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Advancing our understanding of the source, management, transport and impacts of pesticides on the Great Barrier Reef

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Advancing our understanding of the source, management, transport and impacts of pesticides on the Great Barrier Reef

A Report for the Queensland Government Department of Environment and Heritage Protection

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Over the past 5 years, Great Barrier Reef pesticide research has been primarily funded by the Australian and Queensland Governments. The majority of this research has been conducted by Queensland Government Departments for Science Information Technology and Innovation (DSITI) and Agriculture and Fisheries (DAF), Australian Government Department of Environment, the Commonwealth Scientific and Industrial Research Organisation (CSIRO), the Australian Institute of Marine Science (AIMS) and various universities.

ACRONYMS USED IN THIS REPORT

AIMS	Australian Institute of Marine Science
APSIM	Agricultural Production System sIMulator
APVMA	Australian Pesticides and Veterinary Medicines Authority
BSES	Bureau of Sugar Experiment Stations
BMP	Best Management Practice
BRIA	Burdekin River Irrigation Area
CA	Concentration Addition
CDOM	Colour Dissolved Organic Matter
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DoE	[Australian] Department of the Environment
EHP	Queensland Government Department of Environment and Heritage Protection
DNRM	[Queensland] Department of Natural Resources and Mines
DSITI	[Queensland] Department of Science, Information Technology and Innovation (formerly Department of Science, Information Technology, Innovation and the Arts, DSITIA)
DAF	[Queensland] Department of Agriculture and Fisheries
EDC	Endocrine Disrupting Chemicals
ETV	Ecotoxicity Threshold Value
FEAT	Farm Economic Analysis Tool
FGM	Farm Gross Margin
GBR	Great Barrier Reef
GBRCA	Great Barrier Reef Catchment Area
GBRCLMP	Great Barrier Reef Catchment Loads Monitoring Program
GBRMPA	Great Barrier Reef Marine Park Authority
GV	Guideline Value
IA	Independent Action
IWMP	Integrated Weed Management Plan
JCU	James Cook University
MCA	Multiple Criteria Analysis
MMP	Marine Monitoring Program
ms-PAF	multisubstance-Potentially Affected Fraction
NERP	National Environmental Research Program (now NESP - National Environmental Science Programme)
NFS	New Farming System
NPV	Net Present Value
NWQMS	National Water Quality Management Strategy
PWG	Pesticide Working Group
P2R	Paddock to Reef integrated monitoring, modelling and reporting program
SST	Sea Surface Temperature
TV	Trigger Value
WQG	Water Quality Guidelines

ABBREVIATIONS USED IN THIS REPORT

a.i	active ingredient
approx.	approximate
assoc.	association
g.a.i	grams of active ingredient
PSII	photosystem II
ha	hectares
vtg	Vitellogenin

ABOUT THIS REPORT

This report provides a synthesis of the key findings of pesticide research conducted in the Great Barrier Reef (GBR) and is designed to update the previous 2006 – 2010 synthesis report by Devlin and Lewis (2011). The report was commissioned and supported by the Queensland Department of Environment and Heritage Protection (EHP). We have attempted to capture all relevant published pesticide research which has been conducted since 2009 through various funding agencies as well as, where relevant, unpublished or soon-to-be published information.

1. EXECUTIVE SUMMARY

1.1. Scope of report

Five photosystem II (PSII) inhibiting herbicides (ametryn, atrazine, diuron, hexazinone, tebuthiuron) were identified as priority pollutants for management under the 2009 Reef Water Quality Protection Plan for the Great Barrier Reef (GBR). As a result, considerable investment has been made to understand their physico-chemical properties, transport, fate, toxicity and the risk they pose as well as to quantify the water quality benefits and economic feasibility of on-farm management practices to reduce losses to adjacent waterways and into the GBR. To a lesser extent, similar research on proposed 'alternative pesticides' (insecticides, herbicides and fungicides) available to farmers has also been undertaken. Overall, improved understanding has been generated on the physico-chemical properties, transport, risk and management of pesticides in the GBR since the previous synthesis report was released (Devlin and Lewis, 2011; Much of this new research has occurred through various funding programs including the Queensland Department of Environment and Heritage Protection's (EHP) Reef Water Quality (RWQ) science program (e.g. examining alternative pesticides and the economics of the P2R ABCD framework) the Reef Rescue Research and Development Program (e.g. examining pesticide runoff from various industries, management options, pesticide properties, risk and ecotoxicity), the Paddock to Reef Integrated Monitoring, Modelling and Reporting Program (P2R) and the National Environmental Research Program (e.g. pesticide properties and ecotoxicity). Indeed this research has been conducted by a wide range of organisations including universities (James Cook University, University of Queensland and University of Southern Queensland), CSIRO, AIMS and Queensland Government departments (DSITI, DNRM and DAF) often in collaboration across many research groups. This document is designed to update and synthesise the latest research and knowledge on pesticides in the GBR.

Specifically, large advances have been made in obtaining pesticide physico-chemical data (e.g. soil and water half-lives and partitioning); farm-scale runoff of the priority PSII and alternative pesticides from different industries; the exposure and risk of PSII herbicides across the Great Barrier Reef Catchment Area (GBRCA) and lagoon through the use of methods for estimating the joint toxicity of mixtures; improvements in modelling of the priority PSII herbicide loads; the farm economics of implementing herbicide best management practices; ecotoxicological information on a greater suite of foundation species, alternative herbicides, examining cumulative effects with other stressors and the development of improved water quality guidelines for the freshwater, estuarine and marine ecosystems of the GBR.

The report is split into four sections that encompass the recent developments on (1) key sources and pesticide management; (2) pesticide transport, exposure, detection and fate; (3) ecological risk of pesticides and; (4) the economics of improved land management practices. In that regard, the focus of the report is designed to follow the key pesticide information from the paddock through to the marine environment.

1.2. Key sources and management

While very limited specific pesticide usage data are currently available, monitoring programs throughout the GBR and engagement with farmers and industry extension officers have provided insight into the spatial and temporal dynamics of pesticide use. Indeed changes in the detection frequencies, concentrations and loads of pesticides measured in catchment monitoring programs signify considerable changes in industry practices over the past few years. For example, monitoring data from waterways draining sugarcane lands show an increase in the detection, frequency and concentrations of metolachlor, metribuzin and isoxaflutole which temporally correlate with regulatory change (namely temporary bans on usage) for PSII herbicides. Similar changes in pesticide use appear to have occurred in the banana, grains and grazing industries in recent years. Monitoring programs have detected up to 55 different pesticide residues (including metabolites) in waterways of the GBRCA. Despite the apparent shifts in industry practices, the priority PSII herbicides continue to contribute the highest loads to the GBR and are predominately sourced from the sugarcane (ametryn, atrazine, diuron and hexazinone) and cattle grazing (tebuthiuron) land uses. The availability of industry-specific usage data would not only inform monitoring programs but also improve modelling outputs and so a greater linkage with relevant industries is required to facilitate communication between researchers, managers, regulators and end users so these data may become more accessible.

The half-lives of several herbicides under a range of different soil types with varying pH, texture (i.e. particle size) and organic matter contents have been determined under field and controlled laboratory conditions. Results showed that the half-lives of some herbicides varied considerably between soil type and that some herbicides had half-lives much longer or much shorter than values reported in the literature. The data also highlighted the differences between laboratory soil half-lives and field dissipation rates, the latter being influenced by additional factors including washoff and UV light. The outcomes of this research are now being incorporated into the latest Source Catchments model (eWater) to more accurately predict herbicide loads from cropping and grazing lands in the GBRCA.

A number of studies have examined different management options for the runoff of herbicides particularly from the sugarcane and cotton industries. Studies on banded/shielded spray applications, spot spray technology (e.g. Weedseeker®), controlled traffic, shifts to alternate pesticides, timing of application and changes in use in sugarcane ratoons have been conducted and have shown considerable promise in reducing pesticide losses from paddocks. Trials have shown 90% reductions in losses of residual herbicides are possible using banded spraying on irrigated sugarcane paddocks while at least 50-60% reductions are achievable in rain fed systems. Spot spray trials showed that the losses of herbicides from paddocks reduced in proportion to the area sprayed and considerably less herbicides were lost when runoff occurred around 20 to 30 days (or longer) after application, compared to earlier runoff. Rainfall simulation trials throughout the GBRCA have yielded valuable information on the loss pathways of several herbicides (dissolved versus particulate phases); the quantification of (likely) maximum percentage losses of applied active herbicide ingredients; and have allowed the direct comparison of various herbicides in current use. A study on tebuthiuron application in grazing lands also provided important information on movement in soil and loss in runoff, leaching and fate in soils over time after application and examined the differences between two product formulations (flowable versus granular).

1.3. Transport, exposure, detection and fate

Monitoring programs have shown that diverse mixes of pesticides are detected in waterways and groundwaters of the GBRCA and marine environment. These findings demonstrate that multiple pesticides are moving offsite from their point of application. Most monitoring programs show that the highest in-stream concentrations of pesticides coincided with early wet season (or first flush) runoff events, although this is not always the case for larger rivers such as the Fitzroy or streams that receive regular irrigation tailwater inputs, such as Barratta Creek, in the lower Burdekin region. These findings illustrate that some streams in the GBRCA will be transiently exposed to concentrations of pesticides which approach or exceed ecological protection guidelines/thresholds as well as other water guidelines (e.g. irrigation). Depending on the location, exposure to elevated pesticide concentration may last a few hours to several months. Recent research has revealed how pesticides are transported in the waterways of the GBRCA. The pesticides most commonly detected in monitoring programs are predominately associated with the dissolved phase. Flood plume monitoring shows that the pesticides are ‘conservatively mixed’ as the freshwater discharge mixes and becomes diluted with seawater. Moreover research on the degradation rates in seawater of eight common herbicides used in the GBRCA reveal half-lives ranging from months to years. This finding explains the results from passive samplers in the GBR lagoon where herbicides can be detected at concentrations above 1 ng L^{-1} throughout the year. Collectively these studies on the transport, mixing and degradation of herbicides allow simple transport models to be developed to better assess the exposure and risk of pesticides in the GBR (Kennedy et al., 2012a, 2012b).

1.4. Ecological risk

Important research has recently been carried out to determine the ecotoxicity of certain herbicides to relevant freshwater and marine species in the GBRCA and lagoon. Direct toxicity assessments have been completed on freshwater algae for certain herbicides while stream assessments of macroinvertebrate and diatom communities have been performed to examine relationships between herbicide exposure and the sensitivity of different species within these populations. New ecotoxicity data of PSII herbicide effects have also recently become available on estuarine and marine species of the GBR including diatoms, green algae, benthic microalgae, foraminifera, seagrass and corals. The effects of certain pesticides on fish have also been examined. Furthermore, studies have demonstrated the additive and synergistic effects of PSII herbicides with changes in temperature on corals and foraminifera. Collectively these studies have allowed the refinement of water quality guideline threshold values relevant for species of the GBR; permitted more thorough risk assessments to be performed; and helped improve the reporting of herbicide exposure in the Marine Monitoring Program. Indeed the latest risk profiles for the GBR show that the highest impact from pesticides occur in coastal freshwater wetlands with medium impacts to estuarine and inshore marine waters. Finally, research under the current regional Water Quality Improvement Plans have developed ecologically relevant targets for PSII herbicides based on the results of the monitoring and toxicity data.

1.5. Socio economics of improved management practices

The widespread adoption of Best Management Practices (BMPs) that improve water quality at the farm-scale level is heralded as a key mechanism in improving the overall health of GBR ecosystems. Industry and government have together invested significant resources aimed specifically at increasing the adoption of management practices that lead to improved water quality outcomes on farms. However, adoption of new practices by farmers (whether to improve environmental outcomes or productivity) is the result of a complex decision-making process where relative advantage, especially in economic terms, is a key motivator. Farmers will be unlikely to readily adopt unproven practices if the changes are perceived as a high risk to farm profitability. Novel analytical methods incorporating bio-physical, economic and water quality data (using the ‘additive toxicity’ concentration of the herbicides) highlight the private (profitability) and public (improved water quality) benefits of improved herbicide management practices on banana and sugarcane farms.

For sugarcane, a number of key principles and management practice options were identified as having the potential to improve water quality as well as enhance profitability. Nonetheless, these results are found to be critically dependent on regional-specific variables including biophysical characteristics and enterprise structure, especially in relation to farm size. These findings reinforce the notion that future research and policy development should be targeted at the individual, farm-enterprise level in order to enhance adoption rates of these new management practices among farmers.

Key findings from a recent research project indicate that a transitioning from C- to B-class herbicide management practices in sugarcane is the most profitable and cost-effective overall, irrespective of farm size. For example, the Tully analyses indicated that a transition from *C-* to *B-Class* herbicide management was likely to provide the greatest economic benefit per unit abatement of PSII pesticides. Transitioning from B- to A-class herbicide management practices is generally expected to come at an economic cost for a

50 ha farm (although benefits for larger farms were noted). This negative economic outcome is predominantly due to the size of the capital expenditure requirement relative to the farming area. An important implication from this finding is that farm size matters; this is especially the case where capital costs are required for the adoption of new practices. Although the adoption of A-class herbicide management practices tended to be profitable for larger farms, the risk analysis highlighted the importance of ensuring production is maintained in order to remain profitable.

Based on current prices used at the time of the economic study for sugarcane, changing from standard to alternative chemicals will generally come at a financial cost across all herbicide management classes, despite showing potential for water quality benefits. These findings are subject to further research into the use of alternatives for specific agronomic situations, changes in product cost and more recent studies on herbicide toxicity which have questioned the true environmental benefits of a shift in herbicide products from the traditional PSII herbicides.

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2. INTRODUCTION

2.1. Background

Pesticides pose a risk to freshwater, inshore and coastal ecosystems of the GBR. Their presence in waterways and in the GBR lagoon can cause direct and indirect effects which reduces the resilience of aquatic ecosystems to other stressors (e.g. climate change). Diffuse source pollution from agriculture is the largest contributor of pesticides to the GBR, with beef cattle grazing and sugarcane cultivation comprising the dominant land uses in GBR catchments (Brodie et al., 2013b). Varying levels of research have studied GBR-specific pesticide use rates, application methods, off-site transport, the impact on aquatic ecosystems and water quality guidelines. This report summarises the new GBR pesticide research which has occurred since 2010 and contains recommendations for government and industry on future policy directions and potential investments in identified priority research and extension areas.

In this report we focus on all pesticides that have been detected in monitoring programs or known to receive wide usage in the GBRCA including the priority photosystem II (PSII) inhibiting herbicides: ametryn, atrazine, diuron, hexazinone and tebuthiuron as well as several alternative pesticides. We note that the term 'pesticide' is used in this report to collectively refer to herbicides, insecticides and fungicides.

2.2. Stakeholder engagement

This report drew upon a collective of researchers, industry staff and government stakeholders within the 'Pesticide Working Group' (PWG; a forum involving government bodies, research groups and industry). The PWG includes researchers and representatives from a range of stakeholder groups and previous research activities. PWG workshops bring together researchers, managers and industry representatives working specifically on pesticide research, monitoring and management in the GBR. The workshops showcase the latest information from new research projects. The workshops have precipitated regular communication between the groups, facilitating a more coherent discussion on the role of pesticides in GBR, status and management. Hence the PWG provides an important avenue for the report to be presented and evaluated by relevant stakeholders.

The most recent PWG meeting (held in November 2014) recognised the need for a joint industry-government funded project to consolidate the last three to four years of pesticide research outcomes relevant to the water quality and ecosystem health of the GBR. A previous pesticide synthesis report was compiled by the Marine and Tropical Sciences Research Facility (MTSRF) in 2011 (Devlin and Lewis, 2011), however the surge of large scale research efforts on pesticides over the past three to four years has not yet undergone a detailed synthesis process.

A sub-group of researchers from the PWG were commissioned to synthesise all pesticide research conducted since the publication of the previous Pesticide Synthesis Report (Devlin and Lewis, 2011).This was done to improve the understanding of recent research findings and present this in a manner useful for managing, monitoring and regulating pesticides and their impacts.

This project will contribute to increasing the knowledge of, and improving the management of, pesticide use, transport mechanisms and impacts in the GBR catchments. It will also contribute to future updates of Reef Plan (2013) and the 2013 Scientific Consensus Statement (Brodie et al., 2013b).

3. KEY SOURCES AND PESTICIDE MANAGEMENT

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3.1. Summary of key findings

- Herbicide data collected across a multitude of GBRCA land uses (grazing, urban, horticulture, forestry and intensive cropping) showed that diffuse load losses were highest from intensive agriculture.
- The greatest risk window for herbicide losses from paddocks in rainfed farming systems is within 25 days of application. In worst case scenarios, where heavy rainfall followed herbicide application, losses up to 18% of applied active ingredient were documented from some trial sites.
- In irrigated farming systems, where paddocks are typically irrigated 2-4 days after herbicide application, >80% of annual herbicide losses occur in the two irrigations following application. Losses of between 6-8% of applied herbicide active ingredient were common in the first irrigations following application.
- Rainfall simulation trials comparing the movement potential of a range of priority, alternative and knockdown herbicides provided a valuable complement to recent paddock scale pesticide research.
- Rainfall simulation results showed knockdown herbicides were generally lost in the lowest proportionate amounts compared to the residual herbicides. Several alternative residual herbicides such as metribuzin and metolachlor showed very similar susceptibility for offsite movement as the priority PSII herbicides, which suggests care should be taken in their promotion as 'alternatives'. In the case of several other residual alternatives such as isoxaflutole and imazapic, their lower application rates to the paddock meant that their runoff loads were approximately an order of magnitude lower than for the PSII herbicides. If their toxicity is equivalent (or less) than priority PSIIs, their overall environmental risk is likely to be reduced (although further research is required).
- Glyphosate sprayed on soil was still prone to runoff despite purportedly higher soil sorption properties compared to many other herbicides.
- Paddock trials for the grazing herbicide tebuthiuron showed that on a clay soil, granular tebuthiuron had twice the loss in runoff (0.75 kg/ha or 25% as a percentage of a.i. applied) than the dry flowable (liquid) formulation (0.35 kg/ha or 12% of applied active). On a duplex soil the difference in the tebuthiuron losses in runoff were not significant between formulations.
- The majority of herbicide runoff from paddocks was found to be in the dissolved phase with the exception of pendimethalin, glyphosate, diuron and imazapic. Herbicides at the sub-catchment level were also predominately (>80%) transported in the dissolved phase.
- Half-lives measured under a glasshouse trial for several of the alternative herbicides degrade much faster in soil than reported in the international literature. The exception was isoxaflutole which degraded >10-fold slower which may reflect the reduction of UV light in the glasshouse.
- There is a lack of consistent trends between field and laboratory herbicide soil half-lives. Hence the use of the glasshouse trial half-lives is more appropriate in modelling as they exclude losses from runoff, leaching and plant uptake (which are considered separately).

- In the absence of reliable pesticide usage data in catchments and with limited knowledge of management practice changes, changes in pesticide use can often only be inferred from water quality monitoring data.
- Management practices that reduce overall rates of herbicides applied to paddocks hold considerable potential for longer term water quality improvements. Spot spraying paddock trials showed positive correlations between percentage of the paddock sprayed and herbicide runoff concentrations. The application of residual herbicides (e.g. atrazine and diuron) to raised beds through banded application is highly effective in reducing herbicide losses from paddocks (~50-60% reduction in rainfall fed systems and 80-90% in irrigated systems) while maintaining adequate weed control.
- An overall farming management system approach is required to reduce herbicide losses from the paddock. These include factors such as improved on-farm hygiene, more strategic timing of application and product selection, controlling weeds early in the plant crop cycle, and precision/targeted application.

3.2. Introduction

Pesticides are invaluable to agriculture and other industries to ensure pests are controlled and productivity is maintained. The primary pests affecting productivity (and hence requiring control) vary markedly across different commodities in the Great Barrier Reef Catchment Area (GBRCA). Industries such as mixed horticulture and bananas may require herbicides, but their primary pest management focus is on insect and fungi control. Australian sugar production is, alternatively, particularly reliant on a wide variety of herbicidal applications, and a more restricted range of insecticidal controls (Johnson and Ebert, 2000; Cavanagh, 2003). While much research has focussed almost entirely on herbicides in the GBRCA, several other crop pests (insects, fungi) also require control within certain industries. Canegrubs, particularly the greyback canegrub (*Dermolepida albohirtum* (Waterhouse)) are the primary pest insect requiring control by canegrowers in the GBRCA, although crickets (*Teleogryllus* spp.), armyworms (*Spodoptera exempta* (Walker)), wireworms (*Agrypnus variabilis* (Candèze) and *Hetereoderes* spp.*)* and symphylans (*Hanseniella* spp.) require occasional management (Davis et al., 2008). Chlorpyrifos is still used by some growers across the GBRCA, although the purportedly more effective chloronicotinyl insecticide imidacloprid has very recently risen to prominence as the most commonly-applied insecticide for canegrub control (Hunt et al., 2012).

The current herbicide management environment in the GBRCA is the result of a long and dynamic history of target pests, farming system evolution and shifting natural resource management agendas. Recent industry transitions toward new farming practices, particularly minimum or zero tillage systems have exacerbated the reliance on herbicides in industries such as sugarcane, particularly for the control of weeds in ratoon crops (Hargreaves et al., 1999; Johnson and Ebert, 2000). The primary driver for increasing herbicide use in farming systems has been for soil conservation in industries where cultivation was historically commonly used as a weed control strategy (and historically accounted for the majority of paddock tillage events) (Holden et al. 1998). Government and industry research and extension investments for several decades focused on reducing tillage and soil conservation (Prove et al., 1995), with herbicide usage a necessary consequence of reducing or eliminating tillage.

The Australian sugarcane industry has, accordingly, been particularly reliant on residual PSII herbicides (predominantly for pre-emergent weed control) such as ametryn, atrazine, diuron and hexazinone for several decades (see Johnson and Ebert 2000; Davis et al., 2014a). PSII herbicides have a mode of action that blocks photosynthetic electron transport at the photosystem II reaction centre. The Queensland sugar industry has commenced a transition towards a suite of herbicides as alternatives to the priority PSII herbicides currently used. This is likely to have arisen due to a voluntary shift by the industry as part of their improved environmental stewardship and due to recent legislatively imposed restrictions on the use of PSII herbicides (Davis et al., 2014a). Transition towards an 'alternative' herbicide suite is now widely advocated as a key component of improved environmental outcomes for Australia's Great Barrier Reef (GBR), and improved environmental stewardship on the part of the Queensland sugar industry (e.g. Brodie et al., 2013). Herbicides utilised in other industries have also attracted recent attention from a GBRCA perspective. Tebuthiuron is used to control regrowth of Brigalow (*Acacia harpophylla*), tea tree (*Melaleuca spp*.) and other problem woody weeds on grazing lands (Dow AgroSciences 2013a, 2013b; Thornton and Elledge, 2013). It is applied to the soil in a granular pellet form which is then absorbed by plant roots and translocated to target sites in the stems and leaves (Thornton and Elledge, 2013). There has been an increase in tebuthiuron use to remove plantation timber species in several northern Queensland coastal catchments devastated by Tropical Cyclone Yasi in 2011. Many of these plantations are now producing sugarcane again. The urgency to turn these properties back in to sugarcane production may have seen tebuthiuron applied under less than ideal conditions in most Wet Tropics catchments.

This chapter provides a synthesis of the available data on pesticides associated with different land uses in the GBRCA, the current knowledge on the transport of pesticides at the paddock scale and the advances in management practices available to farmers to better mitigate pesticide losses while still providing effective pest control. A summary of the recent research efforts are provided along with the major knowledge/research gaps that remain.

3.3. Sources of pesticides and usage

Annual average modelled load estimates of the five priority PSII herbicides (i.e. ametryn, atrazine, diuron, hexazinone and tebuthiuron) to the GBR vary between 13,800 and 30,000 kg per year (Lewis et al., 2011; Kroon et al., 2012; Barson et al., 2013; Waters et al., 2014). In total, 55 different pesticides (including metabolites) have been detected in monitored waterways of the GBRCA (Table 3-1) and so the preceding estimates of PSII loads are underestimates of the total annual overall 'pesticide' load to receiving environments. Indeed, commonly used pesticides such as glyphosate and paraquat are rarely included in standard analytical suites and hence poor monitoring data are available for pesticides outside of the current standard analytical suite (Davis et al., 2008), although monitoring data for these are now becoming more frequently available. For example, Wallace et al., (2014, 2015) and Smith et al., (2015) have expanded their monitoring to include pesticides outside of the typical monitored suite.

3.4. Land uses as pesticide sources

Many of the pesticides detected in monitoring programs are registered to a multitude of different crops and land uses. Targeted monitoring within the GBRCA has been able to associate various pesticides with specific land uses including sugarcane (Bainbridge et al., 2009; Lewis et al., 2009; Smith et al., 2012, 2015; Davis et al., 2013; O'Brien et al., 2013a; Wallace et al., 2014, 2015), horticulture (i.e. mixed crops in Bowen and Atherton Tableland regions: Lewis et al., 2007; O'Brien et al., 2014a), cotton (McHugh et al. 2008; Silburn et al., 2013), urban (including sewage treatment plants -STPs: Liessmann et al., 2007; Lewis et al., 2009; O'Brien et al., 2014a), bananas (Masters et al., 2014a), grazing (Lewis et al., 2009; Packett et al., 2009; Smith et al., 2012; Thornton and Elledge, 2013; Wallace et al., 2014, 2015), forestry (Leslie, 2010) and broadacre cropping (Packett et al., 2009; Murphy et al., 2013) (Table 3-1). In most cases, the highest concentrations of pesticides in runoff were associated with intensive cropping lands, including sugarcane, cotton and broadacre cropping. While a total of 17 pesticide residues (not including metabolites) were detected in sewage treatment plants (STPs; treated water) in the Cairns region (O'Brien et al., 2014a), the concentrations (and water volumes) were relatively low compared to runoff from diffuse cropping lands. For example, of the 17 pesticide residues detected in the treated STP water, diuron had the highest concentration of 0.685 $\mu g\ L^{-1}$ (and a minimum of 0.049 $\mu g\ L^{-1}$) and the water volume discharged over the monitored three month period (Southern STP) was 2336 ML (O'Brien et al., 2014a; i.e. using the maximum concentration, the total diuron load from this plant over the 3 month period was 1.6 kg). In comparison, diuron concentrations in waterways draining cropping lands can exceed 10 $\mu g.L^{-1}$ (O'Brien et al., 2013a) and loads for certain pesticides can be in the 10's to 100's of kilograms over a short duration (1-2 week) flow event (e.g. Lewis et al., 2009; Packett et al., 2009; Davis et al., 2012; Turner et al., 2012; 2013; Wallace et al., 2014, 2015). Indeed, monitoring and modelling data have shown that the bulk loads of the five priority PSII herbicides predominantly originate from sugarcane, grazing and broadacre cropping (e.g. Turner et al., 2012, 2013; Wallace et al., 2014, 2015; Waters et al., 2014).

3.5. Current pesticide usage

Unfortunately pesticide usage data across land uses and within catchments are generally unavailable or too uncertain to allow any meaningful prediction or modelling of concentrations in runoff on the basis of annual application data. These data limitations make it difficult for the calculation of catchment losses (of active ingredient applied) and to assess their overall risk. While some historical usage data exist for the 1990s (e.g. Hamilton and Hayden, 1996; Johnson and Ebert, 2000; Simpson et al., 2001a), these are now long outdated and are unlikely to reflect current pesticide usage. The Department of Environment's Agricultural Chemical Usage Database displays usage data across river basins from 1997 to 2006, but do not cover all pesticides (e.g. tebuthiuron) and the 'annual application data' have very wide ranges. For example, atrazine application in the Haughton basin for 2006 is listed to range from 12,344.5 to 94,630.8 kg. Hence, monitoring of waterways in the GBR is currently the most reliable method to assess changes in pesticide use and assess their risk in the GBRCA and lagoon (e.g. O'Brien et al., 2013a; Smith et al., 2015). Industry extension staff can also provide important information on general pesticide usage and changes occurring in their respective industries. For example, total pesticide usage in the banana industry is purported to have reduced by 90% in the past 5 to 10 years (J. Armour, pers. comm., 2014).

3.6. Pesticide transport at the paddock scale

3.6.1. Pesticide properties and persistence studies

A variety of inherent physico-chemical and toxicological characteristics define the likelihood of off-paddock transport of pesticides (Simpson et al., 2000; Wauchope et al. 2002). Table 3-1 outlines several key properties of detected over the past 8 years in GBR water quality monitoring programs as well as those known to be in wide use or likely to fill emerging weed control gaps (at least in part) for GBRCA industries. Many of these herbicides, particularly those likely to fill a similar weed suppression role to priority PSII herbicides, often share similar physico-chemical profiles to the priority PSII herbicides that are currently regarded as environmentally problematic. As well as limited ecotoxicological data on relevant target biota (as discussed in Section 5), there are particularly limited data available to inform prediction of the fate of herbicides in tropical environments, specifically in terms of their propensity for off-site movement, and also likely persistence in the environment. The majority of available soil half-life data have been derived in temperate environments (Sanchez-Bayo and Hyne, 2011). Reviews of available fate data for tropical environments indicate that herbicides will generally dissipate more quickly due to higher temperatures and wetter conditions (Racke et al., 1997; Sanchez-Bayo and Hyne, 2011). For example, atrazine dissipation in subtropical Queensland was found to be rapid such that a 90% loss occurred in 36 days, whereas the corresponding loss took 375 days at a site in Tasmania with a colder climate (Kookana et al. 2010). The ability to accurately predict the fate of herbicides is an important aspect to assessing the environmental risks of application and making informed land management decisions.

Table 3-1: Summary table outlining environmentally relevant physico-chemical properties for detected and commonly used pesticides in the GBR catchment. Chemical and ecotoxicological properties compiled using the 'Footprint' Pesticide Properties Database (http://sitem.herts.ac.uk/aeru/footprint/en/index.htm) unless otherwise indicated.

Pesticide	**Solubility in Water**	**Soil Degradation (days/aerobic)**	**Soil sorption**	**Glasshouse half-life**[a]	**Typical tropical half-life**[c]	**Field half-lives in the GBRCA**
	@ 20°C (mg L^{-1})	DT_{50} (typical) (days)	K_{OC}	(days)	(days)	(days)
PSII herbicides covered under Reef Plan targets and Reef Water Quality Program requirements ('Priority' PSII herbicides)						
Ametryn	200	37	316	25, 13-41	25, 17–33	14.7, 20, 231
Atrazine	35	75	100	17, 12–22	13, 5–41	3.7, 8, 10, 12, 15.5, 17, 25, 33
Diuron	35.6	75.5	813	72, 14–200	16, 15–31	23, 38, 69.3, 77, 199; 20[b]
Hexazinone	33000	150	54	51, 33–97	21, 20–21	7, 19, 53, 119, 173
Tebuthiuron	2500	400	80	142, 70–260	-	-
'Alternative' PSII herbicides						
Metribuzin	1165	11.5	95	28, 16–62	-	3, 5, 7, 16.9
Simazine	5	60	130	-	-	-
Terbutryn	25	74	2432	-		-
Bromacil	815	60	32	-	-	-
Prometryn	33	41	400		-	20[b]
Terbuthylazine	6.6	75.1	-	-	-	19.6[b]
Fluometuron	111	63.6	-	-	-	-
'Alternative' herbicides						
Glyphosate	10500	12	1435	25, 18–42	31, 9–50	7.8, 21.4, 42.1
Imazapic	2230	120	137	37, 20–81	-	13, 15.8, 118
Isoxaflutole	6.2	2	145	18, 14–22	-	2.3
Metolachlor	530	90	120	-	-	-

Pesticide	Solubility in Water	Soil Degradation (days/aerobic)	Soil sorption	Glasshouse half-life[a]	Typical tropical half-life[c]	Field half-lives in the GBRCA
	@ 20°C (mg L^{-1})	DT_{50} (typical) (days)	K_{OC}	(days)	(days)	(days)
S-metolachlor	480	15	2261	29, 17–50	33, 14–47	6.1, 13.6, 17, 34, 69.3; 29[b]
Pendimethalin	0.33	90	17581	40, 29–60	32, 13–1396	18, 23.1, 37; 33[b]
Picloram	560	82.8	13	-	-	-
2,4-D	23180	10	88.4	18, 14–22	1, 0.5–1.3	9.4, 11.7, 13.9, 27.6
Triclopyr	8100	39	27	-	-	-
Trifluralin	0.221	181	15800	-	-	-
Asulam	962000	3.2		-	-	-
Imazethapyr	1400	90	52		-	-
Fluroxypyr	6500	1	-	-	-	-
MCPA	29390	24	-	-	-	-
Propazine	8.6	131		-	-	-
Mecoprop	250000	8.2	-	-	-	-
Acifluorfen	250000	54	113	-	-	-
Clomazone	1102	83	300	-	-	-
Metsulfuron-methyl	2790	10	-	-	-	-
Glufosinate-ammonium	500000	7.4	600	-	-	-
Pyrithiobac sodium	728000	60	0.22 to 0.59	-	-	10–14[b]
Haloxyfop	1.6	9	-	-	-	-
Insecticides						
Imidacloprid	610	191	-	-	-	-
Bifenthrin	0.001	26	236610	-	-	-
Chlorfenvinphos	145	40	680	-	-	-

Pesticide	Solubility in Water	Soil Degradation (days/aerobic)	Soil sorption	Glasshouse half-life[a]	Typical tropical half-life[c]	Field half-lives in the GBRCA
	@ 20°C (mg L^{-1})	DT_{50} (typical) (days)	K_{OC}	(days)	(days)	(days)
Clothiandin	340	545	123	-	-	-
Cypermethrin	0.009	60	156250	-	-	-
DEET	2-3	18-24	-	-	-	-
Fipronil	3.78	142	-	-	-	-
Permethrin	0.2	13	1.87	-	-	-
Chlorpyrifos	1.05	50	8151	-	-	-
Diazinon	60	9.1	609	-	-	-
Endosulfan	0.32	50	11500	-	-	-
Malathion	148	0.17	1800	-	-	-
Methamidophos	200000	3.5	1.0	-	-	-
Phosphamidon	1000000	9	-	-	-	-
Prothiophos	0.07	45	24158	-	-	-
2,6-Di-tert-butyl-p-cresol (BHT)	0.6-1.1	<1	-	-	-	-
'Of interest' pesticides not yet detected in GBRCA waterways						
Paraquat	620000	3000	10000000	339, 67–744	41, 36–46	260
Trifloxysulfuron sodium	25700	63.5	306	26, 17–37	-	-
MSMA	580000	200	7000	-	-	-

a – Shaw et al. (2014)
b – Silburn (2003)

Table 3-2: Pesticides detected in several monitoring programs in the Great Barrier Reef waterways have been associated with a number of different land uses.

Land use	Pesticides detected in monitoring	Key References
Sugar	Diuron, atrazine, ametryn, hexazinone, imidacloprid, imazapic, imazethapyr, isoxaflutole, MCPA, metolachlor, terbutryn, chlorpyrifos, metribuzin, fluroxypyr, 2,4-D, glyphosate, pendimethalin	Lewis et al. (2009); Bainbridge et al. (2009); Smith et al. (2012, 2015); Davis et al. (2013); O'Brien et al. (2013b); Wallace et al. (2014, 2015)
Horticulture	ametryn, atrazine, diuron, hexazinone, metolachlor, metsulfuron methyl, pendimethalin, picloram, prometryn, simazine, chlorpyrifos, diazinon, imidacloprid	Lewis et al. (2007); O'Brien et al. (2014a)
Cotton	Dimethoate, fluometuron, prometryn, trifluralin, simazine, endosulfan, pyrithiobac sodium, diuron, metolachlor	McHugh et al. (2008)
	* Pesticide use changed dramatically, from residuals to knockdowns, with glyphosate tolerant and BT cotton	Silburn et al. (2013)
Urban/STP	Diuron, 2,4-D, dichlorprop, atrazine, bromacil, carbaryl, DEET, diazinon, haloxyfop, hexazinone, MCPA, mecoprop, propoxur, simazine, tebuthiuron, terbutryn, triclopyr, malathion, endosulfan	Liessmann et al. (2007); Lewis et al. (2009); O'Brien et al. (2014a)
Bananas	Glufosinate-ammonium, glyphosate	Masters et al. (2014a)
Grazing	Tebuthiuron	Lewis et al. (2009); Packett et al. (2009); Thornton and Elledge (2014); Wallace et al. (2014, 2015)
Forestry	Simazine	Leslie (2010)
Broadacre cropping	Atrazine, metolachlor, diuron, simazine, 2,4-D	Packett et al. (2009); Murphy et al. (2013); Rogusz et al. (2013)

Recent research determined the half-lives of commonly applied sugarcane herbicides in Queensland in a controlled glasshouse environment on common cropping soils (Shaw et al., 2013), providing valuable insights into pesticide persistence in the GBRCA environment. For several of the well-studied herbicides, including atrazine and ametryn, the derived glasshouse half-life values were comparable international values from tropical field studies (Table 3-1). However, investigations of half-lives for several alternative herbicides, that have not previously been studied under local conditions (imazapic, pendimethalin, trifloxysulfuron), found half-lives were on average lower (they degraded faster) than published values. In contrast, the degradation rate of isoxaflutole (Product: 'Balance') was >10 fold slower than international values. Herbicides on cane residues (without rainfall) degraded slower than has been previously reported (Shaw et al., 2013). Adoption of the locally relevant half-life values from this study and Carroll et al. (2012) will improve prediction of herbicide losses under various management scenarios and therefore improve the prediction of loads of herbicides entering the GBR lagoon.

3.6.2. Field versus laboratory studies on persistence

Degradation studies in a controlled environment, such as the glasshouse, were able to eliminate the effect of alternative pathways of pesticide losses that can occur under field conditions, such as offsite transport through runoff or leaching (Shaw et al., 2013). Degradation rates measured in the glasshouse were also able to be compared to the dissipation of herbicides observed across a number of GBRCA field sites (Table 3-1). The half-lives determined in the controlled glasshouse environment were consistent with estimates from the field sites in many instances. For example, the half-lives of diuron measured in a black Vertosol from the Mackay Whitsunday region and pendimethalin measured in a brown Kandosol from the Tully region were similar to the field derived values (Shaw et al., 2013). On a brown Chromosol sandy loam soil from a cane demonstration farm in Bundaberg, the glasshouse derived half-life was the same as the upper estimate from the field for atrazine (17 days). However, the glasshouse derived half-life for this same herbicide was 1.7 times faster than the field derived value in the Wet Tropics. In contrast, degradation of hexazinone on a heavy Vertosol in the Mackay region was slower in the glasshouse than observed in the field. The lack of consistent trends between herbicide degradation rates observed in the field and those observed in the controlled glasshouse environment highlights the difficulty of isolating factors contributing to dissipation in a field scenario. In field scenarios, studies have shown that significant losses occur through leaching, runoff and plant uptake (e.g. >15% of the applied isoxaflutole can be lost through leaching in 25 days (Papiernik et al., 2007). This would mean that the glasshouse degradation rates, which exclude losses due to alternative pathways including runoff/leaching/plant uptake, are more appropriate for use in predicting herbicide fate in agricultural soil water balance models where losses due to degradation are considered as a separate process to loss through runoff/leaching/plant uptake. However, it needs to be considered that where photodegradation is an important loss pathway, glasshouse experiments will underestimate degradation. In certain instances, the degradation rates measured in the glasshouse were faster than observed in Queensland field situations. It is hypothesized that this was lack of consistency in field versus glasshouse results may be due to the maintenance of relatively high soil moisture levels in the glasshouse through the use of a hanging water column, whereas in a field situation the soil will dry out between rainfall events (Shaw et al., 2013).

