The potential benefits of herbicide regulation: A cautionary note for the Great Barrier Reef catchment area

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HIGHLIGHTS

• Herbicides have been identified as a priority pollutants for the Great Barrier Reef.
• There has been recent regulation of herbicides in the Great Barrier Reef catchment.
• Risk assessment identified inconsistent benefits in shifts to alternative herbicides.
• Several alternative herbicides demonstrated similar risks to traditional herbicides.

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ABSTRACT

Industry transitions away from traditional photosystem II inhibiting (PSII) herbicides towards an ‘alternative’ herbicide suite are now widely advocated as a key component of improved environmental outcomes for Australia’s Great Barrier Reef and improved environmental stewardship on the part of the Queensland sugar industry. A systematic desktop risk analysis found that based on current farming practices, traditional PSII herbicides can pose significant environmental risks. Several of the ‘alternatives’ that can directly fill a specific pre-emergent (‘soil residual’) weed control function similar to regulated PSII herbicides also, however, presented a similar environmental risk profile, regardless of farming systems and bio-climatic zones being considered. Several alternatives with a pre-emergent residual function as well as alternative post-emergent (contact or ‘knock-down’) herbicides were predicted to pose lower environmental risks than the regulated PSII herbicides to most trophic levels, although environmental risks could still be present. While several herbicides may well be viable alternatives in terms of weed control, they can still present equal or possibly higher risks to the environment. Imposing additional regulations (or even de-registrations) on particular herbicides could result in marginal, and possibly perverse environmental impacts in the long term, if usage shifts to alternative herbicides with similar risk profiles. One of the emerging policy challenges is ensuring the requisite technical and extension support for cane growers to ensure effective adoption of rapidly evolving farming system technologies, in a very dynamic and scrutinised herbicide management environment.

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1. Introduction

The Great Barrier Reef (GBR) situated on the north-east coast of Australia contains extensive areas of coral reefs, seagrass meadows and fisheries resources (Fig. 1). It has the status of a Marine Park under joint Australian (Federal) and Queensland State Government arrangements and was declared a World Heritage Area in 1981. Despite this protected status, the coral cover on the GBR has declined in recent decades, although the timing and trajectory of the decline are still a matter of some debate (Hughes et al., 2011; De’ath et al., 2012). While the causes of this decline are to some degree reef-specific, terrestrial runoff of sediment, nutrients and pesticides have been identified as one of the key drivers of this decline (Brodie et al., 2012; Brodie et al., 2013). Discharge from rivers adjacent to the GBR lagoon continues to be of poor quality in many locations, and land derived contaminants, including suspended sediments, nutrients and pesticides are present in
the GBR at concentrations likely to cause environmental harm (Brodie et al., 2012; 2013).

Pesticides, a stressor absent prior to European settlement in the GBR (ca. 1850), have been specifically identified as among the most important non-point source pollutants from catchment areas of the GBR (Bainbridge et al., 2009; Brodie et al., 2012). Estuarine and inshore waters of the GBR lagoon are regularly exposed to herbicide runoff from agricultural lands during wet season riverine flood events (December to April) (e.g. Lewis et al., 2009; Davis et al., 2012). Concentrations in these events at times exceed GBR ecological water quality protection guideline trigger values (i.e. GBRMPA, 2009) for several weeks (Lewis et al., 2009, 2012; Shaw et al., 2010; Brodie et al., 2012; Kennedy et al., 2012a,b). The herbicides that have been most commonly detected in the GBR lagoon are photosystem II inhibitors (PSII; herbicides designed to inhibit electron transport at photosystem-II in plants) and include diuron, atrazine, hexazinone, ametryn, simazine and tebuthiuron (Haynes et al., 2000a; Shaw and Müller, 2005; Shaw et al., 2010). Laboratory-based ecotoxicological tests show that GBR marine photosynthetic organisms vulnerable to PSII herbicide exposure at concentrations comparable to those measured in flood plumes include microalgae (Magnarsson et al., 2012, 2013), seagrass (Haynes et al., 2000b; McMahon et al., 2005; Flores et al., 2013) and corals (Jones et al., 2005; Negri et al., 2005). Some organisms appear to recover quickly from short-term exposure (Haynes et al., 2000b; Magnusson et al., 2012), although longer exposure studies on phototrophs such as microalgal communities demonstrate chronic pesticide pollution can induce shifts in community structure (Magnusson et al., 2012). Corals can similarly recover from short-term low level exposure to herbicides, however chronic exposure can lead to decreased photosynthetic rates, bleaching, partial colony mortality, reduced tissue lipid content and reduced fecundity (Brodie et al., 2012). Recent estimates suggest that at least 17,000 kg/yr of these PSII herbicides are exported to the GBR marine environment (Lewis et al., 2011), although this would be an underestimate of the total pesticide load to the GBR, as not all pesticides known to be used in the GBR catchment and entering its waterways are currently being monitored.

