furrows) were irrigated simultaneously commencing on the evening of November 26, 2012 and water flowed out of the furrows on November 27, 2012. Each end of the drainage channel for each bay was blocked off so the water draining from each bay was isolated and constrained to flow out through a pipe (Figure 2). Water samples were collected as soon as flow started (Time 0), then at the following time intervals: 0.5, 1, 2, 4, 6, 8, 10 and 12 hours thereafter.

Water flow was monitored from bays 1 and 3 using a pre-calibrated V-notch weir crate designed to cope with low flow discharges (Figure 2). The depth of water in the crate was regularly recorded by reading the water level height and this was related to flow rate from a previously determined discharge rating curve. In the other two bays water flow was monitored manually by timing how long it took to fill a 20 L bucket at various times throughout the flow event. This technique was also used in bays 1 and 3 and allowed comparison between the data from the V-notch weir crates with that from the bucket technique. Generally good agreement was obtained between the two methods of measuring flow. Water samples were collected in pre-cleaned Nalgene bottles and stored on ice until transported to the laboratory the following day. Samples were then stored at 4°C until they were partially processed in a nearby laboratory by loading onto solid phase extraction (SPE) cartridges. The cartridges were then transported to the analytical laboratory (CSIRO, Adelaide) for extraction and herbicide analysis. In addition, three blank samples (50 mL high purity Milli-Q water) were spiked individually with a known concentration of each herbicide (50 $\mu\text{L} \times 200 \text{ mg L}^{-1}$ stock solution) and taken to the field to check on any herbicide losses during storage and transport to the laboratory. Irrigation water was collected just before it was applied to the field and analysed for herbicide residues and to ensure there was no phosphorus present that could interfere with glyphosate analyses on LC-ICP-MS (all samples were below detection for herbicides apart from 2,4-D which was detected at 16 $\mu\text{g.L}^{-1}$). The spiked samples were treated in an identical manner to the field samples. The SPE cartridges were then transported to the analytical laboratory on ice bricks and eluted using solvent followed by herbicide analysis. The samples for glyphosate and AMPA analysis (100 μL) were injected onto an Agilent 7700 ICP-MS connected to an Agilent 1260 Infinity HPLC tuned to detect mass 31 (P) using Helium as the collision gas. The samples for all other herbicide analysis (20 μL) were injected onto the Agilent 1100 LC. The column was an Alltech Altima C 18 (250 mm x 4.6 mm).

Amounts (μg) of pesticides leaving each irrigation bay for the designated time interval were determined by multiplying concentrations ($\mu\text{g L}^{-1}$) by the total volume (L) of water leaving the irrigation bay during that time interval. The total volume of runoff water leaving the field for a designated time increment was determined by calculating the area under the hydrograph. Since there were only two replicates for each treatment the data were firstly assessed for equality of variances between the two treatments and then statistical differences between the two groups were determined using the appropriate t-test in Excel i.e. assuming equal or non-equal variances.

New/alternative products

The emerging herbicide products available to the sugarcane industry were assessed via two methods. Firstly their runoff physicochemical properties were examined using the rainfall simulation trials (as described above) providing information on the amount and rate of

active ingredient applied, the percent of active ingredient that was lost in surface runoff, the event mean concentration (dissolved phase only) of the runoff following the first ‘event’ after application and their partitioning between dissolved and particulate phases in surface runoff. The inclusion of these emerging products in the rainfall simulation trials also allowed direct comparison to the ‘established herbicides’ used in the sugarcane industry applied at typical label application rates (see Table 2). Runoff dissolved EMC data generated in both the Mackay Whitsunday and Burdekin rainfall simulation trials was combined with a relative toxicity measure to compare the risk of off-site transport of these herbicides. In order for the results from the two rainfall simulation trials to be directly comparable, we up-scaled the diuron EMC ($80 \mu\text{g.L}^{-1}$) by a factor of three (i.e. new value = $240 \mu\text{g.L}^{-1}$) for the Burdekin trial in proportion to the higher application rates in the Mackay Whitsunday region (see Table 2).

The relative toxicity measure applied in this study (h-HEq) was developed using EC_{50} data for population growth and abundance endpoints over chronic exposure times (>72 hrs). Data were collated from the Pesticide Ecotoxicity Database (PED), which includes all EPA-reviewed ecotoxicity endpoints for pesticides registered in the U.S.A.¹. Tests included in the PED were conducted according to U.S. data requirements for pesticide registration (FIRFA 158.540) either Tier I Aquatic Plant Growth-single dose or Tier II Aquatic Plant Growth-multi dose. Equivalency factors were calculated for aquatic plant species only, since all products included in the current study are herbicides. These included duckweed, freshwater and marine algae, and marine diatoms. An equivalency factor could be determined where an effect concentration had been measured under comparable test conditions for the test herbicide and the reference herbicide, diuron. Comparable test conditions were assumed if: a) the same species (or genus in the case of *Chlorella*) was tested; b) test exposure times were >72 hrs and ± 24 hrs; and, c) the dosage regime (either multiple or single) was consistent. The median value of all valid equivalency factors was taken. Where appropriate, additional data points were sourced from studies in the literature, which provided a direct comparison of diuron and a test herbicide. These toxicity studies were first assessed according to quality criteria specified in the ANZECC² water quality guidelines. The herbicide equivalent concentrations are formally calculated using the following functional expression³:

$$HEq = \sum_{i=1}^n C_{iW} REP \quad (1)$$

where,

HEq = herbicide equivalent concentrations;

C_{iW} = the time averaged concentration of each individual PSII herbicide; and,

REP = the relative potency of the herbicide with respect to the reference herbicide diuron.

The application of these toxic equivalency values assumes that the combined effect of these herbicides in a mixture is concentration additive. Further, it should be noted that the

¹ United States Department of Agriculture (USDA) (2011).

² ANZECC (2000).

³ See Kennedy et al. (2012:1).

application of this approach assumes that the dose-response pattern for each of the herbicides follows the same trend, meaning that the dose-response curves should be parallel. The PSII herbicides have a common mode of action and the success of predicting mixture toxicity based on a TEQ approach has been demonstrated in several studies⁴. However, these assumptions have not been tested for the remaining herbicides included in the h-HEq. As these herbicides follow different modes of action (see Table 5), it is less likely that a simple concentration addition model will explain the mixture toxicity. However, concentration addition has been found to be a conservative measure in absence of information on the interactions between different modes of action with relatively small likelihood of underestimating effects⁵. Therefore, this measure represents the best currently available assessment. There is a need for future research to investigate mixture toxicity of herbicides relevant to the GBR on locally important species.

Results

Rainfall simulation trials

The Burdekin rainfall simulation plots gave moderate runoff amounts, averaging ~20 mm or 33% of 60 mm of applied rainfall. Average time to start of runoff was 26 minutes and infiltration before runoff start was 33 mm. In contrast, the sandier Mackay soil gave only ~8 mm of runoff (7% of 107 mm of rainfall), took 51 minutes to runoff and had 70 mm of infiltration before runoff. Thus the Mackay results are for a low runoff situation where more leaching of the less sorbed pesticides from the soil surface occurred before runoff began and lower runoff losses of pesticides are expected. For comparison, Silburn et al. (2013a) had 30 mm of runoff from 46 mm of rain (64%) on a Vertosol with a moist and crusted surface.