The soil half-life of pesticides as well as climatic conditions also influence the amount of pesticide lost from a paddock. Shaw et al (2013) found that soil half-lives increased greatly where soils had low moisture content, presumably because of limited hydrolysis potential and the relative inactivity of micro-organisms which help degrade the pesticide, under such conditions. In the drier regions (i.e. drier soils), such as the cropping lands near Emerald in the Fitzroy Basin, pesticides were detected in paddock runoff up to three years after application (Rogusz et al., 2013). Even in wetter areas, the pesticides with longer half-lives (e.g. diuron) continued to be lost from paddocks following longer intervals between rainfall and pesticide application compared to pesticides with shorter half-lives (e.g. 2,4-D, atrazine and metribuzin) (Nachimuthu et al, 2013).

Pesticide losses from paddocks can also vary from region to region based on soil types, however the extent of this is pesticide specific. Shaw et al (2013) found high variability in pesticide soil half-lives across different soil types, although this was also pesticide specific. For example, the half-lives of commonly-used herbicides in sugarcane such as 2,4-D (14 to 22 days) and atrazine (12 to 22 days) were much less variable across different soil types compared to diuron (14 to 200 days) and paraquat (67 to 744 days), (Shaw et al, 2013). As previously mentioned the spatial variation in rainfall is also likely to influence pesticide losses from paddocks with effects on soil moisture contents (e.g. Rogusz et al., 2013; Shaw et al., 2013).

3.7. Rates of herbicide losses from paddocks

3.7.1. Timing of application and runoff event

Considerable data on the nature and magnitude of pesticide losses from paddocks have emerged from consolidated paddock-scale research occurring over the past 5–10 years. One of the clearest and critical drivers of pesticide loss from paddocks emerging from recent research is the relationship between the date of pesticide application, timing of rainfall and irrigation, and resultant pesticide losses in runoff (Rohde et al., 2013; Armour et al., 2014; Davis et al., 2014b). The longer the time between herbicide application and the first runoff event, the less herbicide was lost in runoff. Also, the amount of infiltrating rainfall during this period, between the herbicide application and the first runoff event (essentially ‘incorporating’ more of the herbicide into the soil profile), reduced the amount of herbicide lost in runoff (Rohde et al., 2013). As a ‘rule of thumb’ it appears the greatest risk of significant herbicide loss is if runoff-producing rainfall occurs within the ~25 days of herbicide application (Rohde et al., 2013; Armour et al., 2014). Different farming systems, particularly the capacity for irrigation in some regions such as the Burdekin and Mackay-Whitsunday, did produce some variation on this theme. In furrow irrigated canefarming systems substantial losses consistently occurred in the first irrigation following herbicide application (with irrigations typically occurring 2–4 days post-herbicide application), with >80% of the annual herbicide load lost from paddocks occurring with the first 2 irrigations (Davis et al., 2013).

Importantly, considerable loss of both priority and non-priority herbicides routinely occurred, across districts when significant rainfall or irrigation occurred soon after application (Rohde et al., 2013; Armour et al., 2014; Davis et al., 2014b). In addition to the PSII herbicides diuron, atrazine and hexazinone, ‘alternative’ herbicides such as pendimethalin, metribuzin, 2,4-D, MCPA, glyphosate and picloram were all detected at similar concentrations (and loads) in runoff from monitored paddocks (Rohde et al., 2013; Armour et al., 2014). The broad propensity for off-site movement in relation to timing of rainfall is clearly demonstrated by the contrasting comparative losses of diuron (a priority PSII herbicide) and pendimethalin (a touted alternative) at the Tully P2R sites (Figure 3-1; Armour et al., 2014). Diuron applied early in the season at Site 1 resulted in low concentrations and loads in runoff during substantial December rainfall (i.e. >50 days after application). In contrast, a late season diuron application at Site 2 (with major wet season rainfall occurring ~2 weeks later) resulted in markedly higher runoff concentrations and load losses in the same rainfall event, even though approximately half the rate of diuron was applied (Figure 3-1). Pendimethalin behaved in the same manner, with higher pendimethalin concentrations measured at Site 1, where it was applied close to rainfall, compared to the much earlier pendimethalin application at Site 2 (both sites received the same herbicide application rate).

Due to the vagaries of climate and soil type, the losses of herbicides (both absolute and as a percentage of the amount applied) varied markedly in field studies; from negligible (< 1% of active ingredient (a.i.) applied) in the cases of long delays between application and rainfall, to substantial (e.g. up to 18% of product applied and >200 g a.i./ha) when there is a short interval between application and rainfall (see Rohde et al., 2013). In contrast, in irrigated systems, losses of herbicides were relatively consistent, losing between 2–12 % of herbicides applied to paddocks in early irrigations following application (Davis et al., 2013), often during the dry season.

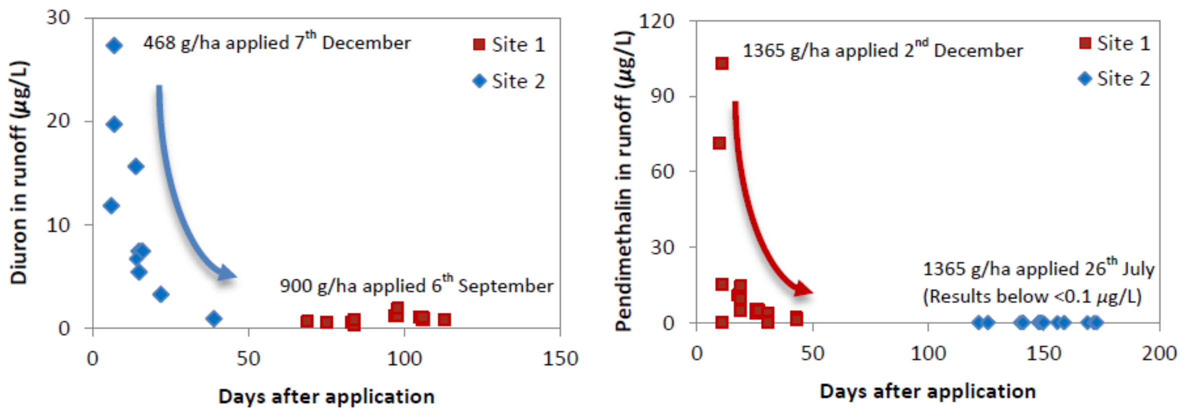

Figure 3-1: Concentrations of diuron (left) and pendimethalin (right) in runoff as a function of the time between herbicide application and run-off inducing rain (modified from Armour et al., 2014)

3.7.2. Rainfall simulator studies on pesticide runoff

A valuable complement to larger, often field-scale studies of pesticide loss under the P2R program was the Paddock Rainfall Simulation Monitoring Program (Cowie et al., 2013). Rainfall simulation is a useful method of assessing pesticide runoff from various management practices by artificially generating runoff from paddock trial plots under controlled conditions. Artificial rainfall is applied in known quantities, at a constant intensity to a small land area (normally several m^2) until runoff occurs for a given amount of time. Rainfall simulation methods have been used successfully in both the Queensland cotton and sugar industries to study management practices for the control of runoff losses (Silburn and Glanville, 2002; Silburn et al. 2002, 2013; Masters et al., 2013). Rainfall simulation trials focussing on herbicide runoff from sugarcane paddocks were conducted in the Bundaberg, Mackay, Burdekin and Ingham cane growing districts, examining several different aspects of herbicide 'Best Management Practice' in the sugar industry. These included the runoff potential of the 'new/alternative' herbicides compared with the priority PSII herbicides, at short times after application, and also the potential water quality effects of 'spot' spraying (comparative losses under 20%, 40%, 60%, and 100% spray coverages on paddocks).

Results of these rainfall simulation trials provided substantial insights into the relative mobility of alternative herbicides compared to the priority PSII herbicides when applied under identical field conditions. Using the Mackay rainfall simulation as an example, the knockdown herbicides such as glyphosate and fluroxypyr, and the residual pendimethalin were lost in relatively lower proportions of a.i. applied (Figure 3-2), although all were detected in run-off (Lewis et al., 2014). The alternative residual imazapic was lost at the highest proportionate amounts of a.i. applied (~2.6 %), with all remaining herbicides such as the knockdown 2,4-D, priority PSII herbicides (diuron, atrazine and ametryn), and alternative residuals such as isoxaflutole, s-metolachlor and metribuzin all being lost in runoff at 1.5 – 2.0% of active ingredient applied. Relative rankings of the proportion of specific herbicide lost during rainfall simulation trials were quite consistent across different districts, although the overall proportions lost did vary between studies (Lewis et al., 2014).

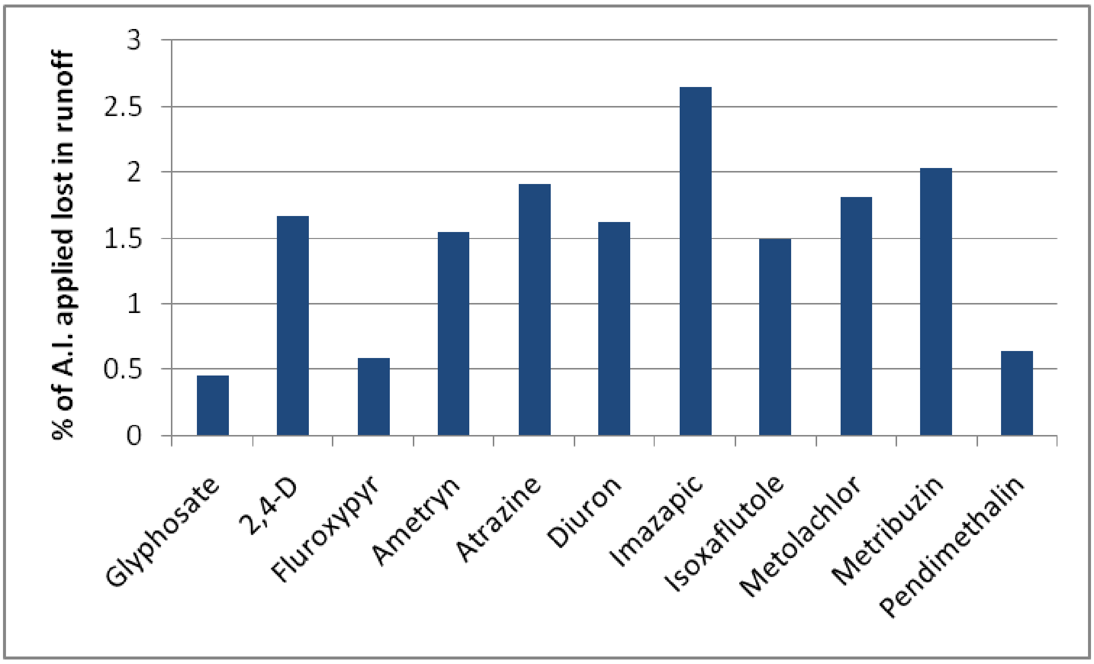

Figure 3-2: Average proportionate losses (%) of herbicide active ingredient (a.i.) during the Mackay rainfall simulation study (modified from Lewis et al., 2014).

3.7.3. Runoff proportional losses versus loads

Presentation of these results in terms of total loads (grams of a.i. per hectare; g.a.i./ha) of herbicide lost does however show a substantially different overview of loss dynamics to comparison of the relative proportions of herbicide applied lost in runoff (Figure 3-2 and Figure 3-3). The total loads of herbicides lost are perhaps the most relevant parameter, particularly with the load-based targets that underpin Reef Plan assessment and reporting. Because of their markedly lower application rates to paddocks (<300 g.a.i./ha), several herbicides such as fluroxypyr, imazapic (which was lost in the highest proportionate amounts of any herbicide) and isoxaflutole all exhibited the lowest total load losses (<3.0 g.a.i./ha) and concentrations from paddocks (Figure 3-3). Ametryn, atrazine, s-metolachlor, metribuzin and 2,4-D, by virtue of their combined mobility and higher application rates, all demonstrated higher total load losses (>30 g.a.i./ha) than diuron (~22 g.a.i./ha), glyphosate (~12 g.a.i./ha) and pendimethalin (10 g.a.i./ha).

Overall results from the lower Burdekin rainfall simulation trial were generally similar to those obtained in the Mackay region, particularly in relation to relative ranked losses of herbicides, although overall proportionate loss rates were higher in the lower Burdekin trial. In this trial, imazapic was again the herbicide lost at the highest proportion of its application rate (~32% of a.i. applied), which was substantially higher than the Mackay trial (i.e. ~2.6 % of a.i. applied) (Lewis et al., 2014). The Lower Burdekin trial also showed glyphosate, fluroxypyr and pendimethalin had the lowest proportional losses of a.i. compared to their application rates Priority PSII herbicides (atrazine, ametryn, diuron) and 'alternative' residuals such as S-metolachlor and metribuzin all had similar loss rates, with 4-8% of a.i. applied being lost in runoff (Lewis et al., 2014).

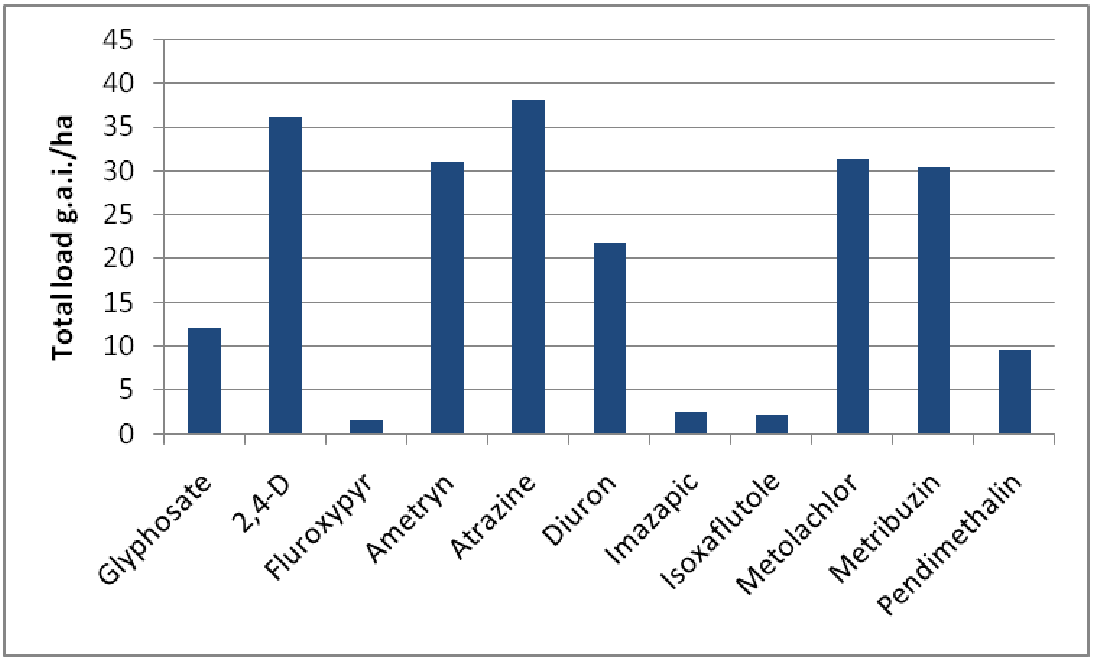

Figure 3-3: Average load losses (grams of active ingredient/hectare) of herbicides during the Mackay rainfall simulation study (modified from Lewis et al., 2014).

3.7.4. Runoff behaviour of alternative herbicides compared to PSII herbicides

The relatively consistent loss patterns of the herbicide suite studied in these rainfall simulation trials provided considerable support for several research findings emerging from field-based research. The results (Figure 3-3) clearly showed that a number of the touted residual alternatives to priority PSII herbicides such as metribuzin and metolachlor can leave paddocks both at similar (and very possibly higher) proportionate and overall rates compared to the priority PSII herbicides they are intended to replace. Several of the knockdowns such as 2,4-D and to a lesser extent glyphosate can also leave paddocks at considerable concentrations and loads. Some of the lower application rate herbicides such as imazapic and isoxaflutole may be as prone to movement as the priority PSII herbicides, and in the case of imazapic, may be even more so. Their lower relative application rates, however, may reduce their overall environmental risk in terms of total load and concentrations of herbicide moving off-site. The results also demonstrated that glyphosate sprayed on the soil is still reasonably prone to runoff even though its soil sorption is considerably greater than many soil residual herbicides (e.g. ~15 times that of atrazine, see Table 3-1). The studies showed that there was high variation in the rates of glyphosate runoff between the different trials, the reasons of which are currently unclear (we note though there was a large difference in the dissolved/particulate partitioning in the runoff between the rainfall simulation sites). Given glyphosate's potentially pivotal role in future industry shifts toward 'minimum till' agriculture and decreased reliance on the priority PSII herbicides it is worthy of further research in terms of its off-site movement potential and environmental impacts.

Similarly, laboratory trials conducted under Reef Rescue Water Quality Research and Development Program quantified the amount of herbicide washing off sugarcane trash using simulated rainfall, to provide insights on the runoff behaviour of a range of priority and alternative herbicides in response to rain in the field, including interactions with farming practices such as green cane trash blanketing (Dang et al., 2012). Many of the alternative herbicides shared a similar susceptibility for off-site movement in surfacewater runoff from cane trash compared to the priority PSII herbicides. An important outcome, however, is that while washoff rates of alternative herbicides such as trifloxysulfuron sodium and imazapic may have been relatively high, the much lower overall application rate of these herbicides resulted in an order-of-magnitude reduction in total load losses compared to the conventional higher application rate herbicides such as atrazine.

Despite its widespread usage in rangeland grazing, data relating to tebuthiuron application and losses in the Australian grazing landscape has been lacking. The research of Thornton and Elledge (2013) has provided some of the first data on the dynamics of tebuthiuron movement in runoff. At the paddock scale under natural rainfall conditions, a runoff event 100 days after application mobilised high concentrations of tebuthiuron (mean 103 µg L^{-1}); however, the total lost in runoff was only 0.05% of the amount applied. Runoff was monitored up to 472 days after application with losses of applied tebuthiuron ranging between 0.05% and 0.45% (Thornton and Elledge, 2013). The highest loss was associated with the runoff event with highest discharge. Much like the loss dynamics documented in other GBR industries such as sugarcane, comparison of individual event hydrographs showed that tebuthiuron concentrations declined exponentially with time across events. Rainfall simulation trials were also used to examine tebuthiuron losses in closer proximity to rainfall, as well as to investigate the effects of different product formulations (granular versus liquid application). On a clay soil, granular tebuthiuron had twice the loss in runoff (0.75 kg/ha or 25% as a percentage of a.i. applied) than the dry flowable (liquid) formulation (0.35 kg/ha or 12% of applied active: Thornton and Elledge, 2013). On a duplex soil the difference in the tebuthiuron losses in runoff were not significant between formulations. These results highlighted, much like the situation in sugarcane research, that timing of rainfall in relation to application date exerts a major effect on losses. Induced rainfall (rainfall simulation) causing significant runoff soon after tebuthiuron application resulted in much greater proportionate losses than the natural rainfall scenario. The importance of time of rainfall after application and the large runoff losses of an alternative herbicide, metolachlor, were also confirmed in grain cropping (Murphy et al. 2013). Glyphosate and glufosinate-ammonium were detected in paddock-scale runoff trials on a banana plot at the South Johnstone research station (Masters et al., 2014a). Concentrations of glufosinate-ammonium fell below detection limits (<0.5 µg L^{-1}) towards the end of the wet season (March), while glyphosate and its metabolite AMPA were detected in all runoff events up to 6 months after the last application. The fungicide mancozeb was below detectable limits (< 5 µg L^{-1}) in runoff and deep drainage (Masters et al., 2014a).

3.7.5. Importance of particulate and dissolved phases in the transport of herbicides in runoff

Pesticides may be transported off paddocks in runoff in the aqueous (dissolved) phase or particulate phase depending on their physico-chemical properties such as water solubility and soil sorption properties (Rice et al., 2004). The importance of physico-chemical properties on the inherent transport potential and ultimate environmental fate of particular herbicides have been long appreciated (Hargreaves et al., 1999; Wauchope, 1978; Willis and McDowell, 1982). While the key chemical properties relating to mobility characteristics (solubility, Koc etc.) are well known (Table 3-1), until recently, much less attention has been paid to the specific partitioning of herbicide transport during runoff off-farm. These data provide critical insights on the ultimate environmental fate (and impact) of herbicides that move off-farm and on the effectiveness of mitigation strategies to minimise off-site transport.

Data from rainfall simulation trials, conducted in the Burdekin, showed that the majority (generally >90%) of the studied herbicides ran off the sugarcane paddock in the dissolved phase with the exceptions of AMPA, diuron, glyphosate, imazapic and pendimethalin (Figure 3-4). Obviously the inherent partitioning behaviour of pesticides plays a role in determining the relative distribution between particulate and dissolved phases. With the exception of imazapic, all herbicides found to be affiliated with particulate phases have higher Koc values (Table 3-1) than those found predominantly in the dissolved phase (Figure 3-4). Other studies have examined partitioning at a catchment scale revealing similar results to the paddock data (Davis et al., 2012; Packett, 2014). At the catchment scale atrazine, ametryn, tebuthiuron, hexazinone, bromacil and metolachlor were >80% in the dissolved phase while 70 to 80% of the diuron measured in runoff was in the dissolved phase (Davis et al., 2012; Packett, 2014). Partitioning at the catchment scale is discussed further in Section 4.7.2.

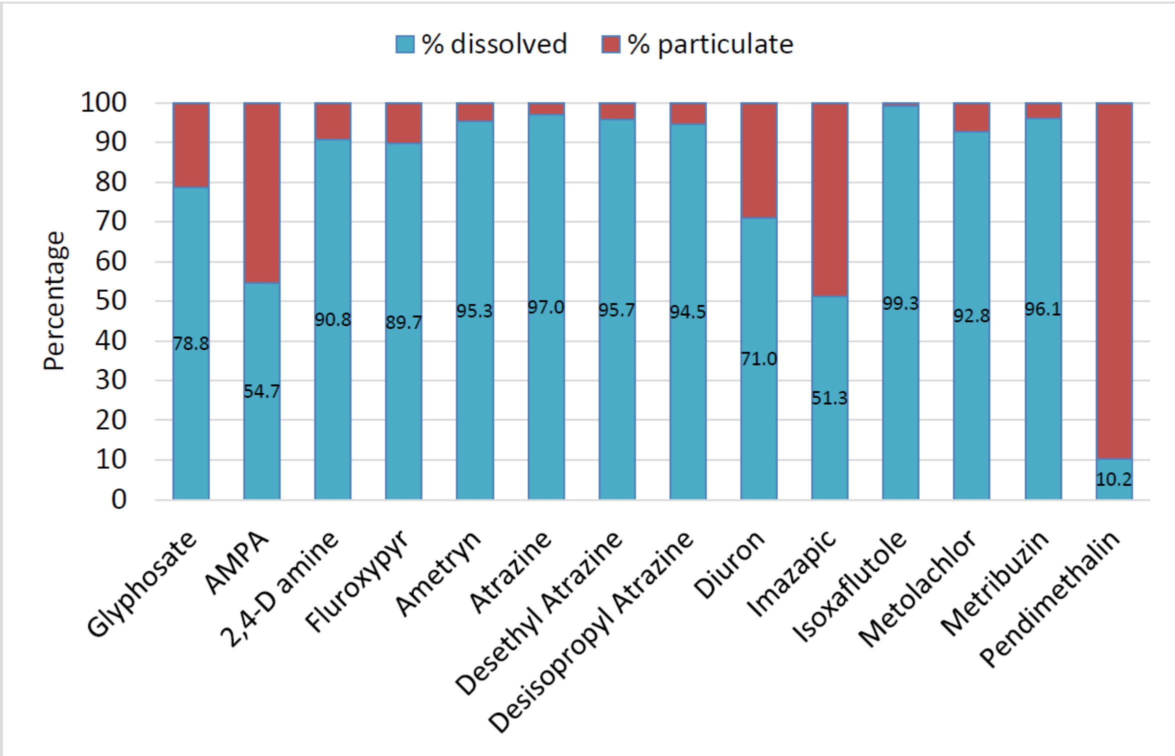

Figure 3-4: Herbicide partitioning (dissolved versus particulate bound) from rainfall simulation trials in the Burdekin Region (from Packett, 2014)

3.7.6. Pesticide losses to groundwater

Contrary to pesticide losses from paddocks in surfacewater, losses to groundwater (i.e. leaching below crop root zones) are relatively poorly understood. Pesticide contamination of groundwaters under agricultural areas is however, a common occurrence at a global scale (Graymore et al., 2001; Cerejeira et al., 2003; Gillom et al. 2006). This issue has received some attention in the GBRCA with numerous historical studies highlighting the potential for soluble herbicides (atrazine, diuron, 2,4-D) to leach past crop root zones (Keating et al., 1996; Adams and Thurman, 1991; Hunter et al. 2001; Simpson et al. 2001b; Baskaran et al. 2002; Klok and Ham, 2004). While losses of pesticides in surfacewater runoff appear responsible for most off-site movement of herbicides (at least on the basis of available data) in the GBRCA, herbicide movement to groundwaters was still quite evident from almost all studies that assessed deep leachate (Rohde et al., 2013; Armour et al., 2014; Davis et al., 2014b).

The herbicides 2,4-D, atrazine, diuron, glyphosate, hexazinone, imazapic, MCPA, metribuzin, metolachlor, propazin-2-hydroxy (propazine), and simazine, were all detected in leachate under monitored canefields during the P2R program. Peak concentrations detected in some samples e.g. 2,4-D (11.5 µg L^{-1}); hexazinone (>10 µg L^{-1}); MCPA (20.6 µg L^{-1}) and metribuzin (41 µg L^{-1}), highlight leachate losses as a notable loss pathway (Davis et al., 2013; Rohde et al., 2013). Surfacewater-drainage studies in Mackay (Rohde et al., 2013) highlighted a clear relationship between herbicide concentrations (diuron and hexazinone) detected in the surface water runoff and in the drainage soil solution samples of monitored paddocks. It was noted that as concentrations in surfacewater decreased, so did the concentrations in groundwater drainage losses. Several pesticide residues were detected for extended periods of time after application, albeit at lower concentrations, in some studies (Rohde et al., 2013). For example, diuron (0.002-0.02 µg L^{-1}) and imidacloprid (0.02–0.09 µg L^{-1}) were detected more than 2½ years after they were applied, highlighting the longevity of some of these compounds in the soil profile (Armour et al., 2014). It is well recognised that due to rapidly declining organic matter content and proportionate microbial activity with depth in the soil profile, once pesticides move into the subsurface layers, they may continue to migrate unattenuated to the groundwater (Kookana et al., 2005). Similarly, calculation of the decline in herbicide concentration in drainage over time at Mackay-Whitsunday cane sites, estimated the deep drainage half-lives of diuron and hexazinone as 58 and 59 days, respectively (~5.25 times greater than surface runoff) (Rohde et al., 2013). While most research attention has focussed on sugarcane, herbicides also appear in deep drainage samples under different GBRCA crops. For example, glyphosate was detected in groundwater leachate under bananas (0.8-1.1 µg L^{-1}) after a 700 mm rainfall event over 4 days (Masters et al., 2014a).

To varying extents many of the herbicides may be sorbed onto soil organic matter or onto clay minerals (Kookana and Simpson, 2000; Kookana et al., 1998). While load losses have not been broadly compiled, cumulative loads of herbicides lost to deep drainage appear relatively low compared to surfacewater losses, and have seldom exceeded 1 g/ha/year, even in scenarios where deep drainage is a dominant water movement pathway for specific paddocks (Davis et al., 2013). Pesticide concentrations in deep drainage are generally an order of magnitude lower than concentrations found in surfacewater runoff from paddocks (Rohde et al., 2013; Davis et al., 2014b). This loss pathway does, however, constitute an information gap, particularly in areas where groundwater contamination appears widespread. Pesticide occurrence in groundwater across a regional scale is also reviewed in Chapter 4.

3.8. Global studies on alternative herbicides

Many of the alternative herbicides, despite being registered in sugarcane for some time (often decades), have previously received minimal monitoring attention in the GBR context, and have only recently been added to standard pesticide analytical suites conducted as part of GBR catchment water quality monitoring programs (see Brodie et al., 2012a; Kennedy et al., 2012b). Due to additional analytical requirements (and hence costs) several herbicides that have been relied on heavily for decades by GBR catchment canegrowers (paraquat, 2,4-D, glyphosate; Simpson et al. 2001a) have also received little, if any, long-term monitoring attention at a catchment scale in the GBR (Davis et al., 2008). Indeed only recently has a wider suite of pesticide analysis been conducted systematically across the GBRCA (Wallace et al., 2014, 2015; Smith et al., 2015) while some targeted analysis at a sub-catchment scale has also been performed (Shaw et al., 2010; Davis et al., 2012; O'Brien et al., 2013b).

While locally relevant GBR catchment data for some specific herbicides are sparse, several of these alternative herbicides (i.e. glyphosate, pendimethalin, isoxaflutole) have been more thoroughly examined in other industries at a global level, particularly within 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; Alletto et al., 2012), metribuzin (Battaglin et al.,2001; Ludvigsen and Lode, 2001; Kjaer et al., 2005; Dores et al., 2006; Plhalova et al., 2012; Oukali-Haouchine et al., 2013), glyphosate (Coupe et al., 2012), 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., 2008b) 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.

3.9. Overall farming system approach

It needs to be emphasised that an overall farming system approach for pesticide management is required to minimise the environmental risk of pesticides. This overall approach includes factors such as on-farm hygiene, timing of application and product selection, getting on top of weeds early in the plant crop cycle and precision/targeted application. While many of these factors are discussed individually below, these should be considered collectively as an overall management approach.

3.9.1. Timing of application and product selection

One of the clearest and most consistent outcomes of recent research was the inverse relationship between herbicide application and timing of rainfall or irrigation, and resultant load losses from paddocks. The timing of application and product selection are overwhelmingly the biggest drivers of offsite pesticide losses and hence one of the key management considerations for minimising herbicide losses off-farm. In addition, the application of longer-lived pesticides early in the year (dry season), and the use of shorter-lived pesticides nearing, or within the high risk wet season period, are critical to minimising herbicide losses from paddocks. The application of herbicides as early as possible in the season allows time for the herbicide to dissipate (as well as act effectively in terms of weed control) before runoff occurs. The research shows that for every 25 days of minimal rainfall after herbicide application, runoff losses off the paddock approximately halve. Given this relationship, the application of irrigation water to sugarcane paddocks in several GBR catchments (lower Burdekin, and to some extent Mackay-Whitsunday), typically 2-4 days after herbicide application, presents particular challenges to managing off-farm pesticide losses. Several practices are available which do offer substantial potential management control of herbicide loss for growers in irrigated systems (see sections 3.9.3 and 3.9.6 in particular).

3.9.2. Early and effective weed control in fallow and plant

Another of the key management lessons emerging from P2R research in particular, was the critical importance of effective weed control in the early stages of the crop cycle to minimise paddock weed seed banks and reducing the long term amount of herbicide required to control weeds in subsequent ratoon crops. Effective early weed control in fallow and plant crops (which included residual control) allowed growers to shift entirely to 'knockdown' herbicides in subsequent ratoon stages of the crop cycle, as well as to reduce overall application rates through use of precision application technologies such as shielded sprayers.

3.9.3. Paddock runoff (tailwater) re-capture/recycling

While capturing paddock tailwater runoff in recycle pits has often been suggested as a key management option for minimising off-site agrochemical losses, recent research suggests that the often extreme nature of wet season rainfall events coupled with relatively short retention times of many on-farm water storages make trapping, particularly of dissolved contaminants (e.g. nitrate, PSII herbicides) relatively inefficient (Brodie et al., 2011; DeBose et al., 2014). Retention of paddock tailwater on-farm is however, a particularly useful practice in some situations. In the lower Burdekin cane district, the capacity for furrow irrigation allows substantial management control of runoff volumes for canegrowers who utilise tailwater recapture. While retention of higher water volumes associated with wet season rainfall events is not viable, tailwater from dry season irrigations, particularly after early season residual herbicide applications, can be recycled or retained on-farm for long periods, maximising the opportunity for significant degradation (Davis et al., 2013). In addition, new technology is being examined to treat some of the herbicides within these storages; early results show the addition of an enzyme (the triazine hydrolase TrzN) to a recycle pit depleted atrazine concentrations by > 90% within 2-3 hours (e.g. Scott et al., 2010).

3.9.4. Capturing spills during pesticide handling and washoff from spray tanks

Small volumes of pesticide residues left in the spray tanks, if not disposed off properly, or a spillage of a few drops of pesticide concentrate could constitute a significant point source of pesticide pollution on farms. To capture spills or the washoff of spray tanks, the "biobeds" have been designed and used in Europe over last 20 years. Biobeds, originated in Sweden in 1992, are usually constructed using a mixture of materials (such as straw, peat, soil) to retain and degrade pesticides, without risking groundwater contamination. Since then the concept has evolved into different forms of beds and filters being used worldwide to manage the point source of pollution (Castillo et al. 2008). Overseas research reviewed by Castillo et al. (2008) has shown that the biobeds can be simple and effective means of minimising potential contamination by pesticides during handling of spray equipments and pesticide products. Biobeds have also been used to remove pesticides from wastewater generated during post harvest operations such as in horticultural production systems (Omirou et al. 2012).

3.9.5. Non-herbicidal weed control

While the complete elimination of tillage and herbicides in weed management is unrealistic for most farmers while maintaining yields, recent weed control advances have suggested substantial reductions in both inputs could be attainable with greater application of ecological knowledge to target weak points in the life-cycles of specific problematic species (Brainard et al., 2013). In most cases, greater exploitation of fallow cover crop and crop residue mulches, either as a physical or allelopathic barrier (biochemical suppression by a cover crop), are potentially a key strategy for suppressing weeds, particularly in warm climates where sufficient biomass may be generated to provide season-long weed suppression. Results could be used to develop more sustainable agronomic practices in regions where fallows are still widely employed (Blackshaw et al., 2001; Kumar et al., 2013). This avenue of research may still be too incompatible for sugarcane at the stage where legume fallow crop mulches will not provide enough cover to suppress weeds. Allelopathic weed control may be possible with some fallow cover crops (E. Fillols, SRA, pers. comm., 2013) and a heavy cane trash blanket is known to suppress many weeds and reduce the need for herbicide control (Fillols, 2012).

3.9.6. Precision application of herbicides

One management strategy that has been suggested to provide significant water quality benefits to sugarcane farmers is to restrict the application of the more problematic herbicides, such as atrazine and diuron, to raised beds only (banded application) and replace their application in furrows/inter-rows with alternative herbicides that have relatively shorter half-lives, lower relative toxicity and/or are less soluble in water. This has been an area of considerable recent research focus in the GBRCA. Rainfall simulator trials conducted in Mackay demonstrated a 54% and 56% decrease in the event mean concentration of atrazine and diuron respectively, from banded applications of the herbicides compared with broadcast applications (Masters et al., 2013). This was attributed to the approximately 50% decrease in area sprayed. Other rainfall simulation studies of the banded application of pesticides on Queensland cotton farms found that the total concentrations of pyrithiobac sodium, metolachlor and diuron in runoff were decreased by 38, 22 and 50%, respectively (Silburn et al., 2013). Results of the 'spot-spraying' component of the rainfall simulation trials also identified significant positive correlations between the percentage of paddock sprayed and subsequent herbicide concentrations in runoff (Lewis et al., 2014), an association evident for all of the herbicides applied to paddocks during the trials. While these outcomes are not particularly surprising, it is one of the first such demonstrations (i.e. 'proof of concept') of the load loss reductions possible with precision application technologies. When considered in conjunction with commercial scale paddock trials of shielded sprayers (discussed in more detail below), these results underline the considerable potential for improved application technologies in providing substantial reductions in herbicide loads leaving paddocks.

The value of field trials in directly quantifying practice change benefits was evident in a 2012 Reef Rescue Research and Development study in the lower Burdekin ('Pesticides in Sugar'). This trial compared the conventional practice of broadcast application of herbicides in sugarcane production across the whole field with the banded application of particular herbicides onto raised beds only using a shielded sprayer (Oliver et al., 2014). The conventional treatment saw atrazine, diuron both, 2,4-D and paraquat applied to the entire paddock with a boom sprayer. Under the alternative banded treatment, atrazine, diuron, paraquat and 2,4-D were applied to the raised beds of the paddock, with only glyphosate and 2,4-D applied to the furrow (which receives applied irrigation water). The results were particularly promising with the banded application of diuron and atrazine to only the raised beds in the cane field decreasing the average total load of both herbicides moving off-site in irrigation tailwater by 90% compared with the conventional treatment. This 90% reduction in off-site movement occurred despite the banded application spray area being only 60% less than the conventional treatment (Oliver et al., 2014). The average total amount of atrazine in irrigation runoff water was 7.5% of the a.i. applied in the conventional treatment compared with 1.8% of the a.i. applied in the banded application treatment (Oliver et al., 2014). Similarly, the average total amount of diuron in runoff water was 4.6% of that applied in the conventional treatment compared with 0.9% of that applied in the banded application treatment (Oliver et al., 2014). This study demonstrates that the application of diuron and atrazine to raised beds only is a highly effective way of minimising migration of these herbicides in drainage water from furrow irrigated sugarcane.

Similarly, spot-spraying technologies used in other industries, such as Weedseeker®, may also have a future role (Griffin et al., 2012), but issues surrounding costs (particularly for the many smaller growers in sugar) and the fact they are currently designed for 'knockdown' rather than residual herbicide application, may limit their cost-effectiveness for overall herbicide management. Recent trials of knockdown herbicide applications in the Mackay district suggests that while Weedseeker® technologies can offer effective weed control, issues such as paddock accessibility and uniformity of weed coverage can significantly affect strategy efficacy and cost-effectiveness (Fillols and Baille, 2013). In these trials, weed control strategies using knock-down herbicides under shields or hoods were very efficient in managing the emerged weeds, although it was noted that a different outcome may have been observed if the wet season had come early and the paddock was not accessible (Fillols and Baille, 2013). Herbicide savings for the spot-sprayed treatments using Weedseeker® weren't as large as expected, however, the weed infestation in this particular trial was light and uniform in coverage (i.e. not in patches) which is a less than ideal situation for cost-effective use of precision application technologies. Cheaper parallels of the Weedseeker® technology are also being trialled in the sugar industry (Allan Blair, QDAFF pers. comm.). Precision application approaches (if correctly implemented as part of an integrated weed management program) will likely reduce the overall application rates of all herbicides to paddocks. This will have demonstrable flow-on effects for off-site water quality. Engineering methods of reducing PSII and residual herbicides such as shields and banded dual herbicide application systems developed by QDAFF are gaining traction in the industry.