2. Recent cane industry herbicide use and policy development in Queensland

The Australian sugarcane industry has been particularly reliant on residual PSII herbicides (predominantly for pre-emergent weed control) for several decades (see Johnson and Ebert, 2000; Davis et al., 2013), with atrazine also being used in grains cropping, and tebuthiuron and simazine originating from the beef grazing industry and forestry plantations, respectively (Lewis et al., 2009). The identification of sugarcane as a major contributor to pesticide pollution in the GBR led in large part to the Reef Water Quality Protection Plan 2009 (Reef Plan) introducing targets to reduce end-of-catchment herbicide loads of diuron, atrazine, hexazinone and ametryn by 50% by 2013. The updated 2013 Reef Plan adjusted this target to a 60% reduction by 2018. (Reef Water Quality Protection Plan Secretariat, 2009). To help achieve these 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 (regulated PSII pesticides) on sugarcane properties in the Wet Tropics, Burdekin Dry Tropics and Mackay Whitsunday catchments. Users of the regulated herbicides have to follow specific requirements including training, restrictions on use near water bodies and revised allowable application rates. The Reef Water Quality Program also aims to reduce herbicide reliance through wider adoption of integrated weed management, including improved weed management planning, farm hygiene and other prevention measures, as well as the substitution of traditional PSII residual herbicides with ‘alternative herbicides’ where appropriate. (http://www.reefwisefarming.qld.gov.au/).

In addition to these specific Reef Plan targets and Reef Water Quality Program requirements, several of these herbicides have received additional recent regulatory scrutiny from the Australian Pesticides and Veterinary Medicines Authority (APVMA). Atrazine, one of the most widely used herbicides in Australian agriculture, has already been the focus of assessment for potential regulatory use amendments as part of the APVMA’s Chemical Review Program (APVMA, 2008a, 2008b). The APVMA has also been undertaking an ongoing review of diuron since 2002, another of the most widely used herbicides in the Australian sugarcane, on the basis of environmental and human health concerns, specifically the potential for diuron to contaminate the marine environment through agricultural runoff (APVMA, 2008a, 2008b). In December 2012, the APVMA announced the final outcomes of its diuron review, with significant changes to conditions of use for diuron products across Australia, and additional region-specific and season-specific restrictions within the sugarcane industry (APVMA, 2012). These include broad label restrictions such as; reduced rates of application; application only on relatively flat land; no spraying when heavy or persistent rain is forecast; and spray-drift buffer zones to protect non-target vegetation and aquatic areas. Additional new provisions related to sugarcane include restrictions on use in the Wet Tropics region, caps on maximum annual application rates and season specific ‘no-spray windows’ in other GBR catchment cane districts (APVMA, 2012).

Sugar industry shifts in recent decades toward environmentally sustainable agricultural practices such as minimum and zero tillage cultivation have, in fact, increased reliance on herbicides (Johnson and Ebert, 2000). However, with both voluntary and more recently legislatively imposed sugar industry practice change away from the PSII herbicides, there is a corresponding shift to ‘alternative’ herbicides to fill this growing gap in weed control measures available to growers (Reef Water Quality Protection Plan Secretariat, 2013). Purported alternatives already in use across the industry include (but are not limited to) non-PSII herbicides such as the ‘knockdown’ (contact), post-emergent herbicides glyphosate, MCPA, monosodium methyarsenate (MSMA), paraquat and 2,4-D, and the residual, pre-emergent herbicides pendimethalin, imazapic, isoxaflutole, metolachlor, S-metolachlor, trifluralin, trifloxysulfuron sodium, as well as the PSII herbicides metribuzin and terbutryn.

Knowledge on the likely environmental fate and off-site ecological effects of these alternative herbicides in GBR sugarcane catchments is, however, currently scarce. A variety of inherent physico-chemical and toxicological characteristics affect the likely environmental risk posed by pesticides (Simpson et al., 2000; Wauchope et al., 2002). Table 1 outlines several of these key properties for commonly applied PSII herbicides in relation to many ‘alternative’ herbicides likely to fill emerging weed control gaps (at least in part) for GBR catchment cane growers. Many of these herbicides, particularly those likely to fill a similar weed suppression role to regulated PSII herbicides, often share similar physico-chemical 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 exhibit higher toxicities to particular aquatic primary producers, at least in freshwater situations (Table 1). Several alternatives do, however, have lower mobility potential and/or lower environmental toxicity. Indeed, there has been surprisingly little structured assessment of the comparative potential environmental effects of broad-scale sugar industry shifts from traditional PSII products to this alternative suite of herbicides. This situation is exacerbated by the lack of locally relevant ecotoxicological data available for the GBR lagoon.
site impacts of pesticides, and can assist in decision-making and policy productive environmental outcomes for the GBR catchment area. S
survived equations, PIRI was developed for use in a uniform land use zone environmental conditions, and land use factors. A point source, steady integrating important factors such as the pesticide properties, soil and potential impact on surface water and groundwater resources, by
designed to provide rating and ranking of pesticides according to their package (Kookana et al., 2005). PIRI is a semi-quantitative index the application of the Pesticide Impact Rating Index (PIRI) software

3. Methods

The GBR cane industry herbicide risk assessment was based around the application of the Pesticide Impact Rating Index (PIRI) software package (Kookana et al., 2005). PIRI is a semi-quantitative index designed to provide rating and ranking of pesticides according to their potential impact on surface water and groundwater resources, by integrating important factors such as the pesticide properties, soil and environmental conditions, and land use factors. A point source, steady state model, which incorporates both process based and empirically derived equations, PIRI was developed for use in a uniform land use zone (i.e., a paddock or collection of paddocks containing the same crop). The PIRI model relies on a range of specific data inputs including land use and application properties (frequency of pesticide application, dosage of pesticide, proportion of active ingredient, proportion of area with pesticide applied, vegetation coverage, and the width of buffer zones); site and environmental properties (days after application to first rain-fall/irrigation event, recharge, depth to groundwater, groundwater value, surface water value, ground slope, rainfall amount, water index, surface water depth, and aquifer porosity); soil properties (fraction organic carbon, bulk density, volumetric field capacity, soil loss, soil type, and soil moisture status); and pesticide properties (solubility, half-life in soil; sorption coefficient based on organic carbon (KOC)). The comparative mobility potential and toxicity to a range of receptor organisms (chosen to represent different trophic levels) can be assessed for a range of pesticides. For further details on PIRI, refer to the paper by Kookana et al. (2005). PIRI has been specifically designed to benchmark new pesticides against existing pesticides, or assess the likely effects of major land use changes (Kookana et al., 2005). As such, it is eminently suitable as a screening tool in a collective pesticide risk analysis for the Queensland sugar industry.

