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Combining weed efficacy, economics and environmental considerations for improved herbicide management in the Great Barrier Reef catchment area

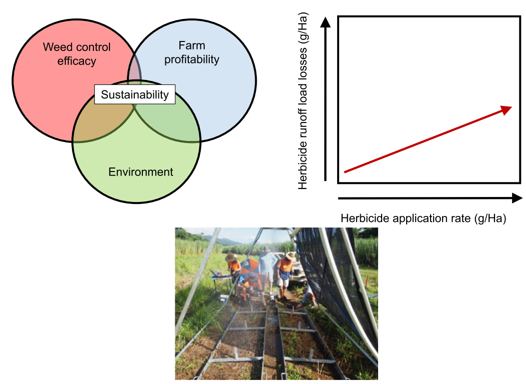
Emilie Fillols [a], Aaron M. Davis [b,*], Stephen E. Lewis [b], Andrew Ward [c]

[a] Sugar Research Australia Ltd, PO Box 122, Gordonvale, 4865, Queensland, Australia
[b] Catchment to Reef Research Group, TropWATER, James Cook University, Townsville, 4811, Queensland, Australia
[c] Mars Wrigley, 1351 Boundary Rd, Wacol QLD 4076, Australia

HIGHLIGHTS

- Off-farm herbicide loss is a management challenge for Great Barrier Reef catchment canefarmers.
- Field efficacy, costs and environmental impact of several herbicide formulations were assessed.
- Several emerging herbicides offered promise as replacements for traditional herbicide mixes.
- Despite slightly higher economic costs, these mixes likely reduce the impact on the environment.

GRAPHICAL ABSTRACT



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ABSTRACT

The current Australian sugarcane industry transition toward adoption of an 'alternative' herbicide strategy as part of improved environmental stewardship is increasingly complicated by recent farming system, regulatory and herbicidal product changes. This study quantified and compared the efficacy, economic costs and environmental risk profiles of a range of established, emerging, and recently registered pre-emergent herbicides across field trials in the Wet Tropics region of North Queensland. Several herbicides were effective on certain weed species, but lacked broad spectrum control. Better efficacy results from products with multiple active ingredients (i.e., imazapic-hexazinone) demonstrated the benefits of using mixtures of active ingredients to widen the spectrum of weed control efficacy. All tested pre-emergent herbicides behaved quite similarly in terms of their propensity for off-site movement in water (surface runoff losses generally >10% of active applied), with their losses largely driven by their application rate. Herbicides with lower application rates consistently contributed less to the total herbicide loads measured in surface runoff. Results demonstrated alternative choices from the more environmentally problematic herbicides (such as diuron) are available with effective alternative formulations providing between 4 and 29 times less risk than the traditional diuron-hexazinone 'full rate'. However, considerable challenges still face canegrowers in making cost-effective decisions on sustainable herbicide selection. Additional research and effective grower extension are required to address information gaps in issues such as specific weed control efficacy of alternative herbicides and potential blending of some herbicides for more effective broad spectrum weed control, while also minimising environmental risks.

* Corresponding author.
E-mail address: aaron.davis@jcu.edu.au (A.M. Davis).

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1. Introduction

The decline of fresh and marine water quality associated with land-based runoff from adjacent agricultural catchments is a major cause of the poor state of many of the coastal ecosystems of Australia's Great Barrier Reef (GBR) World Heritage Area (Waterhouse et al., 2017). Pesticides have been specifically identified as among the most important diffuse source pollutants from catchment areas of the GBR (Brodie et al., 2012). High value freshwater, estuarine and inshore waters of the GBR lagoon are regularly exposed to pesticide runoff from agricultural lands, particularly during wet season riverine flood events (December to April) (e.g. Lewis et al., 2009; Davis et al., 2012). The pesticides that have been most commonly detected in the GBR lagoon are herbicides that inhibit electron transport at photosystem II (PSII) in plants and include diuron, atrazine, hexazinone, ametryn, simazine and tebuthiuron (Haynes et al., 2000; Shaw and Müller, 2005; Shaw et al., 2010). Concentrations during elevated stream flow events can at times exceed ecological water quality protection guideline trigger values for up to several weeks for some of these PSII herbicides (Lewis et al., 2009, 2012; Brodie et al., 2012; Davis et al., 2013; O'Brien et al., 2016; Novic et al., 2018).

Yield loss from weed competition is estimated to cost the Australian sugar industry $70 M annually, with herbicidal control strategies costing the industry an additional $14 M annually, with herbicides themselves also causing yield declines through phytotoxic effects on crops (McMahon et al., 2000). Industry transitions in recent decades toward minimum or zero tillage systems to improve soil conservation have increased reliance on herbicides in sugarcane, with herbicide usage a necessary consequence of reducing or eliminating traditional tillage-based weed control (Hargreaves et al., 1999; Johnson and Ebert, 2000). Due to their convenience and cost-effectiveness, the Australian sugarcane industry has become particularly reliant on PSII herbicides such as diuron, ametryn, atrazine, and hexazinone which are predominantly used as pre-emergent "residual" herbicides with continued activity in the soil for a period of time, reducing weed seed germination and/or growth in the soil (see Johnson and Ebert, 2000; Davis et al., 2014). "Knockdown" herbicides such as 2,4-D, MCPA, fluroxypyr, and glyphosate are also used for post-emergent control (acting via contact with plants). Many of these herbicides are also prone to move offsite in runoff, hence an improved management regime is required to reduce risk to the GBR catchment and lagoon while maintaining weed control efficacy.

In response to herbicide concentrations in the GBR exceeding ecological guideline values, the Reef Water Quality Protection Plan 2009 ('Reef Plan') introduced targets to reduce end-of-catchment 'PSII priority' herbicide loads of diuron, atrazine, hexazinone and ametryn by 60% to be achieved by 2018 (Reef Water Quality Protection Plan Secretariat, 2009, 2013). In the recent Reef 2050 Water Quality Improvement Plan 2017–2022, herbicide load targets were changed to an herbicide concentration target based on the multiple species potentially affected fraction methodology (State of Queensland, 2018; Warne et al., in press). The new concentration target aims to protect at least 99% of aquatic species at river mouths (State of Queensland, 2018). To help achieve these evolving targets, the Queensland Government introduced a package of legislation, extension and research in 2009 known as the Reef Water Quality Program, which included the regulated use of diuron, atrazine, hexazinone and ametryn (referred to as 'priority' PSII pesticides) on sugarcane properties across the Wet Tropics, Burdekin Dry Tropics and Mackay Whitsunday Natural Resource Management regions. The Australian Pesticides and Veterinary Medicines Authority (APVMA) also conducted a concurrent review of diuron, which introduced new application windows and reduced application rates in certain regions. Despite these initiatives as well as improved application methods (e.g. banded application), there is still considerable uncertainty on the most appropriate herbicide mix and application that provides suitable weed control while also achieving desirable water quality outcomes.