These recent studies in the GBRCA have suggested significant water quality benefits can be obtained through the utilisation of precision application technologies while still allowing use of the priority PSII herbicides. There are a range of significant caveats however, associated with widespread adoption of these emerging technologies in the Queensland sugar industry. Practical use of shielded/banded sprayers still requires significant weed agronomy and herbicide knowledge, as well as continual maintenance and calibration of equipment to ensure requisite weed control is achieved. Growers employing this technology will often need ongoing extension/agronomy advice to ensure maximum benefit from practice shifts. The effectiveness of these approaches across the diversity of soil types, weeds and farming systems across the Queensland sugarcane industry are also yet to be fully demonstrated.

3.9.7. Longer term agronomic considerations and management practices to consider in reducing pesticide losses from paddocks

Pesticide management by the agricultural industry is almost invariably more complex than single annual applications, and often involve multiple applications, combinations and rate variations (often at lower than maximum rates) within and between years depending on specific pest pressures and climatic conditions. Similarly, while many of the priority PSII herbicides are most commonly used for pre-emergent (i.e. soil residual) weed control, they are also frequently mixed, or used at lower rates (spikes) to enhance post emergent (contact or 'knockdown') control of both grasses and broadleaf weeds. One of the most glaring information gaps surrounding pesticide monitoring in the GBRCA, is the lack of local-scale usage data. Occasional usage data specific to individual catchments or sales data from individual agrochemical suppliers are available (Davis et al., 2008) but only provide an indicative measure of use for a point in time. In what is often a very dynamic management environment, where major shifts in usage of particular products can occur on a yearly basis, knowledge of practice changes (catchment application rates and products) can often only be retrospectively inferred from water quality monitoring data (see O'Brien et al., 2013a). There are also major changes in use associated with the introduction of herbicide resistant and insecticidal crop varieties, such as glyphosate tolerant and BT cotton (Crossan and Kennedy, 2004) and with development of herbicide resistance in weeds as discussed below.

Agronomic and labelling restrictions (e.g. specific crop, rate, timing, proximity to wetlands and waterways) for registered pesticides limit their widespread viability across the GBR. In addition, pesticide efficacy can be heavily contingent upon soil properties such as moisture, organic carbon content, cation exchange capacity and particle size as well as farming system and geographic location (Davis et al., 2014a). The repetitious use of the same herbicides over an extended period has caused documented cases of herbicide resistance in weeds (Beckie, 2011). For example, 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 within Australia, predominantly in the context of broadacre grain cropping (Owen and Powles, 2010; Beckie, 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 have a range of negative ecological, environmental and agricultural risks in affected industries. Farmers rely on a suite of different products for effective pest control, although the selection of the most efficient, cost-effective and least prone to offsite movement (and environmental effects) can be difficult. A decision support framework to assist farmers to make a more informed choice of pesticide would be beneficial across different industries of the GBRCA (and particularly so for the sugarcane industry).

3.9 Conclusions and research gaps

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. While the spectre of herbicide registration and regulation has been an overarching theme of herbicide management in the GBRCA in recent years, results of this review suggest deriving genuine environmental benefits (and avoiding perverse outcomes) will require a more strategic and carefully considered approach to weed control. Future weed management in the GBR will certainly require more integrated and strategic weed management systems. These need to encompass minimising weed seed production and the size of soil seedbanks particularly in the fallow and early crop cycle, improved farm hygiene, herbicide timing and application techniques, tailoring herbicide applications specifically to weed type and density, weed resistance management that incorporates rotational sequences and/or mixtures of herbicides with different modes of action within and between crop cycles, and protection of the existing herbicide resource. With growers increasingly having to grapple with increased regulation, often unfamiliar herbicide mixtures, long term sustainability issues (i.e. potential development of weed resistance), and rapidly developing application technologies, increased emphasis on technical and extension support surrounding pesticide best practice will certainly be required. For a full list of research gaps for key sources of pesticides and management response, refer to Table 3-3.

Table 3-3: List of research gaps for key sources of pesticides and management

Research Gap	Details
Need to collect/collate high quality usage data	Presently there are very little accurate data on pesticide usage in the Great Barrier Reef catchment area. This limits our ability to assess pesticide losses (relative to amount applied) and to model pesticide loads at a catchment scale.
Comparison of runoff of different pesticides (further	Comparison of particulate and dissolved phases, particularly some of the widely used products like glyphosate that seem to behave variably in different

rainfall simulation sites)	scenarios (may need to be even more comprehensive in mix applications, which has still been a bit patchy). The role of wetting agents in pesticide application (and potential for runoff) are not understood at all.
	While a valuable dataset has been produced on pesticide runoff from paddocks where their runoff can be compared relative to each other, this work has only been conducted on limited soil types and regions and not all common pesticides have been examined.
Evaluate available weed/pesticide management practices, including scope for non-herbicidal weed control (trash blankets)	Some work has been conducted on banded/shielded spraying and other similar practices (e.g. spot spraying), however, runoff trials on a commercial farm have only occurred in the lower Burdekin region (under furrow irrigation). While demonstrations have been carried out in other regions using rainfall simulation, assessing the difference in pesticide losses (e.g. between conventional and banded) in rainfall-runoff event from the Wet Tropics and/or Mackay Whitsunday regions on a commercial/demonstration farm would be highly desirable.
Develop a decision-support tool for weed management and pesticide application in paddocks	With the knowledge currently available on pesticide runoff, soil half-lives, relative toxicity and efficacy (i.e. knowledge of extension officers), a simplified decision support tool could be developed to help farmers better manage weeds (and pesticides) on their property as well as reducing potential pesticide losses.
Examine the efficacy of alternate pesticides for a range of soil types and climate conditions (better linkages with agronomic efficacy research)	Some of the alternate pesticides that have been purported as viable replacements for the more commonly used products have yet to be properly trialled in different regions in terms of their efficacy (i.e. ability to supress weeds) and runoff potential.
Better quantification of the role of deep drainage losses of herbicides to receiving waters (particularly the role of constructed drains in some districts) and losses through deep drainage	While transport via groundwater pathways is usually considered very slow (decades), in the coastal plains of the GBR there are, however, large areas of sugarcane cropping with constructed drains designed to remove deep drainage leachate within days to weeks, to prevent water logging of the cane. There is also some (minimal) evidence that some pesticides will dissipate slowly in sub-soils/regolith (no light, low organic matter, low oxygen, certain pH's; low to negligible microbial activity). Baseflow (returned groundwater) is a large component of streamflow in the Wet Tropics. Thus further quantification of the persistent load of pesticides at low concentrations.
Long term field studies	Need for longer term field studies of whole-of-crop cycle approaches, including fallow and plant cane management, and subsequent ratoons with improved liaisons with industry and growers to map out long-term pros/cons of shifts away from priority PSIIs

4 PESTICIDE TRANSPORT, FATE AND DETECTION

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4.1 Summary of key findings

Pesticides appear to be virtually ubiquitous throughout the GBR and associated coastal ecosystems having been found in sediments and water of rivers, creeks, wetlands, estuaries, inshore and off-shore of the GBR lagoon;

- The priority PSII herbicides still contribute the majority of the pesticide load, although alternative pesticides contribute approximately 20% of the total pesticide load.
- Pesticide concentrations decrease over time and with distance from the source. A number of variables are believed to influence these changes in pesticide exposure as they move through successive ecosystems along the transport pathway, e.g. dilution and mixing, land use with and without pesticide application, degradation and compartmentalisation.
- Some pesticide residues are transported through leachate and into groundwater. The connectivity between groundwater and surfacewater in GBR catchments and coastal environments means that pesticides transported through groundwater are contributing to the loads of pesticides discharged to the Reef. Evidence indicates that the contribution of groundwater to total loads is relatively minor (typically being < 10%) but could be significant in the Wet Tropics. Concentrations in groundwater tend to be lower than surfacewater, although persistence is likely to be higher.
- The half-lives of pesticides in the marine environment are longer than previously thought for a number of pesticides including the priority PSII herbicides, glyphosate, 2,4-D and metolachlor. These findings are consistent with pesticides being detected at relatively stable, albeit relatively low concentrations in the off-shore GBR lagoon.
- Up to approximately 30% of some pesticides are transported in the bound phase and this proportion is likely to decrease with distance from the source.
- Both monitored and modelled pesticide loads are used to assess the mass of pesticides transported off-site and discharged to the Reef. Both methods have different advantages and disadvantages, but ultimately complement each other.
- Temporal variability is greatest in catchments and decreases in marine environments with distance from river mouths.
- Temporal pesticide exposure varies inter-annually and inter- and intra-seasonally. This variation is controlled by environmental (e.g. rainfall) and human (e.g. timing, frequency and rate of application, changes in land management practices) factors.
- Wetter than average (long term median) years have higher pesticide loads but lower pesticide concentrations than average and drier years.
- Chronic exposure has been observed in both freshwater and marine environments. But outside of the area directly affected by flood plumes, chronic exposure to low year-round concentrations (well below concentrations known to cause negative effects) exists.
- Pesticide exposure occurs concurrently with other stressors including high suspended sediment and nutrient concentrations.
- Freshwater ecosystems are exposed to higher concentrations and a greater variety of pesticides than marine ecosystems. Marine pesticide concentrations decrease with increased distance from the mouths of rivers and creeks until low level background concentrations are reached.
- Waterways receiving runoff from sugarcane land use generally have the highest concentrations and variety of pesticides detected.

- Pesticides are known to be present in the water column and sediment bed of waterways, estuaries and wetlands.
- The regional profiles of pesticides in the fresh and marine environment vary and reflect the predominant land use in the adjacent catchment.
- CDOM satellite imagery combined with catchment pesticide concentration data can be utilised to map the spatial extent and intensity of pesticide exposure transported in flood plumes into marine environments.
- It is highly likely that a large part of the GBR and its associated coastal ecosystems are contaminated by pesticides.

4.2 Introduction

To understand the current and future impacts of pesticides to the health and resilience of the GBR and associated aquatic coastal ecosystems[1] we need to be able to assess and predict the ecological risk that pesticides pose to these ecosystems. Ecological risk is "the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors" (USEPA 1992). Without information on both the exposure of organisms to pesticides and the effects of pesticides on organisms, we are unable to determine the severity and extent of impacts caused by pesticides to aquatic ecosystems in the Great Barrier Reef lagoon and associated aquatic coastal ecosystems. This chapter of the Pesticide Synthesis Report focuses on the potential exposure of organisms to pesticides (exposure characterisation), while Chapter 5 will focus on the biological effects of pesticides (effects characterisation).

Exposure of organisms is a function of intensity (concentration), space and time (USEPA 1998). Thus, to be able to define or predict exposure, we need to measure or model all three of these characteristics. The USEPA (1998) suggests that exposure assessments should consider the co-occurrence of the stressor with receptors through the evaluation of the following:

(1) The exposure/transport pathway, i.e. the course a stressor takes from the source to the receptor. For example, air currents, surfacewater, soil, groundwater, or through the food web;
(2) The distribution of the stressor within environmental compartments (e.g. water, sediment, biota); and
(3) The pattern, extent and likelihood of the co-occurrence between stressor and receptor.

The 2006–2010 Pesticide Synthesis Report (Devlin and Lewis, 2011) reviewed the existing knowledge (up to 2010) of pesticide exposure and transport to the GBR. At the time, assessment of pesticide exposure was focused primarily on monitoring the flood plumes that transport agricultural pollutants to the Reef, and the ubiquitous concentrations detected at near shore reefs. Pesticide concentrations were found to be highest during the wet season, co-occurred with elevated levels of suspended solids and dissolved nutrients, and could also be detected in low concentrations continuously throughout the year. Diuron and atrazine were the most commonly detected herbicides, with ametryn, bromacil, hexazinone, imidacloprid, metolachlor, simazine and tebuthiuron also detected. In the majority of instances, pesticides were also detected together indicating that the marine ecosystems were exposed to mixtures of pesticides.

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[1] The Great Barrier Reef "aquatic coastal ecosystems" refers to the rivers, freshwater wetlands, estuaries, and coastline lying adjacent to the Great Barrier Reef.

Knowledge of exposure and transport of pesticides in the adjacent freshwater and coastal ecosystems to the Reef was scarcer and centred primarily on waterways in the, Fitzroy, Mackay Whitsunday, Burdekin and Tully regions. Transport of pesticides focused mainly on calculating the loads of pesticides transported from catchments to the Reef. One of the most significant publications at the time was the calculation of the pesticide baseline loads (Brodie et al., 2009a, 2009b; Kroon et al, 2010) from which the Reef Plan reduction targets were set. Modelled loads were calculated for the majority of major catchments; however, loads calculated from monitoring data were fewer (summarised in Lewis et al., 2009; Packett et al., 2009). Additionally, very little was known of pesticide transport through groundwater; while it was known that pesticides were present in the groundwater of GBR catchments (Baskeran et al., 2001, 2002), their transport and contribution to the loads transported to the Reef was unknown. Lastly, there was also a paucity of data on the fate and compartmentalisation of pesticides in the freshwater, estuarine and marine environments.

Since 2010, our knowledge and understanding of pesticide transport and exposure to the GBR and its coastal ecosystems has substantially increased. In addition, monitoring and analytical methods have also improved which has enhanced our knowledge of the occurrence of pesticides in various environmental compartments. A short description of these improvements will be presented first, followed by our current understanding of:

1. Transport and exposure pathways, including: groundwater and surfacewater transport pathways from the paddock to the Reef; pesticide dissipation and fate; partitioning of pesticides into environmental compartments; and, pesticide loads – monitored, modelled and groundwater loads.
2. Spatial extent of exposure, including: riverine, wetlands, estuaries and marine ecosystems
3. Temporal exposure, including: annual, seasonal, pulsed, and chronic exposures as well as concurrent exposure with other stressors.

Lastly, the gaps in our knowledge of pesticide transport and exposure will be discussed along with the recommended research priorities aimed at filling these gaps.

4.3 Improvements in Pesticide Monitoring

Pesticide monitoring in the GBR lagoon and catchments that discharge to the GBR began in the 1990s. Since that time there have been considerable advances made to pesticide monitoring. These advances include:

- improved quality assurance and quality control procedures;
- improved laboratory extraction methods;
- improved analytical equipment with considerably lower limits of reporting;
- increased numbers of pesticides that can be detected in each analytical suite – this is due to a combination of better extraction methods and improved analytical equipment;
- improved working relationships with farmers and agricultural organisations that has led to greater exchange of information on pesticide usage patterns;
- improved sampling during events and throughout the year; and
- an increased number of sites being monitored.

Given these improvements it would therefore be reasonable to expect an increase in the number of pesticides detected over time, irrespective of any changes in the use of pesticides in agriculture. Indeed, recent pesticide studies have detected more pesticides than earlier work. While this may be due to changes in the number and types of pesticides being used in agriculture, it could also be due to improvements in analytical methods and equipment. Therefore, when making temporal comparisons of exposure to pesticides, particularly in terms of the number of pesticides detected, the results should be interpreted cautiously.

There are two main methods of detecting pesticides in aquatic waterways: grab samples and passive samplers. There has been some discussion in the literature about the merits of the two techniques. Both methods have strengths and limitations and are more appropriate for certain purposes (see Lewis et al., 2012). This chapter will not enter this debate but simply synthesise pesticide monitoring data from both methods.

4.4 Exposure and Transport Pathways

The transport of pesticides from paddocks to receiving waterways occurs via many pathways including global distillation (Wania and Mackay 1993), surfacewater transport, groundwater transport, spray drift and aeolian transport[2]. This chapter will only examine surface and groundwater transport as these are the two principle pathways that have been studied in relation to the GBR. All pesticides applied in catchment areas that discharge to the GBR have some potential to move off-site and ultimately reach coastal ecosystems and the GBR lagoon (Figure 4-1). As pesticides move from the source over time and distance, the transport processes become more complex as physical, chemical and biological interactions occur and the pesticides get dispersed to various ecosystems and environmental compartments. As the pesticides move along these transport pathways and enter new ecosystems, they have the potential to cause adverse effects to non-target organisms.

Figure 4-1: Schematic diagram of the transport pathways of pesticides from paddocks to the Great Barrier Reef and associated coastal ecosystems that are examined in this chapter. Throughout this process pesticides partition between various environmental compartments (e.g. water, suspended sediment and biota).The graduated colour scale represents changes in pesticide concentrations in a typical system along transport routes where orange indicates high concentrations and blue indicates low concentrations.

The processes that control off-site transport of pesticides from paddocks are the first crucial steps in overall transport of pesticides to the GBR (this will be dealt with briefly here, given its importance, but readers are referred to Chapter 3 of the report for greater detail). The fate of pesticides strongly depends on 1) their individual properties such as soil half-life, soil absorption, solubility and; 2) environmental conditions e.g. rainfall. The environmental media in which pesticides leave the paddocks depends largely on their aqueous solubility and the organic-carbon water partition

[2] The transport of soil particles by wind.

coefficient (K_{OC}). Pesticides with higher aqueous solubility and lower K_{OC} values have a higher potential to be mobile in the soil column and leach into water tables and will predominantly be transported off-site in a dissolved form. As the aqueous solubility decreases and K_{OC} increases the proportion of a pesticide in the dissolved form decreases and the proportion transported off-site bound to soil particles (particularly the organic carbon component) increases (e.g. Klok and Ham, 2004; Stork et al., 2008). Thus soluble pesticides, such as atrazine, are commonly transported off the paddock in surfacewater runoff in the dissolved phase, while less soluble pesticides (e.g. pendimethalin) are predominantly transported attached to particulate matter (Lewis et al, 2014; Packett, 2014). Another example is the herbicide paraquat that has a very high K_{OC} (i.e. 1×10^7) and has never been detected in paddock runoff studies (e.g. Davis et al., 2013). This partitioning between dissolved and bound forms is environmentally important because it plays a large role in determining the environmental fate of the pesticide. Soluble forms are more readily transported and are likely to be transported over greater distances than bound forms which will settle out and become part of the sediment in rivers, wetlands, estuaries and the GBR lagoon. The settling out of bound forms is predominantly controlled by the velocity of the water transporting the suspended sediment, the particle size of the suspended sediment and the density of the sediment particles (refer to Fate & Compartmentalisation).

While the majority of the work examining off-site transport of pesticides from paddocks has focused on surfacewater transport, many of the same factors also control the off-site transport of pesticides via leachate, soil pore water and groundwater. Transport of pesticides through leachate and groundwater will be discussed in more detail in the next section.

4.5 Groundwater Transport

Pesticides moving through the groundwater systems of the GBRCA need to be considered when evaluating the transport and exposure pathways of pesticides to the Reef. As previously mentioned, the 2006–2010 Pesticide Synthesis Report (Devlin and Lewis, 2011) contained very limited information about the occurrence of pesticides in groundwater and no information about their transport in groundwater. What is now known is that a high degree of connectivity between groundwater and surfacewater in some GBR regions exists (i.e. the Wet Tropics, lower Burdekin, and Mackay–Whitsunday), and that sizeable volumes of groundwater discharge into riverine and coastal environments (Hunter 2012). A review (Hunter, 2012) and three new field studies of pesticide occurrence in groundwater (Shaw et al, 2012; Masters et al., 2014b; Vardy et al., 2015) have been released since the 2006-2010 pesticide synthesis report (Devlin and Lewis, 2011). The frequency of pesticide detection, and the maximum and mean concentrations from each groundwater study are presented in Appendix A.

Concentrations of the herbicides diuron and hexazinone in leachate (deep drainage) have been found to be highly correlated with surfacewater runoff, but in much lower concentrations (Rohde et al., 2013). The concentrations measured in leachate have been detected up to several orders of magnitude lower than what was detected in surfacewater runoff (Rohde et al., 2013; Masters et al., 2014b), and followed the same decline over time after application as in runoff (Rohde et al, 2013). Compared to transport in surfacewater, pesticides leaching through the unsaturated zone and transported in groundwater are typically slower moving (e.g. in the Burdekin floodplain movement is likely to take years to decades) and pesticides, depending on their physicochemical properties, may bind to subsurface soil. For example, hexazinone concentrations in runoff and drainage were higher than diuron, even though it is applied at approximately one-third the rate (Rohde et al., 2013). This presumably occurs because more diuron is sorbed to soil than hexazinone.

The presence of pesticides in leachate is also dependent on the prevailing land use (Masters et al., 2014b). Pesticides have been detected in leachate from banana plantations (Masters et al., 2014a) and sugarcane farms (Armour et al., 2013) in the Wet Tropics that had shallow groundwater. Twelve herbicides and one insecticide (imidacloprid) were detected in leachate from sugarcane, whereas only glyphosate (herbicide) was detected in leachate under bananas. In the sugarcane leachate, imidacloprid, diuron, tebuconazole, atrazine and simazine were detected frequently, in addition to less common pesticides; propazin-2-hydroxy, hexazinone, flusilazole, 2,4-D, terbutryn, metolachlor, triclopyr and MCPA (Masters et al., 2014b). It should be noted that there was no recorded applications of atrazine or simazine at the study site therefore indicating potential transport from other sites.

Generally pesticides in subsurface soils and groundwater tend to be persistent (i.e. resist degradation) due to low concentrations of organic matter and microbial activity, anaerobic and alkaline conditions, and lack of light. For example, under these conditions, Silburn et al. (2013) noted detection of hexazinone, atrazine and its derivative desethylatrazine in subsoils and leachate five years after their last application. In another example, imidacloprid and diuron were the most frequently detected pesticides in leachate from a sugarcane farm two years after their last application (Masters et al., 2014b).

A field study by Shaw et al. (2012) sampled pesticide residues in 53 bores located in discharge zones of the Burdekin River delta and Burdekin River Irrigation Area (BRIA) where groundwater potentially enters streams or wetlands. This is an area of considerable sugarcane production. Pesticides were detected in 38% of the groundwater samples. All of the pesticides detected were registered for use in sugarcane. All the pesticides detected, except diuron and chlorpyrifos, were expected to be present as they have high leaching potentials. The three most frequently detected herbicide residues were desethylatrazine and desisopropylatrazine (both breakdown products of atrazine) and atrazine that were detected in 32%, 21% and 13% of samples, respectively. Hexazinone, diuron and metolachlor were detected less frequently, in 7.5%, 3.8% and 1.9% of samples, respectively. On only one occasion were pesticides detected at depths greater than 25m – this was for atrazine and its breakdown products. This finding is consistent with diffuse recharge having a longer travel time to reach deeper aquifer layers (Shaw et al., 2012).

The Shaw et al. (2012) study was followed up by another that focussed, amongst other issues, on the temporal variation in concentrations and potential transport of pesticides through the riparian zone of sites in the lower Burdekin (Vardy et al., 2015). This entailed monthly sampling between November 2011 and April 2013 at sites adjacent to the Haughton River, Barratta Creek, Burdekin River and Ramsar listed wetlands in Bowling Green Bay. Atrazine, desethylatrazine and desisopropylatrazine, ametryn and propazin-2-hydroxy (a degradation product of propazine) were detected at three sites. Simazine and metsulfuron-methyl were both detected at two sites. Diuron, hexazinone, imidacloprid, metolachlor, tebuthiuron, 2,4-D, acifluorfen, haloxyfop (acid), isoxaflutole, MCPA and triclopyr were only detected at the Barratta Creek site at Northcote. The study confirmed the finding of Shaw et al. (2012) that generally pesticide concentrations in groundwater were low (most concentrations were less than 0.01 $\mu g.L^{-1}$ and only atrazine was greater than 2 $\mu g.L^{-1}$). The exception was at Barratta Creek, where a larger number of pesticides with elevated and transient concentrations were attributed to creek water entering the groundwater during a higher flow event. Following this surfacewater recharge of the groundwater near Barratta Creek, the composition and concentration of the groundwater was essentially identical to that of the creek water. This change was very rapid but did not persist for more than a couple of months (Vardy et al., 2015). Nonetheless, this shows the high degree of connectivity between groundwater and surfacewater and that for relatively short periods, groundwater can have much higher than usual pesticide concentrations.

Another field study was conducted by Masters et al. (2014b) who sampled groundwater from five to seven bores on three occasions between August 2012 and April 2013, in the Tully-Murray and

Johnstone catchments. Unfiltered samples were analysed for a suite of 232 compounds – predominantly pesticides. Of the seventeen samples analysed, three contained no pesticides, seven contained at least three pesticides and seven contained mixtures of six to eight pesticides. The frequencies of detection were: hexazinone 82%, propazine-2-hydroxy 71%, desethylatrazine and diuron 59%, desisopropylatrazine 47%, imidacloprid 35% (but it only occurred in the Johnstone catchment), atrazine 41%, bromacil 18%, simazine 12%, glyphosate 8% and metsulfuron methyl 6%. This pattern of pesticide occurrence was observed for both the Johnstone and Tully-Murray catchments.

The detection of diuron and glyphosate in both leachates and groundwater (Shaw et al., 2012; Masters et al., 2014a, 2014b; Vardy et al., 2015) highlights the potential for pesticides, which should theoretically be bound strongly to soil, to move into leachates and groundwater. Pesticide concentrations in groundwater have been found to vary over time in the same bores (Masters et al., 2014b; Vardy et al., 2015). The highest concentrations can occur at any time depending largely on local agricultural practices. At some sites pesticide concentrations declined steadily over time while others had persistently low values. This indicates that sampling at only one point in time will not give a reliable indication of pesticide occurrence and concentrations. Rather, groundwater must be sampled repeatedly over time to give a true reflection of pesticide concentrations. The length of time over which sampling should be conducted would logically depend on the rate of groundwater movement and recharge. Groundwater systems with high rates of transport and recharge may need more intense sampling than slower moving and recharging groundwater where more sporadic sampling would adequately reflect temporal variation.

Of concern for the GBR, pesticides can be transported rapidly through groundwater, in shallow, ephemeral or seasonal water tables, and released into creeks and constructed drains (Masters et al., 2014a). In such systems travel distances are relatively short and travel times maybe of the order of weeks. However, the volumes of groundwater and loads of contaminants that return to surfacewater in this way are poorly defined.

4.6 Surfacewater Transport

As we move from the paddock scale to the multiple farm scale, concentrations of pesticides in surfacewater runoff depend not only on pesticide physicochemical properties, application rates and the timing of rainfall, but also on the proportion of the land where pesticides have been applied. Paddocks and farms have various pesticides applied at different times during the year or may have none of a particular pesticide applied at all. Runoff from unsprayed areas can act as diluent when it mixes with runoff from sprayed areas, effectively reducing the pesticide concentrations in the runoff. In addition, when rainfall occurs across the area, the rain will fall on these paddocks at a range of times after pesticide application. These paddocks will thus have different pesticide loads remaining on the sprayed surfaces, as they progress along their particular exponential decay trajectory.

Cook et al. (2013) demonstrated that the seemingly complex problem of estimating runoff concentrations at larger spatial scales could be done using a reasonably tractable mathematical solution, so long as the temporal distribution of application areas can be defined. The model used a first-order decay function and a simple pesticide runoff model (Silburn and Kennedy, 2007; Rattray et al., 2007), and showed that runoff losses from a large number of fields can be represented by a reasonably small number of areas on different decay trajectories. Cook et al. (2011, 2013) and Smith et al. (2011) showed that the model could mimic catchment pesticide runoff over time using a few reasonable assumptions; accounting for dilution from un-sprayed areas was an important part of the modelling. Using this model, it was also found that as the spatial scale increased pesticide dissipation half-lives decreased (Cook et al., 2011; Smith et al., 2011) indicating that once runoff moved to the receiving waterways, additional dilution and decay of pesticides occurred (Thorburn et al., 2013), which is to be expected. Likewise, Davis et al. (2013) found that pesticide concentrations decreased by an order of magnitude over relatively short distances between paddocks and nearby receiving creek systems.

As pesticides then move from the receiving creek systems to higher order streams, concentrations decrease further (Davis et al., 2012; O'Brien et al., 2013b). This is likely as a result of: (i) dilution with water of lower concentration; (ii) deposition of sediment containing sorbed pesticides; (iii) adsorption of pesticides to bottom and bank materials; (iv) sorption by riparian vegetation, and (v) dissipation of the pesticide by volatilisation, or biological or chemical degradation (Finlayson and Silburn, 1996). Variations in pesticide concentrations along a catchment have been demonstrated in the Herbert Water Quality Monitoring Program (O'Brien et al., 2013b, 2014b). Considerable differences were observed between the upper reaches and lower reaches of the Herbert River catchment area. It was found that higher concentrations and more pesticides were detected in the lower catchment area where sugarcane land use becomes prominent. The highest concentrations of diuron and hexazinone were detected in first flush events of small sub-catchments of the lower catchment area. Pesticide concentrations then seem to dissipate as they move further down the catchment towards the Herbert River end-of-system; most likely as a result of dilution from the upper catchment. For example, in 2012–13, 34 µg L^{-1} of diuron was detected at Boundary Creek (a small sub-catchment of the Herbert River) (O'Brien et al., 2014b). This was approximately 23 times the highest concentration detected at the Herbert River end-of-system site (Herbert River @ Ingham; 1.48 µg L^{-1}) in the same year (GBRCLMP data, unpublished). The maximum concentration of hexazinone in 2012–13 was 16 µg.L^{-1} also detected at Boundary Creek, which was 40 times higher than the peak concentration detected at the downstream end-of-system site (0.4 µg L^{-1}). A similar trend was observed at Barratta Creek where pesticide concentrations were found to progressively decrease towards the lower reaches of the creek system (Davis et al., 2012; O'Brien et al., 2013a). Concentrations detected in the estuary of Barratta Creek were at least a half to one-third of the concentrations detected in the upstream site (O'Brien et al., 2013a). This shows that the delivery of irrigation runoff to receiving waterways without rainfall events leads to high pesticide concentrations in the receiving water as there is little dilution (Davis et al., 2013). These elevated pesticide concentrations have been routinely observed in Barratta Creek (Davis et al., 2008, 2012, 2013; Smith et al., 2012; O'Brien et al., 2013a).

Pesticides then continue to move from catchments to the marine environment principally via riverine plumes discharged to the coastal waters of the GBR (Lewis et al., 2009; Lewis et al., 2012; Kennedy et al., 2012b; Petus et al., 2015). Pesticides in flood plumes have been found to reach mangroves, seagrass beds and inshore coral reefs and have been detected 50 km offshore from some river mouths (Lewis et al, 2009). Since 2005, annual riverine plume monitoring has examined the dispersal characteristics of pesticides in flood plumes; pesticide concentrations continue to decrease as freshwater begins to mix with seawater and the flood plume moves further away from the river mouth (Rohde et al., 2006, 2008; Lewis et al., 2009; Devlin et al., 2012a, 2012b; Kennedy et al., 2012a; Lewis et al., 2012). The change in pesticide concentrations at this stage of transport is believed to be principally due to 'conservative mixing behaviour' with the seawater rather than chemical or biological breakdown (Lewis et al, 2009). It is also hypothesised that the herbicide residues in the flood plumes are predominantly in the dissolved phase rather than bound to particulate materials; "the physical removal of sediments near the mouth of the river via flocculation processes would show non-linear characteristics as would the chemical degradation of the herbicide products or uptake by biota" (Lewis et al, 2009). This conservative mixing behaviour between pesticide concentrations and salinity has allowed for the development of mixing models to estimate the spatial exposure of pesticides on seagrass beds and near-shore coral reefs (Kennedy et al, 2012b; Lewis et al, 2013; Petus et al., 2015). The results of these studies will be examined in further detail in Section 5.12.1.

4.7 Fate & Compartmentalisation

4.7.1 Fate

The persistence of pesticides in the marine environment has, until recently, been poorly understood, but is a key factor in affecting their transport within the GBR lagoon and is essential information to inform predictive risk models. The year-round detection of low concentrations (< 10 ng L^{-1}) of pesticides in the Reef lagoon (Shaw and Muller, 2005; Shaw et al., 2010; Kapernick et al., 2006, 2007; Bartkow et al., 2008; Kennedy et al., 2012b; Gallen et al., 2013, 2014) indicates that many of these compounds must be relatively persistent in tropical marine waters. This finding is contrary to the half-lives reported in the literature. However, the half-lives reported in the literature are principally based on freshwater studies and conducted under test conditions that are not consistent with the conditions found in the GBR. The information available on the persistence of herbicides in seawater has until recently been lacking, particularly for test conditions relevant to the GBR. Mercurio et al. (2014, in review; see also Negri et al., 2013) conducted standard flask and pond mesocosm degradation studies (using coastal seawater containing natural bacterial communities) to examine the degradation of glyphosate, four PSII herbicides (diuron, atrazine, tebuthiuron and hexazinone) and two non-PSII herbicides (2,4-D and metolachlor) under a variety of environmental conditions (Table 4-1).

While the flask experiments were performed under modified OECD protocols to provide suitable persistence data for comparative studies, the pond experiments provide the most environmentally relevant data which can be directly applied to spatial risk assessments for herbicides in flood plumes. The flask degradation experiments of individual herbicides indicated that glyphosate was moderately persistent in the marine environment under low light conditions but was highly persistent in the dark, with a minor influence of temperature between 25°C and 31°C (Mercurio et al., 2014). The half-lives (T½) of glyphosate were estimated as 267 ± 21 (SE) days when incubated in the dark at 25°C, 315 ± 29 days when incubated in the dark at 31°C and 47 ± 7 days when incubated in the light at 25°C. The half-life of 47 days under low-light conditions was similar to reported half-lives for glyphosate in fresh water; however, the persistence in the dark at both 25°C and 31°C (267 and 315 days) were by far the longest reported.

The larger volume pond mesocosm experiments (Mercurio et al, in review) examined the degradation of mixtures of the herbicides tested in the flask experiments. Preliminary results indicate that the half-lives of the herbicide mixtures ranged from 32 to 3330 days under the treatment conditions. In general, the half-lives of both PSII and non-PSII herbicides in the mesocosms were shorter than those obtained in the flask experiments, with the exception of the light treatment without sediment. The presence of sediment led to smaller half-lives, but the effect of the presence of light was not clear. The presence of sediment could have acted as an additional source of micro-organisms and/or as a sink for the pesticides (Negri et al., 2013).

These persistence estimates of pesticides in the marine environment represent the first relevant data for application in risk assessments for herbicide exposure in tropical marine systems. The long persistence of herbicides identified in the present study helps explain detection of herbicides in nearshore waters of the GBR year round. Little degradation of the herbicides studied here would be expected during the wet season with runoff and associated flood plumes extending or affecting the GBR. Clearly, further work is required to determine the half-lives of all pesticides commonly used in GBR catchments. The persistence of pesticides in streamflow, impoundments and wetlands in the GBR poorly understood.

Table 4-1 Range of half-lives (t½) in days for each treatment conducted in flasks: Dark 25°C, Dark 31°C, and Light 25°C in degradation Experiment 1 on single herbicides and for each treatment light no sediment, light with sediment, dark no sediment, and dark with sediment in degradation Experiment 2 using mixtures of herbicides.

Experiment	Treatment	PSII Herbicides (atrazine, diuron, hexazinone, tebuthiuron)		Non-PSII herbicides (2,4-D and metolachlor)	
		Dark	Light	Dark	Light
1	25°C	1568 – 5214	556 – 2799	146 – 281	320 – 494
	31°C	818 – 2840		88 – 298	
2	No sediment	300 – 1994	330 – 3330	59 – 147	93 – 1920
	With sediment	201 – 1474	107 – 944	56 – 103	32 – 288

4.7.2 Compartmentalisation (partitioning)

The majority of pesticide monitoring for P2R Program since 2009 has been focused on measuring the concentrations of pesticides in the water column in the dissolved phase, rather than pesticides in the bound phase or sediment bed. Research and monitoring conducted thus far has principally employed grab water sampling techniques followed by extraction of the analytes, or passive sampling. Both methods only measure pesticides in the dissolved phase. While this is logical for measuring the priority PSII herbicides, which are polar with low K_{ow} values and hence high aqueous solubilities (see Chapter 3, Table 3-1), there are many other pesticides known to occur in the receiving waterways of the GBR region which have a high affinity for binding to sediment, particularly insecticides. For example, passive samplers have been reported to detect very low concentrations of highly non-polar insecticides (e.g. Smith et al., 2012; O'Brien et al., 2013a), including the pyrethroids bifenthrin and cypermethrin.

By only quantifying the dissolved concentration of pesticides, we are most likely underestimating the loads of herbicides being exported to the Reef. Two studies have recently examined the compartmentalisation of pesticides in GBR catchments. Davis et al. (2012) compared filtered versus unfiltered concentrations in water samples from Barratta Creek, and found up to a third of the total pesticide concentration was transported in the bound fraction. In particular, of the priority PSII herbicides, diuron had the largest fraction bound to sediment (i.e. approx. 30%). The proportion of ametryn and hexazinone in the bound phase was estimated at 20%, tebuthiuron was 12.5% and atrazine 10%. The bound proportions of desethylatrazine and desisopropylatrazine were estimated at 16.5% and 6.0%, respectively (Davis et al., 2012). A similar assessment conducted in the Fitzroy catchment and for paddock rainfall simulation trials in the lower Burdekin and Mackay Whitsunday regions (Packett, 2014), found that at the sub-catchment and catchment scale, some pesticides were only detected in the dissolved phase (e.g. imidacloprid). Whereas, others were also found in both the dissolved and bound phases, e.g. ≥ 33% of simazine was bound, ≥ 20% of diuron was bound, ≥ 18% of tebuthiuron was bound, ≥ 14% of metolachlor and bromacil was bound, and ≥ 10% of desethylatrazine was bound (Packett, 2014).

Davis et al. (2012) also examined concentrations of pesticides in benthic sediment for a number of sites in Barratta Creek, Bowling Green Bay and nearshore marine sites. Ametryn, atrazine, diuron, metolachlor and tebuthiuron were detected in benthic sediments of Barratta Creek, with diuron detected in the highest concentrations. Furthermore, only diuron was detected in the sediments collected from the Bowling Green Bay and nearshore marine sites. No organochlorine (e.g., DDT, aldrin, dieldrin etc.) or organophosphate (e.g. chlorpyrifos) residues were detected in this study. In 2012-13, sediment cores were collected from a number of freshwater wetland sites in the Lower Burdekin, Mackay-Whitsundays, and Burnett regions (Vandergragt, pers comm.). Two pesticides and a breakdown product were detected; atrazine, diuron and DDE (a breakdown product of the insecticide DDT). Of the residues detected, DDE was found in the highest concentrations (27 $\mu g.kg^{-1}$), at Yellow Waterholes Creek in the Burnett catchment area. The use of DDT has been banned in Australia since 1987 but it is highly persistent, so the detection of DDE is likely to be a legacy of the period when DDT was still registered for use. Diuron was detected at the most sites, namely Sandy Creek in the Mackay-Whitsundays and Yellow Waterholes Creek, Woodgate National Park and South Kolan in the Burnett Catchment. Atrazine was only detected at one site, Mon Repos in the Burnett Catchment. Prior to these studies, diuron was also found to be the dominant pesticide in benthic sediments detected in inter- and sub-tidal areas of the GBR (Duke et al., 2005; Haynes et al., 2000a) and in agriculture irrigation drains and channel in the GBR catchment (Muller et al., 1998).