The rainfall simulation trials showed that the majority of the herbicides ran off the paddock in the dissolved phase with the exceptions of pendimethalin and to a lesser extent imazapic in the Burdekin study (Figure 3). These results are consistent with those of Packett (2013). Importantly, the results show that the application of less herbicide on the paddock typically translated to a proportional reduction in the runoff losses of herbicides from the paddock (see r^2 and p values in Table 3 related to Figure 3). Similar trends were found in the Mackay study although overall runoff losses were lower (data not shown). This is consistent with previous trials on banded versus blanket applications (Masters et al. 2013, Silburn et al. 2013a) and spot spray treatments (Silburn et al. 2013b). The event mean concentrations (EMC) of the herbicides with 100% application matched or were generally higher than previous paddock-scale studies in the GBR catchment area (e.g. Davis et al., 2013; Masters et al., 2013).

⁴ Bengtson-Nash, McMahon, Eaglesham & Müller (2005). Application of a novel phytotoxicity assay for the detection of herbicides in Hervey Bay and the Great Sandy Straits. *Marine Pollution Bulletin* 51, 351–360.

⁵ Belden, Gillion & Lydy (2007).

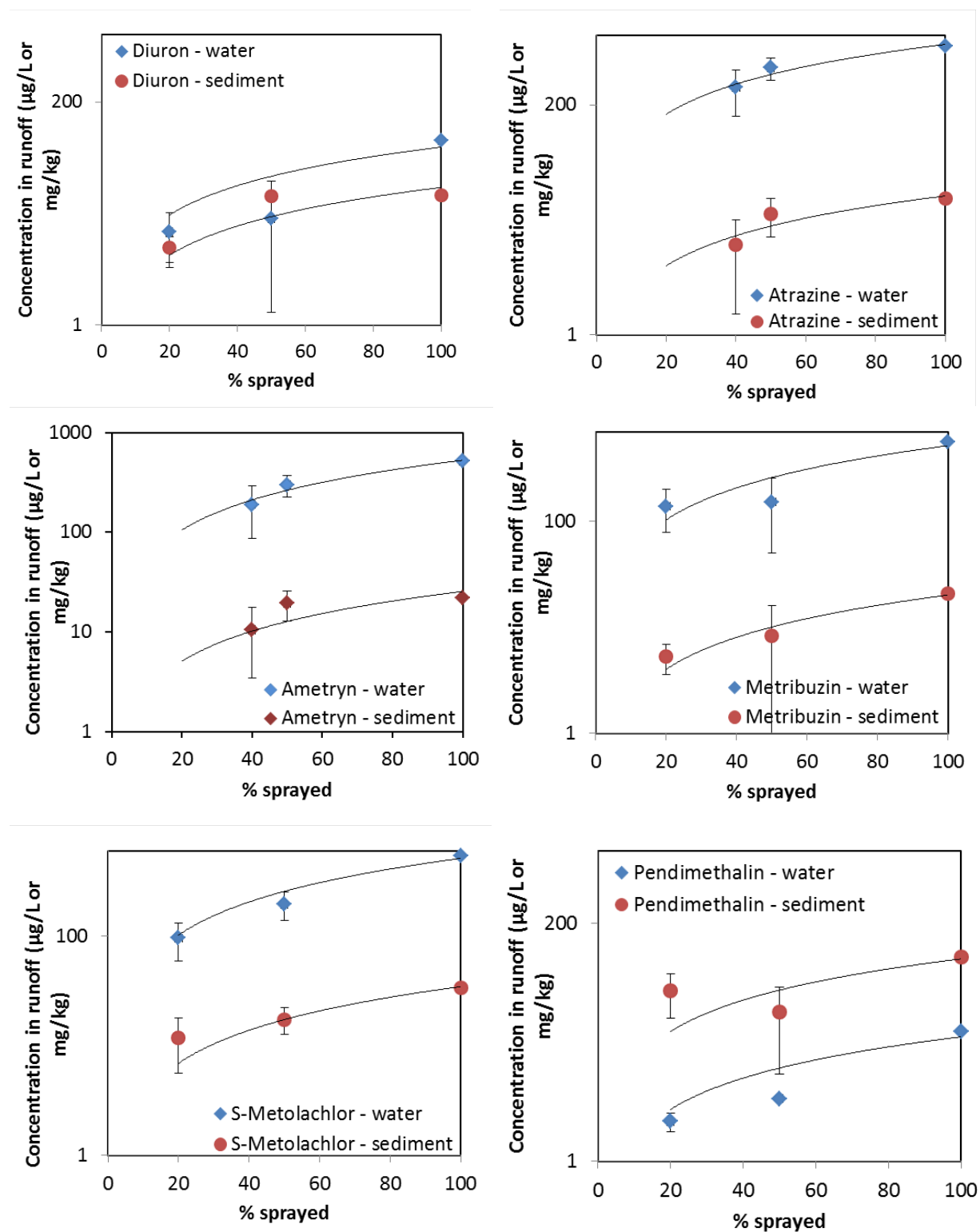


Figure 3. Spot spray trials of the established and emerging (and one metabolite of atrazine) herbicides used in the sugarcane industry with runoff either dissolved in water or attached to sediment (Burdekin 2012 trial).