The Queensland sugar industry has commenced minimising reliance on the priority PSII herbicides and adopting 'alternative' herbicides for weed control (Davis et al., 2014). This reflects both a voluntary shift by the industry as part of their improved environmental stewardship, and also due to the recent legislative imposed restrictions on the use of PSII herbicides. These issues are particularly relevant to canefarmers in the northern Wet Tropics of the GBR catchment area, which have traditionally relied heavily on products such as diuron, in an area that collectively contributes ~50–60% of the GBR's total annual PSII or 'diuron equivalency toxicity' load to the GBR marine environment (Wallace et al., 2016; Huggins et al., 2017). Considerable uncertainty exists over the relative environmental toxicities, mobilities and risk profiles of several existing touted alternative herbicides available to canegrowers (Aslam et al., 2012; Davis et al., 2014; Nachimutu et al., 2016), with several additional new herbicides also recently registered for use in Australian sugarcane.

When selecting herbicidal weed control strategies, growers traditionally face a complex decision process (e.g. weed spectrum efficacy, compatibility with soil type and farming system, weather conditions, label restrictions, length of efficacy, cost, tank compatibility, etc.) and switching to an unknown or newly registered herbicide represents an additional economic risk due to lack of product knowledge that may lead to potential weed control failure or toxicity on cane (Ross and Fillols, 2017). While several paddock-scale studies in the GBR catchment area have provided important insights on the persistence and mobility of herbicides across a range of soil types (e.g. Hargreaves et al., 1999; Simpson et al., 2001; Masters et al., 2013; Silburn et al., 2013; Melland et al., 2016), none have successfully combined mobility, toxicity, efficacy and economic considerations to achieve improved farm stewardship. While historically overlooked, it is this holistic consideration of all of these factors that will ultimately drive grower decision-making regarding practice change on-farm. Indeed, the recent development of proposed guidelines for several key herbicides based on new toxicity data and the application of improved methods (King et al., 2017a, 2017b) provides a novel opportunity to benchmark the new and old herbicide suites in terms of effectiveness and environmental risk. This research contribution examines the weed control efficacies, cost and environmental risk profiles of several alternative pre-emergent herbicides to diuron applied in field trials across the Wet Tropics region of the GBR catchment area and gathers crucial knowledge that will assist growers in their switch to more environmentally friendly herbicides. It highlights that some alternative herbicides may provide reasonable efficacy coupled with relatively lower offsite environmental risk while others show less ability for weed control and present equal or even greater offsite risk. The need for such an approach to combine product efficacy, environmental risk and economic viability in farming systems is receiving increased recognition for effective weed management and industry sustainability (Stewart et al., 2011; Underwood et al., 2017, 2018).

2. Materials and methods

2.1. Study location

Herbicide efficacy field trials were conducted at three different sites spanning much of the length of the Wet Tropics sugarcane industry, near the townships of Tully, Gordonvale and Mossman. As the name implies, Queensland's Wet Tropics receives the highest rainfall rates on the Australian continent. Average annual rainfall at the three trial locations are Tully (4076 mm/yr), Gordonvale (1927 mm/yr) and Mossman (2430 mm/yr) (Australian Government Bureau of Meteorology, 2019). In the Wet Tropics, rainfall can occur throughout the year, but is still strongly seasonal, concentrated in the 'wet season', between November and April, when >80% of the annual rainfall is recorded. Major rainfall is typically generated by monsoonal lows, tropical cyclones and associated rainfall depressions, with rainfall intensities during storms among the highest recorded in the world, often causing substantial riverine flooding (Davis et al., 2017). Wet season commencement (November onwards) also often coincides closely with periods of weed germination and therefore herbicide applications by canefarmers, with later herbicide applications in particular entering high risk weather periods for significant herbicide losses (Davis et al., 2014).

2.2. Study subject: sugarcane crop

Sugarcane (*Saccharum officinarum* L.) is the dominant crop in catchments draining to the northern GBR marine environment, (Ingham to Mossman), occupying approximately 137,000 ha of the Terrain (Wet Tropics) NRM region (ABS, 2018). A semi-perennial crop, in the Wet Tropics, sugarcane is mainly planted in autumn (April–June) and harvested 12–15 months later. The crop is then allowed to re-grow (ratoon) and harvested approximately annually (harvesting season is June–December). Productivity of the crop declines after 3–5 harvests. After the last harvest, the regrowth is sprayed out, and the field is fallowed for ~6 months until the next sugarcane crop is planted. This sequence, planting to planting, is called a cropping cycle, with the crops denoted plant crop, first ratoon crop, etc. Wet Tropics sugarcane is mechanically harvested 'green' (without the crop being burnt prior to harvest) and the crop residue retained on the soil surface as a 'trash blanket' following harvest has occurred since the ~1980's (Prove et al., 1995; Hoghart and Allsopp, 2000).

2.3. Herbicide efficacy field trials

Three field trials were conducted in green cane trash blanketed ratoons to compare the efficacy on weeds of herbicide treatments applied broadcast just after harvest, on three characteristic Wet Tropics soil types varying from well to poorly drained (Table 1). Treatments compared alternative registered pre-emergent herbicides versus PSII-based herbicides applied soon after harvest.

2.3.1. Efficacy trial: design and protocol

Each trial was replicated three times as a randomised complete block (RCB) design including adjacent untreated controls (Table 2). Adjacent controls take into account the weeds spatial distribution across the trial and are a standard feature of herbicide efficacy trials (PP1/152(4) EPPO General Standard). Plot size was two inter-rows wide and 15 m long. The diuron-hexazinone 'high rate' mix (T1) was used as a reference treatment because of its traditional popularity, and local grower's familiarity with its performance. However, since 2013, diuron is now only registered for use at a lower rate (T2) in the Wet Tropics region (see Table 2). Treatments T2 to T7 are currently registered for pre-emergence application in the Wet Tropics, although amicarbazone and the imazapic-hexazinone products have only recently been registered for use. Metolachlor (T5) is traditionally utilised primarily in plant cane weed control on bare soils but is attracting interest from growers as a potential ratoon cane weed control option on trash blankets to replace diuron. Each commercial product was tested separately at their maximum label rate in order to have a better understanding of their weed spectrum control and length of efficacy. These data are foundational to further efficacy data related to product mixes and application at lower rates. When trials were performed, the commercial product Amitron (amicarbazone) was not registered in Australia and the maximum label rate of 1.4 L/ha emulates the Brazilian label. To prevent herbicide uptake from sugarcane, paraquat was added to treatments with a known phytotoxicity issue on sugarcane: diuron-hexazinone 'high rate' (T1), imazapic (T3), isoxaflutole (T4) and imazapic-hexazinone (T7). Paraquat causes rapid destruction of cell membranes and stop translocation of other herbicides in the spray mix. All herbicides were purchased through local agricultural supply resellers.