To populate the data input requirements for the PIRI model, information on a comprehensive range of registered herbicides, their typical application rates, application methods and application frequency, was sourced via interviews from sugar industry agronomy and extension staff across the three major sugarcane growing districts in north Queensland; the Mackay Whitsunday; lower Burdekin; and Wet Tropics regions (see Fig. 1). Modelled herbicide application rates and input data are provided in Supplementary materials (Table S1). These three districts collectively account for ~80% of Australia’s total sugar production, and ~86% of sugarcane area cultivated in the GBR catchment area (Anonymous, 2012). It should be noted that we model application rates for herbicides prior to the imposition of Reef Plan regulatory limits on usage, to compare relative risks even before regulatory constraints on the usage of particular PSII herbicides came into effect. The PIRI database contained the vast majority of registered pesticides relevant to the Australian sugar industry, their chemical properties such as KOC, pesticide half life, dissociation constant, usage information (application

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Solubility in water @ 20 °C (mg L(^{-1}))</th>
<th>Soil degradation (days/aerobic)</th>
<th>Soil adsorption KOC</th>
<th>Impact on Fish Acute 96 h LC(_{50}) (mg L(^{-1}))</th>
<th>Aquatic invertebrates Acute 48 h EC(_{50}) (mg L(^{-1}))</th>
<th>Aquatic plants Acute 7 day EC(_{50}) biomass (mg L(^{-1}))</th>
<th>Aquatic algae Acute 72 h EC(_{50}) growth (mg L(^{-1}))</th>
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<tbody>
<tr>
<td>Ametryn</td>
<td>200</td>
<td>37</td>
<td>316</td>
<td>5</td>
<td>28</td>
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<td>0.059</td>
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<tr>
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<td>75.5</td>
<td>813</td>
<td>6.7</td>
<td>5.7</td>
<td>0.018</td>
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<tr>
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<td>150</td>
<td>54</td>
<td>320</td>
<td>85</td>
<td>0.072</td>
<td>0.0145</td>
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</tbody>
</table>

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spraying type) and toxicity across a range of standard biota used in pesticide ecotoxicology assessments (rat, algae, *Daphnia* sp., rainbow trout etc.). In some cases, where a pesticide of interest was not a priori listed in the PIRI database, or lacked specific ecotoxicology data, relevant physico-chemical and toxicological data were manually entered into PIRI using information derived from the ‘Footprint’ Pesticide Properties Database (PPDB, 2009; http://sitem.herts.ac.uk/aeru/footprint/en/index.htm).

Advice from sugar industry research and extension staff was also used to populate additional district specific model parameters on soil attributes such as soil type, % soil organic matter, and typical soil loss rates from paddocks. Requisite climatic parameters (total rainfall, maximum and minimum temperatures etc.) for the PIRI model were sourced from relevant Bureau of Meteorology (BOM) records in each region (Bureau of Meteorology website, 2013). The dominant proportion of off-site pesticide movement from GBR catchments, particularly in terms of delivery to marine environments, occurs during the north-Australian ‘wet season’ where the majority (~80%) of annual rainfall occurs over a 5 month period (November–March) (Bureau of Meteorology website, 2013). Our environmental pesticide risk therefore also focused on this climatic window. Long-term rainfall and temperature averages for each district were sourced from Ingham (Ingham Composite BOM site 032078) for the Wet Tropics, Burdekin Shire Council for the lower Burdekin (BOM site 033001) and the Mackay district (Mackay BOM site 033119) over the months of November–March (inclusive). Most GBR sugarcane districts rely on rainfall to meet crop water requirements, with the exception of the lower Burdekin region, which has an almost total reliance on furrow irrigation to meet crop water demand (Thorburn et al., 2011; Davis et al., 2013). Typical irrigation volume data for Burdekin crops was also sourced from local studies (i.e. Thorburn et al., 2011) and advice from local researchers. To account for the often marked variability of soil types found across most Queensland sugar districts (see Thorburn et al., 2011), and the resultant effects on alternative pathways for off-site agro-chemical movement, modelling was conducted across a “sand”, “silt” and “clay” soil type in each region. Raw data inputs for each district’s modelling scenarios are provided in Supplementary material (Table S2).

With surface water pollution the primary driver of issues currently surrounding herbicide regulation and registration in Australia, a PIRI risk calculation was performed for each GBR sugarcane district for surface water mobility and surface water toxicity to several different trophic levels of aquatic organisms. PIRI does have the capacity to address some aspects of groundwater impact, although toxicity data are lacking for many herbicides, hence we limit our assessment to surface water pollution. The different trophic levels assessed in PIRI analyses were rainbow trout (used as a measure of toxicity to fish), *Daphnia* sp. (an indicator of potential toxicity to invertebrates), and freshwater algae (the base of the food chain). The model was firstly run using a 4-day delay between herbicide application and first rainfall or irrigation event. Irrigation or rainfall events occurring within a week of herbicide application produce the highest proportionate load losses of applied herbicides, and pose the highest environmental concern (Davis et al., 2013). While we are primarily interested in the environmental risk profiles associated with significant rainfall and irrigation events soon after herbicide application, the comparative environmental risk posed by particular herbicides is also related in part to relative persistence in the environment (Simpson et al., 2000). To account for variability in physico-chemical features such as herbicide soil half-life, we also ran the PIRI model for a Wet Tropics scenario for drier conditions where significant rainfall did not occur until a minimum of 40 days after herbicide application to paddocks.