4.8 Loads

Quantifying the loads (total mass) of pesticides provides information on the mass of pesticides that are transported from paddocks, via groundwater and surfacewater runoff, down catchments and then released to the GBR lagoon. Kroon et al. (2010, 2012) reported baseline pesticide loads from which the Reef Plan reduction targets have been set. Since this time, the P2R program has estimated the annual pesticide loads for the five priority PSII herbicides using monitoring and modelling techniques (e.g. Wallace et al., 2014; Waters et al., 2014). Monitored loads are calculated using the measured aqueous concentrations of the pesticides and the volume of discharge. As such, this method determines load estimates based on the influential conditions that were prevalent within the year of monitoring. Modelling used in P2R program estimates the pesticide loads transported from catchments using a combination of predicted losses of pesticides from paddocks in the sugarcane and grains industries and simpler methods (empirically derived event mean concentration/dry weather concentration times flow) for other land uses over 30-yr climate sequence. The modelling provides load estimates that may differ from the measured seasonal loads because the model is not an exact replica of the catchment or of conditions in a particular season. However, it has the advantage that load estimates can be made for various scenarios, such as with changes in management practices.

Both load estimation methods have advantages and disadvantages and this is why both methods are used in the P2R program. For example, monitored loads are limited in that they only estimate the loads from the variables measured at the gauging stations which are mostly situated at the freshwater zone of waterways (above the tidal influence). In such cases, the contribution from the portion of the catchment below the gauge is not included in the load estimations. In some catchments these areas contain the highest area of sugarcane (e.g. the Johnstone and Herbert catchments). However, new technologies such as acoustic doppler current profilers (ADCPs) permit gauging stations to be located within the tidally affected reaches, and so overcome this limitation. For example the GBRCLMP has established two such stations in the estuaries of the Russell and Mulgrave Rivers and another is to be built in the estuary of the Johnstone River. The second main limitation of monitored loads, is that the method can only calculate pesticide loads for monitored catchments. Neither of these limitations apply to modelled loads where pesticide loads can be generated for the entire catchment (i.e. right to the mouth of the catchment) and for all catchments in the GBR region. Two drawbacks of the modelling approach are (i) the complexity of the methods can mean that the results are viewed with uncertainty (or lack transparency), particularly from the non-scientific community, and (ii) their reliance on sound scientific knowledge (to build the models), which is incomplete, and monitored loads data to calibrate and validate the models.

Monitored loads of the five priority PSII herbicides have been estimated annually since 2009–2010 for up to 15 catchments as part of the GBR Catchment Loads Monitoring Program (GBRCLMP) (Turner et al., 2012, 2013; Wallace et al., 2014, 2015; Garzon-Garcia et al., in prep). Monitored loads of other pesticides have been estimated since 2011–12 (Wallace et al., 2014, 2015; Garzon-Garcia et al., in prep). Prior to 2009/10, smaller datasets for certain NRM regions were developed by individual research projects (Mitchell et al., 2005; Rohde et al., 2008; Lewis et al., 2009; Packett et al., 2009; Davis et al., 2012). Boxplots of the monitored priority PSII herbicide loads calculated annually by GBRCLMP from 2010–2011 to 2012–2013 are presented in Figure 4-2 and Figure 4-3. The loads within each catchment are highly variable over time reflecting the variation in annual climatic conditions (see Temporal Exposure). The loads also vary between catchments, in terms of the absolute magnitude of the loads and also the relative contribution of each PSII herbicide to the load. For example, catchments with a high sugarcane land use area (e.g. Pioneer Catchment) have loads that are generally dominated by diuron, followed by atrazine. Catchments with the highest proportions of grazing and other non-sugarcane land-uses (e.g. Burdekin, Fitzroy and Burnett catchments) have loads dominated by tebuthiuron and atrazine (atrazine in these catchments are sourced to mixed and broadacre cropping lands). Ametryn loads are relatively small compared to diuron, atrazine and tebuthiuron, and are only detected in a small number of catchments, which have a high sugarcane land use area. Hexazinone is present in most catchments but the loads are much smaller relative to diuron, atrazine and tebuthiuron.

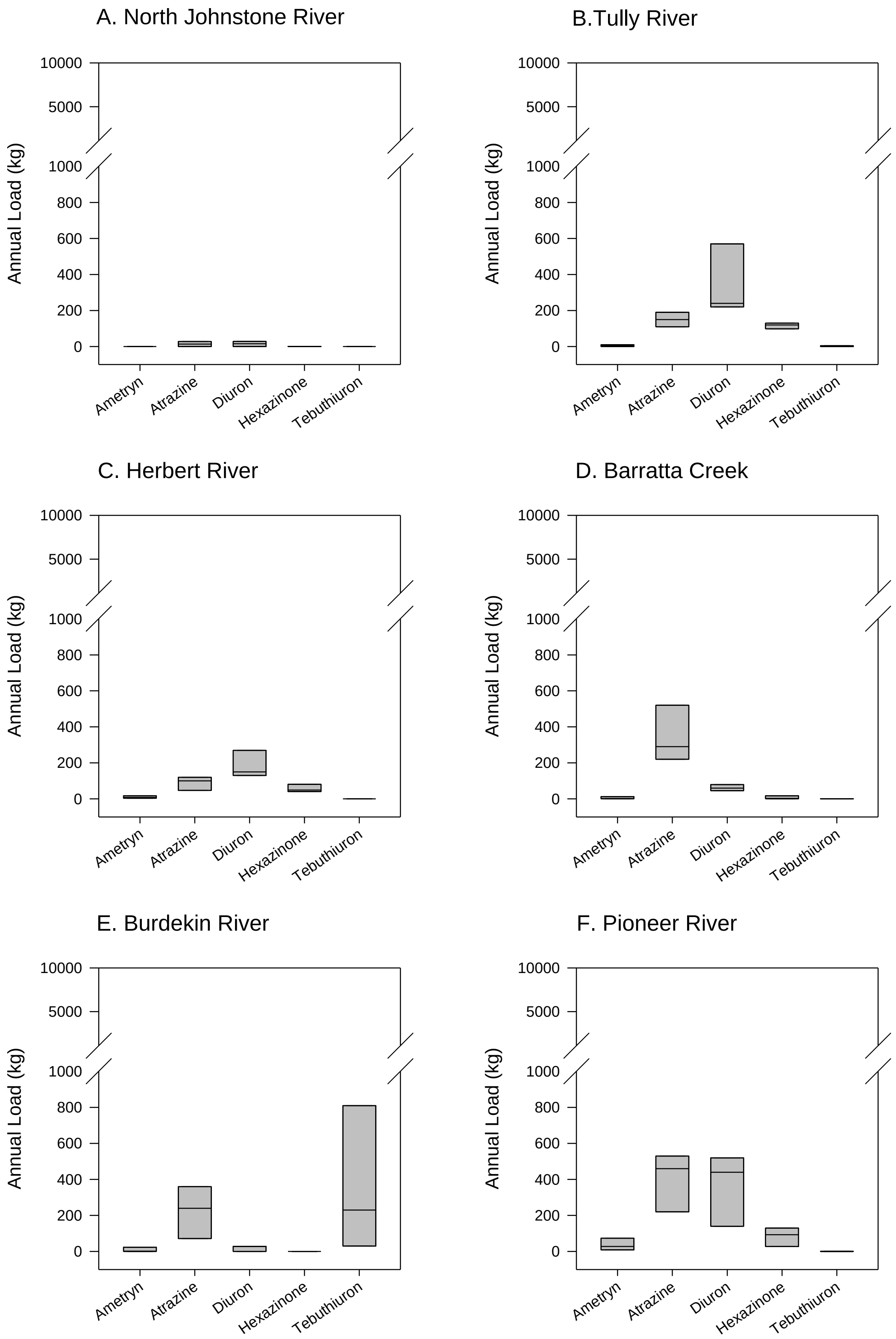

Figure 4-2 Box plots of the annual loads of Photosystem II herbicides estimated for catchments that discharge to the Great Barrier Reef between 2010–2011 and 2012–2013. Data obtained from (Turner et al, 2013; Wallace et al, 2014; Wallace et al, 2015). The top and bottom of the boxes represent the maximum and minimum loads and the centre line represents the median load.

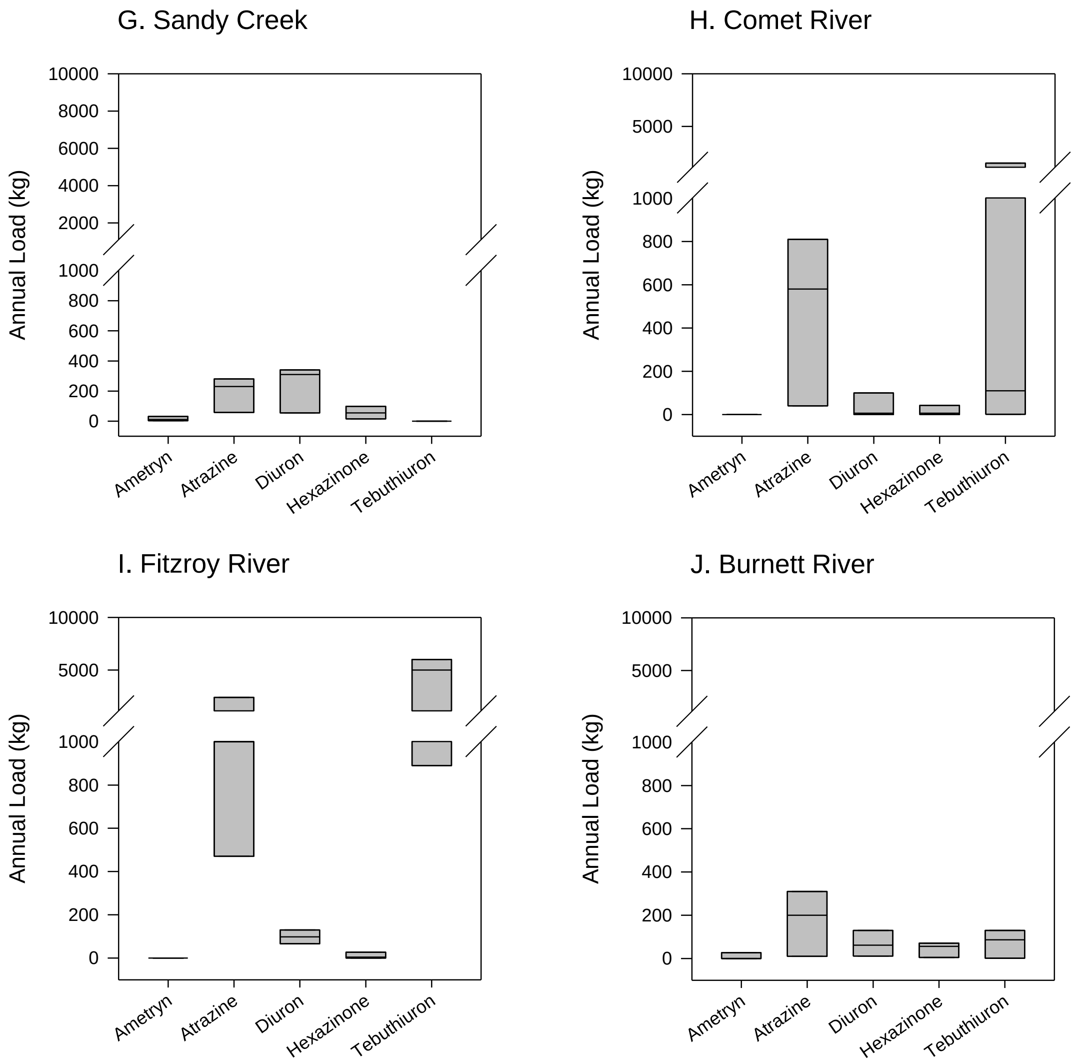

Figure 4-3 Box plots of the annual loads of Photosystem II herbicides estimated for catchments that discharge to the Great Barrier Reef between 2010–2011 and 2012–2013. Data obtained from (Turner et al, 2013; Wallace et al, 2014; Wallace et al, 2015). The top and bottom of the boxes represent the maximum and minimum loads and the centre line represents the median load.

Hateley et al. (2014) has argued that the distance pesticides are transported may play a role in the annual loads discharged to the GBR. This is based on the concept that shorter transport distances provide less opportunity for in-stream or floodplain processes to degrade or remove (through partitioning) pesticides.

It was argued in one of the technical chapters (Lewis et al., 2013) underpinning the Scientific Consensus Statement (Brodie et al., 2013) that the monitored loads are underestimates of the actual loads. There are two main reasons for this. First, the 'end-of-system' sites are generally located well upstream of the end of the tidal influence and therefore do not capture the load contributed by all land downstream[3]. Second, until 2014 (Wallace et al., 2014), the monitored loads only included the five priority PSII herbicides. Yet, 49 pesticides have been detected in the GBR catchments and lagoon (Lewis et al., 2009, Packett et al., 2009, Shaw et al., 2010, Davis et al., 2012, Smith et al., 2012; Turner et al., 2012, O'Brien et al., 2013a; Turner et al., 2013; Wallace et al., 2014, 2015; Garzon-Garcia et al., in prep). The additional pesticides detected include five other photosystem II inhibiting herbicides, a growth inhibitor herbicide, synthetic auxins, insecticides, organophosphates, organochlorins, synthetic pyrethroids and fungicides.

Three studies have determined loads for pesticides in addition to the five priority PSII herbicides (Wallace et al., 2014, 2015; Smith et al., 2015) and a fourth (Garzon-Garcia et al., in prep) will do this for the 2013–2014 data. For 2011–2012 the loads of bromacil, metolachlor, prometryn, simazine and terbutryn were also determined. Their inclusion increased the total monitored pesticide load by 17% (Wallace et al., 2014). Smith et al. (2015) examined the prevalence of 'alternate'[4] pesticides in six catchments (Johnstone, Tully, Herbert, Barratta, Pioneer and Sandy) but could not calculate loads for the Johnstone. They found that in 2012–13 the loads of the 'alternate' pesticides increased the total pesticide load by 13% to 27% depending on the catchment. Of the alternate pesticides, 2,4-D made the largest contribution to the total pesticide load in all five[5] catchments, contributing between 5% and 11%. Load contributions of other prevalent alternate pesticides in each catchment included: metribuzin (≤ 7%), metolachlor and isoxaflutole (≤ 3%), and acifluorfen and MCPA (≤ 2%). Wallace et al (2015) included two additional pesticides (imidacloprid and terbuthylazine) and three extra catchments (Burdekin, Fitzroy and the Burnett) compared to Smith et al (2015) and found that the alternate pesticides overall increased the total pesticide load by 28% from 10,000 to 12,800 kg for 2012–2013. It thus appears that while the monitored PSII based loads underestimate the total pesticide load they are not an order of magnitude underestimates.

Two different approaches have been conducted to model pesticide loads exported from the GBRCA including the Source Catchments model (Waters et al., 2014) and a model developed for the MCA prioritisation process. The Source Catchments model framework applies HowLeaky? to model pesticide losses from the many paddocks which is then up-scaled to a catchment/basin area (Waters et al., 2014). Tebuthiuron losses from grazing lands are calculated using an event mean concentration. The Source Catchments model reports on the summed contribution of PSII herbicide loads for the 35 major river basins of the GBRCA (Waters et al., 2014). The 'MCA' model develops PSII herbicide yield based losses for the key industries in the GBRCA (sugarcane, grazing, horticulture, broad acre cropping) using the available monitored load data. The method for this MCA model is reported in Lewis et al. (2011) and Waterhouse et al. (2012). Initial results from this model reported summed priority PSII herbicide loads for the baseline report (Kroon et al., 2010, 2012) while the recent iterations report individual priority PSII herbicide loads using regionally-specific yield loss coefficients (Lewis et al., 2011; Barson et al., 2014). In terms of total priority PSII herbicide losses to the GBR lagoon, the two modelling methods are comparable, although there are regional discrepancies in particular the Wet Tropics and Mackay Whitsunday regions (Kroon et al., 2013).

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[3] This source of potential underestimation does not apply to modelled loads.

[4] Alternate pesticides were defined in Smith et al (2015) as any herbicide that has been used or could be used by farmers in the GBRCA that is not one of the five priority PSII herbicides; ametryn, atrazine, diuron, hexazinone and tebuthiuron. Alternate pesticides do not, in this report, include insecticides or fungicides.

[5] Note that the pesticide loads for the Johnstone River were not calculated due to insufficient data.

Groundwater discharge may also contribute to surfacewater loads of pesticides in some regions. Vardy et al. (2015) indicated that overall groundwater was estimated to contribute less than 10% to the in-stream pesticide loads in the Lower Burdekin. The groundwater contribution for tebuthiuron and propazin-2-hydroxy was much higher, but this was most likely to be an artefact of a single concentration being greater than the limit of reporting. Unpublished work by the GBRCLMP has identified that groundwater contributes between 40 and 50 % of dissolved inorganic nitrogen in the Tully River. Given these values, it is quite possible that groundwater is also making a significant contribution to the loads of pesticides. Given the high rainfall and discharge of rivers in the Wet Tropics NRM region, the contribution of groundwater in the Wet Tropics to pesticide loads warrants further investigation.

Some groundwater is also directly discharged into the ocean, although the volume of this water is poorly defined (Cook et al., 2004; Williams et al., 2008). The loads of pesticides discharged to the GBR via this mechanism would be much less than the corresponding loads exported via streamflow, but would still add to the total load being discharged to the GBR. Groundwater discharge across the entire alluvial floodplain of the lower Burdekin is in the range of 30 – 150 GL/yr to surfacewater and 50 – 400 GL/yr to the ocean (Cook et al, 2004; Williams et al, 2008). To place the potential contribution of groundwater to pesticide loads entering the Great Barrier Reef in context, these flows could carry loads of 30 – 150 kg (to surfacewater) and 50 – 400 kg (to the ocean) of a contaminant that was present at a concentration of 1 $\mu g.L^{-1}$ concentration, compared to a total average annual load of all PSII herbicides in the Burdekin region of approximately 2,100 kg (Waters et al, 2014). If flows are in the higher end of the above ranges and the combined concentration of PSII herbicides are several µg/L, the total additional load to the GBR from groundwater exports could become significant. Results from the most recent groundwater sampling indicate that concentrations of individual pesticides are < 1 µg/L. Importantly, this load is not being quantified by the P2R program or other R&D projects. In contrast, pesticides present in groundwater discharged into streams, would be accounted for in the catchment loads monitoring (providing it discharges to surfacewater upstream of the gauging station) and modelling.

It is important to note that having the highest loads does not mean that organisms will be exposed to the highest concentrations. It is the combination of concentration, relative toxicity of the pesticide and duration of exposure, rather than loads, that are directly related to biological effects.

4.9 Spatial extent of exposure

As pesticides move from the source they are dispersed to a variety of ecosystems where they may continue to move and/or undergo transformative processes such that different ecosystems are exposed to different concentrations and types of pesticides and their metabolites. Our current understanding of the spatial exposure in the GBR and coastal ecosystems is based on the monitoring of approximately half of the major rivers draining to the GBR, a small fraction of sub-catchments and small creeks draining directly to the coast, a very small fraction of wetlands and estuaries, and a very small fraction of the marine environment. Within those environments, a total of 56 pesticides (including metabolites) have been detected, consisting of 29 herbicides, 16 insecticides, 4 fungicides and 7 herbicide metabolites (Table 4-2 and Table 4-3). Variations in the pesticide exposure characteristics between ecosystems signify potential differences in the ecological risk of pesticides to those ecosystems.

4.9.1 Riverine

It is now well established that riverine ecosystems in the GBR region are exposed to higher concentrations (relative to other ecosystems) and large numbers of pesticides (Davis et al., 2012; Smith et al., 2012; O'Brien et al., 2013a, 2014a, 2014b). Along with freshwater wetlands, creeks and rivers are the principle receiving ecosystems of pesticides in paddock runoff, and are therefore exposed to the highest concentrations of pesticides. Depending on a number of anthropogenic and environmental factors, the level of exposure varies considerably between catchments; i.e. the types of pesticides that are detected, the concentrations at which they are detected and their temporal exposure. These observed differences will mean that the ecosystems within these catchments will face different pressures from pesticide exposure. Here we will focus on the observed differences in pesticide exposure in catchments across the GBR region in terms of the pesticides detected and their concentration levels. Temporal variations will be addressed in the following section.

Prior to 2009, monitoring of pesticides in freshwater ecosystems was limited to a small number of catchments in the GBR region (Devlin and Lewis, 2011). At the time of publication of the 2006-2010 Pesticide Synthesis Report, studies such as Davis et al. (2012) and Smith et al. (2012), which were the first to provide much greater detail on the spatial and temporal distribution of pesticides in GBR catchments, were still in preparation. Since that time, there has been substantial development in the knowledge of pesticide exposure in catchments. For example, pesticides have been routinely monitored in sub-catchments and catchments of the Wet Tropics, Burdekin, Mackay-Whitsundays, Fitzroy, and Burnett-Mary Natural Resource Management (NRM) regions (Appendix B). Since 2009 the GBRCLMP has annually monitored between 11 and 16 sub-catchment and end-of-system sites across all of the above mentioned NRM regions (Smith et al., 2012; Turner et al., 2012, 2013; Wallace et al., 2014, 2015; Garzon-Garcia et al., in prep). In 2011, a three-year study was undertaken to assess spatial exposure of pesticides throughout a catchment as part of the Herbert Water Quality Monitoring Program (O'Brien et al., 2013b, 2014b). In this program, 16 catchment and sub-catchment sites were monitored in the upper and lower reaches of the Herbert Catchment. A number of detailed studies have also examined pesticide exposure in catchments of the Lower Burdekin (Davis et al., 2012a; O'Brien et al., 2013a) and earlier (i.e. pre-2009) catchment monitoring studies have been conducted in the Johnstone (Hunter et al., 2001), Mackay Whitsunday (Mitchell et al., 2005; Rohde et al., 2006, 2008), Black-Ross (Liessmann et al., 2007), Tully-Murray (Bainbridge et al., 2009) and Fitzroy (Packett et al., 2009) catchments. In addition, unpublished pesticide concentration data are also known to have been collected in the Normanby, Daintree and Mossman catchments.

Since 2009, 47 pesticides (and metabolites) have been detected in the Burdekin region (predominantly from Barratta Creek), 40 in the Wet Tropics, 32 in the Mackay-Whitsundays, 16 in the Fitzroy region and 15 in the Burnett-Mary (Table 4-2 and Table 4-3). The number of pesticides detected has continued to rise over time, at least partly as a result of improvements in sampling and analytical methods but also due to changes in pesticide usage. The pesticides detected include the five priority PSII herbicides, 23 other 'alternate' herbicides, 16 insecticides, 4 fungicides and 5 metabolites. The priority PSII herbicides have been detected across almost all NRM regions. The only exception is ametryn which has not been detected in the Burnett-Mary Catchment area (Table 4-2). Pesticides that have been detected across all NRM regions include; bromacil, chlorpyrifos, metolachlor, simazine and the atrazine metabolites, desethylatrazine and desisopropylatrazine (Table 4-2). In 2009–10, Smith et al. (2012) reported that atrazine and diuron were the most commonly detected pesticides in monitored catchments. This was also shown in monitoring data from 2010–12 where atrazine and diuron were detected in nine (2010/11) and eight (2011/12) catchments, respectively, out of nine catchments that were monitored.

The water quality monitoring has clearly shown that not only are ecosystems exposed to multiple pesticides, but that they are invariably simultaneously exposed to mixtures of pesticides (e.g. Smith et al, 2012). This is clear when the raw data from pesticide analyses are examined, but unfortunately it is seldom directly commented on in the literature. During the 2014 – 2015 year a single grab sample from Barratta Creek contained 18 pesticides (GBRCLMP unpublished monitoring data). Mixtures of pesticides can have a combined toxicity that is additive, synergistic or antagonistic (e.g. Warne and Hawker, 1995), therefore the presence of mixtures and the pesticides present in the mixtures should be reported in the literature to assist with assessing ecological risk (refer to Chapter 5).

Pesticide concentrations are also found to vary between catchments and NRM regions. The 2013 Scientific Consensus Statement (Brodie et al., 2013; Lewis et al., 2013) indicated that the in-shore reef lagoon in the Mackay-Whitsundays region had the highest risk of adverse effects from pesticides. This result was based on the concentrations of pesticide mixtures detected at end-of-system sites in Sandy Creek and Pioneer River in 2009-2011. The Burdekin region was also found to have a high risk based on the very high concentrations detected in Barratta Creek during the same period. The Johnstone, Tully, Fitzroy and Burnett catchments were found to have a much lower risk based on the observed mixture concentrations. While this risk assessment was an improvement on previous pesticide risk assessments – it still suffers from a number of limitations including that it focussed on a single day during a flood event.

We are now at a stage to start evaluating what factors are contributing to the variations in pesticides observed between catchments; e.g. land use type, land management practices, geology, hydrology and climatic conditions. The highest pesticide concentrations that have been detected have generally been detected in smaller catchments or sub-catchments, in the lower reaches of catchments, catchments closer to the coast and catchments associated with sugarcane land use (Smith et al., 2012; Davis et al., 2012; O'Brien et al., 2013b, 2014b). O'Brien et al. (2014b) found that a greater number of pesticides and higher concentrations of pesticides were detected in sub-catchments dominated by sugarcane land use, compared to catchments with dry-land grazing, mixed cropping, ex-tin mining and rainforest in the Herbert basin. Proportions of land use in catchments routinely monitored for pesticides by the GBRCLMP are reported in Table 4-4 along with the pesticide risk ratings (determined based on pesticide mixture concentrations) reported by Lewis et al. (2013). Those catchments with High and Very High risk ratings also had the highest proportions of sugarcane. More recently, Kroon et al. (2015) demonstrated that the percent of sugarcane land use in catchments was positively correlated with concentrations of ametryn, atrazine, diuron, hexazinone and imidacloprid.

Given that dilution is also recognised as a contributing factor to in-stream pesticide concentrations (see Section: Exposure and Transport Pathways), it should also be noted that those catchments with Low and Very Low risk ratings had high proportions of Grazing and 'Other' land uses (Table 4-4). These land-use types are known to have lower pesticide loads per km^2 and could therefore act to reduce the total pesticide concentration (Wallace et al., 2014, 2015). In addition, Smith et al. (*in prep-a*) found that pesticide mixture concentrations were negatively correlated with discharge volume, indicating that the size of the catchment and level of rainfall in the catchment could also be influencing factors of in-stream pesticide concentrations.

Table 4-2 Pesticides detected since 2009 in ecosystems of the Great Barrier Reef region. Detections have been collated based on NRM regions; WT = Wet tropics, B = Burdekin, MW = Mackay-Whitsundays, F = Fitzroy, BM = Burnett-Mary. Detections above the limit of reporting have been indicated by a shaded circle (●); Where pesticides have not been monitored is indicated by a clear circle (◌). Blank spaces indicate where monitoring has occurred but pesticides have not been detected (Note: because of changes in analytical methods over time, some pesticides may have not been included in the analysis suite at the time of monitoring and are indicated as 'not detected' due to this)..

Pesticide	Groundwater					Wetlands					Creeks and Rivers					Estuaries					Flood Plumes					Marine				
	WT	B	MW	F	BM	WT	B	MW	F	BM	WT	B	MW	F	BM	WT	B	MW	F	BM	WT	B	MW	F	BM	WT	B	MW	F	BM
Priority PSII herbicides																														
Ametryn		●	◌	◌	◌	◌	◌	●	◌	●	●	●	●	●		◌	●	◌	◌	◌	●		●			●	●	●	●	◌
Atrazine	●	●	◌	◌	◌	◌	◌	●	◌	●	●	●	●	●	●	◌	●	◌	◌	◌	●	●	●	●		●	●	●	●	◌
Diuron	●	●	◌	◌	◌	◌	◌	●	◌	●	●	●	●	●	●	◌	●	◌	◌	◌	●	●	●	●	●	●	●	●	●	◌
Hexazinone	●	●	◌	◌	◌	◌	◌	●	◌	●	●	●	●	●	●	◌	●	◌	◌	◌	●	●	●			●	●	●	●	◌
Tebuthiuron		●	◌	◌	◌	◌	◌		◌	●	●	●	●	●	●	◌	●	◌	◌	◌	●	●	●	●		●	●	●	●	◌
Alternate herbicides																														
2,4-D		●	◌	◌	◌	◌	◌	◌	◌	◌	●	●	●	●	●	◌	●	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌
Acifluorfen		●	◌	◌	◌	◌	◌		◌			●	●			◌	●	◌	◌	◌										◌
Bromacil	●		◌	◌	◌	◌	◌		◌		●	●	●	●	●	◌	●	◌	◌	◌	●					●	●	●	●	◌
Clomazone			◌	◌	◌	◌	◌		◌			●				◌		◌	◌	◌										◌
Fluometuron			◌	◌	◌	◌	◌		◌		●	●	●			◌		◌	◌	◌							●		●	◌
Fluroxypyr			◌	◌	◌	◌	◌	◌	◌	◌	●	●	●		●	◌	●	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌
Haloxyfop		●	◌	◌	◌	◌	◌		◌		●	●	●		●	◌	●	◌	◌	◌										◌
Glyphosate	●		◌	◌	◌	◌	◌	◌	◌		◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌
Imazapic			◌	◌	◌	◌	◌	●	◌	●	●	●	●			◌	●	◌	◌	◌	●					●	●	●	●	◌
Imazethapyr			◌	◌	◌	◌	◌		◌			●	●			◌	●	◌	◌	◌										◌
Isoxaflutole		●	◌	◌	◌	◌	◌		◌		●	●	●			◌	●	◌	◌	◌										◌
MCPA		●	◌	◌	◌	◌	◌	◌	◌	◌	●	●	●		●	◌	●	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌
Mecoprop			◌	◌	◌	◌	◌		◌			●				◌		◌	◌	◌										◌
Metolachlor		●	◌	◌	◌	◌	◌	●	◌	●	●	●	●	●	●	◌	●	◌	◌	◌	●					●	●	●	●	◌
Metribuzin			◌	◌	◌	◌	◌	●	◌	●	●	●	●			◌	●	◌	◌	◌	●									◌
Metsulfuron-methyl	●	●	◌	◌	◌	◌	◌	●	◌		●	●	●			◌	●	◌	◌	◌										◌
Pendimethalin			◌	◌	◌	◌	◌		◌		●	●				◌	●	◌	◌	◌										◌
Prometryn			◌	◌	◌	◌	◌		◌	●	●	●	●	●		◌	●	◌	◌	◌						●	●	●	●	◌
Propazine			◌	◌	◌	◌	◌		◌			●				◌	●	◌	◌	◌										◌
Simazine	●	●	◌	◌	◌	◌	◌	●	◌		●	●	●	●	●	◌	●	◌	◌	◌	●		●	●		●	●	●	●	◌
Terbutryn			◌	◌	◌	◌	◌		◌		●	●				◌	●	◌	◌	◌						●	●	●	●	◌
Terbuthylazine			◌	◌	◌	◌	◌		◌		●	●		●		◌	●	◌	◌	◌										◌
Triclopyr		●	◌	◌	◌	◌	◌	◌	◌	◌	●	●	●		●	◌	●	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌	◌
Trifluralin			◌	◌	◌	◌	◌		◌		●		●																	◌

[1]GBR Marine monitoring program (MMP) categories in HEQ (Gallen et al., 2013) .
[2]Proposed marine ecotoxicity threshold values for protecting 80%, 90%, 95% and 99% of species from diuron (ETVs, [3]Section 5 (Smith et al., In prep-b))
[4]Current GBRMPA water quality guideline for protecting 90%, 95% and 99% of species from diuron (GBRMPA, 2010)
Impacts of diuron on seagrass in experimental systems (Flores et al., 2013; Negri et al., 2015)

Table 4-3 Pesticides detected since 2009 in ecosystems of the Great Barrier Reef region. Detections have been collated based on NRM regions; WT = Wet tropics, B = Burdekin, MW = Mackay-Whitsundays, F = Fitzroy, BM = Burnett-Mary. Detections above the limit of reporting have been indicated by a shaded circle (●); where pesticides have not been monitored is indicated by a clear circle (○). Blank spaces indicate where monitoring has occurred but pesticides have not been detected (Note: because of changes in analytical methods over time, some pesticides may have not been included in the analysis suite at the time of monitoring and are indicated as 'not detected' due to this).

Pesticide	Groundwater					Wetland					Creeks and Rivers					Estuaries					Flood Plumes					Marine				
	WT	B	MW	F	BM	WT	B	MW	F	BM	WT	B	MW	F	BM	WT	B	MW	F	BM	WT	B	MW	F	BM	WT	B	MW	F	BM
Insecticides																														
Bifenthrin			○	○	○	○	○		○		●	●				○		○	○	○										○
Chlorfenvinphos			○	○	○	○	○		○		●	●	●			○		○	○	○										○
Chlorpyrifos		●	○	○	○	○	○		○		●	●	●	●	●	○	●	○	○	○								●		○
Clothianidin			○	○	○	○	○		○		●		●			○		○	○	○										○
Cypermethrin			○	○	○	○	○		○		●	●	●			○		○	○	○										○
DEET			○	○	○	○	○		○		●	●		●		○	●	○	○	○										○
Diazinon			○	○	○	○	○	●	○		●	●		●		○	●	○	○	○							●	●		○
Dieldrin			○	○	○	○	○		○				●			○		○	○	○										○
Fipronil			○	○	○	○	○		○		●	●		●		○	●	○	○	○										○
Endosulfan beta			○	○	○	○	○		○			●				○		○	○	○										○
Endosulfan sulphate			○	○	○	○	○		○			●				○		○	○	○										○
Imidacloprid	●	●	○	○	○	○	○	●	○	●	●	●	●			○	●	○	○	○	●					●	●	●	●	○
Methamidophos			○	○	○	○	○		○			●				○		○	○	○										○
Permethrin isomers			○	○	○	○	○		○			●				○		○	○	○										○
Phosphamidon			○	○	○	○	○		○			●				○	●	○	○	○										○
Prothiophos			○	○	○	○	○		○		●					○		○	○	○										○
Fungicides																														
Chlorothalonil			○	○	○	○	○		○		●					○		○	○	○										○
Flusilazole			○	○	○	○	○		○			●				○	●	○	○	○										○
Propiconazole isomers			○	○	○	○	○		○	●	●	●				○		○	○	○										○
Tebucanazole			○	○	○	○	○		○		●					○		○	○	○										○
Pesticide Metabolites																														
3,4-Dichloroaniline			○	○	○	○	○	○	○	●	●	●	●			○		○	○	○										○
3,4 DiCiAniline			○	○	○	○	○	●	○							○	●	○	○	○										○
DDE			○	○	○	○	○		○	●								○	○	○										○
Desethylatrazine	●	●	○	○	○	○	○	●	○	●	●	●	●	●	●	○	●	○	○	○	●					●	●	●	●	○
Desisopropylatrazine	●	●	○	○	○	○	○	●	○	●	●	●	●	●	●	○	●	○	○	○	●					●	●	●	●	○
Propazine-2-hydroxy[ǂ]	●	●	○	○	○	○	○		○		●	●	●			○	●	○	○	○										○
Terbuthylazine desethyl			○	○	○	○	○		○	○	○	●				○	●	○	○	○										○
Total of all pesticides and metabolites	11	19	○	○	○	○	○	14	○	15	40	47	32	16	15	○	36	○	○	○	13	4	6	4	1	14	16	16	15	○

[1]GBR Marine monitoring program (MMP) categories in HEQ (Gallen et al., 2013) .
[2]Proposed marine ecotoxicity threshold values for protecting 80%, 90%, 95% and 99% of species from diuron (ETVs, [3]Section 5 (Smith et al., In prep-b))
[4]Current GBRMPA water quality guideline for protecting 90%, 95% and 99% of species from diuron (GBRMPA, 2010)
Impacts of diuron on seagrass in experimental systems (Flores et al., 2013; Negri et al., 2015)

Table 4-4 Comparison of pesticide risk ratings and the proportions (as a percentage) of each aggregated land use upstream of GBRCLMP monitoring sites. 'Other' land use includes conservation, mining, urban/utilities, intensive animal and water.

Catchment	Pesticide Risk Rating*	Cropping	Forestry	Grazing	Horticulture	Sugarcane	Other
S. Johnstone	Very Low	0.0	0.0	9.7	2.3	2.8	85.1
Tully	Low	0.0	2.8	5.1	4.5	10.2	77.3
Haughton	Very High	2.9	0.0	79.3	0.1	17.6	0.1
Burdekin	Very Low	1.0	0.6	93.3	0.0	0.1	4.9
Pioneer	High	0.0	25.4	35.0	0.0	21.4	18.2
Plane	High	0.0	10.5	32.6	0.4	48.3	8.2
Fitzroy	Low	6.7	6.6	81.4	0.0	0.0	5.3
Burnett	Very Low	3.8	12.8	79.5	0.2	0.2	3.4

*Based on risk ratings from the Scientific Consensus Statement (Brodie et al, 2013; Lewis et al, 2013).

4.9.2 Wetlands

Studies of pesticides in GBR freshwater wetlands are notable for their absence in the published literature. Recent small-scale pilot studies that sampled 11 GBR freshwater wetlands conducted by the DSITI Wetland Science team detected pesticides in both wetland sediment and water (Vandergragt pers comm.). Locations and characteristics of the studied wetlands and the dominant land uses of the surrounding land are provided in Appendix B.

Analysis of sediments collected during November to December 2012 from wetlands on the Burdekin, Pioneer and Burnett floodplains, identified at least atrazine, DDE or diuron at 7 of 11 sites. Passive samplers deployed in water at two wetlands—DeMoylens Lagoon on the Pioneer Floodplain (January and February 2014) and Mon Repo in the Burnett catchment (March to April 2014) detected a total of 19 pesticides (or metabolites) with 14 pesticides detected at each site. The highest monthly average concentrations were diuron (2.2 – 3.1 µg L^{-1}), atrazine (2 – 2.8 µg L^{-1}), metolachlor (1.8 – 2.3 µg L^{-1}) and metribuzin (1.3 – 1.7 µg L^{-1}).

Freshwater wetland hydrology is highly variable, and is likely—along with surrounding land use—to be a significant influence on the nature of pesticide exposure. For example: in palustrine wetlands fringing rivers or creeks, exposure may be similar to that of the high-water conditions of the adjacent waterways; in depressional wetlands, pesticides may have comparatively longer residence times due to reduced through-flow; floodplain wetlands that connect hydrologically during flood events may retain flood-concentrations of pesticides after floodwaters subside. In the two latter examples it would be expected that the persistence of pesticides will be controlled predominantly by partitioning and degradation. In addition, pesticides may also leach into groundwater from freshwater wetlands. This could be particularly problematic at sites such as the Mon Repo wetland which sits behind the sand dunes of an important sea turtle nesting site. Sea turtles lay eggs in environments which are groundwater fed to keep the eggs moist and therefore there is a probability that the eggs are exposed to pesticides, including those with endocrine disrupting effects (see Section 5.5).