Spraying occurred soon after harvest, at cane spike stage, using a tractor mounted 6-tank research sprayer equipped with a 3 m boom and six 03 air inducted nozzles, spaced every 0.5 m, and spraying at 0.5 m above ground level, which mimics standard grower practices. Rainfall events (timing and amount) were recorded at each site using Onset Hobo rain gauges. The rainfall events and especially the first rain event after spraying are an important consideration as rain often triggers weed germination (unless the soil is already moist before spraying, in that case weed germination occurs immediately) and also activates the pre-emergent herbicides.

2.3.2. Efficacy trial: data collection

For each trial, the first weed control assessment was carried out when the weeds started to emerge in the untreated control plots. Five subsequent weed assessments were conducted within all treatments at each trial, at approximately 2 weekly intervals following that initial assessment. Assessments included a visual estimation of the percentage weed coverage and of percentage coverage of each group of species: grasses, broadleaves, vines and sedges in each plot. The assessments combined in one figure provide an estimate of number, cover, height and vigour of the weeds (virtually the weed volume). A visual assessment is easier to make comparing relative differences to an untreated control than it is by calculating absolute values. The visually assessed percentage weed coverage can be considered as real estimations of a continuous variable and can be analysed with normal statistical procedures (PP1/152(4) EPPO General Standard).

2.3.3. Efficacy trial: statistical data analysis

The efficacy of the herbicide treatment was expressed in percentage weed reduction compared to the adjacent untreated control and calculated using the formula:

$$Efficacy_T = \frac{100\,(W_U - W_T)}{W_U}$$

where $Efficacy_T$ = percentage weed reduction in the treated plot, W_U =

Table 1
Details of the efficacy trial sites.

Trial site	Location	Cane variety Ratoon number	Soil type	Spray date	Weeds in untreated plots	Total rainfall through trial period
1	Tully	Q200 3R	Seasonally wet soils requiring drainage or special management – Hydrosols[a]	21/08/2015	Up to 45% weed coverage Mainly grasses (*Megathyrsus maximum, Digitaria ciliaris*) and broadleaves (*Ageratum conyzoides, Spermacoce latifolia*)	651 mm (20/8/2015 to 14/02/2016)
2	Aloomba	Q200 4R	Deep sandy soils - Tenosols, Rudosols[a]	28/08/2015	Up to 90% weed coverage Mainly grasses (*Echinochloa colona, D. ciliaris,M. maximum*) and broadleaves (*A. conyzoides, Cleome aculeata*)	1141 mm (27/8/2015 to 8/2/2016)
3	Daintree	Q219 2R	Friable non-cracking clay or clay loam soils - Dermosols, Ferrosols[a]	30/10/2015	Up to 20% weed coverage Mainly broadleaves (*A. conyzoides, S. latifolia*) and grasses (*Panicum conjugatum, Paspalum sp.*)	1386 mm (29/10/2015 to 17/3/2016)

[a] (Isbell, 1996).

Table 2
Details of treatments in the efficacy and off-site mobility field trials.

Efficacy trial treatment	Factors assessed	Mobility trial tank mix	Commercial product name	Active	Rate kg or L/ha	Water rate L/ha	Indicative 2018 cost $/ha
T1	Efficacy Mobility	Mix2	Barrage high rate (as reference)	diuron 468 g/L hexazinone 132 g/L	4	300	$74
T2	Efficacy Mobility	Mix1	Barrage low rate (as per new label)	diuron 468 g/L hexazinone 132 g/L	0.9	300	$17
T3	Efficacy Mobility	Mix2	Flame®	imazapic 240 g/L	0.4	300	$10
T4	Efficacy Mobility	Mix1	Balance®	isoxaflutole 750 g/kg	0.2	300	$35
T5	Efficacy Mobility	Mix2	Clincher®	metolachlor 960 g/L	2.7	300	$49
T6	Efficacy Mobility	Mix1	Amitron® Brazilian max label rate (before APVMA registration)[a]	amicarbazone 700 g/kg	1.4	300	$72
T7	Efficacy Mobility		Bobcat® i-MAXX	imazapic 25 g/L hexazinone 125 g/L	3.8	400	$86
T1,T3,T4,T7	Efficacy		Shirquat® 250 added to tank mix to prevent cane foliar uptake	paraquat 250 g/L	1.2	300	$5
	Mobility	Mix1	Soccer®700 WG	metribuzin 700 g/kg	2.2	300	$72
	Mobility	Mix1	Gesaprim® Granules	atrazine 900 g/kg	3.3	300	$34
	Mobility	Mix2	Ametrex®800 WG	ametryn 800 g/kg	2.8	300	$77
	Mobility	Mix3	Amine 625	2,4-D 625 g/L	3.5	200	$20
	Mobility	Mix3	Decoy 400®	fluroxypyr 400 g/L	1.5	200	$51
	Mobility	Mix3	Daconate®	MSMA 800 g/L	6	200	$110
	Mobility	Mix3	MCPA® 750	MCPA 750 g/L	1.45	200	$18
NA		Mix3	Weedmaster® Argo®	glyphosate (potassium and isopropylamine salts) 540 g/L	5	200	$41

[a] Amitron in Australia is now registered at a maximum of 1 kg/ha. 2019 indicative cost per ha is $72.

percentage weed coverage in adjacent untreated control and W_T = percentage weed coverage in treated plot.

A similar calculation was carried out to calculate the percentage reduction for each group of weed species.

Herbicide efficacy data were quantified in each treatment into variables of "total percentage reduction", "grass percentage reduction" and "broadleaf percentage reduction". A linear mixing model considering the measurement dates as repeated measurements was fitted across the data for all three traits using the SAS statistical package. Because our trials are observed over differing sets of time points, the spatial power model SP(POW) structure was fitted, which models the strength of the correlation between two observations as a function of the distance between the two observations. Points closer in time will be more strongly correlated than points further apart in time. The model can be symbolically written for total percent count as:

$$Efficacy_T = Treatment + Date + W_U + Treatment * Date + Replication$$

where $Efficacy_T$ = percentage weed reduction in the treated plot and W_U = percentage weed coverage in adjacent untreated control.

The significance of the fixed terms is tested using asymptotic Wald statistics, so the F-values reported in the analysis of variance table are approximate F values, according to Kenward and Roger (1997). A Tukey's multiple comparison test is used to determine which means among a set of means differ from the rest at a family significance level of 5%.

2.4. Off-site herbicide mobility field trials

To provide a uniform and rapid assessment of the runoff potential (mobility) and relative environmental risk profiles of the tested herbicide formulations, rainfall simulations were paired to two of the three efficacy trial sites (trial 1 and 2 which had the most contrasting soil types). Delayed harvest at efficacy trial 1 (Tully) resulted in rainfall simulations conducted at a different, nearby location with a similar soil type (trial 1a) whereas the rainfall simulation trial 2a (Aloomba) was implemented in the same cane block as efficacy trial 2.

2.4.1. Herbicide mobility trial: design and protocol

An A-frame rainfall simulator based on the specifications of Loch et al. (2001) was used for the herbicide mobility trials. This approach is similar to what has been employed in previous plot scale water quality research in cropping systems, including the Queensland sugar industry (see Masters et al., 2013; Melland et al., 2016).