The resultant chemical risk profile for algae is most relevant to freshwater ecosystems, but likely also provides a reasonable proxy for marine primary producers (i.e. seagrasses, benthic microalgae, coral zooxanthellae) and hence an approximation of risks of herbicides to vulnerable GBR ecosystems. However, the different modes of action of different herbicides (photosystem inhibition, plant growth regulation etc.) and physiology of different primary producers in the GBR that

Fig. 2. An example PIRI model output for surface water mobility risk (left) and surface water toxicity risk impact comparison to freshwater algae (right) for herbicides applied in Wet Tropics sugarcane on a silt soil type. Mobility risk and toxicity risk are combined to give an overall risk rating for each herbicide in this scenario.
span single-celled microalgae through to higher plants (seagrass), admittedly challenge generalised approaches to risk predictions. Following Kookana et al. (2007) an overall risk rating for each herbicide was calculated by averaging potential off-site migration (mobility) with the toxicity rating to give a single overall risk of each herbicide to each specific target organism (e.g. fish, invertebrates, algae) for every herbicide on each soil type in each district (i.e. a ‘low’ mobility averaged with a ‘high’ toxicity would give an overall ‘medium’ risk to a particular target organism). Fig. 2 shows an example output in terms of potential mobility averaged with toxicity risk (fish) to algae. The suite of regulated PSII herbicides (diuron, atrazine, hexazinone and ametryn) all produced similar overall risk profiles to freshwater algae in the ‘medium-high’ to ‘high-very high’ range. A considerable number of herbicides outside this regulated suite, which was intermediate in terms of drainage characteristics and propensity for surface water runoff. Comparative risk ratings of herbicides were also very similar for the rainfall Mackay-Whitsunday and Wet Tropics districts (two ‘wetter’ regions compared to the dry-tropical lower Burdekin district), so we limit presentation of main results for rainfed sugarcane to risk ratings on silt soil types in the Wet Tropics.

### 4.1. Lower Burdekin

PIRI scenarios based on the irrigated lower Burdekin district are outlined in Table 2. As expected, the herbicides used in the sugarcane industry presented a generally higher risk to freshwater algae than to invertebrates and fish. The suite of regulated PSII herbicides (diuron, atrazine, hexazinone and ametryn) all produced similar overall risk profiles to freshwater algae in the ‘medium-high’ to ‘high-very high’ range. A considerable number of herbicides outside this regulated suite, however, also presented similar, and in some cases, even higher risk profiles to algae. Several alternative herbicides (terbutryn, metribuzin, MSMA, paraquat, trifluralin) were all predicted to present risk profiles in the ‘high’ to ‘high-very high’ range. Other ‘alternatives’ with a pre-emergent, residual function such as isoxaflutole, trifloxsulfuron-

### Table 2

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Surfacewater mobility risk</th>
<th>Rating for potential toxicity to algae</th>
<th>Mobility + toxicity (algae)</th>
<th>Rating for potential toxicity to Daphnia</th>
<th>Mobility + toxicity (Daphnia)</th>
<th>Surfacerwater toxicity risk (fish)</th>
<th>Mobility + toxicity (fish)</th>
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<td>Very low</td>
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<td>Very low</td>
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</tr>
<tr>
<td>Ametrelry</td>
<td>Medium</td>
<td>Extremely high</td>
<td>High–very high</td>
<td>Very high</td>
<td>High–very high</td>
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<td>Low-medium</td>
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</tr>
<tr>
<td>Diuron</td>
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<tr>
<td>Flurfloxyrop–p</td>
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<td>Very-low</td>
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<td>Medium–high</td>
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</tr>
<tr>
<td>Trifluralin</td>
<td>Very high</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>Terbutryn</td>
<td>Medium</td>
<td>Extremely high</td>
<td>High–very high</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
</tr>
</tbody>
</table>
sodium and imazapic, returned risk ratings for algae in the 'low' to 'low-medium' range. A number of the other currently widely used herbicides such as glyphosate and 2,4-D were predicted to pose risks to algae in the 'low' to 'medium' range. The herbicides posing the highest predicted risks to invertebrates were ametryn (high-very high; a regulated PSII herbicide), and the ‘alternative’ herbicide pendimethalin (‘medium-high’ overall ‘mobility + toxicity’ rating). MSMA, trifluralin and terbutryn all posed ‘medium’ risks, with all other herbicides posing ‘low-medium’ or risk lower. The two herbicides posing the highest risk to fish were pendimethalin and trifluralin (‘medium-high’). A number of herbicides including the regulated PSII herbicide atrazine, as well as S-metolachlor, metolachlor and terbutryn presented ‘medium’ risks to fishes, with all other herbicides ‘low-medium’ or below in their risk ratings.