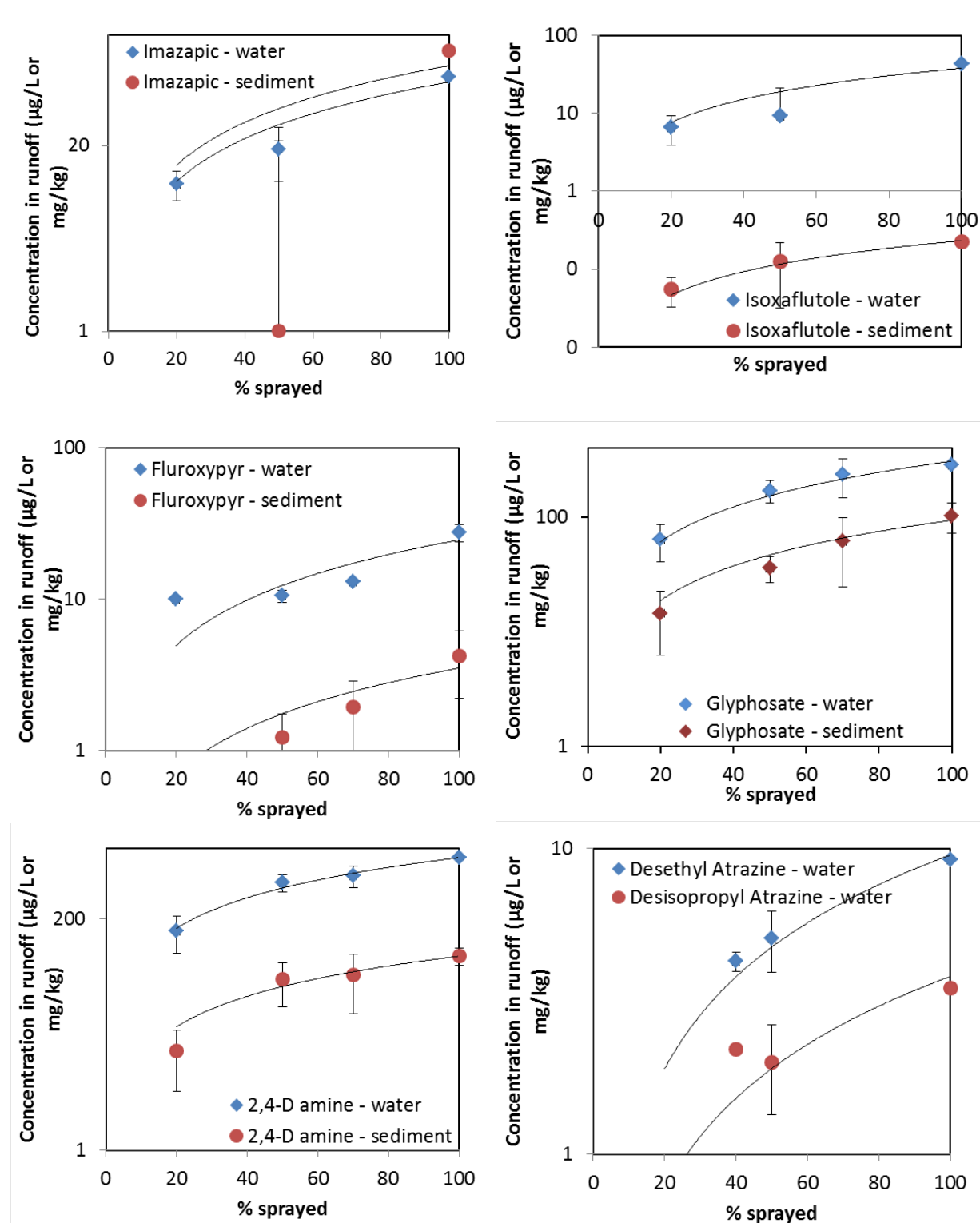


Figure 3 (cont.). Spot spray trials of the established and emerging (and one metabolite of atrazine) herbicides used in the sugarcane industry with runoff either dissolved in water or attached to sediment (Burdekin 2012 trial).

Table 3. Regression analysis results for the loss of herbicides in runoff relative to the percent of the field to which herbicides were applied.

<i>Active Ingredient</i>	<i>Water / sediment bound fraction</i>	<i>R²</i>	<i>p-value</i>
Diuron	Water	0.9422	3.14E-06
	Sediment	0.6321	5.97E-03
Atrazine	Water	0.8509	9.87E-07
	Sediment	0.6232	4.65E-04
Ametryn	Water	0.8567	7.59E-07
	Sediment	0.4636	0.0052
Metribuzin	Water	0.923	9.93E-06
	Sediment	0.756	1.08E-03
S-metolachlor	Water	0.9197	1.18E-05
	Sediment	0.5974	8.75E-03
Pendimethalin	Water	0.9944	2.77E-10
	Sediment	0.7244	1.78E-03
Imazapic	Water	0.9452	2.52E-06
	Sediment	0.8263	2.68E-04
Isoxaflutole	Water	0.9510	1.61E-06
	Sediment	0.5379	0.0158
Fluroxypyr	Water	0.7626	9.67E-05
	Sediment	0.7320	1.91E-04
Glyphosate	Water	0.9619	3.72E-09
	Sediment	0.7972	3.99E-05
2,4-D	Water	0.9764	2.66E-10
	Sediment	0.7383	1.7E-04

Another way of evaluating the runoff of herbicides from paddocks is to examine the ratio of the EMC to the amount applied. Our results from both the Burdekin and Mackay Whitsunday (2012) trials show that less of the 'knockdown' herbicides (glyphosate, fluroxypyr) were lost from the paddock compared to the 'old' PSII inhibitors (diuron, atrazine, ametryn) and the new/alternative herbicides (isoxaflutole, metribuzin, metolachlor) which displayed similar loss rates from the paddock (Figures 4 and 5). The loss of pendimethalin was comparable to the 'knockdown' herbicides, while the 'knockdown' 2,4-D was lost at comparable rates to the PSII inhibitors and most of the new/alternative herbicides. Runoff losses of imazapic were higher in both studies than all other herbicides; given there are little data on imazapic runoff this requires further investigation.

However, because some of the emerging products (isoxaflutole and imazapic) and the newer 'knockdown' fluroxypyr are applied at much reduced rates than older products (Table 2), the actual dissolved runoff losses are also lower (Table 4). In contrast, s-metolachlor and metribuzin, while seen as emerging in the cane industry, are applied at similar rates and ran off at similar concentrations to the older PSII herbicides. Pendimethalin and glyphosate have lower dissolved runoff concentrations due to their higher partitioning coefficient (Table 2).

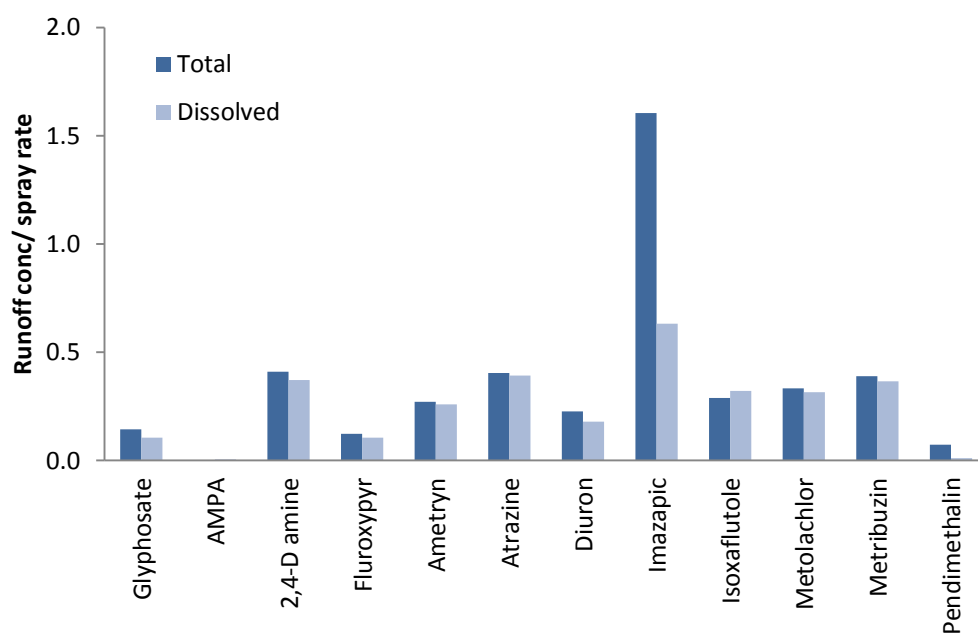


Figure 4. Rainfall simulation 2012 trials in the Burdekin Region suggest that the new/alternative herbicides generally runoff the same as the PSII herbicides in current widespread use with the exception of pendimethalin, which had much lower loss rates.

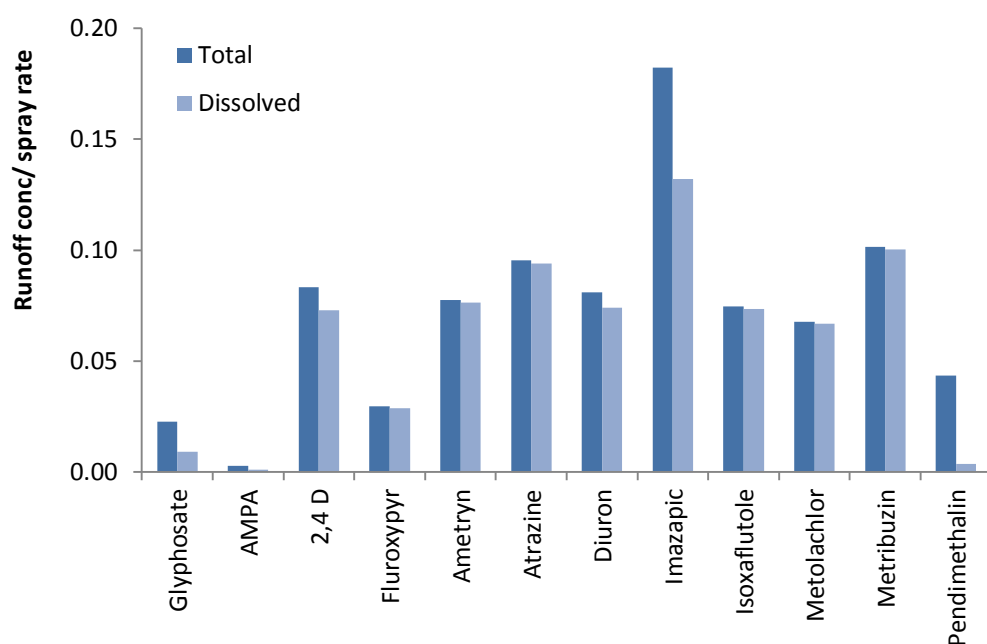


Figure 5. Results from the rainfall simulation 2012 trials in the Mackay Whitsunday Region. The left bar for each herbicide represents the runoff concentration to spray rate ratio of the total sample while the right bar represents the ratio of the filtered (i.e. dissolved herbicide) sample.