Three replicated herbicide treatments for each plot were sprayed on an area 1 m wide by 4 m long using a tractor and the 6-tank research sprayer with a 1.5 m boom (to ensure a correct overlap). Tarps were used to cover and protect the adjacent plots. Cane plants were mowed to <0.5 m tall to prevent the cane canopy from overhanging the plots and intercepting rainfall. The bottom 3 m of the sprayed area was used to carry out the rainfall simulation, whereas the extra top 1 m was used to collect soil and trash samples just after spraying for herbicide analysis. As an adjunct to the pre-emergent herbicide runoff assessment, a range of other "pre-emergent" and "knockdown" herbicides commonly used in green cane trash blanketed ratoons in the Wet Tropics region were also compared. Herbicide treatments were segregated into three different treatment mixes according to their compatibility (mix1, mix2 and mix3) and sprayed onto different plots. When necessary, tank mixes were sprayed separately to facilitate the mixing and avoid precipitation and blockage of the sprayer. Spray water rates for every tank mix were adjusted to obtain a total of 400 L/ha for each plot sprayed with pre-emergent herbicides (mix1 and mix2) and 200 L/ha for each plot sprayed with post-emergent herbicides (mix3) to approach product label requirements (Table 2).

Simulated rainfall was applied to these small field plots (0.75 m wide × 3 m long) two days after the application of herbicides to minimize herbicide degradation and to maximize the risk of herbicide loss in runoff. Plot edges were bound by a metal frame driven 30 to 50 mm into the soil. Runoff was routed through a metal spout for collection. Simulated rainfall was applied at rates (70–80 mm/h) broadly representing a one in two-year average recurrence interval for the region (Melland et al., 2016). Three rain gauges located in each plot recorded the rainfall amount applied during each simulation.

2.4.2. Herbicide mobility trial: runoff collection

Runoff water was collected every five minutes and composited as one sample for each plot (plot runoff collected for 4 to 5 seconds, every five minutes, depending on the flow rates at each site), starting when runoff commenced, and continuing until plot runoff ceased. The composite sample was used to analyse the concentration of herbicides in the water fraction. Samples for herbicide analysis were collected directly into 1 L glass bottles that were covered in aluminium foil. Samples were stored in ice boxes (on site) or in the fridge (4 °C overnight) prior to transport in ice boxes to the receiving laboratory the day after collection. The runoff flow volume for each plot was also measured at the same five minute sample collection periods by timing the plot runoff to fill a 500 mL jug.

2.4.3. Herbicide mobility trial: laboratory methods

Runoff water samples were sent to ACS Laboratories in Kensington, Victoria for herbicide residue analysis. Analysis of concentrations of herbicide active ingredients in paddock runoff water was performed using in-house methods based on established analytical protocols (Munch and Bashe, 1997; Anastassiades et al., 2003; Shoemaker and Bassett, 2005). Glyphosate and its metabolite (or degradation product) AMPA were analysed using method ACS-AM-TM-029 (analytical detection limit of 1.0 μg/L). Water samples were filtered through a 0.22 μm nylon filter and organic solvent was added. Residues of glyphosate and AMPA were derivatized using FMOC and the derivatized compounds were analysed using liquid chromatography—tandem mass spectrometry (LC MSMS).

2,4-D and MCPA were analysed using method ACS-AM-TM-201.1 for "acid herbicides" (analytical detection limit of 2.0 μg/L). Samples were extracted using an acidified organic solvent and cleaned up on modified quenchers cartridges. The residual herbicides were analysed using LC MSMS.

Atrazine, metribuzin, diuron, hexazinone, imazapic, isoxaflutole, metolachlor, ametryn and fluroxypyr were analysed using method ACS-AM-TM-201 for "non-acid herbicides" (analytical detection limits between 0.5 and 2.0 μg/L). Samples were extracted using a buffered organic solvent and cleaned up on modified quenchers cartridges. The residual herbicides were analysed using LC MSMS.

MSMA organic arsenic was extracted using a suitable organic solvent, the extracts were filtered to remove particulates that may contain inorganic arsenic and analysed by inductively coupled plasma atomic emission spectroscopy (ICP AES).

Breakdown products were detected in the majority of samples analysed over the course of this study and their concentrations were added to the parent compound for our analysis.

2.4.4. Herbicide mobility trial: runoff data analyses

To directly compare rainfall simulation results, we conducted two separate analyses of the herbicide runoff data (all results are presented as the mean of each specific treatment with standard deviation of the replicated treatments). Measured runoff volumes were used to convert dissolved herbicide concentrations in water into total runoff loads of active ingredient (ai) lost (g/ha) from each plot. This analysis allows for direct comparisons to be made between the different herbicides in terms of surface water loads lost to the environment. Because this data representation may be related to variable product application rates, we also quantified the percentage losses of the total herbicide applied to the paddock (the load of the herbicide in surface runoff divided by the total amount of active ingredient applied). This analysis allows comparative assessments of the relative amounts of herbicide lost.

To more holistically compare potential environmental impacts of herbicide application strategies, herbicide "toxic equivalency factors" (TEFs) were calculated relative to diuron (e.g. Lewis et al., 2013; Davis and Pradolin, 2016). We have revised this calculation in light of new data and to produce estimations for amicarbazone and MSMA. In that regard, the studies of Smith et al. (2017a, 2017b) showed that the application of the 75th percentile concentration from Species Sensitivity Distribution (SSD) curves was the most optimal method to calculate TEFs. In this study, we have applied the SSD 80th percentile values for diuron, ametryn, hexazinone, 2,4-D, glyphosate, imazapic, isoxaflutole, metolachlor, metribuzin, fluroxypyr and MCPA calculated by King et al. (2017a, 2017b) who compiled the latest available ecotoxicity data; we note the 75th percentile values were not provided and the 80th percentile provided the closest approximation. For these herbicides, the TEFs were calculated by dividing the diuron 80th percentile value by the corresponding herbicide value. The freshwater values were used in all cases with the exception of 2,4-D and MCPA which only have marine 80th percentile values, whereby these concentrations were applied with the corresponding diuron 80th percentile marine value.

The herbicides which had no 80th percentile data included atrazine, amicarbazone and MSMA. For atrazine, Smith et al. (2017b) provided a TEF based on the 75th percentile which we have adopted; however, for amicarbazone and MSMA there are limited toxicity information and so a different approach was required. In both cases we examined comparable ecotoxicology data for autotrophs from the Pesticide Properties Database (http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm) to provide an 'indicative TEF'. This included acute EC_{50} biomass concentrations for *Lemna gibba* (aquatic plant) for amicarbazone (0.21 mg/L) and MSMA (93 mg/L) where the comparable diuron value (0.0183 mg/L) provides indicative TEFs of 0.087 and 0.0002, respectively. While these TEFs have high uncertainty, they provide at least some indication until additional ecotoxicity data can be generated.