### 4.2. Wet Tropics and Mackay-Whitsunday

The PIRI modelling for the two rainfall-fed sugarcane districts of the Wet Tropics and Mackay-Whitsunday produced very similar patterns and rankings of pesticide mobility and off-site toxicity across all modelled soil types, and we only present results here for a Wet Tropics silt soil type. Results were also similar to the lower Burdekin scenario in terms of relative ranking of herbicides (Table 3). There was, however, a minor shift towards slightly higher risk ratings for some herbicides, likely due to higher predicted surface water mobility risks in these two districts. Several herbicides such as diuron, metolachlor, and metribuzin all had slightly higher mobility risk ratings in the Wet Tropics and Mackay Whitsunday regions compared to the Burdekin, a result that flowed on to subsequent overall ‘mobility + toxicity’ ratings for these herbicides. This slight difference almost certainly reflected the higher wet season rainfall totals (1800 mm for Ingham, one of the ‘drier’ parts of the Wet Tropics and 1300 mm for the Mackay-Whitsunday district) in rain-fed districts compared to the dry-tropical climate experienced in the lower Burdekin cane farming district (~860 mm), which necessitates some form of irrigation to meet crop water demands.

Like the Burdekin scenario modelling, the suite of regulated PSII herbicides (diuron, atrazine, hexazinone and ametryn) all produced similar overall risk profile ratings to freshwater algae in the ‘high’ to ‘very high’ range. A considerable number of herbicides outside this regulated suite (terbutryn, metribuzin, MSMA, paraquat, trifluralin), however, again presented similar, and in some cases (S-metolachlor, pendimethalin, trifluralin), even higher risk profiles to algae than several of the regulated PSII suite. Several of the other currently widely used herbicides such as glyphosate and 2,4-D were predicted to pose risks to algae in the ‘low-medium’ to ‘medium-high’ range. The herbicides posing the highest predicted risks to invertebrates were ametryn (‘high-very high’ risk), and two alternative herbicides pendimethalin and trifluralin (‘high’ overall ‘mobility + toxicity’ rating). Glyphosate and diuron posed ‘medium-high’ risks to invertebrates. A range of herbicides such as S-metolachlor, diquat fluzifop-P, metolachlor, metribuzin, MSMA, and terbutryn posed ‘medium’ risks to invertebrates, with all other herbicides of ‘low-medium’ risk or lower. In the Wet Tropics modelling, risks to fish were slightly higher than the Burdekin, with two herbicides (pendimethalin, trifluralin) posing an overall ‘high-very high’ risk to fishes. A higher risk for a number of herbicides (ametryn, atrazine, diuron fluzifop-P, glyphosate, S-metolachlor, metolachlor, metribuzin, MSMA and terbutryn) with predicted risks in the ‘medium’ or ‘medium-high’ risk category occurred in the Wet Tropics compared to the Burdekin.

Detailed results of the PIRI model Wet Tropics scenario where major rainfall was delayed for at least 40 days post-application are presented in...
Table S1. In terms of general results, herbicides with longer soil half-lives (~100 days or longer) tended to remain in the same surface water mobility risk category as the scenario with a 4-day delay between application and rainfall. Persistent herbicides such as MSMA, metolachlor, trifluralin, pendimethalin and atrazine, therefore, remained at a ‘high’ risk of surface water mobility. Longer half-life herbicides such as hexazinone and paraquat similarly remained in the ‘medium’ mobility risk category. Shorter half-life herbicides such as metribuzin, glyphosate, ametryn and diuron presented lower mobility risks if there was a substantial delay between rainfall and application. Alternative herbicides such as isoxaflutole (a very short half-life) and trifloxysulfuron sodium notably decreased to a ‘very low’ risk of surface water mobility under the 40-day rainfall delay scenario. Decreases in any surface water mobility risk rating for any herbicide were subsequently reflected in lower overall environmental risk ratings when mobility and toxicity ratings were combined (Table S3).

5. Discussion

A desktop assessment was conducted to determine the relative risk posed by emerging ‘alternative’ herbicides compared to more traditional (and now regulated) PSII herbicides used in the sugarcane industry throughout the GBR catchment area. The PIRI semi-quantitative model was used to rank the pesticides in terms of relative risk of off-site runoff in surface water and also environmental toxicity across a range of indicative trophic levels. Results of PIRI analyses suggested that the risk profiles of several of the proposed ‘alternative’ herbicides in the Australian sugarcane industry, with regard to both susceptibility to offsite movement and environmental toxicity, are very similar to the risks posed by currently regulated PSII herbicides. In some cases, these ‘alternatives’ appear likely to present potentially greater environmental issues under standard application rates and bioclimatic regimes of GBR catchments compared to several of the more traditional and now regulated herbicide suite. Given this risk modelling used application rates and practices allowed prior to reef specific regulations of PSII herbicides (atrazine, diuron, hexazinone and ametryn), the comparative risk of several ‘alternatives’ may be even more pronounced under the newly imposed regulatory regime.

While many of the regulated PSII herbicides have capacity for both pre-emergent (i.e. soil residual) and post-emergent (contact or ‘knock-down’) control of both grasses and broadleaf weeds, their most common usage in the Queensland sugarcane industry is for residual weed control. Several of the alternatives that can directly fill a specific pre-emergent (‘soil residual’) weed control function similar to PSII herbicides such as S-metolachlor, trifluralin, pendimethalin, and metribuzin all posed similar environmental risk profiles to regulated PSII herbicides. This, however, should not be a surprising outcome given the broad similarities in physico-chemical and toxicological characteristics of many of these emerging ‘alternative’ herbicides presented in Table 1. Several alternatives with a pre-emergent residual function such as isoxaflutole, trifloxysulfuron sodium and imazapic, did return risk ratings in the ‘low’ to ‘very low’ range. While these herbicides share some characteristics with regulated PSII’s, their much lower overall application rates almost certainly contribute to lower overall risk profiles. Many of the ‘alternative’ post-emergent (contact or ‘knock-down’) herbicides that are currently widely used in the Queensland sugarcane industry such as glyphosate, 2,4-D, MSMA, MCPA and paraquat were predicted to pose lower environmental risks than regulated PSII herbicides to most trophic levels, although several still posed risks in the ‘medium’ to ‘high’ range.