Further studies are needed to determine pesticide exposure in wetlands with different hydrological and land use contexts.

4.9.3 Estuaries

The presence of pesticides in estuarine sites has received little attention to date. Catchment monitoring is principally conducted in the freshwater reaches above the tidal zone and therefore do not account for the influence of tidal mixing on pesticide exposure. Albeit more recently (since 2013-14) GBRCLMP catchment monitoring sites have been installed in the tidal zone of the Russell and Mulgrave Rivers in the Wet Tropics. Note however, the monitoring results from these two sites had not been published at the time of writing this report. The 2006-2010 Pesticide Synthesis Report (Devlin and Lewis, 2011) reported that the presence of pesticides in estuarine waters, sediments and biota had been observed by some authors (e.g. Duke et al., 2005; Lewis et al., 2009; Mortimer, 2000). Since this time, the only published studies monitoring pesticides in estuaries have centred on the Barratta Creek estuary, which lies within a Ramsar wetland in the lower Burdekin (Davis et al., 2012; O'Brien et al., 2013). In these studies, water and sediment samples were analysed for the presence of pesticides. The pesticides that were detected in the estuary (Table 4-2 and Table 4-3; 'Estuaries' of the Burdekin (B)) are consistent with what has also been detected in Barratta Creek (Davis et al., 2012, 2014c; O'Brien et al., 2013a). In general, pesticides in the Barratta Creek estuary were fewer and found in lower concentrations than what was detected in the upstream sites of Barratta Creek (Davis et al., 2012; O'Brien et al., 2013a). Nevertheless, these results do demonstrate that estuaries are exposed to large number of pesticides with concentrations of certain pesticides exceeding relevant guidelines for extended periods (>1 month; O'Brien et al., 2013a). Unfortunately, at this stage our knowledge of pesticide exposure in the GBR estuaries is still fundamentally inadequate to make an assessment of pesticide exposure, and therefore risk, to these ecosystems.

4.9.4 Marine

Annual monitoring of pesticides has been conducted at 14 inshore sites in the GBR since 2005 as a component of the Australian Government's Reef Rescue Marine Monitoring Program (MMP). Passive samplers have been deployed at the sites which cover five NRM regions; Cape York, Wet Tropics, Burdekin, Mackay Whitsunday, and Fitzroy (Table 4-2 and Table 4-3). Flood plume monitoring has also been conducted as part of the MMP, mainly from the mouth of the Tully and Herbert Rivers in the Wet Tropics. In addition to pesticide monitoring, satellite remote sensing has been used to provide a large spatial estimate of pesticide exposure in the marine environment (Kennedy et al., 2012b; Lewis et al., 2013; Petus et al., 2015).

While a wide spectrum of pesticides have been detected in GBR catchments, a much smaller proportion has been detected in the marine and flood plume monitoring (Table 4-2 and Table 4-3). Most commonly detected in the marine monitoring have been the more water soluble and mobile herbicides (Brodie et al., 2012b; Davis et al., 2013; Lewis et al., 2009). The MMP has reported the presence of fifteen pesticides (and two metabolites) since 2005 (Table 4-2 and Table 4-3; Kapernick et al., 2006, 2007; Bartkow et al., 2008; Bentley et al., 2012; Gallen et al., 2013, 2014). This includes the five priority PSII herbicides which were detected in the marine waters of each of the monitored NRM regions, with the exception of Cape York (a relatively pristine site) where ametryn and tebuthiuron were not detected (Kennedy et al, 2012b). In addition, six other herbicides — bromacil, imazapic, metolachlor, prometryn, simazine and terbutryn and atrazine metabolites, desethylatrazine and desisopropylatrazine have been commonly detected in all the marine waters of NRM regions (except Cape York) and, flumeturon has only been detected in the marine waters of the Burdekin and Fitzroy NRM regions (Table 4-2 and Table 4-3). Three insecticides, chlorpyrifos, diazinon and imidacloprid, have also been detected in the marine environment; imidacloprid has been detected in marine waters of all monitored regions; diazinon has been detected in marine waters of the

Burdekin and Mackay-Whitsunday regions; and, chlorpyrifos in the Mackay-Whitsundays only (Table 4-2 and Table 4-3). Across all sites, diuron has been the most prevalent pesticide detected in the MMP followed by atrazine, whereas the catchment monitoring indicated that atrazine was the most frequently detected followed by diuron (Lewis et al., 2009; Kennedy et al., 2012b; Lewis et al., 2012; Smith et al., 2012; Turner et al., 2012, 2013; Wallace et al., 2014, 2015; Garzon-Garcia et al., in prep). This may indicate differences in the degradation of atrazine and diuron.

Site-specific trends are evident (Kuhnert et al., 2015) and pesticide profiles in the marine environment generally match those detected by end of catchment monitoring (Turner et al., 2013; Wallace et al., 2014). Similar to the observations in catchments, the regional profiles of pesticides in the marine environment vary and reflect the predominant land use in the adjacent catchment. For example, atrazine is commonly detected in the Burdekin region and tebuthiuron in the Fitzroy region, corresponding to the adjacent sugarcane and grazing land use respectively (Bainbridge et al., 2009; Lewis et al., 2009; Turner et al., 2012, 2013; Gallen et al., 2014; Wallace et al., 2014, 2015). Other factors contribute to the high spatial variability observed in pesticide detections in marine waters including the influence of discharge from multiple rivers and the distance of a monitoring site from a river mouth (Petus et al., 2015).

The spatial extent of flood plumes of the thirty major rivers draining to the GBR cannot logistically be monitored on a routine basis to assess the extent of pesticide exposure in the marine environment. To overcome this, remotely sensed data has provided a platform for quantifying the spatial extent of flood plumes and subsequently the spatial extent of pesticide exposure (Kennedy et al., 2012b; Lewis et al., 2013; Petus et al., 2015). Schroeder et al. (2012) developed a relationship between Colour Dissolved Organic Matter (CDOM) that can be quantified using satellite imagery, and salinity. This, combined with the conservative mixing behaviour of pesticides in flood plumes means that satellite imagery can be used to estimate the salinity of flood plumes and hence the degree of dilution that the pesticides in the flood plume have undergone. This technique has been applied by Kennedy et al. (2012b) and more recently by Lewis et al. (2013).

4.10 Temporal Exposure

The variability of temporal pesticide exposure can range from negligible to very high depending on the spatial location, the ecosystem and the season. Generally, the temporal variability becomes lower with greater the distance from the source of pesticides. Thus, variability is typically high in catchments, lower but still significant in estuaries and the inner-shore of the GBR, but minimal in the outer reef (Section 4.9.4). This temporal variability occurs at the annual, inter-seasonal and intra-seasonal level and affects the type of exposure to pesticides that the various ecosystems experience.

4.11 Annual exposure

There can be marked inter-annual variability in loads of pesticides transported to the GBR (Turner et al., 2012, 2013; Wallace et al., 2014, 2015). Between 2010–2011 and 2012–2013 the monitored loads of pesticides at individual sites and summed across sites varied by a factor of two to seven (Turner et al., 2013; Wallace et al., 2014, 2015). For example, the total monitored loads of tebuthiuron during these years ranged from 1100 to 7000 kg. This variability in pesticide loads is largely due to the variations in annual rainfall, rainfall in the preceding year(s) (antecedent rainfall) and related factors such as percent groundcover. Higher annual rainfall generally leads to higher annual loads but lower pesticide concentrations due to increased dilution (Smith et al., in prep-a). In fact, Smith et al (in prep-a) has found a statistically significant ($p \leq 0.05$) negative linear relationship between pesticide concentration and river discharge that holds for all the monitored catchments. All other factors being equal, higher annual rainfall will lead to higher river discharge and therefore larger flood plumes and greater areas of the estuaries and inner shore portion of the GBR being affected by flood plumes (Kennedy et al., 2012a). However, the biological effects are likely to be lower in years of high discharge, due to the diluted pesticide concentrations.

Pesticide loads and concentrations can also be affected by farm management practices, changes to pesticide use labels and changes in prices. For example, in late 2011 and late 2012 the Australian Pesticide and Veterinary Medicine Authority (APVMA, 2012) changed the labels of diuron products which restricted its application rate and the window it could be applied. This combined with encouragement from extension officers to use knockdown products rather than residuals, led to changes in the pesticides applied to sugarcane and the detection of pesticides in catchments. For example, immediately before the introduction of the restrictions a large increase in diuron concentrations occurred in some catchments (Smith pers. comm.). O'Brien et al. (2014a) found that diuron concentrations in Barratta Creek decreased between July 2011 and July 2013, although diuron concentrations peaked just prior and just after the December 2011 no spray window announcement. However, analysis of diuron concentrations in Barratta Creek for an additional year revealed that in 2013-2014 the concentrations were no lower and may have been higher than before the restrictions were introduced (Warne et al., 2014). Analysis from 2010 to 2014 across all the catchments monitored by the GBRCLMP found the effects of the restrictions on diuron concentrations were varied – some decreasing, others increasing or staying the same (Warne et al., 2014).

Commensurate with the decreased diuron concentrations measured in Barratta Creek, between July 2011 and July 2013, O'Brien et al. (2014a) reported increased concentrations of metolachlor and metribuzin. These have been suggested as potential replacements of diuron (Fillols and Callow 2010; Seeruttun et al, 2010). Generally, both the median and maximum concentrations of imidacloprid have also increased since 2009 (Turner et al., 2014). Smith et al. (2015) examined temporal variability for seven alternate pesticides (fluometuron, metolachlor, prometryn, simazine, terbutryn and metribuzin) across nine catchments between 2009 and 2013. The temporal trends of each alternate pesticide in each catchment were unique, with both increases and decreases in concentration and detection frequencies observed (Smith et al, 2015).

4.12 Seasonal exposure

It is well established that transport of pesticides in waterways is highly seasonal – with the vast majority transported during the wet season or during storm events (e.g. Reinert et al, 2002). This is the reason that monitoring for pesticides is predominantly event-based e.g. the GBRCLMP. Generally the concentrations and loads of pesticides that occur in GBR catchments during the dry season are considerably lower than during the wet season (e.g. Smith et al, 2012; O'Brien et al, 2014b; Smith et al, in prep-a). More specifically, the first flushes in catchments are responsible for a disproportionally large percentage of the annual pesticide load. A number of studies (Devlin and Lewis 2011; Cook et al., 2011, 2013; Smith et al., 2011; Davis et al., 2012; O'Brien et al., 2013a, 2014a) have shown that first flushes are major contributors to the annual loads. Indeed, Davis et al. (2012) found that the majority (>50%) of the annual herbicide loads was delivered in the early 'first flush' flows at sites in the lower Burdekin floodplain.

Pesticide exposure characteristics fall into three main groups:

(1) Long-term (chronic) exposure of relatively stable, low-level concentrations and mixtures of pesticides, typical in the off-shore reefs. Whilst the highest concentrations of pesticides in the marine environment are detected during the monsoon period, ambient monitoring during the dry-season has demonstrated that they persist throughout the entire year (Lewis et al, 2012; Shaw et al, 2010; Kennedy et al, 2012b; Gallen et al, 2014);

(2) Where there is a rapid increase in pesticide concentrations late in the dry season or early in the wet season followed by a gradual decline over the wet season (e.g. refer to Figure 4-4). This most frequently occurs in large catchments such as the Fitzroy and Burnett and those estuarine, coastal and in-shore areas affected by their flood plumes; and

(3) Where there is an initial increase in pesticide concentrations followed by a series of short duration increases followed by a decline (i.e. pulses) (e.g. refer to Figure 4-5). This exposure scenario usually occurs as a result of multiple spraying events during the wet season and most frequently occurs in the small coastal catchments such as Barratta and Sandy Creeks and the Pioneer River (Smith et al, in prep-a) and those estuarine, coastal and in-shore areas affected by their flood plumes.

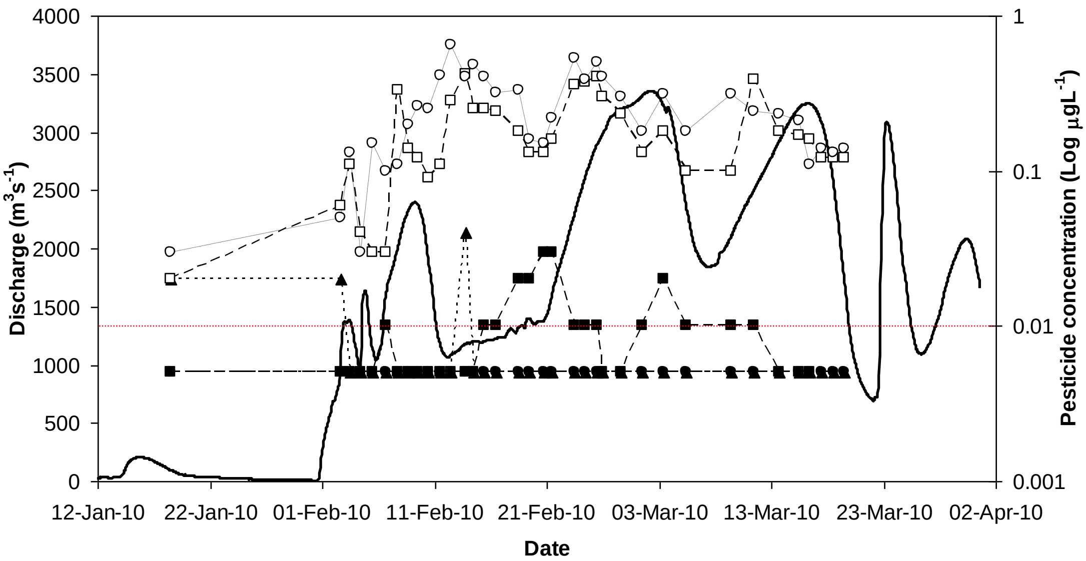

Figure 4-4: Discharge ($m^3\ s^{-1}$) and pesticide concentrations ($\mu g\ L^{-1}$) for Fitzroy River during the 2009/2010 wet season. Symbols represent the five priority PSII herbicides; diuron (▲), atrazine (□), hexazinone (■ ametryn (●) and tebuthiuron (○). Solid black line represents discharge ($m^3\ s^{-1}$), red line represents the limit of reporting ($\mu g\ L^{-1}$). Reproduced from Smith et al. (2012).

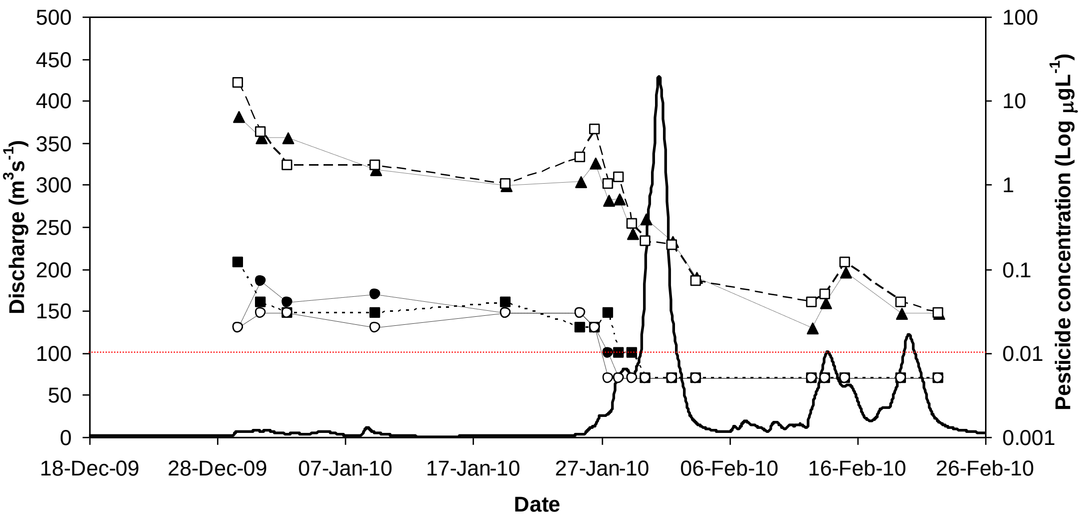

Figure 4-5: Discharge ($m^3\ s^{-1}$) and pesticide concentrations ($\mu g\ L^{-1}$) for Barratta Creek during the 2009/2010 wet season. Symbols represent the five priority PSII herbicides; diuron (▲), atrazine (□), hexazinone (■), ametryn (●) and tebuthiuron (○). Solid black line represents discharge ($m^3\ s^{-1}$), red line represents the limit of reporting ($ug\ L^{-1}$). Reproduced from Smith et al. (2012).

The ecological risk posed by pesticides is a function of their aqueous concentrations and the length of time organisms are exposed to the concentrations. Therefore, ecosystems exposed to these different exposure scenarios will face different ecological risks and how this risk is quantified should reflect these differences. Differences in temporal exposure have only been considered in a very simplistic sense so far in the GBR. While it is well known that pesticides are transported with high levels of total suspended solids and nutrients, to date there have been no assessments of the exposure and transport of these stressors as mixtures.

4.13 Conclusions and research gaps

In order to determine and/or model the probability of ecological risk from pesticides to the GBR and associated coastal ecosystems, the exposure characteristics to pesticides must be quantified in terms of type of pesticide, concentration, spatial extent and temporal variability. Our current state of knowledge of these four factors is presented below:

(1) Type of pesticide: A total of 56 pesticide residues (including metabolites) have been detected since 2009, consisting of 29 herbicides, 16 insecticides, 4 fungicides and 7 herbicide metabolites (Table 4-2 and Table 4-3). The types of pesticides detected in freshwater and marine environments reflect the upstream land use and the physicochemical properties of the pesticides. Pesticides with high aqueous solubility are generally more readily leached or transported off-site and detected in waterways. The composition of pesticides detected is constantly changing reflecting changes in pesticide use (voluntary or mandated). The number, concentrations and loads of the alternative pesticides appear to be increasing with time and this trend is likely to continue. Pesticides invariably occur as mixtures.

(2) Concentration: it is understood that as pesticides move longitudinally through waterways and out to the Reef, concentrations decrease due to dilution, compartmentalisation and degradation processes. However, the contributions and significance of these processes for determining pesticide concentrations in various ecosystems along the transport pathway is largely unknown. The proportion of each pesticide transported in the dissolved and bound phase depends on their physicochemical properties. PSII pesticides are transported mainly in the dissolved phase. The available data on degradation in the marine environment indicate that they persist for considerably long periods (32 – 3330 days). Pesticide concentrations are highly variable close to the source but this variability decreases markedly as the distance from the source increases.

(3) Spatial exposure: our current understanding is based on the monitoring of approximately 40% of the major waterways draining to the GBR, a small fraction of sub-catchments and creeks, a small fraction of wetlands and estuaries, and a very small fraction of the marine environment. It is highly likely that all parts of the GBR and its associated coastal ecosystems are contaminated by pesticides. Findings to date suggest a strong influential role of land use on the spatial exposure of pesticides, which decreases with increased distance from the source. Waterways downstream of sugarcane generally have the highest concentration of pesticides, particularly PSII herbicides. Contamination of the GBR and associated coastal ecosystems by pesticides is widespread and likely to be ubiquitous. CDOM satellite imagery is being used to help map the exposure of pesticides in the marine environment.

(4) Temporal exposure: temporal variability (annual, seasonal pulsed and chronic) of pesticide exposure has been demonstrated across ecosystems and catchments and is controlled by both human and environmental factors. Wetter than average years have higher pesticide loads but lower pesticide concentrations than average and drier than average years. Larger catchments and ecosystems further from the source have smaller intra-seasonal variations in pesticide

concentrations. The risk posed by pesticides is time and concentration dependent and there is potential for recovery between exposures, therefore risk posed by pesticides is highly dependent on the temporal exposure in an ecosystem. In addition, quantification of pesticide exposure with concurrent exposure to other stressors is critical to determine the total risk of GBR and associated aquatic coastal ecosystems.

Data and knowledge on pesticide transport, fate and exposure characteristics in the GBR is essential to make any assessment of the impacts of pesticides to the Reef and its associated coastal ecosystems. Exposure data coupled with effects data (discussed in Chapter 5) can generate probabilistic and deterministic assessments of the ecological risk posed by pesticides to the GBR, therefore ultimately assessing Reef Plan's (2013) long-term goal; the quality of water entering the reef from broadscale land use has no detrimental effect on the health and resilience of the Great Barrier Reef. This Chapter has identified the spatial extent of our knowledge of pesticide exposure through various monitoring programs, however this only accounts for a small fraction of the area likely to be exposed to pesticides. Due to the extensive size of the GBR and coastal waterways, and the variability observed in pesticide exposure (type, concentration and temporal), modelling approaches are considered to allow us to extrapolate our estimation of pesticide exposure. The transport, fate and exposure data generated to date can provide an essential basis for improved modelling pesticide exposure in catchments and the marine environment to estimate ecological risk. Key knowledge gaps are listed in Table 4-5

Table 4-5: Key knowledge gaps that remain in understanding transport, fate and exposure of pesticides in the GBR.

Research Gap	Details
Groundwater transport and delivery	The transport of pesticides in groundwater and the contribution of pesticides from groundwater to the Reef is still largely unknown;
Contribution to concentrations	quantification of the contribution of environmental and anthropogenic variables (e.g. land use, discharge volume, distance from the source) for predicting pesticide concentrations in waterways as they move from the source to the Reef
Half lives in freshwater	quantification of pesticide half-lives and their influence on pesticide concentrations in freshwater and estuarine waters of the GBR;
Extent, exposure	extent of exposure of pesticides in sediment beds and the ecological impact of the exposure relationship between pesticide loads and pesticide exposure and risk has not been quantified and is still largely unknown
Bound and dissolved phases	further work on the partitioning of pesticides used in GBR catchments between bound and dissolved phases is required – this would permit more accurate estimates of the load of pesticides being transported to the GBR by sediment.
Temporal variability	temporal exposure of pesticides in different ecosystems is largely unknown and has not been formally quantified. Temporal variability of pesticide concentrations between sampling times needs to be examined, particularly in terms of pesticide load estimations, sampling regimes and quantification of pesticide concentrations over time. Whether observed inter-annual changes in pesticide concentrations in catchments are due to changes in land management practices.
Cumulative stressors	While co-occurrence of pesticides with other stressors has been observed, no formal quantification or probabilistic assessment of pesticides with other stressors has been undertaken.

4.14 Suggested research priorities

The following research priorities are recommended for enhancing our knowledge and understanding of pesticide transport and exposure in the GBR and its associated aquatic coastal ecosystems:

1. Determine the relationships between landscape scale variables (e.g. land use, rainfall) and pesticide exposure variables (i.e. spatial and temporal exposure, pesticide type and concentration) to permit us to estimate pesticide exposure in unmonitored waterways.
2. Monitoring the transport and exposure characteristics of the pesticides, particularly 'alternate' pesticides, and those that are known to be used that are not routinely monitored (e.g. glyphosate, paraquat).
3. Determining the fate, compartmentalisation, and the temporal and spatial variability of pesticides in various environmental media particularly sediment, groundwater and flood plumes.
4. Longitudinal monitoring of a catchment to measure changes in pesticide concentrations with distance downstream and identify 'hot spots' of peak pesticide exposure.
5. Linking pesticide concentrations and loads at end-of-system sites with concentration and spatial exposure in marine and estuarine ecosystems.
6. Generating pesticide concentration and salinity relationships for all catchments, to estimate exposure in marine environments by CDOM satellite imagery.
7. Quantifying temporal exposure in ecosystems (i.e. pulsed and chronic) in relation to ecosystem effects.
8. Determining the influence of climatic variables on the inter-annual changes in pesticide concentrations, i.e. can we prove that changes in catchment pesticide concentrations are due to changes in land management practices?

5 ECOLOGICAL RISK OF PESTICIDES

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5.1. Summary of key findings

- Current water quality guidelines may not be appropriate to protect foundation GBR species during the summer wet season given recent research showing interactions of herbicides and sea surface temperature (SST) on toxicity.
- Ecotoxicological studies using GBRCA benthic diatom species suggest acute exposure to atrazine can result in median effect concentrations (EC50, concentrations that effect 50% of individuals) at ~40 to greater than 1000 µg L^{-1}.
- The benthic green algae *Nephroselmis pyriformis* is one of the most sensitive tested of all plant species to diuron with <0.5 µg L^{-1} and 2.1 µg L^{-1} causing a 10% and 50% inhibition of photosynthesis (IC10 and IC50, respectively), respectively. These concentrations are below the maximum values measured in catchment and estuarine monitoring programs.
- Diuron was consistently the most toxic herbicide of diuron, atrazine, hexazinone and tebuthiuron to four diatom species commonly found in GBR estuaries. Importantly, mixtures of the PSII herbicides often detected in water samples from estuaries were shown to have additive impacts on two species of estuarine microalgae.
- Chronic exposures of diuron to complex microbial biofilms were shown to lead to changes in the structure of microbial communities that may have flow-on effects to species further up the food chain.
- Since current pesticides rarely accumulate in biota, demonstrating field exposure is difficult. Monitoring biomarkers for invertebrate exposure, coupled with water analysis remains a worthwhile approach linking exposure with impacts although further laboratory experiments using local species are needed to validate this approach in the GBR and adjacent catchments.
- Barramundi exposed to the active ingredient atrazine showed no biochemical changes consistent with endocrine disruption with the exception of increased plasma testosterone (T) concentrations. In contrast, exposure to environmentally relevant concentrations of commercial herbicide formulations increased hepatic vitellogenin (vtg) transcription and plasma 17β-E concentrations, and reduce plasma 11-KT concentrations and the androgen/estrogen ratio, suggesting estrogenic and anti-androgenic responses to the additives in the commercial formulations.
- Wild male barramundi in rivers discharging into the GBR lagoon show evidence of exposure to estrogenic compounds which is strongly associated with pesticide run-off from sugarcane land use in the GBR catchment. Moreover, altered liver vtg transcript abundance in wild juvenile coral trout (*Plectropomus leopardus* and *P. maculatus*) further suggest that this exposure extends out into the GBR lagoon itself.
- Precise acute PSII herbicide toxicity threshold data for the tropical seagrasses *Zostera muelleri* and *Halodule uninervis* are now available. The sensitivities of the seagrasses were similar to that of microalgae for the herbicides atrazine, diuron, hexazinone and tebuthiuron. This confirmed that photosynthesis in seagrass can be affected at concentrations lower than the current GBRMPA water quality guidelines for ecosystems protection.
- A miniature and more rapid toxicity test for PSII herbicides by using isolated leaves of the seagrass species *Halophila ovalis* has also been developed. The study validated the utility of the isolated leaf technique by demonstrating the inhibition of photosynthesis by diuron was identical for isolated and potted leaves and similar to inhibition levels in other seagrass species.
- Chronic exposures of seagrass to diuron affected photosynthesis in *H. uninervis* and *Z. muelleri* over a 79-day exposure. While most of the plants survived prolonged herbicide exposure concentrations

of > 0.6 μg L^{-1}, diuron caused considerable impacts on energetic status that may leave the plants vulnerable to other stressors that they are exposed to simultaneously or sequentially such as low light levels during flood plumes. Concentrations of diuron above > 0.6 μg l^{-1} caused reduced growth and mortality.

- Acute 24-h exposure of the tropical crustose coralline algae (CCA) *Neogoneolithon fosliei*, indicated that this species was 3- to 10-fold less sensitive to the PSII herbicides atrazine, diuron, and hexazinone than coral.
- Simultaneously exposed coral to PSII herbicides and SSTs up to 32°C confirmed that atrazine, diuron and hexazinone can enhance the sensitivity of corals to thermal stress (i.e. photo-physiological effects and bleaching). The majority of combinations of PSII herbicides and thermal stress had an additive effect, and it was calculated that above 30°C reducing diuron concentration by 1 μg L^{-1} would protect photosynthetic efficiency from an equivalent increase in SST of 1.8°C or damage to photosystem II by an increase of 1°C. The combined effects of diuron and thermal stress were also additive in several species of foraminifera-hosting diatoms, dinoflagellates or rhodophytes.
- The greater amount of new ecotoxicological studies has allowed new ecotoxicity threshold values to be developed for fresh, estuarine and marine waters for key pesticides in the GBR. In turn, risk assessments have drawn on these data to better appreciate risk in the GBRCA and lagoon using a variety of methods.

5.2 Introduction

To understand the risks posed by agricultural pesticides to tropical ecosystems we need to understand:

- The types of agricultural pesticides present in the GBR lagoon and catchments. This can be informed by usage data (Chapter 3) and monitoring of waterways (Chapter 4, Table 4-2 and 4-3), modelling or prospective ecological risk assessments.
- The spatial and temporal exposure of organisms to pesticides in creeks, rivers, wetlands, estuaries and the reef lagoon. This can be achieved by monitoring pesticides using grab samples and passive samplers, bioindicator programs and combining these data with monitoring, modelling and/or satellite imagery (Chapter 4).
- The toxicity of the pesticides to relevant local species of high conservation and economic value such as crabs, fish, seagrass and coral (this Chapter). Much of these currently available ecotoxicity data come from international studies that mainly use temperate species that may not be representative for tropical ecosystems.
- Factors that affect toxicity of pesticides including other contaminants or abiotic (physical and chemical) stressors, and the “pulsed” nature of many exposures (this Chapter).
- How to combine and model the exposure and toxicity data above to assess the spatial and temporal risk of pesticide to freshwater, estuarine and marine ecosystems of Queensland (This Chapter).

The risk assessment process outlined above has been incrementally applied to the GBR and its catchments since the identification of significant concentrations of pesticides in the GBR lagoon 15 years ago (Haynes et al., 2000a). The presence of pesticides in these waters remains an issue for ecosystem health with the recent Consensus Statement on Land Use Impacts on GBR Water Quality and Ecosystem Condition stating that “pesticides pose a risk to freshwater and some inshore and coastal habitats” (Brodie et al., 2013b). However, it should be noted that this assessment was based on existing data which have a number of limitations and are therefore likely to underestimate rather than overestimate the actual risk (Lewis et al., 2013). Refining our understanding of the risks posed by pesticides to organisms and ecosystems of high conservation value will inform regulators and managers of the likelihood and consequences of pesticide pollution and are necessary to develop guidelines and policy targets for improved management of the GBR (Reef Plan, 2013). In this chapter we summarise and assess recent findings on relevant pesticide toxicology and in combination with exposure data from Chapter 4 we describe how pesticide risk assessments have been applied and improved in recent years. Finally we look ahead to the needs and challenges that we have to better quantify the risks posed by pesticides to the organisms and habitats of the GBR and its catchments.

5.3 Wetland species

5.3.1 Background

The highest concentrations of pesticides in Queensland waters can be found in the freshwater ecosystems including creeks, rivers and wetlands (See Chapter 4 and (Lewis et al., 2013)). Recent systematic monitoring of pesticides across the GBR and the GBRCA has revealed widespread contamination of rivers and streams at concentrations above current ecosystem protection trigger values (Smith et al., 2012). The highest in-stream herbicide concentrations and greatest load transport typically occur under early wet-season conditions, when they are washed from fields to waterways by intense rain. However, some of the major sub-catchments (e.g. the lower Burdekin cane growing region) exhibit consistently elevated pesticide concentrations (above available ecosystem protection guideline values) throughout much of the dry season, due to continual paddock tailwater inputs from irrigated cane farms (Davis et al., 2013; O'Brien et al., 2014a). These temporal dynamics of herbicides in GBRCA freshwater environments result in periods of both acute (short-term, high concentration) and chronic (long-term, lower concentration) exposure (e.g. Lewis et al., 2013; Chapter 4).

5.3.2 Acute and chronic pesticide impacts in tropical freshwater species

The most commonly detected pesticides in the GBRCA are the priority PSII herbicides atrazine, ametryn, hexazinone, diuron and tebuthiuron, as well as some alternative herbicides such as metolachlor, metribuzin and 2,4-D, and the insecticide imidacloprid (refer to Chapter 4 for details). Currently, there is limited local ecotoxicological information (acute and chronic) on the effects of pesticide residues in GBRCA catchment freshwater streams (Bainbridge et al., 2009; Davis et al., 2013; Wood et al., 2014). However, studies elsewhere in Australia and overseas are finding that pesticide concentrations below national guideline levels can adversely impact local and regional freshwater biodiversity and ecosystem functions (Schäfer et al., 2012a, 2012b; Beketov et al., 2013).

The direct lethal effects of important GBRCA herbicides such as atrazine have been demonstrated on non-GBRCA periphyton and phytoplankton populations at concentrations as low as 20 µg L^{-1} (Graymore et al., 2001). Some of the first ecotoxicological studies using GBRCA species suggested an acute exposure of ~40 µg L^{-1} atrazine could cause EC50s of for some freshwater benthic diatoms, but other taxa were considerably more tolerant with EC50 concentrations >1000 µg L^{-1} (Wood et al., 2014). Wood et al. (2014) used different methods to that of Graymore et al. (2001) and the differing sensitivity that these studies found probably does not mean that GBRCA freshwater algae are more tolerant than those from other systems. Currently, a biomonitoring index is being developed based on data from Wood et al. (2014) and new data from studies on the sensitivity of GBRCA freshwater benthic diatoms exposed to other herbicides and altered light levels. This index is designed along the lines of SPEAR (SPEcies At Risk) (Liess and Ohe, 2005) and it assesses the proportion of the benthic diatom community at risk from herbicides and will be useful to show herbicide toxicity in rivers. Until more relevant Australian ecotoxicology studies can be performed we remain reliant on larger datasets of herbicide toxicity based on temperate northern hemisphere freshwater species.

Insecticides are also detected in GBRCA waters (Chapter 4) and can impact on tropical Queensland fish at low concentrations. For example, the freshwater eastern rainbowfish *Melanotaenia splendida splendida* was found to be sensitive to the neurotoxic insecticide chlorpyrifos (Humphrey and Klumpp, 2003), with LC50s for eggs and sperm as low as 20 µg L^{-1} and indicators of stress such as larval length were impacted at concentrations as low as 6 µg L^{-1}. More broadly the typical 96 h acute lethal dose of chlorpyrifos to temperate aquatic fish is less than 10 µg L^{-1} (Barron and Woodburn, 1995). There is little relevant local toxicological data available for new insecticides found in Queensland rivers and estuaries such as imidacloprid (but see Section 5.5).

A number of recent reviews have highlighted that indirect and sub-lethal effects are a more pervasive manifestation of herbicide contamination of freshwater environments (Rohr and McCoy, 2010). Phototrophic community composition can be affected by chronic herbicide exposure although responses could be variable depending upon taxonomic, seasonal, and community interaction factors (Pesce et al., 2011). Diuron appears particularly toxic to temperate freshwater primary producers, with chronic effects observed at concentrations as low as 0.1 µg L^{-1} (Ricart et al., 2009; Pesce et al., 2011). The affect of long-term, low-dose pesticide exposures can produce effects (e.g., biodiversity changes, tolerance acquisition, and functional changes) that only become apparent in organisms after several generations (Pesce et al., 2011). For freshwater fish and amphibians, ecologically relevant concentrations (i.e. measured in the field) of the widely used herbicide atrazine consistently produces a number of sub-lethal effects such as: reduced growth rates; variable effects on timing of metamorphosis; elevated locomotor activity and reduced antipredator behaviours; immune capacity reductions; elevated infections; and inducement of diverse morphologic gonadal abnormalities (Rohr and McCoy, 2010). Recent documentation of sub-lethal pesticide effects in the form of altered levels of biomarkers for endocrine function in juvenile populations of barramundi (*Lates calcarifer*) from freshwater habitats of the GBRCA (Kroon et al., 2015), suggests that exposure to herbicides and associated chemicals is an issue that warrants increased research attention.

The results for individual herbicide stressors may however, underestimate real world effects and recent trends are toward studies in which lower herbicide concentrations are considered, and compound mixtures or successive treatments tested (Pesce et al., 2011). This trend is very relevant to the GBRCA context, where complex 'cocktails' of pesticide compounds in receiving environments appear the rule rather than the exception (Smith et al., 2012; Davis et al., 2014c). Additionally when chemical pollutants are combined with other natural stressors the combined effects is found to be synergistic in 55–80% of reported cases (Holmstrup et al., 2010) and such synergistic effects are known for pesticides (Beketov and Liess, 2005). The potential impacts of multiple pesticides and stressors are addressed in Section 5.6.

5.4 Estuarine species

Tropical estuaries flowing into the GBR lagoon can contain high dissolved concentrations of herbicides and detectable concentrations of insecticides (Chapter 4). Estuaries of Queensland directly link freshwater habitats and the GBR lagoon and can filter and trap sediments, nutrients and pollutants from agriculture and urban sources. Tropical estuaries are more diverse and ecologically complex than their temperate counterparts and represent important nurseries, migratory routes and habitats for GBR species of high economic, social and environmental value such as prawns, crabs and fish. The herbicide concentrations in estuaries vary considerably, with a maximum of up to 15 µg L^{-1} of atrazine during wet season runoff events and consistent background concentrations (0.1- 0.5 µg L^{-1}) recorded during dry periods (Mitchell et al., 2005; Packett et al., 2009; Davis et al., 2012; Smith et al., 2012). Despite their recognised ecological importance and known contamination issues, Queensland estuaries remain understudied in relation to potential impacts of pesticides to their key biota. Here we review recent studies on the effects of pesticides on tropical estuarine organisms including microalgae, mangroves, invertebrates and fish. We also summarise the findings of field-related studies on biomarkers for pesticide exposure in tropical estuarine habitats.

5.4.1 Microorganisms

Microalgae and cyanobacteria are at the base of complex food webs and are therefore critical to the health of estuarine ecosystems. As microalgae rely on photosynthesis for growth and reproduction, they can be particularly sensitive to herbicides that block this process such as PSII inhibitors, including diuron and atrazine. The majority of studies on the impacts of PSII herbicides on tropical organisms, including microalgae, have used Pulse Amplitude Modulation (PAM) fluorometry, a non-invasive fluorescence technique, to measure the change in quantum yield of PSII (Jones et al., 2003; Ralph et al., 2007). The most sensitive parameter measured by PAM fluorometers is inhibition of effective quantum yield ($\Delta F/F_m'$) which is proportional to reduced photosynthetic efficiency under experimental light levels and provides a link to reduced photosynthetic carbon fixation (energy) (Genty et al., 1989; Ralph et al., 2007). PAM fluorometry has also been used to measure inhibition of the maximum quantum yield (F_v/F_m) which is proportional to damage to PSII due to oxidative stress caused by PSII herbicides blocking electron transport under illuminated conditions (Genty et al., 1989; Osmond et al., 1999). Typical dose-response curves from which herbicide concentrations that inhibit 10 and 50% of $\Delta F/F_m'$ and F_v/F_m (IC10 and IC50) can be derived experimentally (Flores et al., 2013). The relevance of photosystem effects as an ecologically relevant endpoint is important to consider. For PSII herbicide effects on microalgae the argument is relatively clear. PSII herbicides inhibit electron transport in photosystem II and this effect provides a link to reduced photosynthetic carbon fixation (energy) and is directly quantified using a PAM fluorometer (Genty et al., 1989; Ralph et al., 2007). For microalgae which have few internal energy resources to draw upon, the impacts of PSII herbicides on photosynthesis causes proportional reductions in growth (Magnusson et al., 2008) (Figure 5-1) and this type of non-traditional endpoint can included in to support water quality guideline derivations as long as their ecological relevance has been demonstrated (Warne et al., 2015). The application of a photo-physiological endpoint for non-PSII pesticides is not suitable.