To quantify the herbicide risk relative to diuron, the herbicide active ingredient concentration leaving each treatment were divided by the 'high rate' diuron concentration (i.e. mobility) and then multiplied by their relevant TEF (Lewis et al., 2013). Hence when the combined mobility-risk factor is >1 then the herbicide was assessed as greater environmental risk than the diuron "high rate" application. When more than one active ingredient was applied in a treatment, the individual relative herbicide risk of all active ingredients lost in the treatment were summed into a single index. For example, for products with two active ingredients (i.e. Barrage and Bobcat®i-MAXX), the total combined relative risk was calculated as the sum of the individual relative risk of each of the actives. This additive approach to quantify impact of overall herbicide mixtures has not been validated for herbicides that have different modes of action and it is unlikely that a simple addition model would fully explain mixture toxicity (Smith et al., 2017a); however, this approach still provides an approximation of risk.

3. Results

3.1. Herbicide efficacy field trials

The weed populations in all three efficacy trials consisted mainly of grasses and broadleaf weeds, however, there were variations in the level of weed infestation, the specific weed species, and eventual weed coverage in the absence of herbicidal control in each trial (Table 1). Four and a half months after harvest, the untreated plots at each trial site ranged between 20% and 90% weed ground coverage. The combined analysis of the percentage reduction of the total weed coverage for trials 1, 2 and 3 showed no significant difference for the interaction Treatment x date ($P = .57$), whereas significant differences existed between treatments ($P < .001$). Average percentage reductions across all assessment dates are presented in Fig. 1a. The combined analysis for the percentage grass reduction showed no significant difference for the interaction ($P = .92$) and between treatments ($P = .41$), whereas the combined analysis for the percentage broadleaf weed reduction showed significant differences between treatments ($P < .001$) ($P = .06$ for the interaction; Fig. 1A). Detailed overviews of results are available in Fillols et al. (2018).

Results indicated no significant differences in reduction of the total weed populations between diuron-hexazinone full rate (T1) and other treatments except for metolachlor (T5), which resulted in significantly lower overall weed control (Fig. 1A). Several significant differences did, however, emerge between treatments with regard to level of weed control on specific weed types. Results indicated that diuron-hexazinone low rate (T2), imazapic (T3), isoxaflutole (T4) and metolachlor (T5) resulted in lower broadleaf control. Against broadleaved weeds, amicarbazone was as effective as diuron-hexazinone high-rate and imazapic-hexazinone, however its efficacy against grasses was quite low and short lasting (< 30 days). Results also indicated that the performance of imazapic (T3), isoxaflutole (T4) and diuron-hexazinone low rate (T2) was shorter lasting (<30 days) on broadleaves compared to the three better performing herbicides including diuron-hexazinone 'high rate' (T1), amicarbazone (T6) and imazapic-hexazinone (T7), that maintained reductions above 85% for 70 days (Fig. 1B). In particular, isoxaflutole performed poorly on the broadleaf *Spermacoce latifolia*. Imazapic, isoxaflutole and metolachlor were more effective against the grasses in the trials. Diuron-hexazinone applied at the recently regulated low rate (T2) did not perform well (Fig. 1A), especially on grasses (Fillols et al., 2018). Metolachlor (T5) was the worst overall performing herbicide, proving largely ineffective for trash blanket weed control across all sites.

3.2. Off-site herbicide mobility trails

Surface runoff volumes were highly variable for each of the plots across the rainfall simulations for the two sites. At trial 1a, the runoff varied from 16 to 56 mm with a mean of 36 mm. Runoff from trial 2a ranged between 21 and 51 mm with a mean of 40 mm. The differences in runoff highlight considerable variability across even an individual paddock and likely reflect factors such as preferential wheel traffic-compaction, fine scale soil pore variability, antecedent soil moisture, differences in soil type or the presence/absence of trash (and interactions between these factors), both within and between sites. In any case, across all simulations, the rainfall applied to the paddock (~ 80 mm/h) and the surface runoff from the plots highlight that a high proportion of surface runoff (in the order of 20–70%) can occur during intense rainfall events.

The herbicide surface runoff losses as a percentage of active ingredient applied showed high variability between herbicides and between the two sites (Fig. 2). The results demonstrated that under certain

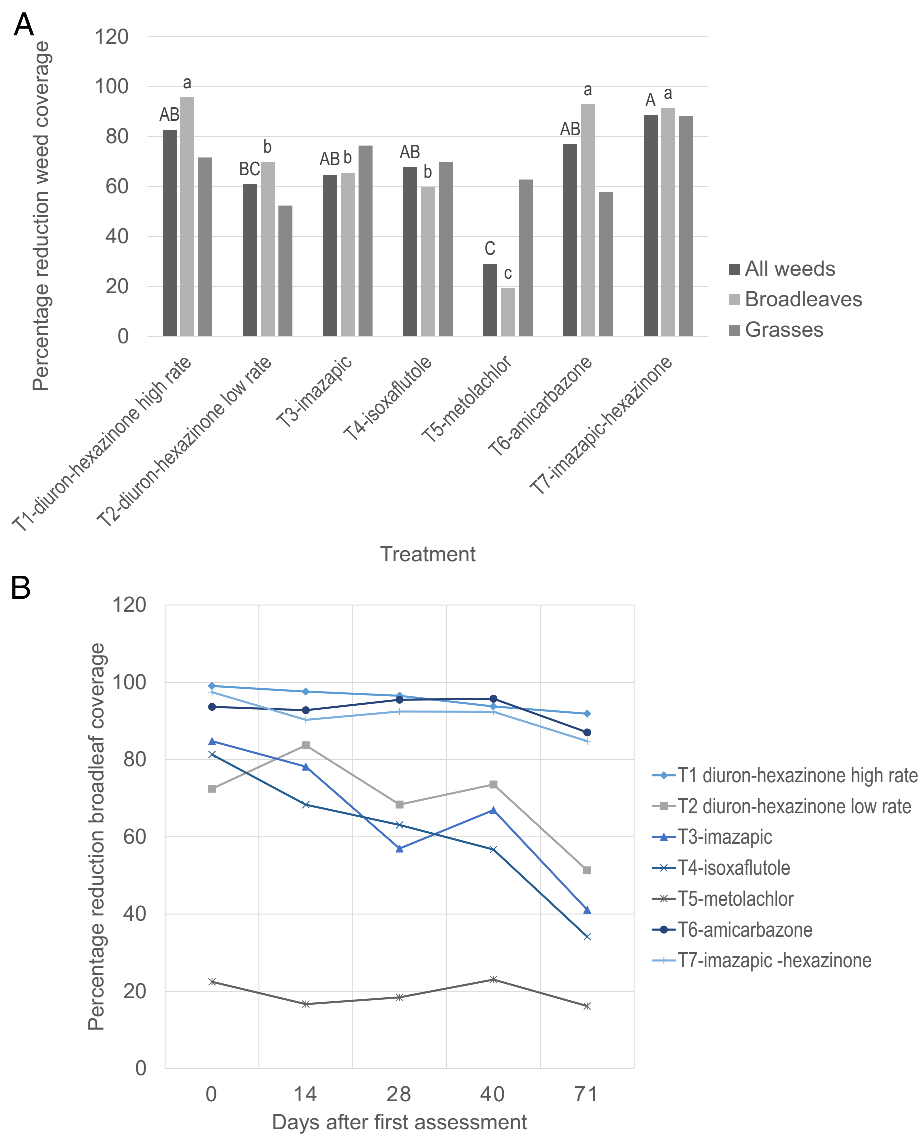

Fig. 1. A. Mean percentage reduction of total weed coverage, broadleaves and grass coverages compared to the adjacent untreated controls for the three trials. Means with the same letter are not significantly different ($P > 0.05$). Fig. 1 B. Mean percentage reduction of broadleaf weed coverage for each assessment date compared to the adjacent untreated controls for the three trials.