Herbicide relative risk to the Great Barrier Reef

We were able to use the differences in the mean EMCs (relative to diuron) and the predicted toxicities (relative to diuron) to produce an overall risk of these herbicides to the GBR. For example, a particular herbicide that is 10 times less toxic than diuron but runs off the paddock twice as much as diuron would be rated as an overall risk of 0.2 (~5 times less of a risk than diuron). Our analysis shows that of the main herbicides used in the sugarcane industry, ametryn has the highest risk, which is 1.4 and 2.2 times greater than diuron based on the rainfall simulation trials in the Mackay Whitsunday and Burdekin regions, respectively (Table 4). In all cases, the herbicides in the Burdekin trial presented a much higher (approximately 2-fold higher) relative risk than the Mackay Whitsunday trial, although all of the herbicides examined, with the exception of ametryn, had a lower relative risk than diuron in both trials (Table 4).

Table 4. Mean EMC (dissolved phase) measured in rainfall simulation studies (at 2 days after application) combined with the relative toxicity score (see Table 5) to provide an assessment of the relative risk of offsite transport for commonly applied herbicides in the sugarcane industry. N/A – Event mean concentrations not available

<i>Herbicide</i>	<i>Predicted GBR relative toxicity</i>	<i>Mean EMC (dissolved phase detected in paddock runoff (100% applied)) Mackay Whitsunday</i>	<i>Risk relative to diuron based on predicted toxicity and runoff potential Mackay Whitsunday</i>	<i>Mean EMC (dissolved phase detected in paddock runoff (100% applied)) Burdekin</i>	<i>Risk relative to diuron based on predicted toxicity and runoff potential Burdekin</i>
Atrazine	0.15	162	0.243	783	0.489
Diuron	1.0	100	1.0	240*	1.0
Ametryn	1.0	137	1.37	518	2.158
Metribuzin	0.12	151	0.181	563	0.282
S-Metolachlor	0.3	116	0.348	543	0.679
Pendimethalin	0.006	6	<0.001	18	<0.001
Isoxaflutole	1.3	11	0.143	43	0.233
Imazapic	1.6	13	0.208	61	0.407
Glyphosate	0.001	25	<0.001	284	0.001
2,4-D	0.011	158	0.017	805	0.037
Fluroxypyr**	0.004	8	<0.001	28	<0.001
Hexazinone***	0.35	181	0.634	N/A	N/A
Paraquat****	0.002	N/A	N/A	0.1	<0.001
Propazine	0.02****	N/A	N/A	N/A	N/A
Trifloxysulfuron sodium	33****	N/A	N/A	N/A	N/A
Asulam	0.07****	N/A	N/A	N/A	N/A

*EMC has been up-scaled to reflect difference in application between the Mackay Whitsunday and Burdekin trials (see text)

**Only two replicates and concentrations in one of the samples below limit of reporting (LOR). Assumption of 0.5xLOR was applied in calculating the mean.

***Data from a comparable rainfall simulation trial (Masters et al., 2013).

****Indicative relative toxicity only. Values derived using EC50 data for plants reported in the PPDB and may not refer to the same species or have been derived under comparable test conditions.

*****Despite several field trials in the Burdekin, paraquat has always been below detection limits (0.1 µg.L⁻¹).

Table 5. Relative potencies for herbicides based on EC₅₀ values for population growth or abundance endpoints (h-REP) with respect to the reference herbicide diuron (REP=1).

<i>Active Ingredient</i>	<i>h-REP (Median)</i>	<i>h-REP (n)</i>	<i>h-REP (Range)</i>	<i>Mode of Action^b</i>
Diuron	1	-	-	Inhibitor of photosynthesis at PSII
Hexazinone	0.35	5	0.29-2.9	Inhibitor of photosynthesis at PSII
Atrazine	0.15	22	0.00062-0.86	Inhibitor of photosynthesis at PSII
Ametryn	1.0	21	0.059-1.7	Inhibitor of photosynthesis at PSII
Metribuzin	0.12	3	0.081-0.29	Inhibitor of photosynthesis at PSII
S-metolachlor	0.30	3	0.026-0.62	Inhibitor of cell division
Pendimethalin	0.0059	5	0.0032-0.015	Inhibitors of microtubule assembly
Imazapic as ammonium salt ^c	1.6	2	0.046-3.1	Inhibits the production of amino acids necessary for cell division and growth
Isoxaflutole	1.3	2	0.017-2.7	Acts by indirect carotenoid biosynthesis inhibition
Haloxypyr-R-methyl ester	0.00039	5	0.00016-0.00065	ACCase inhibitor
Imazethapyr	0.80	2	0.000041-1.6	Acetolactate synthase (ALS) inhibitor
Fluroxypyr as metpyl ester	0.0036	4	0.0015-0.0093	Synthetic auxin
Acifluorfen as sodium salt ^c	0.022	2	0.009-0.035	Cell membrane disruption - PPO inhibitor
Glyphosate as ipa	0.00052	3	0.0002-0.0011	Inhibition of lycopene cyclase.
Paraquat dichloride	0.0015	6	0.0002-0.13	Photosystem I inhibitor
2,4-D amine	0.011	2	0.000047-0.022	Synthetic auxin

^a Kennedy et al. (2012).^b Pesticides Properties Database (PPDB), University of Hertfordshire.^c Due to a lack of data meeting the established criteria, data of lower quality were accepted for these comparisons.

As the rainfall simulation trial was performed 2 days after herbicide application, it represents a 'worse-case scenario' for herbicides lost from paddocks, although we note that such scenarios can occur in practice (i.e. it is common for growers in the Burdekin region to irrigate within 2 to 4 days after herbicide application). To estimate runoff losses for a storm at longer times after application we used the mean soil half-life data generated by Shaw et al. (2013) to predict the EMC in runoff. This assumes runoff losses decrease in proportion to how much soil degradation of the herbicide would have been expected to occur over a 30 day (i.e. 1 month) period. This approach is based on a well-known relationship between the pesticide concentration in soil and surface runoff (see Leonard et al., 1979; Leonard, 1990; Silburn and Kennedy 2007) and allows a range in our relative risk outputs to be generated from two days after application to 30 days after application. This approach leads to lower runoff EMC's for compounds which have shorter half-lives.