A summary of recent toxicity (IC50) values for the effects of PSII herbicides on tropical estuarine and marine species derived from PAM fluorometry can be found in Table 5-1. Lower IC50 values indicate greater toxicity and one of the most sensitive species tested has been the benthic green algae *Nephroselmis pyriformis*. The IC50 and IC10 values of diuron to this species are 2.1 $\mu g\ L^{-1}$ and <0.5 $\mu g\ L^{-1}$ (Magnusson et al., 2010). These effect concentrations are below those regularly encountered in estuarine ecosystems (Mitchell et al., 2005; Lewis et al., 2009; Packett et al., 2009; Davis et al., 2012; Smith et al., 2012) and below the current GBRMPA water quality guideline trigger value for diuron (0.9 $\mu g\ l^{-1}$; 99% species protection) (GBRMPA, 2010) and proposed ecological threshold values (Section 5.14). Magnusson et al. (2010) reported IC50 values for diuron, atrazine, hexazinone and tebuthiuron on 4 diatom species and showed that diuron was consistently the most potent of these four PSII herbicides commonly detected in GBR estuaries (Table 5-1). Importantly, mixtures of the PSII herbicides often detected in water samples from estuaries were shown to have additive impacts on two species of estuarine microalgae (Magnusson et al., 2010). Interestingly, the herbicide diuron was detected at concentrations up to 11 $\mu g\ kg^{-1}$ in dry season estuarine sediments and the toxicity of interstitial waters from this contaminated sediment was slightly higher than could be explained by the herbicides detected analytically (Magnusson et al., 2013). Chronic exposures of complex microbial biofilms to diuron was shown to lead to changes in the structure of microbial communities (Magnusson et al., 2012) that may have flow-on effects to species further up the food chain.

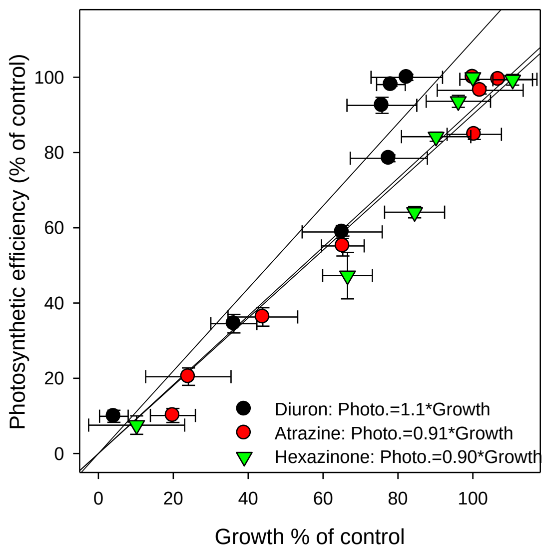

Figure 5-1. A comparison of the effects of 72 h exposures of diuron, atrazine and hexazinone on the growth and photosynthetic efficiency in the diatom *Navicula* sp. $r^2 > 0.98$ in each case. Redrawn from Magnusson et al. (2008).

5.4.2 Mangroves

At the other end of the size scale, mangroves represent the largest plants found in estuarine habitats and these intertidal trees may also be susceptible to PSII herbicides. While the extent of mangrove habitats are relatively dynamic, they are in global decline (Duke et al., 2007), and the unusual dieback of mangroves in coastal and estuarine systems in the Mackay region in the 1990s raised the possibility that herbicides from agricultural sources may have contributed to these declines (Duke et al., 2005; Duke, 2008). Toxicology trials on several mangrove species, including *Avicennia marina* revealed that mangrove seedlings could be impacted by diuron, ametryn and atrazine but that the concentrations affecting photosynthesis were well above those detected in sediments and pore water after the dieback event (Bell and Duke, 2005). Abbot and Marohasy (2011) instead proposed that burial of the mangrove's breathing root pneumatophores by sediments during flood plumes as an alternative hypothesis to explain the dieback. Other herbicides have the potential to impact on mangroves. For instance glyphosate and imazapyr (both amino acid synthesis inhibitors) have been used to eradicate exotic mangroves in Hawaii (MacKenzie and Kryss, 2013), while 2,4-D and 2,4,5-T were used to effectively defoliate mangrove habitats during the Vietnam War (Van et al., 2014).

Table 5-1: Comparison of PSII herbicide concentrations (µg l^{-1}) that inhibit effective quantum yield (photosynthetic efficiency $\Delta F/F'_m$) by 50% across tropical estuarine and marine taxa. (updated from Flores et al. (2013)).

Taxa/Species	Duration	Diuron	Atrazine	Hexazinone	Tebuthiuron	Reference
Diatom						
Navicula sp.	4 h	2.6	36	5.7	94	(Magnusson et al., 2010)
Cylindrotheca closteriuma	4 h	4.4	77	6.9	77	(Magnusson et al., 2010)
Phaeodactylum tricornutuma	4 h	2.7	34	6.6	51	(Magnusson et al., 2010)
Phaeodactylum tricornutuma	2 h	18	45	22		(Muller et al., 2008)
Green alga						
Nephroselmis pyriformis	4 h	2.1	14	2.4	12	(Magnusson et al., 2010)
Seagrass						
Zoestra muelleri	72 h	2.5	13	4.4	29	(Flores et al., 2013)
	77 d	2.4				(Negri et al., 2015)
Halodule uninervis	72 h	2.4	18	6.9	30	(Flores et al., 2013)
	77 d	2.8				(Negri et al., 2015)
Halophila ovalis	24 h	3.5				(Wilkinson et al., 2015)
Coral						
Acropora millepora	7 d	2.9	47	14		(Negri et al., 2011)
Seriatopora hystrix	14 h	2.3	45	8.8	175	Jones et al. (2003)
Acropora formosa	14 h	5.1	37			(Jones and Kerswell, 2003)
Montipora digitata	10 h	5.9	88			(Jones and Kerswell, 2003)
Porites cylindrica	10 h	4.3	67			(Jones and Kerswell, 2003)
Seriatopora hystrix	10 h	2.9				(Jones and Kerswell, 2003)
Foraminifera						
Heterostegina depressa	24 h	11				(van Dam et al., 2012b)
Crustose algae						
Neogoneolithon fosliei	7 d	8.5	180	152		(Negri et al., 2011)
All species						
Mean for all species		*5.1*	*54*	*23*	*67*	
GBRMPA (2010) guideline		*0.9*	*0.6*	*1.2*	*0.02*	(GBRMPA, 2010)
Proposed ETVs		*0.08*	*2.8*	*0.9*	*4.3*	(Table 5-3 this report, Smith et al. in prep-b)

5.4.3 Invertebrates

The effects of insecticides on a range of freshwater invertebrates such as crabs and shrimp have been the focus of multiple studies; however similar ecotoxicological studies on estuarine species are rare. Examples that do exist are generally for temperate (non-Australian) species such as the American blue crab *Callinectes sapidus*, the juvenile stages of which are very sensitive to concentrations of a pyrethroid insecticide (lambdacyhalothrin) at concentrations as low as 0.22 µg L^{-1} (LC50) (Osterberg et al., 2012). GBR-relevant studies are restricted to biomarker responses in animals collected from the field. The analysis of mud crabs *Scylla serrata* from 11 estuarine environments along the GBR revealed contamination of legacy insecticides, such as DDT and dieldrin, which can bioaccumulate in food webs, but no contemporary insecticides or herbicides were detected in the crab tissue (Negri et al., 2009a). Biomarkers for exposure to contaminants revealed significant differences between crabs from different catchments including acetylcholinesterase inhibition in crabs from the Burdekin and Normanby Rivers indicating exposure to organophosphate or carbamate insecticides or potentially arsenic which was elevated in Normanby River crabs (van Oosterom et al., 2010). Since current pesticides rarely accumulate in biota, demonstrating exposure can be difficult. Monitoring biomarkers for invertebrate exposure, coupled with analysis of environmental samples (water and sediment) remains a worthwhile approach linking exposure with impacts (Davanso et al., 2013; Farcy et al., 2013) although further laboratory experiments using local species are needed to validate this approach in the GBR.

5.4.4 Estuarine Fish

Recent studies have indicated that temperate estuarine fish are sensitive to insecticides such as pyrethroids and organophosphates (Parent et al., 2011; Sànchez-Nogué et al., 2013) but there remains a paucity of studies testing dose-responses of pesticides on tropical estuarine fish of the GBR. As with estuarine invertebrates of the GBR, fish from multiple rivers have been assessed for a range of biomarkers that indicate exposure to pesticides and other contaminants. In one study multiple biomarkers indicated that barramundi (*Lates calcarifer*) from more polluted rivers exhibited lower acetylcholinesterase activity and elevated EROD activity and DNA damage – all indicators of exposure to contaminants (Humphrey et al., 2007). In particular, fish from the Herbert and Johnstone rivers exhibiting reduced acetylcholinesterase activity may have been exposed to organophosphate or carbamate insecticides even though the pesticides were not detected in water samples.

Several agricultural pesticides detected in rivers discharging into the GBR, as well as in the GBR lagoon itself, are known to elicit endocrine-disrupting effects in wildlife (United Nations Environment Programme and the World Health Organization, 2013). These pesticides include herbicides (e.g. 2,4-D, atrazine and its metabolite desethyl atrazine, pendimethalin, simazine), organophosphates (e.g. chlorpyrifos), legacy organochlorines (e.g. dieldrin, endosulfan, lindane), and insecticides (e.g. fipronil, permethrin). A recent study exposed barramundi to the herbicide atrazine but no biochemical changes consistent with endocrine disruption were observed except increasing plasma testosterone (T) concentrations (Kroon et al., 2014). In contrast, exposure to environmentally relevant concentrations of commercial herbicide formulations can increase hepatic vitellogenin (vtg) transcription and plasma 17β-E concentrations, and reduce plasma 11-KT concentrations and the androgen/estrogen ratio, suggesting estrogenic and anti-androgenic responses to the additives in the commercial formulations (Kroon et al., unpublished data).

Recent field work has indicated that exposure to estrogenic compounds occurs in wild male barramundi (*Lates calcarifer*) in rivers discharging into the GBR lagoon, and that this is strongly associated with pesticide run-off from sugarcane land use in the GBR catchment (Kroon et al., 2015). Moreover, altered liver *vtg* transcript abundance in wild juvenile coral trout (*Plectropomus leopardus* and *P. maculatus*) further suggest that this exposure extends out into the GBR lagoon itself (Kroon et al., 2015). Vitellogenin (*vtg*), the precursor of fish egg-yolk protein, is a well-established biomarker of exposure to estrogenic compounds in the environment (Wheeler et al., 2005). Other potential sources of EDCs present in the GBR region, such as sewage treatment plants, industrial waste, and intensive animal production, do not match the occurrence and spatial patterns of altered *vtg* transcription documented in this field work, although some influence from point sources cannot be excluded (Kroon et al., 2015). Whether pesticide exposure patterns in the GBR rivers and lagoon are sufficient to ultimately influence population dynamics of these and other fish species, and the sustainability of their fisheries, remains to be determined.

5.5 Coastal and reef species

5.5.1 Background

As pesticide-contaminated floodwaters leave the rivers and estuaries they enter the GBR lagoon influencing intertidal and nearshore habitats and reaching many 10's of km offshore past coral reefs and inter-reefal habitats. Nearshore habitats, including seagrass beds, play critical roles by providing food and shelter for green turtles (*Chelonia mydas*) and dugongs (*Dugong dugon*) as well as many other organisms. These habitats absorb nutrients from run-off and are an important carbon sink (Waycott et al., 2009). Seagrass loss on the GBR is strongly linked to chronic light attenuation during flood events (Collier et al., 2012b) and since PSII herbicides may also affect primary production in seagrass (Haynes et al., 2000b; Ralph, 2000) there has been mounting concern that herbicides may contribute to this seagrass decline (Waterhouse et al., 2012, 2013). Along the rocky shores and further offshore, corals can also be exposed to PSII herbicides and impacts on photosynthesis of coral symbionts has been a focus of continued research since the early 2000s (Jones and Kerswell, 2003; Jones et al., 2003; Negri et al., 2005). While PSII herbicides have remained the main focus of toxicology research, some efforts have also been made to assess the risks of insecticides used in GBR catchments to coastal and reef species (Markey et al., 2007; Negri et al., 2009b; Botté et al., 2012). Here we review recent studies on the effects of pesticides on coastal and reef organisms including seagrass, foraminifera, algae, coral and fish.

5.5.2 Seagrass

Herbicide contamination of seagrass meadows in Queensland is well documented (Haynes et al., 2000a; McMahon et al., 2005) and the majority of studies on the impacts of herbicides on tropical seagrass use PAM fluorometry as described in the previous section. Short term exposure to PSII herbicides can affect photosynthesis in seagrasses at concentrations as low as 0.1 to 0.5 µg l^{-1} (Haynes et al., 2000b; Ralph, 2000; Chesworth et al., 2004; Macinnis-Ng and Ralph, 2004) (Figure 5-2). Flores et al. (2013) was the first study to generate precise acute PSII herbicide toxicity threshold data from concentration response curves for tropical seagrasses using potted *Zostera muelleri* and *Halodule uninervis* in 72-h exposure studies. The sensitivities of the seagrasses were similar to that of microalgae for the herbicides atrazine, diuron, hexazinone and tebuthiuron (Table 5-1). This confirmed that photosynthesis in seagrass can be affected at concentrations lower than the current GBRMPA water quality guidelines for ecosystems protection (GBRMPA, 2010) (Figure 5-2). Wilkinson et al. (2015) recently developed a miniature and more rapid toxicity test for PSII herbicides by using isolated leaves of *Halophila ovalis.* The study validated the utility of the isolated leaf technique by demonstrating the inhibition of photosynthesis by diuron was identical for isolated and potted leaves and similar to inhibition levels in other seagrass species (Table 5-1). The development and validation of this bioassay has been used to test an additional 10 PSII herbicides including a herbicide being considered for registration for use on cane farms (Wilkinson, NERP Project 4.2 unpublished). Future applications for this method could include contribution to monitoring programs and water quality guideline development.While photosynthesis in seagrass has been shown to be vulnerable to acute exposures to PSII herbicides (Table 5-1), much less is known of the potential whole–plant effects of herbicides. It seems logical that if herbicides can reduce the photosynthetic capacity and efficiency of the plant then this should have flow-on effects to plant energetics and health (Ralph et al., 2007a; Gao et al., 2011). Limited data indicate that growth in seagrass seedlings (Gao et al., 2011) and mature plants (Mitchell, 1987; Johnson and Bird, 1995) can be reduced by chronic exposures of atrazine, however this has not been demonstrated in GBR-relevant scenarios. Recent studies have demonstrated that chronic exposures of seagrass to diuron affected photosynthesis in *H. uninervis* and *Z. muelleri* over a 79-day exposure at concentrations as low as 0.3 µg L^{-1} (Negri et al., 2015). Although most of the plants survived prolonged herbicide exposure, concentrations of diuron > 0.6 µg l^{-1} caused measureable impacts on energetic status which may leave the plants vulnerable to other abiotic stressors that occur simultaneously or sequentially such as low light levels during flood plumes. At 1.7 µg L^{-1}, inhibition of photosynthesis by diuron drew down upon energy reserves such as starch in the root-rhizome complex of the plants (> 40% reduction) and eventually reduced growth and elevated mortality at concentrations at this concentration diuron (Figure 5-2).

A recent risk assessment identified nearshore environments in the Mackay Whitsunday region as being at the greatest risk of exposure to the highest concentrations of herbicides (Brodie et al., 2013b). There is only limited information available on the total area of seagrass in the Mackay Whitsundays since the original survey of the region in 1987 (Coles et al., 1987). Subsequent surveys in 1999–2000 provided some evidence of localised loss of seagrass in the Central Whitsundays correlated with point and non-point source discharge, while other areas recorded an increase in seagrass area (Campbell et al., 2002). More recent surveys conducted through the MMP indicate declines in seagrass abundance across the region since 2009 (e.g. McKenzie et al., 2014), which have largely been attributed to the cumulative impact of record floods and cyclones (Devlin et al., 2012b). However, given the demonstrated impact of diuron on the energetic status of seagrass in laboratory experiments (Negri et al., 2015), it is possible that exposure to chronic, low levels of pesticides with intermittent acute exposure in the wet season (Gallen et al., 2013; Lewis et al., 2013) may have increased the vulnerability of seagrass to other pressures (e.g., low light characteristic of flood conditions (Collier et al., 2012a)). The cumulative impact of multiple stressors, including herbicides, on seagrass warrants further investigation (see Sections 5.10 and 5.11).

5.5.3 Corals

Corals are the keystone builders of coral reefs and are often very sensitive to a range of stressors including climate change and water quality. Corals rely on their symbiotic dinoflagellate partners *Symbiodinium* spp. to harvest sunlight for carbon fixation (energy) to survive in their preferred clear-water, low nutrient habitats. A range of PSII herbicides, including diuron and atrazine, have been shown to impact coral symbionts by reducing photosynthetic efficiency and increasing damage to PSII (Table 5-1). The impact on photosynthesis is very rapid (within minutes) and, although reversible (Negri et al., 2005) can cause chronic impacts on exposed corals. Laboratory experiments demonstrated that long-term exposure of coral to diuron (10 µg L^{-1}) can result in coral bleaching (Negri et al., 2005; Cantin et al., 2007) and the bleaching along with reduced photosynthesis caused by the herbicide exposure can lead to reduced energy status and reproductive output (≥1 µg L^{-1}), and mortality (10 µg L^{-1}) in some species (Cantin et al., 2007) (Table 5-2). Cantin et al. (2009) also demonstrated that corals hosting different *Symbiodinium* types are affected to different extents with energy transfer for corals hosting “high-performance” Clade C1 symbionts more affected by diuron than for corals hosting Clade D symbionts.

While the main focus of toxicology research on GBR corals has been on interactions with herbicides, some toxicity studies have shown sensitivity to insecticides and fungicides used in GBR catchments. For example Markey et al. (2007) demonstrated that the settlement of coral larvae (but not fertilisation of eggs) was sensitive to insecticides including chlorpyrifos and endosulfan (EC50s 1 µg L^{-1}) as well as the fungicide MEMC (EC50 2.5 µg L^{-1}). Although the effects were not observed at concentrations likely around coral reefs the study did highlight the sensitivity of early life phases of corals to some insecticides in comparison to a lower sensitivity in adult colonies (the reverse was true for herbicides (Negri et al., 2005). In contrast to the agricultural insecticides tested, the “natural” insecticide derived from the bacterium *Bacillus thuringiensis,* which is widely applied in wetlands and mangrove habitats of the GBR to control mosquitoes, did not affect coral larvae and sponges even at very high concentrations of 5000 µg L^{-1} (Negri et al., 2009b)

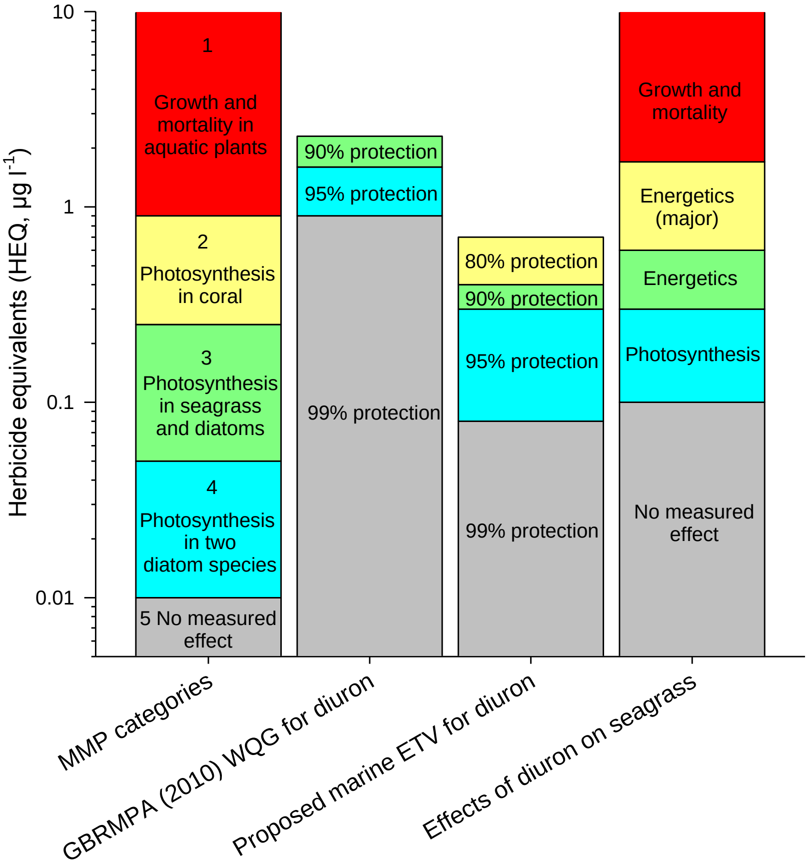

Figure 5-2: A comparison of risk categories and existing guidelines[1,2,3,4] and proposed ecotoxicity threshold values (ETVs) based on herbicide equivalents (= the potency of diuron, µg l^{-1}). Seagrass toxicity data from Flores et al. (2013) and Negri et al. (2015). Data for risk categories and guidelines can be found in Table 5-3.

[1]GBR Marine monitoring program (MMP) categories in HEQ (Gallen et al., 2013) .
[2]Proposed marine ecotoxicity threshold values for protecting 80%, 90%, 95% and 99% of species from diuron (ETVs, [3]Section 5 (Smith et al., In prep-b))
[4]Current GBRMPA water quality guideline for protecting 90%, 95% and 99% of species from diuron (GBRMPA, 2010)
Impacts of diuron on seagrass in experimental systems (Flores et al., 2013; Negri et al., 2015)

5.5.4 Other calcifying species

Other marine species tested, including foraminifera and crustose coralline algae, which both build calcareous skeletons, are less sensitive to herbicides such as diuron (Table 5-1). For example van Dam et al. (2012b) exposed thirteen tropical species, hosting a range of diatom, dinoflagellate, red or green algae symbionts to diuron and in general the IC_{50} for inhibition of photosynthesis was greater than 10 µg L^{-1}. Uptake of the herbicide was also slower and, while not highly sensitive to effects on photosynthesis, damage to the photosystems of the symbionts (reduced Fv/Fm) occurred at very low concentrations, indicating that whole animal effects may occur, especially in combination with high light stress. Acute 24 h exposure of the tropical crustose coralline algae (CCA) *Neogoneolithon fosliei*, indicated that this species was 3- to 10-fold less sensitive to the PSII herbicides diuron, atrazine and hexazinone than coral (Table 5-1) (Negri et al., 2011). CCA has a more flexible photosystem arrangement that can be less reliant on PSII function and may only be sensitive to herbicides in the presence of other stressors such as sediments (Harrington et al., 2005).

Table 5-2: Updated summary of effects of PSII herbicides (diuron equivalents) on GBR/tropical photosynthetic species from the Scientific Consensus Statement adapted from (Brodie et al., 2013b).

<0.1 µgL^{-1}	No observed effect on photosynthesis in corals (Negri et al., 2011); seagrass (Haynes et al., 2000b; Flores et al., 2013; Wilkinson et al., 2015) and microalgae (Magnusson et al., 2008; Magnusson et al., 2010). The effect on primary production is **insignificant**.
0.1-0.5 µg l^{-1}	Photosynthesis is reduced by up to 10% in corals (Jones and Kerswell, 2003; Negri et al., 2011); seagrass (Haynes et al., 2000b; Flores et al., 2013; Wilkinson et al., 2015) and microalgae (Magnusson et al., 2008; Magnusson et al., 2010). The effect on primary production is measurable but **minor**.
0.5-2.3 µg l^{-1}	Photosynthesis is reduced by between 10% and 50% in corals (Jones and Kerswell, 2003; Negri et al., 2011); foraminifera (van Dam et al., 2012b); seagrass (Haynes et al., 2000b; Flores et al., 2013; Wilkinson et al., 2015) and microalgae (Magnusson et al., 2008; Magnusson et al., 2010). Seagrass condition (energy storage) is reduced (Negri et al., 2015). The community structure of tropical microalgae can be affected by concentrations of diuron as low as 1.6 µgL^{-1} (Magnusson et al., 2012). The effect on primary production is **moderate**.
2.3 – 10 µg l^{-1}	Photosynthesis is reduced by between 50% and 90% in corals (Jones and Kerswell, 2003; Negri et al., 2011); seagrass (Flores et al., 2013; Wilkinson et al., 2015) and microalgae (Magnusson et al., 2008; Magnusson et al., 2010). A 50% reduction of growth and biomass of tropical microalgae and seagrass condition was also reported in this concentration range (Magnusson et al., 2008; Negri et al., in prep). The community structure of tropical microalgae is significantly affected and this causes significant changes in the tolerance of microbial communities to herbicides (Magnusson et al., 2012). The effect on primary production is **major**.
>10 µg µg l^{-1}	Causes reduced growth and mortality in seagrass(Gao et al., 2011; Negri et al., 2015) and loss of symbionts (bleaching) in corals (Jones et al., 2003a; Negri et al., 2005). The effect on health and survival of foundation species of the GBR can be **catastrophic**.

5.5.5 Marine Fish

Marine fish, like those in estuaries (Section 5.8) can be potentially affected by insecticides or via effects on the endocrine system from pesticides that are known endocrine disrupting chemicals. Two tropical species of reef damselfish have been tested for sensitivity to the acetylcholinesterase-inhibiting insecticide chlorpyrifos. This class of insecticide is common and acts by inhibiting nerve enzymes which results in the triggering of constant stimulation in nerves leading to paralysis and death (Fulton and Key, 2001). In the first study, high concentrations of chlorpyrifos were found to cause developmental abnormalities in *Pomacentrus amboinensis* (Humphrey et al., 2004). In a more recent study, chlorpyrifos caused measureable effects on muscle cholinesterase activity in *Acanthochromis polyacanthus* at 1 µg l^{-1} chlorpyrifos and this effect increased with concentration, eventually leading to changes in liver function at 10 µg l^{-1} (Botté et al., 2012). As described above, altered hepatic *vtg* transcript abundance in coral trout (*P. leopardus* and *P. maculatus*) suggests that exposure to estrogenic compounds occurs in marine fish (Kroon et al., 2015). The documented patterns of altered *vtg* transcription in coral trout are consistent with the distribution of agricultural pesticides in the GBR lagoon, particularly with higher maximum concentrations in the central and southern GBR lagoon (Kennedy et al., 2012b; Lewis et al., 2013).

5.6 Multiple pesticides and stressors

Although pesticides can be detected in rivers, estuaries and the marine environment of north Queensland all year they are predominantly flushed into the GBR lagoon during flood events (Packett et al., 2009; Shaw et al., 2010; Davis et al., 2012; Kennedy et al., 2012b; Lewis et al., 2012). Under these circumstances pesticides are frequently detected:

(1) In the presence of other pesticides. For example multiple PSII herbicides are often detected in combination or different classes of pesticides can be detected together.

(2) Under conditions of low salinity, low light, high suspended solids and nutrients

(3) During the warmest months.

Furthermore, these conditions can occur simultaneously or sequentially and impacts on the environment can be broadly considered "cumulative". Each of these scenarios has the potential to increase the vulnerability of biota to pesticides. Here we review recent studies that document the potential impacts of pesticides in mixtures and in combination with other stressors related to flood plume conditions.

5.7 Pesticide mixture toxicity

When pesticides that have the same mode of action (e.g. the PSII herbicides atrazine and diuron) and co-occur in water samples the total effect on an organism is additive i.e. the total effect on an organism conforms to the concentration addition model of joint action (Berenbaum, 1985). For example, laboratory studies have shown that the effects of herbicides diuron, atrazine, simazine and tebuthiuron on photosynthesis in the Queensland estuarine microalgae *Navicula* sp. and *Nephroselmis pyriformis* conform to concentration addition (Magnusson et al., 2010), and the same principles apply for freshwater temperate species (Faust et al., 2001). Therefore, the toxicity of a mixture of PSII herbicides can be calculated using the "concentration addition" (CA) method by adding together the concentration x relative toxicity of each component of the mixture (Berenbaum, 1985). This method has been applied for multiple GBR scenarios to assess whether PSII herbicide mixtures (i) exceed guidelines, (ii) pose a risk to the GBR biota or (iii) to report against water quality targets (Kennedy et al., 2012b; Lewis et al., 2012; Smith et al., 2012). Recent studies have calculated the atrazine equivalent concentrations of PSII herbicide mixtures to be up to 807 µg l^{-1} at sites within the GBRCA (Smith et al., 2012), concentrations likely to be highly toxic to sensitive biota. Even when concentrations of individual PSII herbicides are very low, the additive toxicity of complex low-concentration mixtures of can exceed toxicity thresholds (Faust et al., 2001).

The toxicity of pesticide mixtures in water samples (or passive samplers) from the GBR and adjacent catchments have also been assessed in bioassays, often using inhibition of photosynthesis (PAM fluorometry) on microalgae as a toxic endpoint (Bengtson Nash et al., 2005a, 2005b; Shaw et al., 2009; Shaw et al., 2012; Magnusson et al., 2013). In these studies the toxic effect on microalgae usually matched the expected additive toxicity from the individual PSII herbicides detected analytically. Sometimes however, photoinhibition was higher than expected based on analytical results, indicating the presence of unidentified toxins in water samples (Shaw et al., 2009; Magnusson et al., 2013). The pairing of passive samplers with assays has also been used to successfully assess the toxicity of insecticide or other pesticide mixtures using sensitive endpoints such as inhibition of settlement of invertebrate larvae (Shaw et al., 2009).

When pesticides with different modes of action, for example diuron and metolachlor co-occur, it is more appropriate to calculate the combined toxicities using the Independent Action toxicity model (IA) which has been applied successfully to predict the combined effect of herbicides and thermal stress on foraminifera (van Dam et al., 2012a). However, there is currently very little data to enable the use of IA (the full concentration-response relationship for each component of the mixtures is needed) for multiple pesticides relevant to the GBR. Freshwater habitats of the GBRCA are often contaminated with multiple pesticides including insecticides and herbicides (Smith et al., 2012) and the impacts on biota are often unpredictable (Relyea, 2009). It has therefore been recommended (Smith et al., in prep-c) that the toxicity of mixtures to freshwater and marine organisms be calculated using the ms-PAF method (de Zwart and Posthuma, 2005) that assesses the potentially affected fraction (PAF) of species (s) that will theoretically be affected at a specified environmental concentration of each component of the mixture. This method is an application of the method used to derive Australian water quality guidelines (ANZECC and ARMCANZ, 2000) and can draw upon global toxicity data when specific GBR toxicity data are not available.

5.8 Pesticides in flood plume conditions

The highest pesticide concentrations in the GBR lagoon coincide with low salinity and high concentrations of suspended solids and nutrients during the summer wet season (Devlin et al., 2012a, 2012b; Kennedy et al., 2012b; Davis et al., 2014c). In fact, the widespread introduction of pesticides in the latter half of last century also overlapped with continued expansion of coastal agriculture that has resulted in increases in land-sourced pollution and low salinity, compounding the potential for multiple stressors from plumes to impact marine habitats of the GBR (Brodie et al., 2012a; Schaffelke et al., 2013). Complex interactions between these multiple stressors are likely, but remain largely unstudied in the GBR and GBRCA context, and we currently rely on international studies to predict potential effects.

Changes in water quality have the potential to either increase or decrease the impact of pesticides. For example the pyrethroid insecticide deltamethrin (used on cotton) potentially binds to particulates in high turbidity water and can become less available (and effectively less harmful) to freshwater fish and shrimp (Thomas et al., 2008). The extent to which the presence of suspended solids decreases the toxicity of pesticides varies with the physico-chemical properties of the pesticides (e.g. Phyu et al., 2013). PSII herbicides in contrast are far more water soluble and only a small fraction binds to suspended solids in flood plume conditions (Davis et al., 2012). Therefore, suspended sediments (and changes in salinity) would not be expected to greatly reduce the bioavailable fraction of PSII herbicides under flood plume conditions, rather its presence combined with a combination quality pressures is more likely to increase impacts of these herbicides. For example, Harrington et al. (2005) demonstrated that the presence of sediments increased the negative effect of diuron on crustose coralline algae.

Reductions in light penetration due to increased suspended sediments from river plumes can contribute to the loss of seagrasses globally (Collier et al., 2012a). Recent research indicates very similar responses in seagrass to chronic shading and herbicide exposure, including changes in energetics and reduced growth (Negri et al., in prep). We therefore expect that chronic exposure of seagrasses to herbicides during flood plume events is likely to exacerbate seagrass loss. While herbicide exposure under low light acts on seagrass in a similar way to shading, recent studies demonstrate that damage to the photosystems in seagrass is exacerbated by diuron under high irradiance (Wilkinson et al., 2015) and this may have implications for intertidal seagrasses simultaneously exposed to herbicides and high light conditions.

Nutrients and herbicides are commonly used agricultural chemicals that can both directly impact microalgal growth in different ways, with unpredictable outcomes. For example, individually, nutrients and atrazine have contrasting effects on microalgal growth, with nutrients typically stimulating and atrazine inhibiting (Murdock et al., 2013). Complex combinations of these two antagonistic pollutants can impact on microalgae in vastly different ways from their influence when introduced separately (Murdock et al., 2013). Very little research has examined the potential for reduced salinity to affect pesticide toxicity in marine organisms. The only study on potential interactions between low salinity and diuron effects did not find any additional impacts in coral symbionts over a short 10-h exposure (but the low salinity of 27 psu had no effect on its own) (Jones et al., 2003).

The impacts of pulsed and chronic exposures to pesticides are considered in the context of water quality guidelines in Section 5.11.3.

5.9 Combined effects of pesticides and thermal stress

Wooldridge (2009) hypothesised that reducing the nutrient concentrations on the GBR would improve the resilience of corals from increases in sea surface temperatures (SST) of up to 2.5°C. Reef management and policy widely assumes that improvement in water quality can ''buy time'' for corals to adapt or acclimatize to increased SST (Brodie et al., 2013b). River discharges containing the highest loads of pesticides occur in January-March, coinciding with maximum water temperatures in the GBR and the potential combined impacts these stressors may intensify as the climate changes. Organisms such as corals exist very close to their upper thermal threshold and are likely to be particularly sensitive to further stressors including pesticides. A study that simultaneously exposed coral to PSII herbicides and SSTs up to 32°C confirmed that atrazine, diuron and hexazinone can enhance the sensitivity of corals (photo-physiological effects and bleaching) to thermal stress (Negri et al., 2011). The majority of combinations of PSII herbicides and thermal stress had an additive effect, and it was calculated that above 30°C reducing diuron concentration by 1 µg l^{-1} would protect photosynthetic efficiency from an equivalent increase in SST of 1.8°C or damage to photosystem II by 1°C. The combined effects of diuron and thermal stress were also additive in several species of foraminifera-hosting diatoms, dinoflagellates or rhodophytes, with the impact on photosystems again proving additive (van Dam et al., 2012a). While similar experiments have not been published on seagrass or organisms from tropical estuaries, the evidence so far indicates that pesticides have the potential to increase the vulnerability of tropical species to elevated SSTs, and that effective management of local water quality can reduce negative effects of global stressors such as elevated SST. Results from these studies also raise the issue that water quality guidelines for pesticides (often derived from temperate species and under benign laboratory conditions) may not be appropriate to protect foundation species of the GBR during the summer wet season (e.g. Fig. 5-2).

These studies have highlighted how the assessment of risk posed by a pesticide may be complicated by enhancement or suppression of its effect by another co-occurring stressor. In addition, recent reviews of the combined action of pairs of stressors in a range of ecosystems suggest non-additive outcomes such as synergies (when the combined impact of several stressors is greater than the sum of the impacts of individual stressors) or antagonisms (when combined stressor impact is less than the sum of the individual impact) are often more common than simple additive effects (where the combined effect is equal to the sum of the individual stressor impacts) (Darling and Côté, 2008; Magbanua et al., 2013). It is becoming increasingly apparent that complex interactions among multiple stressors occur commonly in freshwater, estuarine and marine ecosystems impacted by agricultural land-use practices, and that the consequences of stressors will often be unpredictable on the basis of knowledge of single effects. The integrated management of catchment land use needs to be informed by knowledge of the combined effects of multiple stressors.

5.10 Comparison of water quality guidelines for pesticides

5.10.1 New water quality guidelines

The current Australian and New Zealand Guideline for Fresh and Marine Water Quality (ANZECC and ARMCANZ, 2000) do not include guideline values (GVs, previously termed trigger values, TVs) for many pesticides and those that have GVs often are of 'low reliability' (i.e. based on ecotoxicity data for a limited number of species and taxonomic groups). For this reason, the current GVs are now under revision as part of the National Water Quality Management Strategy (NWQMS) (http://www.environment.gov.au/water/quality/national-water-quality-management-strategy#revision).

The Australian Government has recently called for tenders to derive guideline values for over 30 chemicals, with at least 18 being for pesticides. Independent of the review of the NWQMS, the Queensland Department of Science, Information Technology and Innovation (DSITI) set about calculating a set of ecotoxicity threshold values (ETVs). These were derived using the revised method (Batley et al., 2014; Warne et al., 2015) of calculating GVs for the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. They are termed ETVs, rather than GVs, because at this point in time they have no national standing. To address this, the ETVs will be submitted for consideration as national GVs as part of the current revision of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality and subsequently for inclusion in the Great Barrier Reef Water Quality Guidelines.

ETVs for six pesticides (ametryn, atrazine, diuron, hexazinone, imidacloprid and tebuthiuron) were derived, whenever possible, separately for freshwater and marine ecosystems. However, when there were insufficient data to derive an ETV for a particular ecosystem, toxicity data from different ecosystems were combined (e.g. a freshwater GV could be generated using data from freshwater and estuarine species).

The derived ETVs are compared to the current TVs for fresh, estuarine and marine waters (Table 5-3). Toxicity data for two tropical Australian phototrophic species (i.e. species that photosynthesise) were commissioned as part of this work. The species were *Isochrysis galbana* (a marine microalga) and *Lemna aequinoctialis* (a freshwater macrophyte). A comparison between current and proposed guideline values for diuron can be found in Figure 5-2, alongside the current Marine Monitoring Program categories and toxicity concentrations to seagrass in recent publications.