conditions (i.e. heavy rainfall shortly after application), very high surface runoff losses of herbicides (> 10% of a.i. applied) are possible. The pre-emergent herbicide losses at both sites were higher than 10% lost, with higher losses at trial 1a (highest loss of 60% for hexazinone) on poorly drained hydrosol compared to trial 2a on deep sand (highest loss of 29% for hexazinone). These values are consistent with Masters et al. (2013), who obtained comparable herbicide loss values on a moderately drained brown chromosol.

The standard deviations for some of the herbicides (error bars) lost in surface runoff largely reflect the variability in runoff across the treatment plots, rather than any marked differences in relative loss behaviour of herbicides between sites (i.e. relative load loss patterns were generally consistent between sites). When comparing the herbicide losses as percentage of applied, hexazinone and imazapic tended to have higher runoff losses (>15% loss at both sites) than other herbicides. These results are expected as hexazinone and imazapic are highly soluble in water (solubility of 33,000 and 2230 mg/L respectively) and are relatively mobile in soil (K_{oc} of 137 and 54 mg/L respectively). However, most of the pre-emergent herbicides had similar losses to diuron (± 20%). Their behaviour can be explained by their physico-chemical properties with the exception of amicarbazone and metribuzin which should have been found in runoff in higher amounts according to their properties. For the knockdown herbicides, 2,4-D generated the most losses with 10 to 25% loss in runoff, whereas fluroxypyr and glyphosate were the least prone to runoff. These results are consistent with Cowie et al. (2013) who also compared the runoff behaviour of 2,4-D and fluroxypyr versus pre-emergent herbicides. Glyphosate has a relatively high K_{oc} of 6920 mg/L and therefore low mobility, and the solubility of fluroxypyr in water (6500 mg/L) is lower than the other knockdown herbicides.

The grams per hectare surface runoff herbicide losses also generally displayed consistent trends across the sites with diuron, metribuzin, atrazine, metolachlor, ametryn and 2,4-D having relatively higher loss rates, while diuron (lower rate), hexazinone (lower rate), isoxaflutole, imazapic and fluroxypyr generally had lower amounts lost (Fig. 3). The main driver for the differences in grams per hectare surface runoff herbicide losses at each site clearly was the difference in herbicide application rates.

Degradates of several herbicides including atrazine (breakdown products, desethylatrazine and desisopropylatrazine) and diuron (3-(3,4-dichlorophenyl)-1-methylurea (DCPMU)) were frequently detected in surface runoff but made very minor contributions to the herbicide runoff loads. The relatively low amounts of these compounds in plot runoff is unsurprising given the short time period between product application and rainfall application in this study. The major exception where a significant component of an herbicide breakdown product that left plots was isoxaflutole. Isoxaflutole presents a somewhat special case, as it 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). All metabolite concentrations were added to the parent compound in this study (i.e. referred to as Total Isoxaflutole).

With the exception of the ametryn treatment that presented significant environmental risk compared to even the high rate diuron-hexazinone treatment, all other treatments demonstrated lower impact relative to diuron "high rate" on the environment (Table 3). Ametryn's TEF (0.64), high application rate (1600 g/ha), moderate water solubility (200 mg/L) and moderate mobility in soil (K_{oc} of 316 mg/L) are compiling factors that resulted in a total relative risk similar to diuron in both trials (Table 3). The recently registered imazapic-hexazinone formulation was several times less of a risk relative to using the traditional diuron-hexazinone full rate, but still had a relatively high risk (4 to 9 times less risk than diuron) compared to imazapic, isoxaflutole and amicarbazone applied separately, which were environmentally 11 to 77 times less of a risk than diuron full rate at these sites. As expected most knockdown herbicides (2,4-D, MSMA, fluroxypyr, MCPA, glyphosate) resulted in low environmental risk (often 1000 times less risk than diuron). It was also observed that the relative risk ranking order of the tested herbicides was very similar between the two sites, despite the fact the sites had very different drainage properties, highlighting that grower recommendations related to herbicide environmental impact can be driven by a simplified risk matrix (Table 4).

4. Discussion

4.1. Weed control efficacy

The recently registered imazapic-hexazinone mix was the most efficient pre-emergent herbicide across all trial sites, regardless of the soil type and the weed composition. Like the similarly performing, but no longer permissible diuron-hexazinone high rate application, it had a particularly long period of efficacy regardless of the soil type and the rainfall amount when compared with other herbicides like imazapic and isoxaflutole. In our trials, it was particularly stable during an atypical dry period that preceded its incorporation before the first significant rainfall and had a long period of activity after activation (Fillols et al., 2018). Some herbicides like imazapic, isoxaflutole and amicarbazone

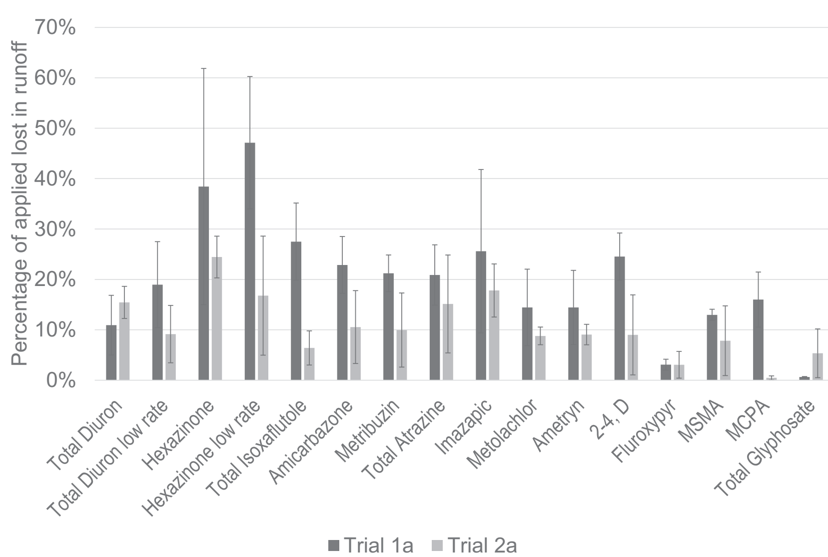

Fig. 2. Herbicide runoff losses at trial 1a and trial 2a in percentage of applied product lost.