When we apply this new 30 day scenario, all herbicides in the Mackay Whitsunday region (including ametryn) have a lower relative risk than diuron and all herbicides examined, with the exception of paraquat, have a reduced relative risk compared to diuron (Table 6) at the two day scenario (Table 4). This is because diuron has a longer half-life (72 days) than the other herbicides examined in this study (with the exception of paraquat which has a half-life of 339 days). The relative risk of herbicides for the 30 day scenario in the Burdekin region is

also reduced, although ametryn continued to have a higher relative risk than diuron (Table 6).

Table 6. Predicted EMCs (dissolved phase) and relative risk if rainfall occurred 30 days after application based on the mean soil half-life data reported in Shaw et al. (2013).

<i>Herbicide</i>	<i>Predicted GBR relative toxicity</i>	<i>Mean EMC (dissolved phase detected in paddock runoff (100% applied)) Mackay Whitsunday</i>	<i>Risk relative to diuron based on predicted toxicity and runoff potential Mackay Whitsunday</i>	<i>Mean EMC (dissolved phase detected in paddock runoff (100% applied)) Burdekin</i>	<i>Risk relative to diuron based on predicted toxicity and runoff potential Burdekin</i>
Atrazine	0.15	59	0.125	283	0.251
Diuron	1.0	71	1.0	169	1.0
Ametryn	1.0	62	0.882	235	1.390
Metribuzin	0.12	59	0.100	218	0.155
S-Metolachlor	0.3	57	0.242	267	0.473
Pendimethalin	0.006	3	<0.001	10	<0.001
Isoxaflutole	1.3	4	0.076	16	0.124
Imazapic	1.6	7	0.163	34	0.318
Glyphosate	0.001	11	0.000	129	0.001
2,4-D	0.011	59	0.009	302	0.020
Fluroxypyr*	0.004	3	<0.001	9	<0.001
Hexazinone	0.35	114	0.565	N/A	N/A
Paraquat	0.002	N/A	N/A	0.1	<0.001

*Fluroxypyr based on field half-life in the Burdekin (14.1 days: Shaw et al. 2013)

Banded/shielded spraying furrow irrigation trial

Full results of this work can be found in Oliver et al. (2014). In summary, the total volume of water leaving each irrigation bay ranged from 123 to 155 kL, which equated to 148 to 187 kL.ha⁻¹ or 15 to 19 mm. The measurement of flow using the calibrated V-notch weir crates and the manual bucket measurements agreed quite well for the two bays (Bays 1 and 3) when both techniques were used (Figure 6). This good agreement gave confidence in the flow data generated for Bays 2 and 4 where the manual bucket measurements were used.

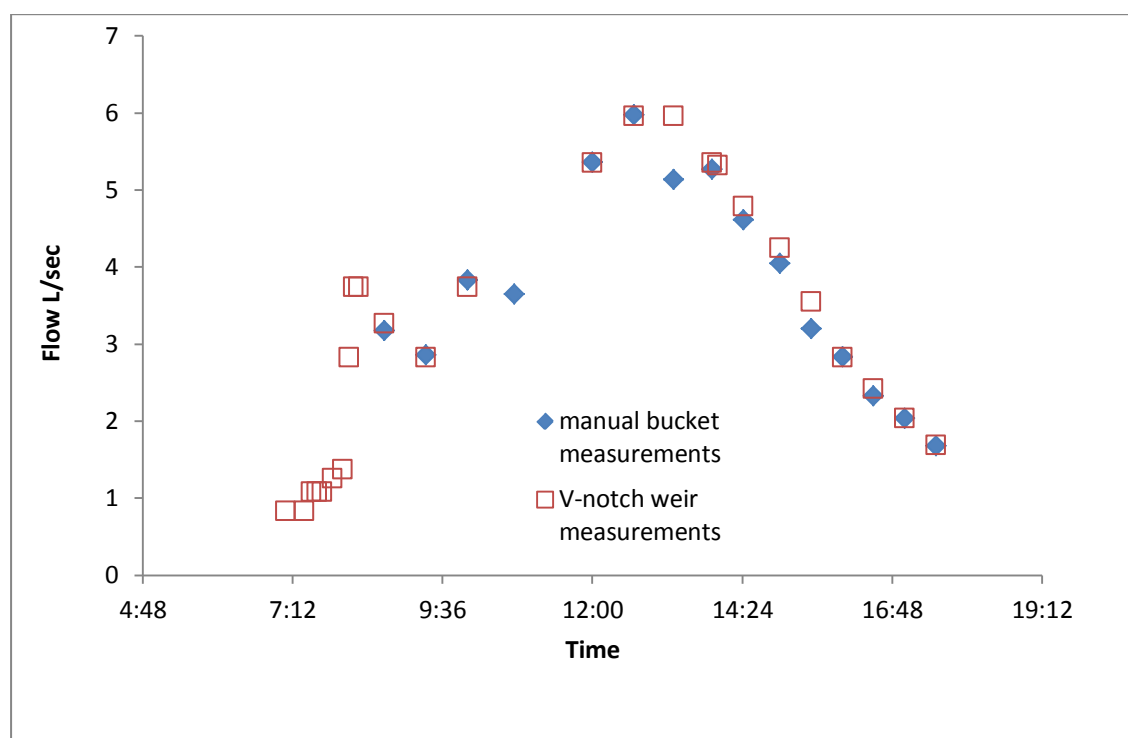


Figure 6. Example of the flow data from Bay 1 derived from the V-notch weir crate that had been calibrated prior to the field experiment and from the manual measurements made using volumes of water collected in the bucket at designated times throughout the irrigation event.

The concentrations of atrazine, diuron and 2,4-D in water were highest in the first 2-3 samples but generally decreased exponentially over time. A similar result was found by Masters et al. (2013) with rainfall simulation studies in sugarcane fields. The range of concentrations in water from the Conventional bays in this study was 0.02 – 1.31 mg L⁻¹ for atrazine, 0.07 – 0.60 mg L⁻¹ for diuron and 0.10 – 1.59 mg L⁻¹ for 2,4-D with mean concentrations for the irrigation event being 0.52 mg L⁻¹, 0.31 mg L⁻¹ and 0.50 mg L⁻¹ for atrazine, diuron and 2,4-D, respectively. In comparison, the range of concentrations in water from the banded sprayed bays were 0.01 – 0.12 mg L⁻¹ for atrazine, <0.01 – 0.06 mg L⁻¹ for diuron and 0.10 – 0.60 mg L⁻¹ for 2,4-D with mean concentrations for the irrigation event being 0.04 mg L⁻¹, 0.02 mg L⁻¹ and 0.35 mg L⁻¹ for atrazine, diuron and 2,4-D, respectively (Figure 7A, 7B and 7C). The concentrations of atrazine and diuron (Figure 7A and 7B) were statistically ($P < 0.001$) greater in water samples from Conventional bays than from Banded bays, but there was no significant difference between treatments in the concentrations of 2,4-D in water (Figure 7C), which reflects that there was little difference in the amount of 2,4-D applied in both treatments.