Not unexpectedly, the studied herbicides collectively posed the greatest toxicological risk to aquatic algae out of all of the assessed trophic levels. Due to their focus on freshwater ecotoxicological subjects, the PIRI risk predictions are especially relevant to freshwater ecosystems. Other recent pesticide risk assessments have also suggested that freshwater environments, by virtue of their closer proximity to agriculture in the GBR catchment, face some of the greatest risks of herbicide exposure (Davis et al., 2013; 2014) of any ecosystem types in the GBR catchment area. Results are also likely to be at least broadly transferable to other phototrophs in marine-estuarine GBR ecosystems such as phyto-microbenthos (Magnusson et al., 2012), seagrass (Flores et al., 2013) and coral zoanthellae (Shaw et al., 2012), all of which are likely vulnerable to herbicide exposure. Notably, while much of the concern surrounding herbicides typically relates to their potential effects on primary producers, several of the ‘alternative’ herbicides also posed higher potential threats than currently regulated PSII herbicides to higher level consumers such as aquatic invertebrates and fish. Any expected environmental benefits of broad-scale industry shifts away from regulated PSII to an alternative herbicide suite are not consistent, and need careful consideration to ensure substantial environmental benefits. Our study also only targeted herbicides, but a number of insecticides are in wider use in the sugarcane industry (imidacloprid, clothianidin, chlorpyrifos) as well as some fungicides (MEMC). All of these compounds have well known toxicity to aquatic animals, both invertebrates and vertebrates, and with emerging concerns surrounding some of these pesticides (Di Prisco et al., 2013), further analysis including these compounds is needed in the future.

5.1. Global studies on ‘alternative’ herbicides

Many of these ‘alternative’ herbicides, despite being registered in sugarcane for some time (often decades), have previously received minimal monitoring attention in the GBR context, and are only recently being added to standard pesticide analytical suites conducted as part of GBR catchment water quality monitoring programs (see Brodie et al., 2012). Due to additional analytical requirements (and hence costs) several herbicides that have been relied on heavily for decades by GBR catchment cane growers (paraquat, 2,4-D, glyphosate) have also received little, if any, monitoring attention at a catchment scale in the GBR (Davis et al., 2008). Beyond desktop modelling, there is currently very little relevant regional information to gauge the true capacity for off-site movement of alternative herbicides under GBR catchment cane farming systems and climatic regimes. While locally relevant GBR catchment data are sparse, several of these alternative herbicides (i.e. metolachlor, pendimethalin, isoxaflutole) have, however, seen much greater use in other industries at a global level, particularly northern hemisphere cropping systems. Paddock and catchment monitoring data from these areas can also shed valuable insights into the potential environmental issues associated with these emerging herbicides from an Australian sugarcane and GBR perspective. Studies of the movement dynamics and environmental detection frequency for herbicides such as isoxaflutole (Meyer et al., 2007; Lin et al., 2003; Allietto et al., 2012), metribuzin (Battaglin et al., 1998; Ludvigsen and Lode, 2001; Kjaer et al., 2005; Dores et al., 2006; Pilhalova et al., 2012; Oukali-Haouchine et al., 2013), metolachlor (Meyer et al., 2007; Erickson and Turner, 2002; Kolpin et al., 2002; Thurman et al., 1991; McConnell et al., 2007; McMillin and Means, 1996; Vallotton et al., 2008) and pendimethalin (Freitas et al., 2012) all underline a significant capacity for off-site movement across a range of farming systems and climatic regimes. Many of the environmental detections of these herbicides occur at frequencies and concentration exposure levels likely to pose significant risks to a range of aquatic fauna.

As in many other industries, glyphosate, one of the cheapest and widely used herbicides globally (Woodburn, 2000), is being increasingly advocated as a desirable alternative herbicide in the Australian sugarcane industry, in large part due to perceived environmental benefits. In spite of the reported strong sorption to soils and short soil half-life, researchers have nevertheless 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 for several bacteria and fungi, as well as for both invertebrates and vertebrates in terrestrial.
and aquatic ecosystems (Reylea, 2005a, 2005b; Druart et al., 2011; Vera et al., 2010; Helander et al., 2012). It is noteworthy that in addition to the glyphosate parent compound, there are risks associated with the main metabolite of glyphosate degradation, AMPA, or surfactants, which might be more toxic than glyphosate itself (Tsui and Chu, 2003). While there is little doubt glyphosate has many proven benefits from an agronomic perspective for its economical, broad-spectrum weed control, emphasis on its purported relative environmental benefits likely need to be made with more circumspection.

There are also several emerging issues with restricting the range of available herbicides (through either regulation or advocacy) in the GBR sugar industry that will likely pose potential additional challenges to growers. The repetitious use of the same herbicide over an extended period has caused documented cases of herbicide resistance in weeds (Beckie, 2011). The global emergence of glyphosate as a cornerstone of no-till agriculture in recent decades (Woodburn, 2000; Helander et al., 2012) has caused 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; Beckie, 2006, 2011). In addition to resistance issues, extended use of glyphosate has been suggested in some cases to benefit disease causing microbes and cause yield declines (Kremer and Means, 2009). Intensive use of a limited range of herbicides can accordingly have a range of negative ecological, environmental and agricultural risks in affected industries.