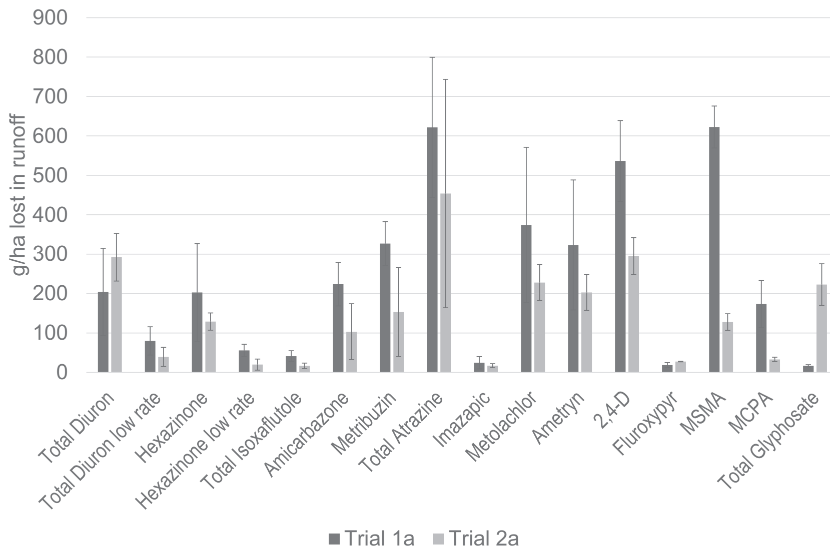

Fig. 3. Herbicide runoff losses in g per hectare of active ingredient at trial 1a and trial 2a.

were effective, but only on certain weed species. The better results from the imazapic-hexazinone or diuron-hexazinone pre-mix products demonstrated the benefits of using two active ingredients to widen the spectrum of efficacy (i.e. imazapic or diuron as a grass control and hexazinone as a broadleaf control). Combining several of the herbicides according to the likely pre-emergent weed problem is a possible option for growers, but requires more targeted assessment. At the newly registered rate for the Wet Tropics NRM region, the diuron-hexazinone (lower rate) product applied on its own appears to not be an effective pre-emergent weed control option.

4.2. Loads of herbicide in runoff

Rainfall simulation results indicate that significant amounts of many applied herbicides (up to 60%) can be lost to the environment via surface runoff if rainfall occurs soon after application, consistent with previous rainfall simulation and irrigation trials conducted on sugarcane paddocks in the GBR (e.g. Davis et al., 2013; Silburn et al., 2013; Oliver et al., 2014; Davis and Pradolin, 2016; Melland et al., 2016). The high generated amounts of surface runoff combined with the recent application of herbicides (two days prior to simulation) does admittedly represent an almost 'worst-case' scenario where highest surface losses of herbicides would be expected. Rainfall events of this magnitude (and significantly larger) are not, however, uncommon across the Wet Tropics, particularly in early stages of the wet season. Indeed, comparable load losses in similar real-world scenarios have been documented in long-term paddock scale trials in the GBR catchment area (Rohde et al., 2013).

All tested pre-emergent herbicides behaved quite similarly, with their runoff losses largely driven by their application rate. Herbicides with lower application rates (i.e., isoxaflutole, imazapic, low rate diuron) consistently contributed less to the total herbicide loads documented in runoff water. Average loads of the pre-emergent herbicides from the two runoff trials were plotted against their application rate and linear regressions fitted to the data had $r^2 > 0.79$ for both trials (Fig. 4). For the tested pre-emergent herbicides, 17% of the amount

Table 3
Calculation of risk relative to diuron for each treatment at trials 1a and 2a.

T	Active per ha	TEF (to diuron)	Mean runoff concentrations in ppb		Total risk relative to diuron [a]		Relative risk ranking order	
			Trial 1a	Trial 2a	Trial 1a	Trial 2a	Trial 1a	Trial 2a
T1	diuron 1872 g	1	563	722	1.25	1.11	1	1
	hexazinone 528 g	0.26	533	310				
T2	diuron 421.2 g	1	210	105	0.442	0.163	3	3
	hexazinone 118.8 g	0.26	150	51				
T3	imazapic 96 g	0.23	63	41	0.026	0.013	10	10
T4	isoxaflutole 150 g	0.32	110	49	0.063	0.022	9	9
T5	metolachlor 2592 g	0.047	1017	550	0.085	0.036	8	7
T6	amicarbazone 980 g	0.087	603	267	0.093	0.032	7	8
T7	imazapic 95 g	0.23	63	41	0.247	0.113	5	5
	hexazinone 475 g	0.26	479	279				
x	ametryn 1600 g	0.64	887	490	1.01	0.434	2	2
x	metribuzin 1125 g	0.23	890	395	0.364	0.126	4	4
x	atrazine 2970 g	0.036	1647	1167	0.105	0.058	6	6
x	2,4-D 2187.5 g	0.0002	1630	705	0.0006	0.0002	13	13
x	fluroxypyr 600 g	0.002	57	67	0.0002	0.0002	14	14
x	MSMA 4800 g	0.0002	1850	79	0.0007	0.00002	12	15
x	MCPA 1087.5 g	0.005	535	305	0.005	0.002	11	11
x	glyphosate 2700 g	0.002	50	528	0.0002	0.0015	15	12

x: treatments not included in the efficacy trials.
[a] *Total Risk relative to diuron* $= \sum_{n=1}^{\infty} \frac{TEF_n\, RO_n}{RO_d}$ Where TEF: individual active ingredient TEF to diuron, RO: individual active ingredient mean runoff concentration, RO_d.: diuron high rate mean runoff concentration and n: individual active ingredient.

Table 4
Summary of efficacy, cost and relative risk, for tested pre-emergent treatments.

T	Active per ha	Indicative cost per ha	Average efficacy on weeds	Total risk relative to diuron	Risk ranking compared to diuron
T1	diuron 1872 g hexazinone 528 g	$74	Very efficient	1.11 to 1.25 times higher risk	1
T2	diuron 421.2 g hexazinone 118.8 g	$17	Moderate efficacy	2 to 6 times lower risk	3
T3	imazapic 96 g	$10	Moderate efficacy (mainly on grasses)	38 to 77 times lower risk	10
T4	isoxaflutole 150 g	$35	Moderate efficacy (mainly on grasses)	16 to 45 times lower risk	9
T5	metolachlor 2592 g	$49	Poor efficacy on trash blanket	12 to 28 times lower risk	7
T6	amicarbazone 980 g	$72 (cost at 1 kg/ha)	Good efficacy (mainly on broadleaves)	11 to 31 times lower risk	8
T7	imazapic 95 g hexazinone 475 g	$86	Very efficient	4 to 9 times lower risk	5
x	ametryn 1600 g	$66	x	2.3 times lower to 1.01 times higher risk	2
x	metribuzin 1125 g	$43	x	3 to 8 times lower risk	4
x	atrazine 2970 g	$18	x	10 to 17 times lower risk	6

x: treatments not included in the efficacy trials.

applied in trial 1a and 12% of the amount applied in trial 2a were lost in runoff water, illustrating the importance of application rate for these herbicides, as well as the influence of the local environmental conditions. The free draining soil type at trial 2a limited the average herbicide loss via surface runoff to 12% of herbicide applied compared to the poorly drained hydrosol which increased the average herbicide loss via surface runoff to 17%. These results provide field validation of similar outcomes documented in modelled loss dynamics and environmental risk assessments targeting Queensland sugarcane herbicides and climatic regimes (Davis et al., 2014). However, we note that losses to groundwater were not quantified in this study. Hence, we could not evaluate associated herbicide losses to groundwater that might be expected on more free draining soils found in the Wet Tropics, a process that can be an important off-site loss pathway for nitrogen from cane farms (Rasiah et al., 2005; Armour et al., 2013).