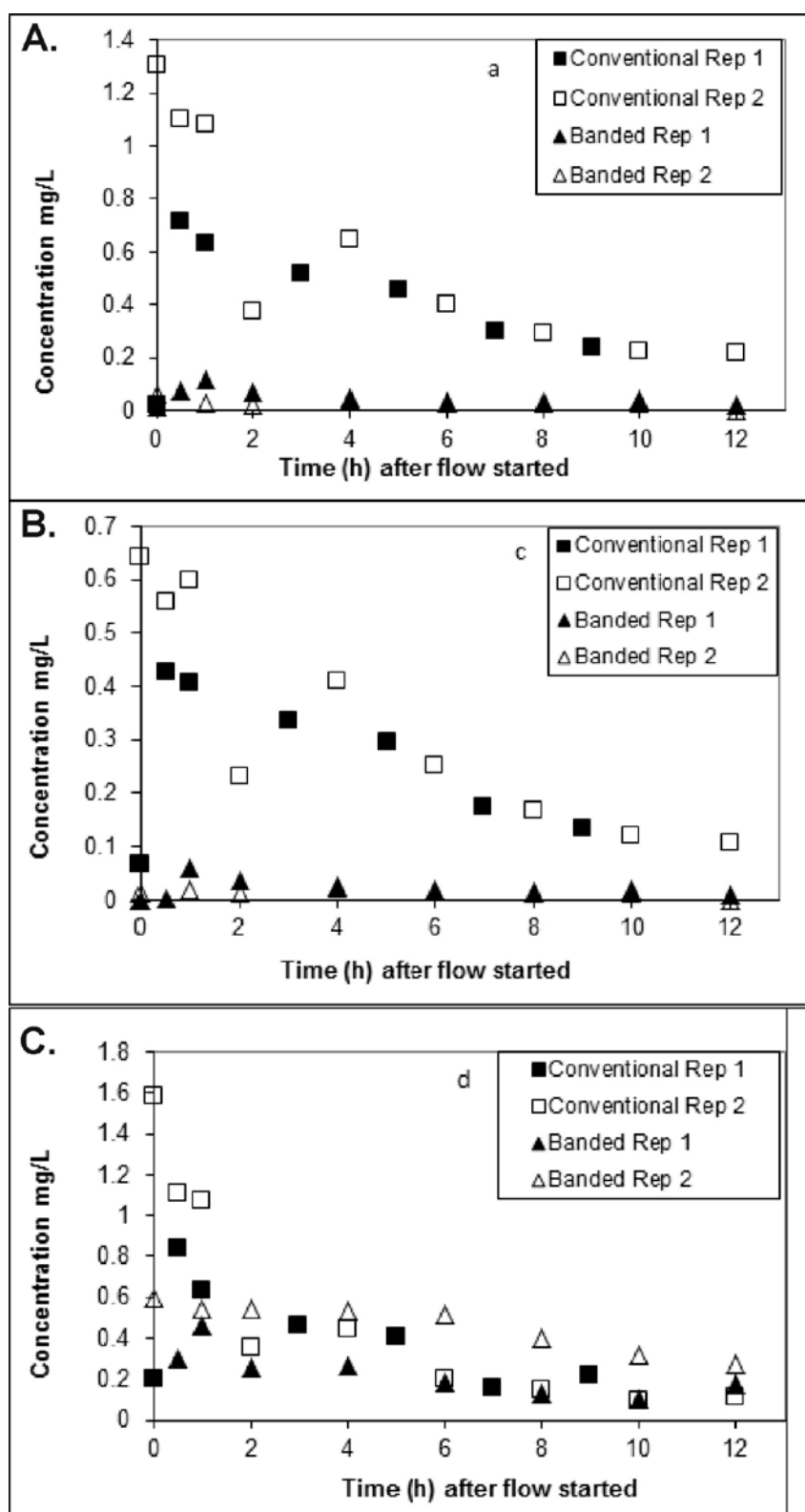


Figure 7. Concentrations of atrazine (A), diuron (B) and 2,4-D (C) in the trial. For atrazine and diuron there was a significant difference in the concentrations between the conventional (broadcast) application and the banded/shielded sprayer while 2,4-D displayed no significant difference.

There was a 90% and 92% decrease in the average load of atrazine and diuron, respectively, moving off-site in water from Banded bays compared with Conventional bays. However,

atrazine and diuron were applied only to raised beds in the Banded bays with glyphosate and 2,4-D applied to the furrows, while in the Conventional bays the herbicide treatments were applied across the whole area. Thus, less atrazine and diuron were applied to the total area of the Banded bays compared with the Conventional bays. For both diuron and atrazine 747 g (900 g ha⁻¹) was applied to the Conventional bays compared with 306 g (370 g ha⁻¹) to the Banded bays (hence 60% less atrazine and diuron applied). When the differences in amount applied to the two treatments were taken into account, there was still a significant ($P < 0.001$) decrease in the amount of atrazine and diuron moving off-site from Banded bays. The average amount of atrazine moving off-site as a fraction of the amount applied in this experiment was 7.5% from the Conventional bays compared with 1.8% from Banded bays. Including the load of the atrazine metabolites moving in runoff water had a marginal effect on the total load deriving from the original parent compound in drainage water from the Conventional bays where 58.9 g (7.9%) of total atrazine and metabolites was lost in surface drainage water under this treatment.

Similarly, the average amount of diuron moving off-site as a fraction of the amount applied in this experiment was 4.6% from the Conventional bays compared with 0.9% from the Banded bays. These results indicate that applying atrazine and diuron to the raised beds only (Banded bays), rather than applying across the whole field (Conventional), significantly ($P < 0.001$) decreased the load of atrazine and diuron moving off-site. This result is due to the delay in water “wetting up” the raised beds resulting in a lack of or a decrease in contact between the herbicide on the raised bed and the irrigation water draining from the irrigated field through the furrows. Ultimately this resulted in a decrease in the herbicides moving off-site in discharging irrigation water from the Banded bays.

Discussion

The finding that the runoff from the paddock was roughly in proportion to the area sprayed (Figure 3) was expected and this clearly demonstrates that reductions in the use of certain herbicides through WeedSeeker® or similar technology which can reduce the amount of herbicide applied by up to 80% (Figure 8). The use of banded/shielded sprayers also reduces residual herbicide (e.g. atrazine, diuron, hexazinone, ametryn and other emerging products) application by 50% (Masters et al., 2013) to 60% (Oliver et al., 2014) (see also Silburn et al., 2013a). Furthermore, application of banded/shielded spraying in furrow irrigation systems in the Burdekin reduces residual herbicide runoff by 90% (Oliver et al., 2014), consistent with results of Silburn et al. (2013a). Hence these new technologies, should they be adopted completely in the sugarcane industry across the GBR catchment area, would be expected to reduce PSII herbicide loads (and the emerging or alternative herbicides) delivered to the GBR lagoon by >50% and hence are likely to achieve water quality targets. We note that concentration and loads of the ‘knockdown/contact’ herbicide 2,4-D did not change between the broadcast/boom and banded spraying as it was applied across both the rows and inter-rows/furrows even in the banded method. However, the toxicity and risk of 2,4-D is much lower than that of diuron (~ 10 fold lower risk than diuron: Table 4) and hence 2,4-D provides a reasonable option to apply across the paddock.



Figure 8. The WeedSeeker technology has been applied in the Mackay Whitsunday region and can reduce application of some herbicides by up to 80% (from <http://reefcatchments.com.au/files/2013/02/WeedSeekerSm1.pdf>).

Although diuron and atrazine have similar solubilities in water (35 and 35.6 mg L⁻¹, respectively) (Footprint Pesticides Properties Database, 2013) and were applied at the same rate of 1 kg ha⁻¹ in both treatments for the furrow irrigation trial, the atrazine concentrations in irrigation runoff water were almost double those of the diuron concentrations. This most likely reflects the differences in sorption behaviour of the two herbicides since the sorption coefficient (K_{oc}) of atrazine is only 100 L kg⁻¹ (range of 89 to 513 L kg⁻¹) while diuron is 813 L kg⁻¹ (range of 498 to 1358 L kg⁻¹) (Footprint Pesticides Properties Database, 2013). Similar findings were observed in the rainfall simulation trials (Table 4). Herbicide runoff partitioning studies on the lower Burdekin floodplain have similarly highlighted the relative propensity for diuron to sorb to particulate matter (Davis et al., 2012).