Agronomic and labelling restrictions for many of the suggested alternatives to regulated PSII herbicides (particularly several with lower predicted environmental risks from PIRI modelling) will also limit their widespread viability to many cane growers across the GBR. The efficacy of several prominent alternative herbicides is heavily contingent upon soil properties as well as farming system and geographic location. Non-PSII alternatives such as imazapic have existing restrictions on usage within 50 m proximity to wetlands and waterways, limiting application in areas with high numbers of waterways (e.g. the Wet Tropics). Isoxaflutole is adsorbed to organic matter and clay particles in the soil and is still active and achieves good weed control in high organic carbon (OC) soils. Soils with low OC and cation exchange capacity (CEC), however, have a reduced capacity to adsorb this particular herbicide in the soil matrix, which may result in the herbicide leaching past the weed root zone into the cane root zone (Bayer Crop Science, 2011). In addition to potential off-site movement, this characteristic makes the herbicide prone to leaching on certain soil types, potentially causing crop damage. Because of the significant concerns for leaching potential, Australian isoxaflutole labelling states the herbicide is not to be applied if CEC is less than 4.5 or soil organic carbon is 1% or less, a characteristic that will preclude its use from large areas of GBR cane land, particularly in the Wet Tropics.

The efficacy of metribuzin, one of the proposed alternatives to diuron, is highly dependent on sufficient soil moisture. Dry conditions with minimal rainfall cause very rapid breakdown of metribuzin following application, reducing longer-term weed control efficacy. As such, there are likely to be limitations on its effectiveness under certain climatic conditions in GBR catchments. The role of available ‘alternative’ herbicides in herbicide mixtures also poses potential risks from an environmental, if not agronomic perspective. The currently registered allowable usage of trifloxysulfuron sodium in Queensland sugarcane, an herbicide which rates a low overall environmental risk in the PIRI modelling, is only available as a formulation with ametryn, a regulated PSII herbicide which consistently rates as one of the highest environmental risk herbicides of any assessed in this study. With ametryn by far the dominant component of the herbicidal active ingredient in this registered product, shifts by growers away from perceived problematic herbicides such as diuron and atrazine, to ‘alternatives’ may again yield questionable environmental benefit.

The complex chemical dynamics of some herbicides also poses problems for risk assessment. A prime example is isoxaflutole, an herbicide applied at low doses (between 75 and 150 g/ha), it has the potential for widespread use in the next decades, particularly as a substitute for atrazine. 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 (see Table 1), it rapidly degrades to DKN, which has a longer half-life of 8–61 days (Pallett et al., 2001). In this sense, isoxaflutole acts as 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 KOC than its parent compound (Mitra et al., 1999). Lack of knowledge of the aquatic ecotoxicology of DKN makes informed risk assessment of this chemical currently difficult.

The variability in specific herbicide’s behaviour evident across the international scientific literature also highlights a substantial challenge for pesticide modelling efforts, including this study. By necessity much of the data input underpinning the PIRI model is based on literature values, often derived in environments very different from GBR catchments. Recent GBR pesticide modelling has highlighted the value of using locally derived parameters for physico-chemical properties of herbicides (half-lives, soil partitioning etc.) in improving model predictions of pesticide runoff (Anzooman et al., 2013). Paratax for example, an herbicide with a medium mobility risk rating according to PIRI predictions, has been rarely detected in paddock runoff from Queensland sugarcane sites (see Davis et al., 2013). Future pesticide modelling and risk assessment research should test locally calibrated (or measured) parameters for herbicide environmental and toxicological properties to ensure model relevance, and emerging research (Shaw et al., 2013) may offer this scope for more refined assessments.

5.2. Potential perverse environmental outcomes from pesticide regulation in the GBR

The processes by which imposition of regulatory compliance may become counterproductive are numerous and diverse, as are the generic pathways which give rise to them (Grabosky, 1995; Maclean, 2009). Results of this study do highlight several issues that current (and future) contemplation of pesticide regulation should consider. Reactive regulation of specific practices, with minimal consideration of the broader implications, may set the stage for a range of ineffective or potentially perverse environmental outcomes. Ad hoc regulation of individual herbicides within the Australian sugarcane industry may well simply shift usage to a new suite of herbicides that appear in many cases to provide marginal or poorly defined improvements to water quality, or alternatively increase risks of development of weed resistance. Similarly, broad scale shifts by growers to alternatives from traditional PSII herbicides could also maintain or increase the risk to the environment via other mechanisms. One of the key drivers of the sugarcane industry’s long-standing reliance on regulated PSIIIs is their demonstrated weed control capacity and cost-effectiveness. Increased regulation or deregistration of familiar and proven herbicides may force growers to begin testing and experimenting with new and unfamiliar chemical formulations, essentially ‘learning on the go’, with what are large-scale experiments of product efficacy. In addition to agronomic and economic effects, poor initial weed control measures may then prompt ‘recovery’ sprays with more powerful mixes, possibly in closer proximity to high risk wet season rainfall periods. Such approaches could have unpredictable, if not highly questionable, environmental outcomes for local wetlands and GBR ecosystems.

In addition many of the currently used group of herbicides, as well as many of the ‘alternatives’ were ‘grandfathered’ into the current regulatory regime without any new ecological risk assessment (King et al., 2013). Some of these herbicides have completed recent reviews (atrazine in 2008 and diuron in 2012), although the majority haven’t been subject to this process. Given the long timelines to conduct these
reviews (average period 14 years) it’s unlikely that any adequate new reviews or re-assessments will be completed in the near future (King et al., 2013).