This work generated ETVs for two herbicides (ametryn and imidacloprid) that have previously not been included in the Australian and New Zealand Guideline for Fresh and Marine Water Quality (ANZECC and ARMCANZ, 2000). For three of the remaining four herbicides the reliability of the ETVs is higher than the current GVs – meaning we have greater confidence that they will provide the specified degree of protection. Should the proposed ETVs be nationally adopted as GVs this will lead to higher estimates of the risk posed by atrazine, diuron (marine only) and hexazinone (as the ETVs are lower than the current GVs) but lower estimates of the risk posed by diuron (freshwater) and tebuthiuron (as the ETVs are higher than the current GVs). Collation of ecotoxicity data for risk characterisation

Risk characterisation of individual chemicals and mixtures relies on the availability of ecotoxicity data. While it is preferable to base this solely on local endemic species, this is largely impossible due to there being insufficient ecotoxicity data for local tropical species to meet the minimum data requirements of the species sensitivity distribution method of calculating water quality guidelines. Therefore, we have to predominantly rely on the ecotoxicity data available in the scientific literature, irrespective of where the species live.

The quality and reliability of water quality guideline values, risk assessments and consequent management actions depends on the quality of the ecotoxicity data used. Thus, it is critical that a data quality assessment scheme, such as that developed by Hobbs et al. (2005) is employed to ensure high quality and defensible data underpin the guideline values and hazard and risk assessments of the ecosystems of the GBR and adjacent catchments. The Pesticide GBR Ecotoxicity Database (Smith et al., In prep-a) was developed to store ecotoxicity data that were determined to be of acceptable quality (based on Hobbs et al., 2005) to provide a single data source available to all groups involved in reporting on pesticide risk for the Paddock to Reef Program. To date, the data for the six pesticides have been quality checked and entered into the database; ametryn, atrazine, diuron, hexazinone, tebuthiuron and imidacloprid. Ultimately, all pesticides detected in the GBR and adjacent catchments should be included in this database to ensure pesticide risk is properly assessed.

5.2 Pesticide exposures over time scales relevant to the GBR and its catchments

To date, risk characterisations of pesticides detected in GBR ecosystems has been limited to comparing pesticide concentrations with effects produced by a single exposure period defined in water quality guidelines, trigger values or by concentration addition models or ms-PAF (Lewis et al., 2009, 2012, 2013; Davis et al., 2012; Kennedy et al., 2012a; Smith et al., 2012). However, we recognise that none of these scenarios adequately describes pesticide exposure in the GBR and its coastal and catchment ecosystems. In Chapter 4, temporal exposure was shown to (i) be highly seasonal, co-occurring with the wet season over the spring and summer months; (ii) occur in repeated pulses of high concentrations in the smaller catchments and sub-catchments; and (iii) be chronic, particularly at low levels in the marine areas. The following outlines the potential risks resulting from these types of temporal exposure patterns.

Table 5-3: Proposed ecotoxicity threshold values (ETVs, µg l^{-1}) that should protect 99%, 95%, 90% and 80% of phototropic species[6] from exposure to six herbicides and the corresponding current Australian and Great Barrier Reef trigger values (Smith et al., in prep-b).

Chemical	**Status[@]**	**Media[#]**	**Reliability[$]**	**PC99[^]**	**PC95[&]**	**PC90[*]**	**PC80[+]**
Ametryn	ETV	F & M	HR	0.02	0.1	0.3	0.7
	Aus & NZ	NA	NA	NA	NA	NA	NA
	GBR	M	MR	0.5	1.0	1.6	
Atrazine	ETV	F	VHR	3.7	6.0	8.1	12.0
	Aus & NZ	F	MR	0.7	13	45	150
	ETV	E[1]	HR	2.2	3.4	4.4	6.3
	ETV	M	HR	2.8	3.8	4.6	6.1
	Aus & NZ	M (M adopted from F)	LR – ECL	0.7	13	45	150
	GBR	M	MR	0.6	1.4	2.5	
Diuron	ETV	F (F & E)	HR	0.2	0.3	0.4	0.7
	Aus & NZ	F	LR – ECL	0.2	0.2	0.2	0.2
	ETV	M (M & E)	MR	0.08	0.3	0.4	0.7
	Aus & NZ	M	LR – ECL	1.8	1.8	1.8	1.8
	GBR	M	MR	0.9	1.6	2.3	
Hexazinone	ETV	F	MR	0.2	0.7	1.3	2.4
	ETV	M (F & M)	HR	0.9	1.2	1.5	2.0
	Aus & NZ	F & M	LR – ECL	75	75	75	75
	GBR	M	LR	1.2	1.2	1.2	1.2
Imidacloprid[¥]	ETV	F	MR	0.03	0.1	0.2	0.7
	ETV	M (F & M)	MR	0.03	0.1	0.3	0.9
	Aus & NZ	NA	NA	NA	NA	NA	NA
	GBR	NA	NA	NA	NA	NA	NA
Tebuthiuron	ETV	F & M	LR	4.3	8.8	12.0	17.0
	Aus & NZ	F	HR	0.02	2.2	20	160
		M (adopted from F)	LR – ECL	2.2	2.2	2.2	2.2
	GBR	M	LR	0.02	2	20	

[@] Aus & NZ = the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ, 2000), GBR = Water Quality Guidelines for the Great Barrier Reef Marine Park (GBRMPA 2010). [#] the ETV or TVs were calculated using F = freshwater, M = marine water, NA = not available, F & M = freshwater and marine water, F & E = freshwater and estuarine, M & E = marine and estuarine organisms. $ HR = high reliability guideline value, MR = moderate reliability guideline value, VHR = very high reliability guideline value, LR = low reliability trigger value for values from ANZECC and ARMCANZ (2000) or ETVs for values proposed by the current project, LR – ECL = low reliability environmental concern level. ^ PC99 = the concentration that should theoretically protect 99% of organisms in the ecosystem being considered. [&] PC95 = the concentration that should theoretically protect 95% of organisms in the ecosystem being considered. *PC90 = the concentration that should theoretically protect 90% of organisms in the ecosystem being considered. [+] PC80 = the concentration that should theoretically protect 80% of organisms in the ecosystem being considered.[1] Estuarine Guideline Values are not normally derived for the Australian and New Zealand Guidelines for Fresh and Marine Water Quality, due to insufficient toxicity data. However, for atrazine sufficient estuarine toxicity data were

[6] These ETVs should provide a higher degree of protection when all species (not just phototrophic species) are considered. This occurs because the herbicides a specific mode of action (they inhibit the photosystem II component of photosynthesis) and as such, phototrophs (organisms that photosynthesise) are far more sensitive to these chemicals than other organisms (e.g. mammals, fish, crustaceans) that do not photosynthesise.

5.2.1 Effects of seasonal exposure

Exposure to high pesticide concentrations most often occurs seasonally based on the timing of rainfall with pesticide application periods. The main period of pesticide exposure occurs with the tropical wet-season during the spring/summer months when days are longer and temperatures are higher. Important seasonal or life cycle stages may coincide with the seasonal runoff of pesticides and understanding this co-occurrence between ecological cycles and pesticide runoff is necessary to generate a more accurate assessment of risk in the GBR and coastal ecosystems. For example, the summer wet season when pesticide concentrations are high coincides with the slow growth periods for many tropical seagrass species (warm, low light)(Waycott et al., 2004) and the impact of this seasonality to pesticide risk is unknown. Laboratory bioassays which we currently use to assess the toxicity of pesticides, do not consider these important ecological cycles.

5.2.2 Effects of pulsed exposure

Pulsed exposures to pesticides are always unique events (Chapter 4) and the nature of pulsed exposures in GBR catchments has been examined by Smith et al (in prep-a). Accounting for the effects of pulsed exposures in a risk assessment can be complex as they usually involve multiple exposure and recovery periods. The frequency and magnitude of the pulses, and the potential for recovery in the periods between them, will determine whether cumulative impacts are likely. The cumulative effects of pulsed pesticide exposures will vary depending on both the organisms and the pesticides involved. This has been examined in laboratory tests demonstrating the capacity of organisms to recover after exposure to different types of pesticides. As an example, recovery of phototrophs from pesticides such as metsulfuron-methyl is slow, thus, if the lag time before recovery is longer than the period between pulses, the effect on the organism will be equivalent to a continuous exposure (Boxall et al., 2013). Conversely, phototrophs have the capacity to recover growth rate and photosynthetic functioning quickly from PSII herbicides after exposure has ceased (Vallotton et al., 2008a). It has been demonstrated that pulses of PSII herbicides with alternating recovery periods exert a greater effect than a single short pulse but have a smaller effect on growth than a continuous exposure (with no recovery periods) of an equivalent time-weighted average concentration (Macinnis-Ng and Ralph, 2004; Vallotton et al., 2008a).

Using a probabilistic ecological risk assessment, Smith et al (in prep-a) examined the potential for exposure and recovery in GBR catchment ecosystems during the 2010-11 and 2011-12 wet seasons. Days of exposure (≥ 1% of species potentially affected) were compared to days of recovery (< 1% of species potentially affected) such that, an exposure:recovery (E:R) value > 1 indicated more days of exposure than recovery and a value < 1 indicated more days of recovery than exposure during the wet season. The highest E:R ratio was recorded at Sandy Creek in 2010-11 with a ratio of 4.8 days of exposure to every day of recovery. Barratta Creek and Pioneer River were the only other two sites where the E:R ratio exceeded one in 2010-11 and 2011-12. This type of characterisation of the temporal exposure observed in GBR catchments is a basic assessment to demonstrate variations exist between catchments. The periodic sequence of exposure and recovery is likely to vary temporally as the wet season progresses, and this variation is likely to differ between sites and between years of sampling. This type of characterisation does not generate a reliable assessment of risk related to the pulsed exposure patterns observed. To do so would require more sophisticated modelling techniques.

5.2.3 Chronic Exposure

In some catchments, where pesticide concentrations are high, concentrations do not reduce to recovery levels between pulses, generating a chronic exposure of high concentrations. For example, monitoring data from the Pioneer River indicates that in 2011–12 atrazine equivalent concentrations remained above the atrazine TV of 13 µg l^{-1} for at least 33 consecutive days (Smith et al., In prep-a). The standard ecotoxicity tests have an exposure period of 3 to 7 days for phototrophic species. Therefore a continual exposure of high pesticide concentrations over 33 days is likely to cause a much greater impact to the ecosystem than what we can currently predict when we compare concentration levels against TVs or ecotoxicity data sourced from the literature. As pesticides are transported away from the paddock sources, the frequency and intensity of the concentration pulses reduces and a low-level chronic type of exposure is observed. As described in Chapter 4, temporal exposure in estuarine and marine areas generally have lower pesticide concentrations, however it is likely that they have a prolonged exposure period compared to the riverine ecosystems as some pesticides have been detected all year round in marine habitats (Shaw and Muller, 2005; Kennedy et al., 2012b; Gallen et al., 2014). Empirical studies have demonstrated impacts associated with chronic exposure of PSII herbicides on GBR species including: changes in the structure of microbial communities in estuarine environments (Magnusson et al., 2012); effects on seagrass energetics and growth from a 79-day diuron exposure (Negri et al., in prep), and; bleaching, a reduced energy status and reduced reproductive output in some coral species as a result of chronic diuron exposure (Cantin et al., 2007).

5.3 Spatial assessment of the risks posed by pesticides to the GBR and associated systems

5.3.1 Background

There has been much progress on understanding the spatial and temporal risks of pesticides in the GBR since the maximum recorded concentrations of individual herbicides in riverine flood plumes were plotted, contoured and compared with ecological protection guidelines for the Great Barrier Reef Marine Park and laboratory-measured effect concentrations (Lewis et al., 2009). Indeed, risk assessments of pesticides in the GBR have greatly improved with more ecotoxicological and monitoring data and the development of better methods to calculate guidelines and assess the effects in situations where multiple pesticides are present (see previous sections). Assessments on the risks of a combination of herbicides include Smith et al. (2012) who calculated atrazine-equivalent PSII concentrations using monitoring data collected within the GBRCA and Lewis et al. (2012) and Kennedy et al. (2012a, 2012b) who calculated diuron-equivalent PSII concentrations from flood plume monitoring data (grab and passive samplers) in the GBR lagoon. Other tools such as the Pesticide Impact Rating Index (PIRI) has been applied to examine the relative risks of the pesticides used in the sugar industry (Davis et al., 2014a) and horticulture (Lewis and Glendenning, 2009) and the Predict the Ecological Risk of Pesticides in freshwater ecosystems (PERPEST) model has been applied to examine the effects of the multitude of pesticides detected in Barratta Creek and the Haughton River (Davis et al., 2013). Collectively these assessments highlighted that certain pesticides posed a considerable ecological risk to aquatic ecosystems at particular times of the year and allowed a more comprehensive region-wide GBR assessment to be completed.

The landscape-scale assessment of pesticide hazard to the process and values of GBR catchment palustrine (swamp) and lacustrine (lake) systems has been assessed and mapped at a landscape-scale (DSITIA, unpublished data). Of the 299,685 ha of lacustrine and palustrine wetlands in the GBR catchments, 21 436 ha or 7.2% of the total exists within areas assessed as having Moderate to Very High Hazard for pesticide inputs. These are concentrated in coastal lowlands and inland cropping areas of the GBR.

The recognition that most herbicides are transported in the GBRCA in the dissolved phase (Davis et al., 2012; Packett, 2014) allowed a new risk assessment approach to be conducted as part of the 2013 Scientific Consensus Statement (Brodie et al., 2013a, 2013b; Lewis et al., 2013) which built upon earlier work by Kennedy et al. (2012b). This approach used the concentrations of the key PSII inhibiting herbicides monitored under the GBRCLMP (Turner et al., 2012, 2013; Wallace et al., 2014) and applied (i) additive diuron-equivalent concentration and (ii) multiple substances potentially affected fraction (ms-PAF) models using the latest available ecotoxicological data. The periods of highest diuron-equivalent concentrations that coincided with considerable flow for each of the major river catchments in each GBR natural resource management region (excluding Cape York) were identified (Tully, Burdekin, Pioneer, Fitzroy and Burnett Rivers). These diuron equivalent concentrations were coupled with offshore salinity values (calculated using the relationship between satellite-derived colour dissolved organic matter (CDOM) and seawater salinity data; Schroeder et al., 2012) to estimate the maximum possible diuron-equivalent concentrations across the GBR lagoon. The data were contoured to identify risk areas considered as catastrophic, major, moderate, minor, insignificant and no risk using a combination of expert judgement and known ecotoxicological thresholds for keystone plant communities in the GBR (i.e. phytoplankton, seagrass and coral zooxanthellae) (Lewis et al., 2013).

The results of this assessment revealed that the Mackay Whitsunday region exhibited the highest risk of PSII herbicides in the GBR with concentrations of 'major' and 'moderate' consequence impinging on 24 km^2 of coral reefs and 140 km^2 of seagrass meadows within this region. Under this scenario considerable inhibition of photosystem II would be expected to occur in both coral and seagrass species. The Wet Tropics region was rated as having the second highest risk with a relatively large area (250 km^2) of seagrass species classified under a 'minor' risk. However, a limitation of this risk assessment was that only the major river within each Natural Resource Management region was assessed using this method. Additional analysis using the ms-PAF method showed that Barratta Creek within the Burdekin region reached a 'catastrophic' risk (i.e. >70% of phototrophic species potentially affected) for one of the analysed events; this result is of concern given that Barratta Creek feeds into high value Ramsar-listed wetlands. Indeed the smaller creeks that contain relatively large areas of intensive agriculture (> 20%) such as Barratta and Sandy Creeks yielded the highest pesticide concentrations in monitoring programs (Smith et al., 2012; Lewis et al., 2013).

Of the five ecosystems that were recognised within the GBR, we suggest that the freshwater reaches of rivers and freshwater/coastal wetlands face the highest risk from pesticides (PSII herbicides and some non-PSII pesticides) (catastrophic to moderate) followed by the estuarine reaches of the rivers (major to minor), coastal nearshore zone which includes intertidal and subtidal seagrass meadows (moderate to insignificant), the inner shelf (moderate to insignificant) and the mid and outer shelf (insignificant to no risk). These risk categories depend on the specific region and the land use characteristics of the adjacent catchment(s). This risk classification most likely is an underestimate of the actual risk as the current risk assessment does not consider (a) all pesticides known to occur in waters of the GBR (including other PSII herbicides such as metribuzin), (b) all modes of action by which PSII herbicides exert their toxicity, (c) the risk posed by combinations of pesticides with the other contaminants found in flood plumes (e.g. elevated TSS and nutrients) nor other environmental stressors (e.g. climate change), (d) the cumulative impacts from the multiple plumes that occur each year. Accounting for the cumulative impacts from the multiple plumes alone could easily increase the risk classification by one class e.g. from minor to moderate or from moderate to major. Finally, there is insufficient knowledge about the long-term effects of low level exposure to pesticides, as experienced in the mid and outer shelf (or for other environments in the catchment to reef continuum), to have confidence in the current assessment that pesticides pose only an insignificant to no risk to these ecosystems. Long-term toxicity tests should address this knowledge gap, but more toxicity data for locally relevant species and local conditions are required to fully assess the risk posed by pesticides (Lewis et al., 2013).

Pesticide risk assessments for the GBRCA and lagoon are ongoing and similar methods have been applied for additional rivers of the GBR under various Water Quality Improvement Plans and under the MMP (Petus et al., 2015). Risk assessments of the future will benefit from additional monitoring and ecotoxicological data as well as new tools for the calculation of effect-equivalent concentrations of the multitude of pesticides detected in catchment and marine monitoring programs. A similar framework (i.e. calculation of additive PSII herbicide concentrations) has been applied in the setting of ecologically relevant targets for rivers of the Wet Tropics and Burnett Mary as part of their regional Water Quality Improvement Plans (Brodie and Lewis, 2014; Brodie et al., 2014).

5.4 Conclusions and knowledge gaps

The ecological risks posed by pesticides to the GBRCA and GBR depend on their occurrence (Chapter 4) and their impact on species relevant to these ecosystems (this Chapter). Recent research has provided regulators and managers with relevant ecotoxicology data for the most common pesticides, the PSII herbicides, to a range of marine organisms. This has enabled comparisons between current and proposed water quality guideline values for PSII herbicides with effects on species of high conservation value such as corals and seagrasses. Broadly we conclude:

1. There are large gaps in our understanding of how (in particular) alternative or emerging pesticides affect nearshore, estuarine and freshwater species relevant to the GBR and GBRCA. This information is needed to develop and/or improve water quality guidelines.
2. The highest risk of pesticides is to freshwater and estuarine ecosystems where the greatest concentrations are measured. However, the impact of pesticides on freshwater and estuarine organisms are poorly known and this needs to be a focus of future toxicology studies and field assessments (monitoring and biomarkers) to improve future risk assessments.
3. Complex mixtures of pesticides as well as climate and cumulative exposures generally increase risk to sensitive biota and this needs to be further investigated in GBR-relevant scenarios and applied in future risk assessments.
4. Communication between industry, researchers, regulators and managers on all aspects of pesticide risk improved over the course of NERP and associated research programs. This should continue with a strong focus on how changes in land practices can translate to improved water quality (reduced impacts of pesticides) and relies on ongoing and improved risk assessments from the sources, through the catchments and into the GBR lagoon.

Table 5-4: Research gaps in pesticide impacts in freshwater.

Research Gap	Details
Modelling pesticide risk requires the collation and quality assessment of published pesticide ecotoxicity data.	Expand the GBR pesticide ecotoxicity database to include all pesticides detected in GBR catchments and the GBR lagoon (and additionally emerging pesticides, breakdown products and commercial pesticide formulations) such that ecological risk can be modelled for all of these pesticides. This will provide farmers and industry representatives with information as to which pesticides have the highest to lowest risk to freshwater and marine ecosystems.
Risk analysis	The highest risk of pesticides (i.e. based on concentrations and exposure) is to the freshwater and estuarine ecosystems of the GBR catchments. It is here where we will likely see the greatest impacts of pesticides to the freshwater communities. In addition, the connectivity of these communities with the marine ecosystems means that they play an important role in the resilience of the Reef (Nyström et al., 2008). • Examine what the pesticide loads mean to the Reef in terms of risk and determine if there is a relationship between pesticide load reduction and a reduction in pesticide risk. • Studies should include a wider range of target pesticides including sediment-bound insecticides, fungicides, emerging herbicides and additives in commercial pesticide formulations • Biomarkers for exposure and/or effects based for example on enzyme, immune and endocrine outcomes are needed. • The influence of flood plume stressors (low salinity, high nutrients and

	suspended solids) on the sensitivity of keystone species and communities to pesticides needs to be addressed. • Continue to work on updating pesticide risk assessments using latest monitoring data, ecotoxicology data and risk assessment tools to better update our understanding of pesticide risk to various freshwater, estuarine and marine ecosystems.
Monitoring	Improve biological and chemical monitoring (for example: community structure, passive sampling and grab sampling) of nearshore GBR habitats of high conservation value to evaluate the success of land management policies to protect the GBR.
Community impacts	To date, little is known of the impact that pesticides are having to the freshwater and estuarine communities of the GBR catchments. In addition, it is likely that through biological monitoring we can demonstrate to farmers and stakeholders a clear relationship between measured pesticide concentrations and the impairment to these communities. Methods in metabarcoding and ecogenomics could provide a sensitive way to correlate water quality characteristics with changes in the structure and functioning of a freshwater community • Quantify the sensitivity of species/communities of the highest conservation value, under conditions relevant to freshwater, estuarine and nearshore marine environments, to priority pesticides – ensuring guideline concentrations protect species and communities that we value the most. • Improved focus on understanding the sensitivity of key near-shore marine species to pesticides is required to ensure water quality guidelines successfully protect species/ecosystems of high conservation value: seagrass – e.g. germination studies, and key fisheries species – e.g. reproduction studies and fitness effects. • Experimental validation is required of mixture and joint toxicity models (e.g. ms-PAF) to selected key freshwater, estuarine and marine organism ecotoxicology tests with pesticides having the same mechanism and those with different mechanisms. • Quantification of the influence of climate change stressors (temperature, OA etc.) on the sensitivity of keystone species to pesticides is required
Site specific studies	Irrigation tailwater in the lower Burdekin region is thought to be the cause of exceptionally high concentrations of pesticides detected at Barratta Creek during low flow periods. Barratta Creek feeds into Bowling Green Bay, a Ramsar Wetland which is of high ecological importance. It is unknown what the extent of the pesticide risk is to Barratta Creek and Bowling Green Bay.
Ecotoxicology	Improved focus on quantifying the toxicity of pesticides to key nearshore, estuarine and freshwater/wetland species to ensure water quality guidelines successfully protect species/ecosystems of high conservation value (algae, plant, invertebrates, fish). • Conduct further ecotoxicology tests on species that have high ecological, cultural and commercial value using protocols that satisfy criteria for inclusion in water quality guidelines (e.g. Batley et al., 2014)
Cumulative pressures	Assess the impacts of (i) multiple pesticides, (ii) additional stressors related to flood plumes (e.g. low salinity, nutrients and light) and climate change (e.g. high temperature, increased OA), and (iii) repeated pulses (flood plumes) and chronic exposures on organisms/communities of high conservation value - towards incorporating these influences in species sensitivity distributions and future water quality guidelines. • Test the cumulative impacts of pulsed exposures to pesticides relevant to GBR scenarios

	• Investigate how guidelines can accommodate data on multiple stressors and pesticide mixtures
Communication	• The current procedure for reporting improvements of pesticide impact to the GBR is based on changes in the loads of pesticides transported to the Reef, however the ecological risk of pesticides is based on the pesticide concentrations and exposure period. We need to examine what the pesticide loads mean to the Reef in terms of risk and determine if there is a relationship between pesticide load reduction and a reduction in pesticide risk. Establish an ongoing role for the Pesticide Working Group to facilitate communication between researchers, managers, regulators and end users. • Develop a criteria/formula so 'state of pesticides' can be incorporated into the Reef Plan report card process

6 ECONOMICS OF CHANGING PESTICIDE PRACTICES

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6.1 Summary of key findings

- The majority of economic studies concentrate on pesticide management practices in sugarcane, with only a limited number of published studies completed for other agricultural industries in the GBRCA.
- The extent of economic and water quality benefits associated with improved management practices in sugarcane were found to be critically dependent on regional-specific variables including biophysical characteristics and enterprise structure, especially in relation to farm size and location.
- Despite the water quality results showing that all progressive changes in sugarcane herbicide management practices provide a positive level of PSII herbicide abatement, some management practices were found to have an adverse impact on farm profitability.
- Progressing from C- to B-Class herbicide management practices in sugarcane is generally expected to be profitable and provide the highest return on investment (IRR) across all farm sizes and regions. The magnitude of the return on investment has a positive relationship with farm size, primarily because the capital expenditure is spread across a greater productive area on larger farms.
- Transitioning from C- to B-class herbicide management practices in sugarcane is generally the most cost-effective regardless of farm size show, providing the greatest economic benefit per unit abatement of PSII pesticides. In turn, this was then followed by progressive changes from *C-* to *A-Class* and then from *B-* to *A-Class*, with a bare fallow and high tillage farming system exhibiting a relatively lower per unit cost-effectiveness between comparative herbicide management classes.
- The profitability of moving from C- to A-Class herbicide management practices in sugarcane varies across districts, with the payback period extending beyond 10 years in Mackay for a fifty hectare farm. Payback periods were found to be less than 3 years for larger farms in other regions.
- The economic implications of transitioning from B- to A-Class practices in sugarcane are largely dependent on capital costs and the farmer's ability to successfully implement these commercially unproven practices. Negative economic outcomes were observed for transitions from B-to A-class management practices for a 50 hectare farm.
- Progressing to improved herbicide management in sugarcane was found to reduce PSII-equivalent herbicide (PSII-HEq) losses in all regions. Moving from C- to B-Class was generally shown to reduce losses by up to 50 per cent, whilst a progressive shift to A-class showed significant improvements to water quality by decreasing losses up to 98 per cent in some cases. The dramatic decrease in herbicide losses when shifting to A-Class management is largely attributed to the use of non-PSII herbicides (i.e. greater reliance on knockdown herbicides).
- Risk analysis illustrates the importance of ensuring production is maintained in order to remain profitable. This is especially the case when progressing to A-Class herbicide management in sugarcane, which is based on practices under research and not thoroughly tested on a commercial scale.
- In the case of banana farms, a system based change in management practices (including weed, pest and disease management as well as soil and nutrient management) resulted in positive financial returns when shifting from D- to C-Class and C- to B-Class practices over 5-year investment periods. Conversely, the investment required for a shift from B- to A-Class was found to have a slightly negative return.

- Farmer surveys in sugarcane showed that practices which had the highest adoption rates were generally perceived to increase farm profitability and had perceived characteristics that would appear to incentivise adoption. Other management practices had characteristics that could be deemed as potential barriers to adoption and may explain why growers have been slow to adopt.
- Sugarcane farmers were also classified into either adopters or non-adopters in order to analyse whether there was a statistical difference between their perceptions. On average, the findings indicated that adopters were more inclined to perceive practice adoption as resulting in greater profitability than non-adopters; while adopters perceived practices to have greater compatibility within their existing farming system.

6.2 Introduction

Pesticide usage is a major component of the overall farming system for Australian cane crop growers and is generally recognised as a necessary input in order to remain productive and competitive. Two crops in particular are examined in this chapter; namely, bananas and sugarcane. Although grazing systems are an important agricultural industry within Australia, pesticide use is not deemed a high priority within the GBRCA for this industry. Therefore, the grazing component has been omitted from this review.

Today, sugar and banana production remain the economic backbone of many coastal communities (Garside, 2003; Hall and Gleeson, 2013). These industries provide vital socio-economic benefits within many coastal towns in Queensland, creating employment opportunities for those directly associated with farm enterprises as well as flow-on effects for community organisations and local businesses that service those enterprises. The flow-on effects from local household expenditures into recreational activities and domestic holiday/leisure tourism provides a substantial contribution to the economic value of the GBR (see Deloitte Access Economics, 2013).

The widespread adoption of Best Management Practices (BMPs) that improve water quality is considered a key mechanism in improving the overall health of the Great Barrier Reef (GBR) ecosystem. Ideally, BMPs which focus on soil health, farm production efficiency and precision agriculture will assist in aligning both economic and environmental interests toward the common goal of a sustainable agricultural industry over the long term. In particular, Smith (2008) specifically highlighted farm design issues including initially determining land suitability (environmentally and economically) before production. This necessarily involves identification, development and management of appropriate drainage measures, grassed spoon drains and headlands to buffer and filter runoff, and using unsuitable cropping land as wetlands to trap sediment and 'polish' runoff.

6.2.1 Bananas

Producing approximately 85 per cent of Australia's bananas, the North Queensland coast has become synonymous with banana production (Bagshaw and Lindsay, 2009). According to an economic report prepared by Hall and Gleeson (2013), the production of North Queensland bananas, during the 2010-11 financial year, added close to $1 billion and 8 300 full-time equivalent jobs to the economy. Grown from an area of 11 500 hectares, banana production accounted for 33 per cent of Queensland fruit production by value. The market price for bananas is influenced strongly by changes in the supply of bananas. Damage caused to banana plantations by severe tropical cyclones can severely disrupt short-term banana supplies due to the close proximity of North Queensland growing regions. These impacts can make a substantial difference to Australian banana prices as witnessed after ex-Tropical Cyclones Yasi and Larry.

The Banana BMP environmental guideline (King, 2013) prescribes the use of an integrated approach to pest and disease management, which includes the use of physical, biological, cultural and chemical control options. Also, the guidelines recommend an assortment of chemicals be used intermittently to alleviate chemical resistance as well as the introduction of targeted application strategies such as bell injection, which has significantly reduced the quantity of insecticides used in the banana industry (King, 2013). Importantly, chemical control should only be utilised when its cost is less than the projected damage caused by the pest.

The Australian Pesticides and Veterinary Medicines Authority website (http://apvma.gov.au) lists a broad range of pesticides that are registered to control certain weeds, insects and diseases associated with banana production in Queensland. CropLife Australia (2014) advocates the use of particular insecticide chemical groups to control weevil borer and rust thrip such as organophosphates, phenylpyrazoles, pyrethroids and neo-nicotinoids. For the control of yellow sigatoka, they recommend a rotation program of several fungicide chemical groups including anilinopyrimidine, DMI, and quinone. On top of these pests, an assortment of chemicals are registered for the control of nematodes and black sigatoka as well as a variety of moths, thrips, mites, fruit flies, leaf spot and speckle. Banana growers also have a range of herbicides registered for the control of particular weeds as well as banana sucker eradication. These include knockdown herbicides such as paraquat, fluazifop-p, 2,2-DPA-sodium, 2,4-D and glyphosate along with two pre-emergent herbicides comprising of diuron and oryzalin.

A guide to banana production published in 1998 (Lindsay, *et al*., 1998) estimated annual insect and disease management costs at around $5 000 per hectare in a ratoon crop, emphasizing the importance producers place on effective management. In comparison, annual weed management costs were estimated at less than $100 per hectare. While these costs may have changed in recent years, no further research was found to have been undertaken in this area to provide an up-to-date estimate. There is also a lack of research examining the impact to water quality from pesticide use. Masters *et al*. (2013a) monitored runoff and deep drainage from a banana plot after applying glufosinate-ammonium and glyphosate to control weeds and mancozeb to control yellow sigatoka. Considering the broad range of pesticides available for use in banana production, the rate and extent of pesticide movement is practically unknown.

6.2.2 Sugarcane

Sugarcane production has been the predominant agricultural industry for coastal Queensland since the middle of the 19th century. The Queensland sugar industry produces approximately 95 per cent of Australia’s total raw sugar which is typically worth around $1.7 – $2 billion in production to the Australian economy (CANEGROWERS, 2014). Cane farmers are price-takers and Australian sugar prices are highly exposed to volatility in residual world market prices since 80 per cent of its product is exported and export price parity is applied to the domestic market (Sugar Industry Oversight Group, 2006). In the last 20 years the sugar industry has come under increasing economic pressure from a range of factors including increased international competition, industry deregulation, increasing input costs, pest and disease outbreaks, extreme weather events and relatively weak world sugar prices for a prolonged period. Long-term production issues associated with traditional intensive cropping systems have also pressed the industry to adopt improved management practices to become sustainable. This led to improved farming practices being developed to improve production and profitability.

While adopting improved management practices has helped the cane industry to improve environmental sustainability, meeting Reef Water Quality Protection Plan (Reef Plan, 2013) water quality targets remains a challenge. With respect to the use of pesticides in the sugar cane industry, herbicides are commonly used to manage weeds and to prevent economic loss to crop production. Weeds are the most significant pest for growing sugarcane and are an important issue affecting productivity and profitability (Fillols and Callow, 2011). Herbicides are widely used to control undesirable competing plant growth and are thus a key component of an Integrated Weed Management Plan (IWMP). Methods such as mechanical cultivation and herbicide application are typically used to control grass, broadleaf weed, sedge and vine (Calcino *et al*., 2008). The Bureau of Sugar Experiment Stations (BSES) has highlighted the potential for monetary loss as a consequence of yield losses if weed control is delayed or omitted. Research suggests that yields of ratoon cane can potentially be reduced by 7-30 per cent through weed infestation (McMahon, 1989, in Fillols and Callow, 2011). Accordingly, the effective and timely use of herbicides is an important element of an IWMP.

Management of the green-cane trash blanket is considered an efficient practice to manage weeds in ratoon cane. This is not applicable in areas where cane is burnt prior to harvest, such as in the Burdekin Region. Fillols (2012) reports on a number of experiments undertaken by the BSES investigating the optimal thickness of the green-cane trash blanket in addition to the optimal timing of the herbicide applications. The results showed that, in comparison to bare soil, trash at all levels reduced weed coverage and contributed to additional yield and profitability. In particular, increasing the level of trash led to improved management of broadleaf weeds and grasses and strategies involving early pre-emergent herbicides were more efficient.

6.3 Economics of improved pesticide management

Many facets of the farming system impact on weed management requirements. Past economic studies investigating the profitability of improved weed management have predominantly focused on a systems-based approach, with pesticide management as a component within the suite of changes. The following subsections review literature investigating the economic implications of moving to improved pesticide management practices on banana and sugarcane farms.

6.3.1 Bananas

While pesticides are commonly used by banana producers, little research has investigated the economic implications of shifting to improved management. Roebeling, *et al.* (2007) established that a shift to improved interrow management, which is switching from herbicide application to slashing, would increase operating costs by about $50 per hectare and decrease the farm gross margin (FGM) by between 3 per cent and 9 per cent. A later study by Van Grieken *et al.* (2010) examining whole-of-farming systems changes, including weed, pest and disease management as well as soil and nutrient management, found that investments into improved farming systems resulted in positive financial returns when shifting from D- to C-class and C- to B-class practices over 5-year investment periods. Conversely, the investment required for a shift from B- to A-Class was found to have a slightly negative return. Unfortunately, no studies have focused on the incremental economic implications of shifting to improved pesticide management as part of a farming system. In addition, there is a paucity of economic information relating to contemporary BMP.

6.3.2 Sugarcane

Past economic research examining management practice change has been undertaken using either a case study approach or a representative approach. A case study uses operation and production information generated from a particular farm and is usually based on historical production information. In comparison, a representative study uses data consistent with appraisals from technical specialists, surveys and land capability assessments to reflect a specific suite of management practices and/or farming system and often utilizes modelled production data from the Agricultural Production System sIMulator (APSIM).

6.3.2.1 Case studies

Several case studies have analysed the potential for legume fallow break crops to reduce herbicide requirements (see, for example, Poggio and Hanks, 2007; Young and Poggio, 2007). Growing a well-managed legume crop can also increase soil cover over the wet season and therefore reduce the amount of erosion from surface water movement which, in turn, reduces the potential for sediments containing nutrients and chemicals to enter waterways. In particular, Poggio and Hanks (2007) compared the current situation of a bare fallow with conventional farming practices to alternative fallow practices including (a) legume (Ebony cowpeas) fallow with conventional practices; (b) legume fallow with zonal tillage practices; and (c) legume fallow with new farming system (NFS) practices. Results from the study showed that scenario (c) (i.e. well managed legume fallow with NFS practices) produced the highest FGM and the greatest operating return, which was attributed to reduced tractor operations, savings in fertiliser usage and lower weed control costs. Scenario (b) was also shown to produce a significantly higher FGM than a bare fallow due to reduced tractor labour hours. On the other hand, the legume fallow with conventional farming practices (scenario (a)) produced a similar FGM and operating return to the existing practice of the bare fallow. In this case, the accrued savings from lower fertiliser and weed control costs tended to be offset by increased costs associated with the additional cultivation requirements for the legume crop.

In a similar case study analysis using the FEAT tool, Young and Poggio (2007) compared the economic performance of a conventional farming practice to a NFS involving reduced tillage and the use of a soybean rotational crop that is harvested for seed production. They found similar results (i.e. increased FGM and higher operational return for the new system) based on the assumption that the legume crop increases the cane yield. Greater economic performance was attributed to lower variable costs (from less tractor hours and lower input costs) and the additional revenue from the soybean crop.

6.3.2.2 Representative studies

Roebeling *et al.* (2004) examined the cost-effectiveness of implementing BMPs for water quality improvement at the plot level for the Douglas Shire Water Quality Improvement Program. The study evaluated several BMPs with a focus on nutrient, soil and water quality using APSIM and a specialized hydrological model combined with cost-benefit analysis. Results of the study found that improved practices such as reduced tillage, legume fallow crops and reduced nitrogen application are economically viable at the farm level. Nevertheless, the improvement in water quality resulting from the adoption of these management practices is likely to be relatively small. The authors concluded that far stronger positive effects on water quality are likely to result from the provision of incentives that lead to the adoption of management practices that are otherwise not economically viable at the farm level (e.g. spoon-shaped cane drains).

In a more recent article Roebeling *et al.* (2007) examined the cost-effectiveness of implementing various BMPs for water quality improvement in the Tully-Murray catchment. The study used APSIM in conjunction with water quality models and cost-benefit analysis to analyse the economic effect on FGM together with the implications for water quality. Results showed that a majority of the BMPs were attractive from a financial-economic perspective as well as leading to improved water quality based on the effectiveness of these BMPs in reducing water pollutant delivery (i.e. fine suspended sediment, DIN, and persistent herbicide delivery.

Another paper by Strahan (2007) analysed the economic benefits of changing to more sustainable cane farming practices in two catchments of the Mackay Whitsundays region based on the Mackay Whitsunday natural resource management body’s farm management classification system (ABCD framework). The study involved modelling representative cane farms and assessing the economic implications of the various practice changes using FEAT. A risk analysis was also performed using @risk which resulted in a set of distribution curves showing the probability of likely farm business profit for each management level. Taking into account the required capital investment, the viability of each option was evaluated using a standard discounted cash flow investment analysis.

The results indicated that significant benefits are achievable by adopting the higher level sustainable farm management practices. In comparing the relative impacts of each practice change, significant gains could be achieved by progressing from conventional (C-class) to best management (B-class) practices and these changes provide relatively greater benefits to profitability at lower cane prices. These improvements were predominantly achieved from realising savings to the cost of production which are independent of the price of cane. However, changing from C-class to B-class requires significant changes. For example, changing from C- to B-class practices involves upgrading the ripper and fertiliser box, acquiring a new spray unit and a bed former, in addition to matching row spacing with machinery width to achieve controlled traffic. Whilst making significant changes over the entire farm involves a higher level of whole farm planning, thus requiring more time to do so, there is reduced chemical use and cultivation. Strahan (2007) suggests it will take at least five years to implement these changes over the entire farm.