Based on the runoff of these herbicides from paddocks (EMC in water) and their predicted relative toxicities to diuron, we were able to provide a relative risk ranking of the herbicides used in the sugarcane industry (Tables 4 and 6). Ametryn is considered as having the highest risk to the GBR based on the trials in the Mackay Whitsunday (1.4 fold higher than diuron) and Burdekin (2.2 fold higher) at 2 days after application and somewhat less at 30 days. If ametryn was to become more widely used in the sugarcane industry (generally applied in combination with atrazine) given the current restrictions to diuron, it would do little to reduce the overall risk of PSII herbicides to the GBR. Currently, ametryn is found at much lower concentrations compared to diuron and atrazine in the GBR catchment and lagoon (Lewis et al., 2009; Smith et al., 2012). In particular, we note that the product Krismat, another emerging herbicide in the sugarcane industry, is a mixture of ametryn and trifloxysulfuron sodium, both of which are considered more toxic than diuron. Indeed, trifloxysulfuron sodium may be up to 33 times more toxic than diuron (Table 4), although it is applied at a much lower rate and would be expected to runoff less than diuron. This product was not evaluated in the rainfall simulation trials and we recommend that it be the subject of future investigations.

The other herbicides examined in the rainfall simulation trials presented a lower risk profile relative to diuron across the two regions (Tables 4 and 6). It has been shown here that a 60 to 90% reduction in diuron loss from paddocks can be achieved by banded application (Masters et al., 2013; Silburn et al., 2013a; Oliver et al., 2014). If residual herbicides were used as banded applications for most spray events (e.g. in the plant cane crop, occasionally a

broadcast residual control may be required), this adoption would likely deliver the water quality targets for herbicide loads. The assessment provided here allows comparison of the individual products that are commonly used as part of a weed management strategy in sugarcane. We note, however, that herbicides may not be direct substitutes for one another. For example, the knockdown herbicide glyphosate will not replace the residual herbicide diuron as it has a different usage pattern and cannot be used to achieve residual weed control in the row of a cane crop. Scenarios of the suite of herbicides in use with a strategy reliant on diuron (or other residual PSII herbicides) need to be compared to a strategy with reliance on alternative herbicides to assess the overall water quality risks of herbicide practices.

The 'knockdown' herbicides glyphosate, fluroxypyr and 2,4-D are predicted as having a much lower environmental risk than diuron (>25 times less risk and mostly > 50 times less risk) and appear to provide good alternatives when applied via the banded/shielded sprayer method (i.e. 2,4-D and glyphosate application in the furrow/inter-row of the paddock). As we have noted previously there are some limitations in our risk assessment that make this only a preliminary assessment. This includes the assumption that the dose-response pattern for each of the herbicides follows the same trend that is parallel, which may not be the case as these alternative herbicides have different modes of action (Table 5).

The paddock runoff data are based on a simulated rainfall event (70-80 mm.hr⁻¹) that represents approximately a 1 in 5 (Mackay Whitsunday) to 1 in 10 year (lower Burdekin) recurrence interval. Indeed, this estimate is likely to be conservative as similar events have been recorded in the lower Burdekin over the past 2 successive seasons (i.e. 2012/12 and 2013/14). Hence, these data are likely to provide a reasonable estimate of what would be expected to occur under these scenarios and we note that similar concentrations of herbicides have been measured in irrigation tailwater runoff trials conducted in the lower Burdekin (Davis et al., 2013; Oliver et al., 2014). While the EMCs in paddock runoff may be higher than under more common rainfall occurrences, the relative ranking amongst the herbicides are also not expected to change.

Herbicide information gaps

While this study significantly expanded knowledge of the environmentally relevant properties of a range of sugarcane industry herbicides, several additional information gaps emerged from this research. A number of key herbicides which will assume greater importance for growers for which significant knowledge gaps still exists include:

- There is a need to differentiate metolachlor and s-metolachlor in future studies as these herbicides are likely to have different risk profiles.
- The properties, runoff potential and toxicity of the metabolite of isoxaflutole (DKN) need to be determined as this is the 'active' herbicide and may be more problematic than the parent compound.
- Ecotoxicity studies should use the 'Glyphosate' products rather than only the active ingredient so that all surfactants and the metabolite (AMPA) are examined.

A summary of these herbicides and more details on these specific issues are provided below:

Metolachlor is a member of chloroacetanilide herbicide family that has been widely used in the agriculture sector for pre-emergence control of certain broadleaf and annual grassy weeds in the field of corn, soybeans, sorghum, peanuts, potatoes, pod crops, cotton, and on highway rights-of-way and woody ornamentals (USEPA, 1995), and is registered for use in over 70 crops worldwide. Metolachlor was initially introduced into the market as a racemic product which contains both R and S enantiomers in an even ratio. Racemic metolachlor (metolachlor) is now being replaced worldwide by S-metolachlor, the product enantiomerically enriched with the herbicidally active 1'S isomers (Muller *et al.*, 2001). S-metolachlor is physically and chemically equivalent to metolachlor but is more active in the site of action of susceptible plants. Recent ecotoxicological work suggests S-metolachlor was more toxic to *freshwater algae* than *racemic*-metolachlor (Liu and Xiong, 2005). With both racemic metolachlor (Clincher, Bouncer) and S-metolachlor (i.e. Dual Gold) used in sugarcane, there is a need to differentiate the environmental risk profile of these two chemicals, but these issues are yet to be specifically assessed as part of environmental monitoring effort in the GBR.

Isoxaflutole (IXF) is a pre-emergence herbicide (commercial formulation; Balance) used to control annual grasses and broad-leaf weeds in sugarcane (*Saccharum officinarum* L.) and maize (*Zea mays* L.). Applied at low doses (between 75 and 150 g ha⁻¹), it is used as a substitute for atrazine and has the potential for widespread use in the next decades. Isoxaflutole is specifically designed to rapidly undergo hydrolysis to form the herbicidally active diketonitrile (DKN) degradation product through the opening of the isoxazole ring (Pallett *et al.*, 2001; Beltran *et al.*, 2003). While isoxaflutole has a very short half-life in soil, it rapidly degrades to a relatively stable and phytotoxic degradate, diketonitrile (DKN), which has a half-life of 8-61 days (Pallett *et al.*, 2001). In this sense, IXF acts a precursor (or proto-herbicide) rather than a parent compound. The aqueous solubility of DKN is 50 times greater than that of isoxaflutole (326 mg L⁻¹ vs. 6.2 mg L⁻¹) (Beltran *et al.*, 2002), and also possesses a lower K_{oc} than its parent compound (Mitra *et al.*, 1999). This enhanced potential mobility of DKN has been confirmed in numerous lysimetry studies (Lin *et al.*, 2003; Alletto *et al.*, 2012), which showed that DKN was more readily leached than atrazine and its metabolites after rainfall. Cumulated losses of DKN in French maize systems (where cumulative water applied never exceeded 750 mm/year) ranged from 1.8 ± 0.6 up to 31.5 ± 15.1% of applied dose according to the cropping system and year (Alletto *et al.*, 2012). Studies of streamflow dynamics of IXF and DKN in U.S. rivers documented the presence of DKN in ca. ¾ of analysed samples (Meyer *et al.*, 2007). More details of the specific environmental and physicochemical features of DKN in an Australian context would be of considerable value to future risk assessment exercises.