4.3. Relative risk to diuron

The concentrations of the alternative herbicides in runoff from several treatments demonstrated considerably lower impact than the traditional diuron-hexazinone full rate, ranging from 4 to 9 times less of an environmental risk (imazapic-hexazinone) to up to 11 to 77 times less risk (imazapic, isoxaflutole and amicarbazone). Herbicides such as imazapic, isoxaflutole and amicarbazone may be more effective for weed control if used in mixtures to extend their efficacy spectrum. Based on nominal TEF mixes from this study, the combination of imazapic + isoxaflutole (11 to 29 times less risk), imazapic + amicarbazone (8 to 22 times less risk), or isoxaflutole + amicarbazone (6 to 19 times less risk) may provide improved environmental outcomes than imazapic-hexazinone, while still providing effective weed control at relatively lower costs (discussed below). When herbicides are used in combination, rates are also likely to be reduced while maintaining their efficacy, therefore potentially decreasing their offsite environmental risk even further. However further work would be required to assess the efficacy of a range of herbicide blends and rates.

The combination of environmental risk, efficacy and economic data are clearly valuable to produce a simplified decision-making tool for farmers to achieve effective and sustainable management practices. The various efficacy and environmental scenarios documented here converge on very similar conclusions despite the different weed types, pressures and different soil types assessed across the three trials. Efficacy, economic and environmental risk data can be used in combination as a powerful communication tool for growers, as they collectively display a holistic overview of the various pros and cons of alternative strategies to diuron in trash blanketed Wet Tropics ratoons (Table 4). Selecting the right herbicide to control the weed population in a paddock is hitherto a complex decision taking into account multiple agricultural factors such as soil type, weather, crop stage, weed species, weed stage, cane variety and presence of trash as well as economic factors. Hence the additional runoff risk factor that growers need to consider must be simplified to facilitate adoption. We suggest these data could be presented as the risk relative to diuron (in times of xx times more or less risk) or in a risk ranking order (e.g. Table 4).

It should also be noted that our study focusses on only projected herbicidal impacts on environmental health from a purely off-site water quality perspective. Continued herbicide use on paddocks has also been shown to often exert significant impacts on soil micro-, meso- and macro-fauna, significantly depressing some groups of microorganisms (Roper and Gupta, 1995). In Australia, however, little information is available about the effects of herbicides on soil microbial populations,

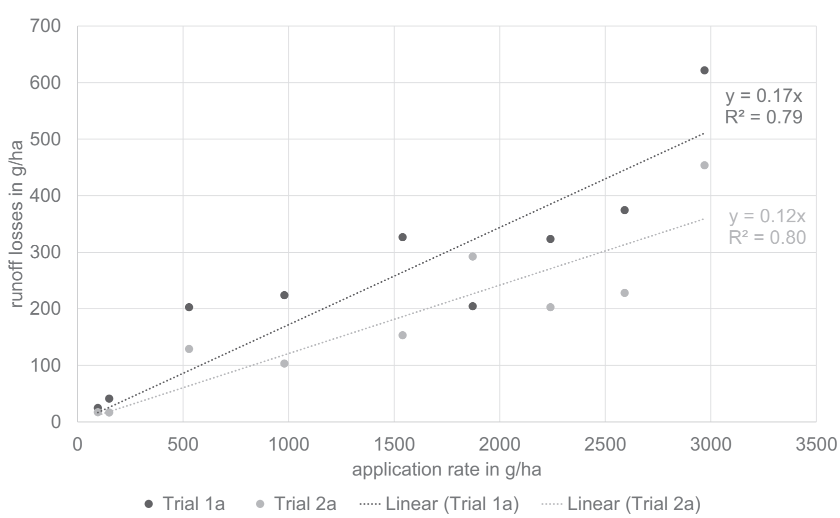

Fig. 4. Loads of all tested pre-emergent herbicide active ingredients in runoff (g/ha) compared to their application rate (g/ha) for trial 1a and 2a.

and this would be a useful avenue of future research to better quantify the specific relative environmental impacts of herbicide practice change.

The dynamics of changing herbicide registration, application rates and regulation has been an overarching theme of herbicide management in the GBR catchment area in recent years, and one that will almost certainly continue. Effects of regulatory changes to available product efficacy (e.g. diuron-hexazinone), new chemicals, variable efficacy depending on weed types, economics and environmental risk will all interact to influence individual grower decision-making outcomes. One of the greatest emerging challenges for both industry, extension staff, government policy makers, and regulators is ensuring that the requisite, but rapidly growing amount of technical, environmental and extension support is available for growers to make informed decisions in what is now a heavily monitored, dynamic and regulated herbicide management environment.

5. Conclusions

This study is one of the first to combine efficacy, environmental risk and economic data to demonstrate that various efficacious and cost-effective alternatives to high rate diuron applications are available for Great Barrier Reef catchment canegrowers, and that several are also more environmentally sustainable. This study used the latest toxicity data and recommended methods to calculate toxic equivalent factors (TEFs) coupled with local mobility data to determine relative environmental risk. We note that for some of the newly registered herbicides there is still a lack of local mobility data as well as relevant local-scale toxicity information that hinders a fuller and more comprehensive assessment of local environmental risk. Results also highlight some of the challenges facing canegrowers in making cost-effective decisions on herbicide selection, while also minimising potential environmental risks. Given the limited weed spectrum controlled by several individual herbicides, identifying suitable product blends and rates as well as their resultant weed control and environmental risk is another current information gap deserving further research. Effective and sustainable use of all herbicides, particularly newer, more unfamiliar products, will require a sound knowledge of the weed issues in the paddock, weed control spectrum of specific active ingredients, environmental risk profiles of candidate herbicides, stage of crop cycle and climatic risk periods to make a more informed herbicide choice.

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CRediT authorship contribution statement

Emilie Fillols: Conceptualization, Methodology, Funding acquisition, Investigation, Formal analysis, Writing - review & editing. **Aaron M. Davis:** Investigation, Formal analysis, Writing - review & editing. **Stephen E. Lewis:** Investigation, Formal analysis, Writing - review & editing. **Andrew Ward:** Conceptualization, Methodology, Funding acquisition.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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