5.3. The future of pesticide management in the GBR?

Whether the ‘carrot’ (i.e. incentives) or ‘stick’ (i.e. regulations) approach is best to expedite adoption of improved management practices by agricultural industries remains contentious (Posthumus and Morris, 2010). Rather than direct forms of government intervention-regulation there has, however, undoubtedly been a long-term trend in the Australian rural policy (including within the GBR catchment) towards initiatives that emphasise various forms of self-regulation for dealing with apparently intractable challenges that occur at the agri-environmental interface (Dibden and Cheshire, 2005; Lockie and Higgins, 2007). In spite of some positive developments, particularly on issues of education and awareness of environmental issues, the adoption of more sustainable management practices on Australian farms remains slow, and the changes driven by voluntary self-regulation are more often described as incremental rather than revolutionary or systemic (Lockie and Higgins, 2007). Furthermore, there is an increasing recognition that these self-regulatory measures have had minimal impact on actual natural resource condition beyond the scale of individual paddocks (fields) and properties, with indicators of regional or catchment resource condition such as water quality continuing their widespread national decline (Commonwealth Scientific and Industrial Research Organisation, 2003). This has been attributed to the predominant focus of practices maintaining productivity at the farm level; the significant number of farmers who still have not implemented them; and difficulty in translating the resulting patchwork of individual actions into cumulative, demonstrable results at a broad scale (Commonwealth Scientific and Industrial Research Organisation, 2003; Lockie and Higgins, 2007). Recent steps toward pesticide regulation and registration pressures likely represent a recent shift toward hybrid governance of agri-environmental issues, and perhaps represent a policy admission, that the recent self-regulation has produced only marginal environmental improvements at best. Results of this study suggest regulatory imposition needs to be better underpinned by measured consideration of the broader consequences of possible industry responses to regulation.

On a more promising note, recent research funded by the Australian and Queensland Governments under Reef Plan has identified improved management practices that can drastically reduce losses of PSII (and other) herbicides from paddocks, primarily via improved placement, timing, application methods and lower overall application rates (Masters et al., 2013; Silburn et al., 2013; Oliver et al., 2014). Regardless of regulatory considerations, future weed management in the GBR will certainly require more integrated and strategic weed management systems that encompass: minimised weed seed production and the size of soil seed banks, particularly in the early crop cycle; improved farm hygiene; improved herbicide timing and application techniques; weed resistance management incorporating rotational sequences and/or mixtures of herbicides with different modes of action within and between crop cycles; protection of the existing herbicide resource; and integration of non-herbicide weed management tools. One of the greatest emerging challenges for both industry and regulators is ensuring the requisite technical and extension support required for growers in what is now a very dynamic and monitored herbicide management environment. It is inevitable (if not already being manifest) that growers will increasingly have to grapple with increased regulation, often unfamiliar herbicide mixtures, the spectre of developing weed resistance, and rapidly developing application technologies. Much of the recent focus of Reef Plan initiatives has targeted the environmental science of best management practice and predicted improvement in water quality outcomes (see Carroll et al., 2012), and incentive funding for grower adoption of ‘best management practice’ (Brodie et al., 2012). Support for ongoing extension of research results and ensuring effective adoption of new farming systems and technologies and weed management strategies within the broader industry has thus far been a largely secondary concern, but one that needs emphasising.

6. Conclusions

Cane industry shifts towards alternative herbicides are now widely regarded as a key component of improved environmental outcomes for the GBR, and improved environmental stewardship on the part of the Queensland sugar industry. This desktop analysis found based on current farming practices, that while regulated PSII herbicides can pose significant environmental risks, many of the touted ‘alternatives’ present similar environmental risk profiles, regardless of farming system and bio-climatic zone being considered. While many herbicides may be viable alternatives in terms of weed control, they may still pose an equal or higher risk to the environment. Some of the apparently environmentally beneficial chemical characteristics of alternatives compared to traditional Australian sugarcane PSII herbicides also become questionable when subject to closer critical scrutiny. Several alternative herbicides (particularly those used at lower application rates and with shorter half-lives) have potential to limit off-site losses, but their properties, environmental fate and toxicology and broad scale applicability to all weed control scenarios are much less understood at this time. As a result, the apparent expectation that simply restricting or prohibiting the use of specific herbicides currently regarded as environmentally problematic will drastically reduce the risk of off-site environmental impacts of herbicides appears equivocal. Imposing additional regulations (or even de-registrations) on particular herbicides could result in negative environmental impacts in the long term, if usage simply shifts to alternative herbicides with similar risk profiles.

There will remain an ongoing need for residual herbicides in the Queensland sugar industry in weed management situations requiring pre-emergent, longer-term weed control. Rather than simply limiting or removing capacity for applying certain herbicides on an ad hoc basis, enhanced environmental outcomes are going to hinge more on generally improved on-farm pesticide management, and environmental stewardship practices that reduce the need for pesticides, rates of herbicides applied and reduce risk of off-site movement, regardless of the particular herbicides being used. In an industry grappling with a new chemical management environment, ongoing technical support and advice on the specific agronomic practicalities of using both traditional and emerging alternative herbicides and associated environmental risks are going to become increasingly important to the industry and individual growers.

Conflict of interest

All authors are of this manuscript have no current or potential conflict of interest including any financial, personal or other relationships with other people or organisations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, this work.

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