Glyphosate is the main nonselective, systemic herbicide used against a wide range of weeds. Its worldwide use has expanded because of extensive use of certain agricultural practices such as no-till cropping, and widespread application of glyphosate-resistant genetically modified crops (Helander *et al.*, 2012). The mode of herbicidal activity of glyphosate is based on inactivation of an enzyme of the shikimate metabolic pathway. Glyphosate kills non-selectively and efficiently nearly all herbaceous plants. Glyphosate is considered by some to be more environmentally benign in comparison with other herbicides because: (1) it strongly sorbs to soil particles, limiting the potential for transport; (2) it has a shorter half-life compared with many other herbicides; (3) the use of glyphosate has resulted in a reduction

in the number of herbicide applications to control weeds; (4) the use of glyphosate results in lower fossil fuel usage owing to an increase in conservation tillage; (5) it has a low toxicity to mammals, birds and most aquatic fauna because the shikimate pathway does not occur in animals (Franz *et al.*, 1997; Giesy *et al.*, 2000). However, recent evidence has cast doubts on its safety. The half-life time of glyphosate may be much longer in many ecosystems than generally presumed. The half-life for glyphosate has been observed to range from 1.7 to 142 days, with an average of about 40 days. The variability in half-life is thought to be due to the variability in microbial activity and extent of soil sorption among the various sites that were studied. Repeated applications of glyphosate can also apparently increase its soil half-life due to effects on microbial communities (Giesy *et al.*, 2000; Helander *et al.*, 20012). Less is known about the metabolite of glyphosate, aminomethylphosphonic acid (AMPA). It has lower water solubility (5.8 g L^{-1} at 25°C) and a longer soil half-life (ranging from 76 to 240 days).

In spite of the reported strong sorption to soils and the short half-life in soil, researchers have reported frequent detections of glyphosate, and its main metabolite AMPA, in runoff and catchment waterways (Coupe *et al.*, 2012). Toxic effects of glyphosate, and surfactants used in herbicide formulations are documented in several bacteria and fungi, as well as in both invertebrates and vertebrates in terrestrial and aquatic ecosystems (Druat *et al.*, 2007; Helander *et al.*, 2012). Owing to the high water solubility of glyphosate-based formulations and their extensive use in the agro-environment, these herbicides are a concern to water ecosystems. Negative effects of herbicides in freshwater systems have been shown as reduced reproduction of frogs and fish, decreased survival of algae (Vera *et al.*, 2010), and increased populations of toxic, bloom-forming cyanobacteria which are capable of using the glyphosate as a phosphorus source (Helander *et al.*, 2012). Exposure to glyphosate can also significantly affect amphibians, with research documenting decreases in the number of surviving tadpoles, toads and frogs in nature following glyphosate exposure (Relyea 2005a; 2005b). It is noteworthy that in addition to glyphosate itself, risks of herbicides might be associated with the main metabolite of glyphosate degradation, AMPA, or surfactants, which might be more toxic than the glyphosate itself (Tsui and Chu, 2003).

There are also a range of emerging agronomic issues with glyphosate that will likely pose challenges (and potential environmental issues) for many industries into the future. The repetitious use of the same herbicide over an extended period has caused documented cases of herbicide resistance in weeds. The mode of action of glyphosate is so unique that weed resistance development was regarded most unlikely, and it took 20 years before the first glyphosate-resistant weeds appeared. During the past decades, glyphosate has become the backbone of no-till agriculture with almost 90% of all transgenic crops worldwide being glyphosate-resistant and in many areas hardly any other herbicides are used (Helander *et al.*, 2012). This causes a very strong selection pressure for increasing glyphosate resistance in weeds. Presently, glyphosate resistance has been documented in more than 20 weed species, including in an Australian context (Owen and Powles, 2010; Beckle *et al.*, 2011). In addition to resistance issues, extended use of glyphosate has been suggested in some cases to benefit disease causing microbes (Johal and Huber, 2009).

Conclusions

A series of rainfall simulation trials were conducted across the Burdekin and Mackay Whitsunday regions to examine the runoff behaviour of the key herbicides used in the sugarcane industry. Further, the water quality benefits of shielded/banded spraying in the furrow irrigated Burdekin region were quantified. This study showed that reduced application of herbicides on the paddock through new technologies available to the industry (such as WeekSeeker® and banded/shielded spraying) leads to proportional (or greater) reductions in offsite herbicide loss. These technologies show that reductions of 60% or more are possible and hence, if widely adopted across the sugarcane industry, would likely achieve water quality targets for pesticide loads to the GBR. An assessment of the risk of the different herbicides used in the sugarcane industry suggest that, with the exception of ametryn, all the other herbicides examined in the rainfall simulation trials pose less of a risk relative to diuron (currently considered the herbicide of most risk in the GBR). Furthermore if the first paddock runoff occurred 30 days after application, the risk profile of all the herbicides (with the exception of paraquat) relative to diuron reduced even further, a reflection of their shorter half-lives. The application of the 'knockdown' herbicides such as glyphosate, fluoxypyr and 2,4-D are predicted as having a much lower environmental risk than diuron (mostly >50 times less risk) and appear to provide good alternatives when applied via the banded/shielded sprayer method.

Future Directions

This study has provided valuable data on the properties, dynamics and management of herbicides commonly applied in the sugarcane industry. The results have allowed us to better model the loss of herbicides from sugarcane lands, understand their transport pathways, examine the potential benefits of the new/alternative herbicides that may become used more widely in the sugarcane industry and improved management options for the industry to reduce off-farm herbicide losses. We recommend the following:

- That all pesticide monitoring, modelling, research and toxicology data collected across the Reef Rescue R&D and Paddock to Reef Integrated Monitoring, Modelling and Reporting Programs and projects under the National Environmental Research Program and Reef Protection R&D program be synthesised. We hope to utilise the Pesticide Working Group to produce a special issue collection of papers based on results from these research and monitoring programs which will start the process, although further coordination may be required to produce one consolidated document.
- That all the data and knowledge under these programs (and consultation with industry) be used to produce a 'best management practice approach' document for herbicide application in the sugarcane industry. We need some more consultation with industry to work out the best way to go forward as there are numerous options that could be available (SafeGauge for pesticides; other decision-support based tools; best management practices developed by the sugarcane industry).
- That the final outputs of this research be presented to growers through shed meetings and extension field days.

- That short targeted (and relatively lower cost) herbicide fate trials (such as banded shielded spraying) be continued to build our knowledge on the new/alternative products (potential agronomic and water quality benefits) and also conduct trials where the timing of application can be examined. Specifically, further examination of Flame (imazapic) Krismat (trifloxysulfuron sodium), Balance (isoxaflutole and particularly its metabolite DKN) and metolachlor (r and s metolachlor species) are recommended.
- That relevant ecotoxicological data (i.e. coral, phytoplankton) be developed so that the relative toxicity of the new/alternative herbicides can be more thoroughly examined (and better recommendations can be made on their use to the industry). Based on our preliminary toxicity analysis (data from algae and plants) we can suggest that s-metolachlor, metribuzin, pendimethalin, isoxaflutole and trifloxysulfuron sodium be prioritised for ecotoxicological testing on seagrass species of the GBR as these would appear to have the highest risk.

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Appendix 1: Publications

Oliver, D.P., Anderson, J.S., Davis, A., Lewis, S., Brodie, J. and Kookana, R. (2014) Banded applications are highly effective in minimising herbicide migration from furrow-irrigated sugar cane. *Science of the Total Environment*, 466-467, 841-848.

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