A series of similar papers relating to Paddock to Reef Monitoring, Modelling and Reporting work (East, 2010; Poggio and Page, 2010a, 2010b; Poggio and Page, 2010c; Poggio et al., 2010a, 2010b, 2010c; Van Grieken, *et al*., 2010) evaluated the transitioning to improved sugarcane management practices in the Tully, Burdekin, and Mackay Whitsunday regions using APSIM. Specifically, they compared FGM, conducted capital budgeting analysis on investments associated with the transition, and performed risk analyses for cane yields and prices. Irrigation management and legume yield were also examined, as were the effects on viability considering factors such as farm size, capital investments and legume fallows.

The Paddock to Reef work found that it generally benefitted the farmer to transition from dated (D-class) to C-class practices. In all but the Mackay Whitsunday case study, it was economically viable to transition from the C- to B-class practices, depending on the capital investment required and the length of the investment horizon. Transitioning from B- to aspirational (A-class) practices is harder to achieve and is largely dependent on the farmer's ability to successfully implement these commercially unproven practices. Negative NPVs were generally observed for transitions from B- to A-class (except in the Mackay Whitsunday case study), which highlights that appropriate incentives may be required to be provided to growers to achieve this level of change if deemed necessary for environmental improvement.

6.3.3 Reef Water Quality Economic Research Project

More recently, research by Poggio *et al*. (2014) evaluated a multitude of management practice options in order to identify profitable abatement opportunities for PSII herbicides and their alternatives from three major sugarcane production districts located in the GBR catchment. Evaluation of the management practices are each classified on the basis of their perceived potential to improve water quality on cane farms, in particular these include:

- moving between C-class, B-class and A-class practices for herbicide management;
- moving from C-class to B-class practices for tillage and fallow management; and,
- moving from standard to alternative chemicals.

The key findings from the research are listed as follows (Poggio *et al*., 2014: p i):

- “The results identified a number of key sugarcane management practice options that have the potential to improve water quality (or facilitate this process) and are also expected be worthwhile economically to implement.
- The economic and water quality results were found to be critically dependent on regional-specific variables including biophysical characteristics and enterprise structure, especially in relation to farm size and location.
- Progressing from C- to B-class herbicide management is generally expected to be profitable and provide the highest return on investment (IRR) across all farm sizes and cane districts. The magnitude of the return on investment has a positive relationship with farm size, primarily because the capital expenditure is spread across a greater productive area on larger farms.
- The period it takes to payback the initial investment when moving from C- to B-class herbicide management is expected to be 2 years for 50 ha farms and one year for 150 ha and 250 ha farms.
- The water quality modelling for Tully indicated that progressing from C- to B-class herbicide management results in a reduction of up to 14 g/ha/yr (~41%) in PSII-equivalent herbicide (PSII-HEq) losses, depending on fallow and tillage practices. Relative reductions across other cane districts are shown to be up to 10 g/ha/yr (~52%) in Mackay; up to 26 g/ha/yr (~52%) in the Burdekin Delta; and up to 55 g/ha/yr (~48%) in the BRIA.
- The profitability of moving from C- to A-class herbicide management varies across districts: the payback period for 50 ha farms taking six years in Tully; eight years in the Burdekin; while the initial investment is not recoverable over 10 years in Mackay. Payback periods for 150 ha farms are two years for Tully and the Burdekin and three years for Mackay. Similarly, it is two years for all 250 ha farms.
- Water quality modelling showed progressing from C-to-A-class herbicide management results in a reduction of PSII-HEq losses of up to 29 g/ha/yr (~83%) in Tully; up to 15 g/ha/yr (~76%) in Mackay; up to 49 g/ha/yr (~98%) in the Burdekin Delta; and up to 109 g/ha/yr (~97%) in the BRIA.
- Moving from B- to A-class herbicide management is expected to come at an economic cost for 50 ha farms. This is predominantly due to the amount of capital expenditure required relative to size of the farming area. Alternatively, a small farm will need to look at other avenues to improve the utilisation of capital expenditure or potentially use a contractor if suitable services are available within the region.
- A change from B- to A-class herbicide management is expected to be profitable for 150 ha and 250 ha farms. Results highlight the importance of farm size and the efficient utilisation of capital expenditure.
- Moving from B- to A-class herbicide management shows significant improvements to water quality: a reduction of up to 15 g/ha/yr (~72%) in PSII-HEq losses for Tully; up to 5 g/ha/yr (~50%) in Mackay; up to 23 g/ha/yr (~95%) in the Burdekin Delta; and up to 55 g/ha/yr (~94%) in the BRIA.
- Risk analysis illustrates the importance of ensuring production is maintained in order to remain profitable. This is especially the case when progressing to A-class herbicide management, which is based on practices under research and not thoroughly tested on a commercial scale.
- When progressing to improved herbicide management, the combination of fallow and tillage management tends to have a relatively negligible impact on the economic results between comparative scenarios in Tully. In Mackay, progressing to improved herbicide management under a legume fallow and low tillage farming system is marginally more profitable.
- In the Burdekin, progressing to improved herbicide management from C-class under a bare fallow and high tillage farming system is substantially more profitable than moving under a legume fallow and low tillage system.
- PSII-HEq losses are greater under a bare fallow and high tillage farming system than under a legume fallow and low tillage system across all cane districts.
- Despite showing potential water quality benefits, changing from standard to alternative chemicals at current market prices will generally come at an economic cost irrespective of the combination of

fallow and tillage practices." These finding are subject to further research into the use of alternatives for specific agronomic situations, changes in product cost and more recent studies on herbicide ecotoxicities which has questioned the true environmental benefits of a shift in herbicide products from the traditional PSII herbicides.

6.4 Socio-economics

Over the past several decades the changing farm business environment has provided challenging conditions for sugarcane growers to maintain profitability. A fall in the real sugar price since 1990, coinciding with an increase in the real costs of production, has caused a cost-price squeeze. In addition to this, growers face volatile output prices, production variability and increased pressure to achieve improved environmental outcomes. These circumstances highlight the need for growers to continually adopt Best Management Practices (BMPs) that improve their profitability and sustainability. BMPs have been developed on the basis that they are perceived to be beneficial for production as well as the environment. However, growers are less likely to adopt new management practices in the absence of information regarding their prospects for improved profitability.

Industry and government have together invested a significant amount of resources aimed specifically at increasing the adoption of management practices leading to water quality improvement. Unsurprisingly, non-adoption or low-adoption of new conservation practices is often explicable in terms of a failure to provide clear evidence of any relative advantage[7] in economic terms (see Pannell et al., 2006). Rogers (2003) identified the relative advantage of a new practice as a key motivator of adoption. Moreover, several studies emphasise the importance of grower perceptions toward the complexity, observability, trialability and compatibility of management practices in determining adoption (Gould et al., 1989; Adesina and Zinnah, 1993; Adesina and Baidu-Forson, 1995; Van der Meulen et al., 1996; Wossink et al., 1997; Pannell et al., 2006; D'Emden et al., 2008). A recent paper by Reimer et al. (2012) examining the influence of growers' perceptions on the adoption of best management practice found that relative disadvantages and incompatibility were the primary barriers to adoption while relative advantage, compatibility, and observability were the most important factors affecting a farmer's decision to adopt improved practices that lead to water quality improvements.

A recent study by Thompson et al. (2014) collected survey data from over 60 North Queensland cane farmers from Ayr, Ingham, and Tully with the purpose to develop a profile of grower's perceptions toward the characteristics and economic impacts of various management practices. Practices that had high adoption rates, among the growers surveyed, were perceived to increase farm profitability. Figure 6-1 identifies the distribution of growers that perceived practice adoption would either increase or decrease farm profitability. These practices included vary herbicide rate between blocks (95 per cent adoption) and directed herbicide application (93 per cent). Conversely, the least adopted practice, knockdowns and strategic residual use excluding Diuron, Atrazine, Ametryn and Hexazinone (23 per cent), was perceived to decrease farm profitability.

The second least adopted practice electronic records (36 per cent adoption rate) are also a case in point. Given that most growers perceive the practice to have very little impact on profitability (see Figure 6-1)

[7] Relative advantage is the perceived net benefit to be gained by adopting an innovation relative to the practice it supersedes and is a function of several perceived attributes including a practice's impact on short-term production costs and yields, medium to long-term profitability, the variability (or riskiness) of production and the required establishment costs (Pannell et al., 2006).

there is minimal financial incentive for adoption. Moreover, the average grower perceives that adoption requires new skills and information (see Figure 6-2), which is likely to be a constraint to adoption.

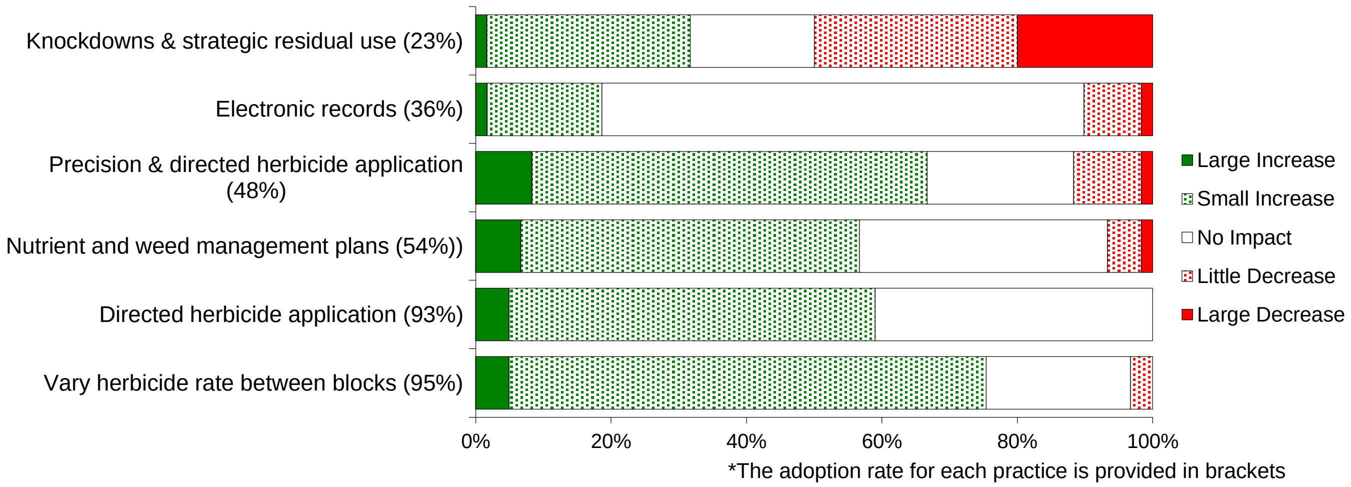


Figure 6-1: A comparison of the perceived impact to profitability from practice adoption

Similarly, practices with relatively high adoption rates had perceived characteristics that would appear to incentivise adoption. In these cases, the majority of growers agreed that these practices were compatible with existing farming systems and they were easy to trial. On the other hand, these growers tended to disagree that the practice requires a high capital investment, new skills and contractors to implement. Other management practices had characteristics that could be deemed as potential barriers to adoption and may explain why growers have been slow to adopt. For instance, while perceived as being profitable, precision and directed herbicide application had the third lowest (48 per cent) adoption rate. This is unsurprising, however, given that the majority of growers strongly agreed that adopting precision and directed herbicide application requires a high capital investment and to a lesser extent new skills.

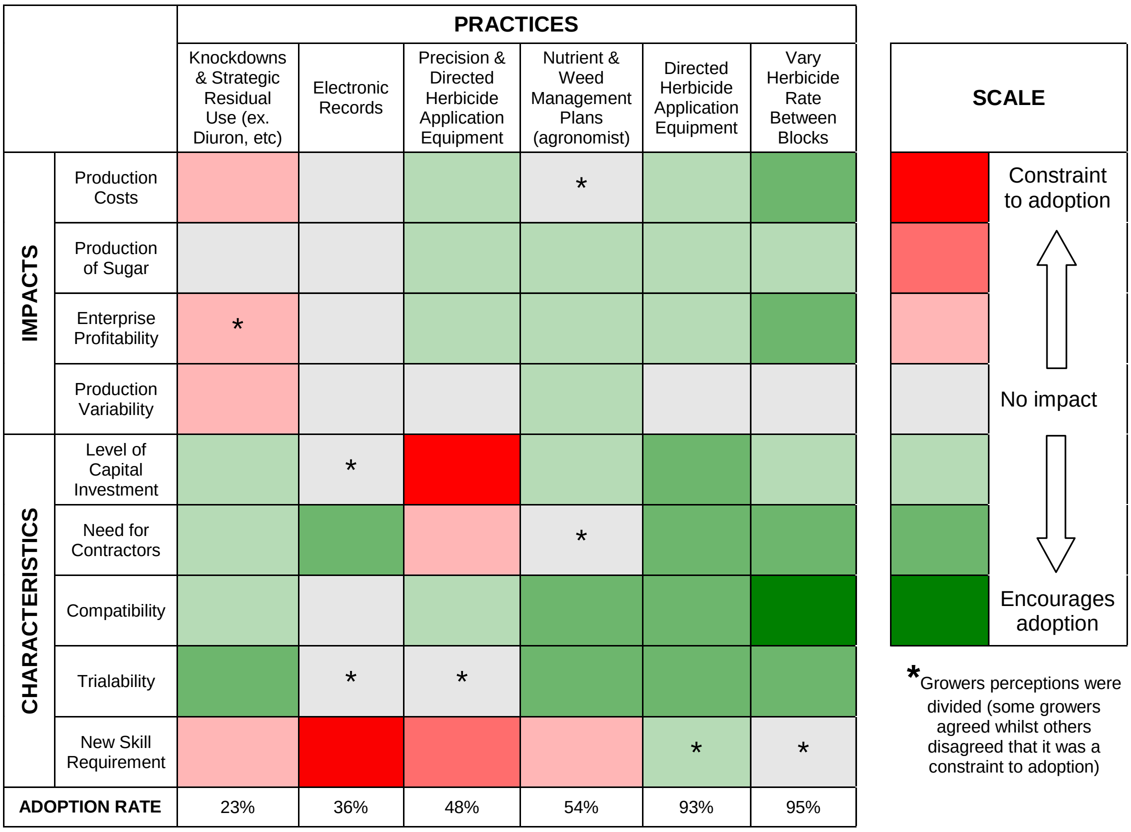


Figure 6-2: Average perceptions of the practice presented as a heat map.

Growers were also classified into either adopters or non-adopters in order to analyse whether there was a statistical difference between their perceptions. Finding evidence about the differences in perceptions between growers may provide further opportunities to better target extension and ultimately enhance practice adoption. Accordingly, profitability and compatibility within the existing farming system were both found to be critical factors that affect the adoption decision. On average, the findings indicated that adopters were more inclined to perceive practice adoption as resulting in greater profitability than non-adopters; while adopters perceived practices to have greater compatibility within their existing farming system. A practice being perceived as having a relatively high capital investment requirement was also found to be an important consideration affecting the decision to adopt precision and directed herbicide application.

Interestingly, farm and farmer characteristics (e.g. age, education, farm size, etc) were generally found to be relatively insignificant in determining whether to adopt a new practice. Notable exceptions to this were: the farmer's age in the case of adopting precision and directed herbicide application and electronic records; and farm size in the case of adopting precision and directed herbicide application.

Another interesting avenue is concept work that develops an integrated framework in which appropriate policy mechanisms to improve adoption by growers can be assigned directly to social and economic barriers to adoption. For instance, Pannell (2008) developed an adoption framework (see Figure 6-3(A)) that seeks to objectively identify the appropriate policy mechanisms to encourage farmers to modify their current land use. In particular, the framework proposes that the relative levels of private (internal) and public (external) net benefits should play a critical role in the selection of policy approaches to encourage environmentally beneficial land usage. Figure 6-3(B) refines the model to account for lags to adoption and learning costs, and assumes that managers require a benefit:cost ratio ≥ 2.0. Gaining a firmer understanding of the relationship between these private and public net benefits, as well as to what extent these benefits are measurable across the various sugar cane regions, will ideally enable a more targeted policy approach.

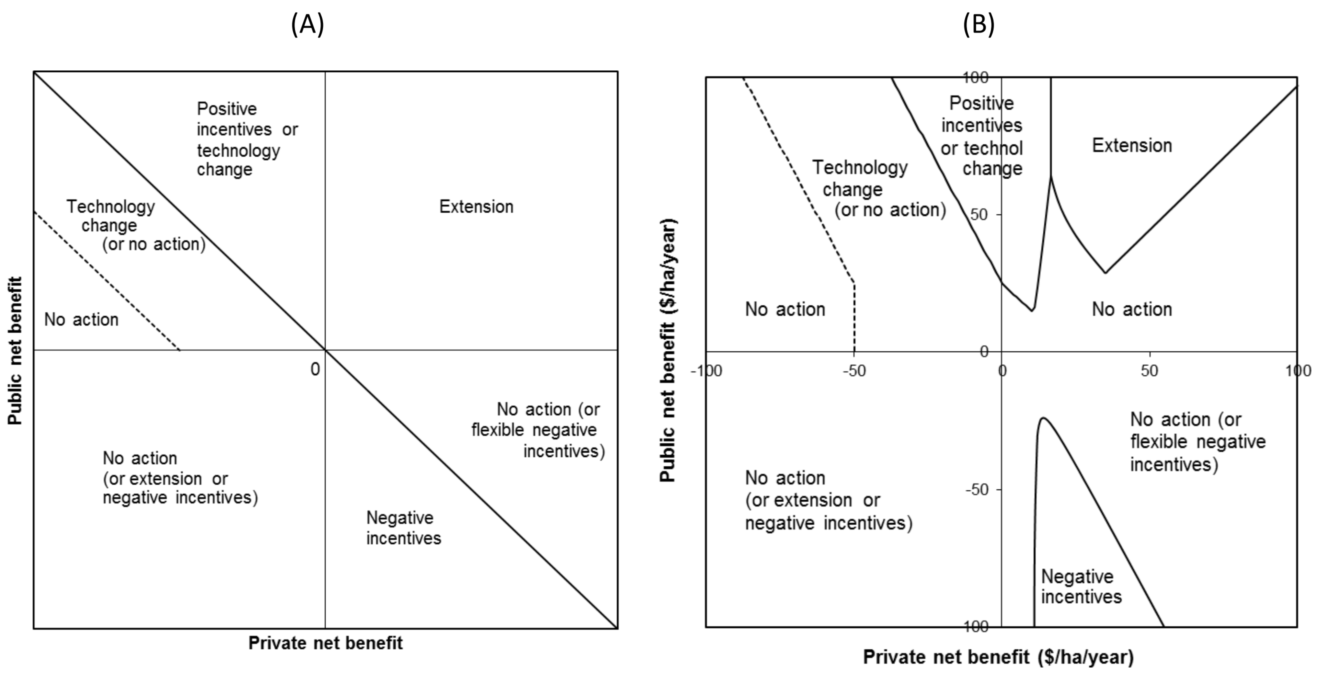


Figure 6-3: Efficient policy mechanisms for encouraging land use on private land (Source: Pannell, 2008).

6.5 Summary and Discussion

In this chapter, a number of key aspects involving both industry economics and water quality issues have been discussed. Finding tractable solutions to minimise nutrient and pesticide runoff entering the GBR catchment have become primary issues for concern for industry and government. The efficient adoption of BMPs that maintain or improve production and profitability, while improving water quality, is considered a key mechanism in improving the overall health of the GBR ecosystem. Surprisingly, there has been limited economic work carried out linking practice change to environmental and social issues in the GBR catchment. In the past, the relevance of employing economics to solve problems primarily concerned with the efficient and effective allocation of resources often failed to find traction within many of the public programs seeking to find innovative solutions that improve the environment while at the same time increasing the profitability of industry.

The extension of relevant and up-to-date information to growers is considered an essential function to help improve on-farm decision-making and boost the adoption of best management practices. Nevertheless, a review of past literature on banana production systems in the GBRCA has found a severe shortage of research examining the economic implications of moving to improved pesticide management. Only two papers were found that examine improved pesticide management. The first paper, written eight years ago, examines a management change from spraying glyphosate to employing slashing operations to control interrow weeds and finds an economic cost associated with adoption. The second paper examines a whole farming system change, and provides no assessment of the incremental change to profitability from moving to improved pesticide management in isolation of a whole system change. Surprisingly, no case studies exploring improved pesticide management were found. Examining the economic implications of pesticide management and improved management practices more broadly is critical for adoption and validation in a commercial setting. In conclusion, an important outcome of this review was to expose a number of research gaps that currently exist for economic work in the banana industry.

Recent economic conditions within the sugar industry indicate that cane businesses are under substantial pressure from cost-price squeeze and volatility from market and production risks (see, for example, Smith *et al*., 2014). In this operating environment it is clear that priority should be given to identifying BMPs that are cost-effective and profitable to implement. This is especially the case considering recent research by Thompson *et al*. (2014), which indicated that BMPs with high adoption rates tend to have a positive relationship with grower perceptions about their impact on profitability.

Smith *et al.* (2012, 2014) highlighted the fact that previous studies had tended to analyse practice change from an academic perspective, placing little emphasis on the heterogeneity of farm enterprises across individual landholders and regions. Each sugarcane production region has unique biophysical and socio-economic characteristics that influence the sugarcane production system and management practices used by the landholder. In order for landholders to proactively adopt these practices it is thus critical to identify specific management practices that are most likely to lead to both water quality improvement and increased profitability. Whilst there is abundant literature on sugarcane management practices that minimise environmental risk, often that literature lacks an accompanying economic assessment of implementing those management practices. What is starkly apparent is the paucity of studies that undertake economic analyses of the cost to change individual practices as part of a broad system and how this affects the farm business at both an operational and economic level.

Recent studies by Poggio *et al.* (2014) and Van Grieken *et al*. (in press) aimed to address some of these issues. These studies undertook economic work at the practice level and integrated water quality data into the analysis to identify the most cost-effective practices that achieve desirable water quality outcomes. Analysing at a practice level for pesticides and nutrient management is beneficial in terms of being able to isolate an incremental change in management practice and its resultant impact on farm profitability, water quality, and adoption characteristics. Enterprise heterogeneity was also taken into account by incorporating location, farm size, soil type, and management practice characteristics.

6.6 Management priorities

Identifying farm management practices that are profitable to implement while also leading to improved water quality is critical to enable the efficient adoption of best practices and to ensure the long term sustainability of industry.

A key finding by Van Grieken *et al*. (2010) was that whole-of-farming systems changes for banana production was profitable for growers transitioning from D- to C-class and C- to B-class management but not for growers moving from B- to A-class management. However, the study did not examine improved pesticide management independent of the whole farming system, which raises the question of how pesticide management changes affect farm profitability in isolation. For that reason, further research would be needed to determine the financial implications of a change to improved pesticide management.

For sugarcane production, findings from the RP62c project indicate that progressing from C- to B-class herbicide management practices is the most profitable and cost-effective overall, irrespective of farm size. The payback period was expected to be two years for 50 hectare farms and one year for larger farms. In terms of water quality improvement, progressing from C- to B-Class management was found to reduce PSII-equivalent herbicide losses by approximately 50 per cent.

Moving from C- to A-class herbicide management practices in sugarcane was also found to be profitable in many cases; however, the payback period for 50 hectare farms was shown to take from six to over ten years amongst the regions. For larger farms, this period decreased to between two and three years among regions. Due to the inherent volatility surrounding the farming environment as well as the requirement of farm businesses to maintain their financial viability in the event of downturns, a short payback period is essential. Bearing these factors in mind, growers may not interpret a six to over ten year payback period as viable. Another point to consider is that growers need to have the financial capacity to afford their progression to A-class practices, which is likely to be a greater barrier for smaller growers. Corresponding water quality modelling showed significant reductions in PSII-HEq losses of between 76 per cent and 98 per cent.

Moving from B- to A-class herbicide management practices in sugarcane is expected to come at an economic cost for 50 hectare farms due predominantly to the amount of capital expenditure required relative to farming area. In light of research by Rogers (2003) and Pannell *et al*. (2006), growers are unlikely to adopt practices that are not perceived as having a positive net benefit compared to the practice it supersedes. On the other hand, progressing from B- to A-class is expected to be profitable for some 150 hectare (except for Mackay) farms and all 250 hectare farms, which highlights the importance of farm size and the efficient utilisation of capital expenditure. In the case of 150 hectare farms where the change was found to be profitable, an expected payback period between four and six years was observed, while 250 hectare farms ranged between three and five years. Moving from B- to A-class has varied water quality improvements among the regions with reductions in PSII-HEq losses of over 90 per cent in the Burdekin and 50 per cent in Mackay.

The degree of risk associated with new practices plays an essential role in the adoption decision. If a new practice has limited adoption on a commercial basis and the efficacy of the new practice is uncertain then growers may be unwilling to adopt or require a high rate of return in order to outweigh the possibility of negative outcomes. For instance, potential risks for A-class herbicide management practice adoption in sugarcane include poor herbicide efficacy or phototoxicity to the crop, thus resulting in adverse impacts on crop yield. An analysis was therefore undertaken to examine how sensitive the relative advantage is to a decrease in yield when shifting from A- to B-class management. The results indicate that just a one per cent decrease in yield will result in a negative economic outcome across all regions. Consequently, evidence validating the efficacy of A-class herbicide management is crucial before the extensive adoption of A-class herbicide management is likely to occur.

Attributes of farming systems were also found to influence both water quality and profitability when adopting improved herbicide management practices in sugarcane. Because pesticide runoff is greater under bare fallow and high tillage farming systems, in comparison to legume fallow and low tillage systems, transitions to improved herbicide management practices produce relatively larger water quality benefits. In terms of profitability, there were dissimilarities among regions. In both Tully and Mackay, legume fallow and low tillage farming systems were found to be marginally more profitable when progressing to improved management. In the Burdekin, legume fallow and low tillage farming systems were also found to be more profitable when progressing from B- to A-class, however, bare fallow and high tillage systems were found to be more profitable when progressing from both C- to B-class and C- to A-class management.

6.7 Conclusions and knowledge gaps

Several research gaps were identified by the literature review. Firstly for bananas, a central focus should be to evaluate the economic, water quality and social implications from adopting improved management practices, including pesticides as an independent component of the whole farming system. This will require the development of a number of case studies, using actual farm data, to examine the financial consequences of transitioning to improved pesticide management within prominent banana growing regions. The outputs from these case studies would then provide the necessary economic data and framework to develop representative scenarios to examine how the transition would affect (economic, water quality and social) a particular range of banana farms common to each region. The intergration of economic, water quality and social data will also enable the prioritization of management practices to better inform policy decisions and investment in natural resource management programs. Secondly, a focus should be given to examining the interaction of particular farming practices (e.g. tillage and fallow management) on the profitability of improved pesticide management. Finally, practices are continually being improved as new information comes to light (e.g. Best Management Practices); therefore future research will need to evaluate the most current practices.

In regards to sugarcane production, there are a number of avenues for further economic research that will build on recent economic work to support policy development in the future. A targeted analysis focused on specific case studies would serve to confirm the findings from studies undertaken using stylised scenarios, especially in light of the heterogeneous nature of each region. This is particularly the case regarding A-class management practices, which are based on practices under research and not thoroughly tested on a commercial scale. Accordingly, this would necessarily involve continuing to work together with agronomists, extension officers and individual growers to demonstrate the practical implications of these management practices in a commercial setting. Furthermore, this would assist with the communication efforts to increase adoption and to verify the bio-physical, economic, and water quality results.

There is also a need to better understand the economic implications for achieving concrete ecological targets to achieve the environmental aims set out in Reef Plan. The recent economic work undertaken in the cane industry provides a very solid foundation for this work to occur. In turn, this would enable the current economic and water quality modelling results to be used to determine the costs and benefits of achieving these aims as well as optimal combinations of growers to target by farm size and by region.

Preliminary work has been undertaken to demonstrate the practical application of the policy mechanism proposed by Pannell (2008) through the merger of the empirical results from Poggio *et al*. (2014) into the theoretical frameworks. This work aims to assist natural resource management organisations and policy-makers to choose appropriate policy mechanisms that encourage growers to adopt improved herbicide management practices and maximise the net benefit of intervention. An example of this work is presented in Figure 6-4.

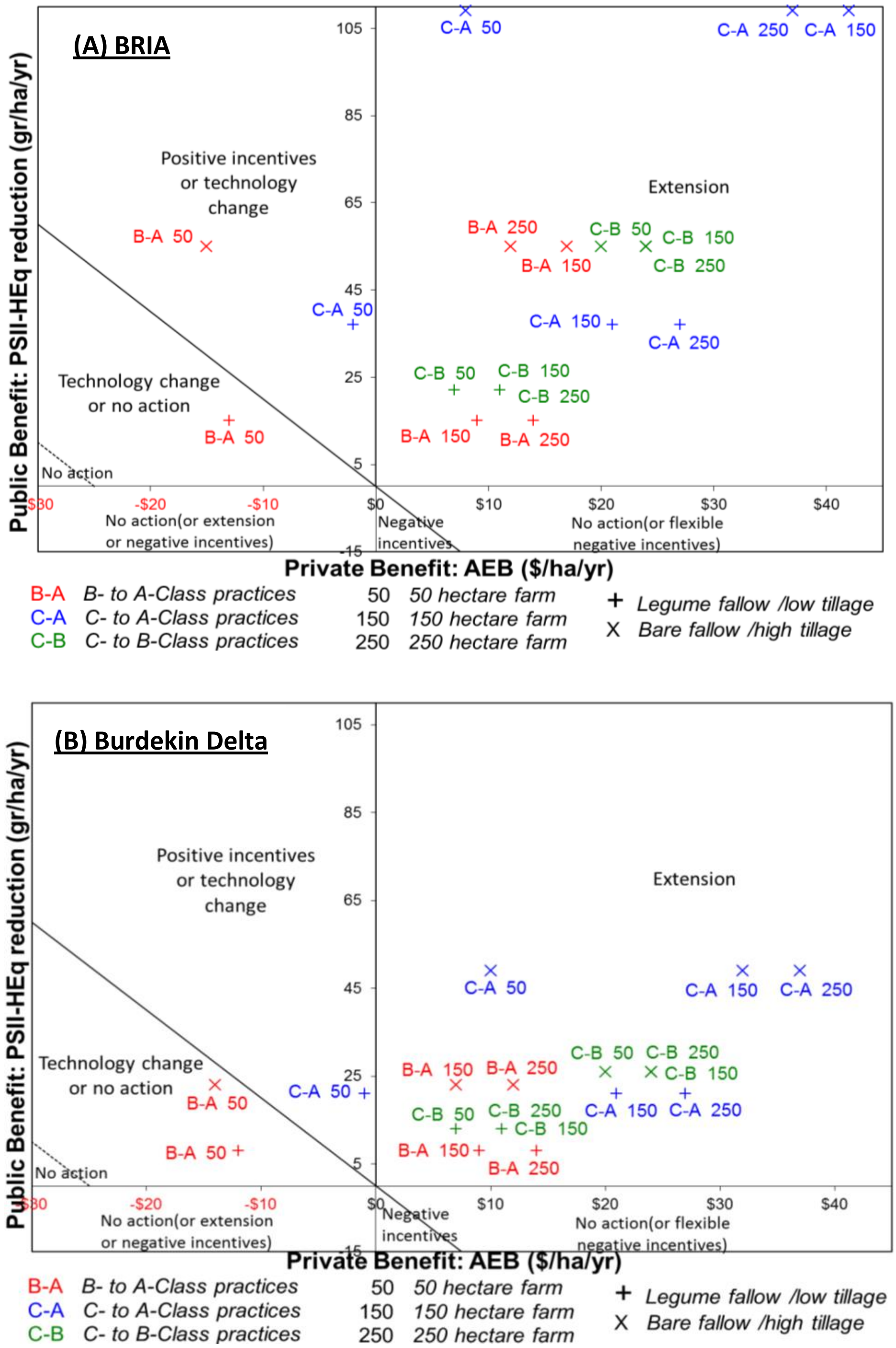
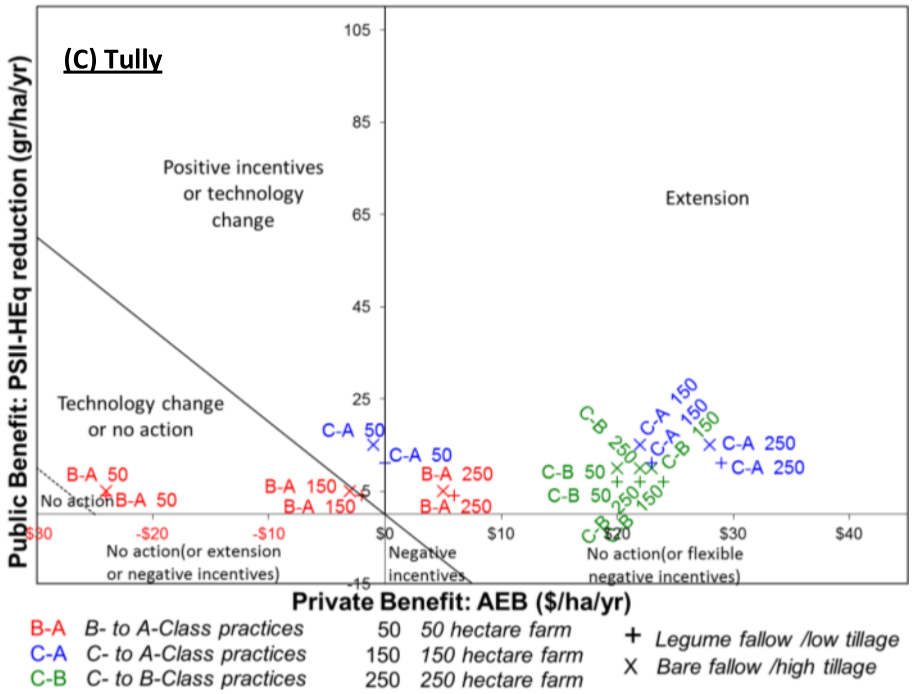


Figure 6-4: Efficient natural resource management policy mechanisms to encourage improved herbicide management.



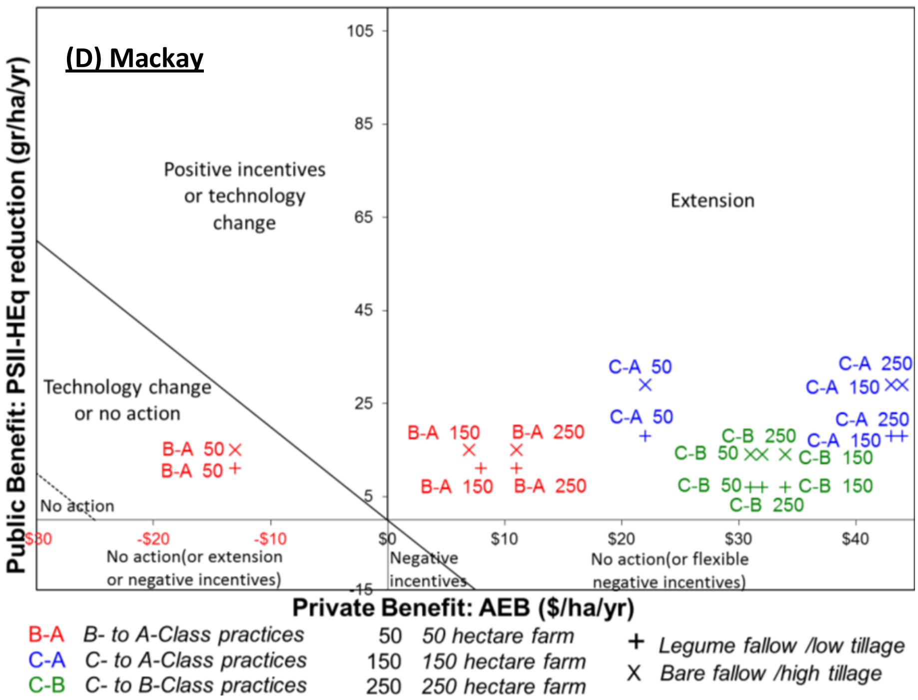


Figure 6-4 (Cont.): Efficient natural resource management policy mechanisms to encourage improved herbicide management.

*The frontier dividing the positive incentives zone from the technology change zone has been monetised assuming that one gram of annual PSII-Heq reduction per hectare has a public benefit of $0.50. This value was selected purely to illustrate an example of the frontier and has not been calculated based on any prior research.

An important issue with integrating this new work into Pannell's (2008) model is that the public benefits on the y-axis are not represented in monetised value. Instead, these values are plotted in terms of the physical level of PSII- HEq (equivalent herbicide) abatement when implementing each change in herbicide management. While, in its present form, the graph in Figure 6-2 is not functionally equivalent to the Pannell model, transposing the conceptual aspects of the model onto the findings from Poggio *et al.* (2014) tends to produce intuitive results.

For instance, extension efforts[8] are best targeted on encouraging growers to shift to improved herbicide management where there is likely to be a relatively large public as well as private benefit in doing so. This is commonly represented on the graphs by transitions from C- to B-class herbicide management and from C- to A-class management. This is particularly true for larger farms and growers that employ a bare fallow and high tillage combination. On the other hand, encouraging growers to transition from B- to A-class herbicide management may warrant positive incentives[9] or require technology innovations[10], especially smaller farms. Some of these practices are shown to come at a cost to the grower to adopt.

Growers that employ practice changes located in the zone of the graph where both the public and private benefit is large should receive a relatively higher priority for extension, at the expense of practice changes with a large private and small public benefit. However, it is important to note that A-class practices are currently not commonly used in the industry and are thus largely unproven commercially. Therefore, this level of operational risk suggests that more field work may be required to reinforce these findings.

In order to fully implement Pannell's (2008) policy mechanism model, the public benefits are first required to be converted to a monetary value that is directly proportional to the physical abatement levels. The assignment of appropriate monetised values for the public benefits will enable a direct comparison with the private benefits and overcome scaling issues regarding the non-monetised y-axis, which is critical to the interpretation of Pannell's model. However, this is non-trivial matter that will require an investigation into the feasibility of deriving these values in the absence of any market-traded prices or suitable proxy measures currently available.

As mentioned earlier, the policy mechanism model was refined to account for lags to adoption and learning costs, and integrates a benefit:cost ratio ≥ 2.0. When these parameters were included into the model the zones for positive incentives and extension shifted upwards and to the right. If these refinements were incorporated to the above graphs, the growers that are progressing to practices with a small private benefit and large public benefit may be located in the positive incentives or technology change zone. Nonetheless, the parameters required to refine the model would need to be derived via targeted future research in order to confirm these expectations.

Recycling pits are another area that needs particular research attention. Work undertaken by Poggio *et al.* (2014) acknowledges that there is a lack of knowledge about the water quality and economic implications of irrigation recycling pits. Addressing this information gap would increase the accuracy of the water quality results in the Burdekin region and provide a better understanding of the economic implications. Key research gaps for sugarcane and bananas are listed in Table 5-5.

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[8] Extension includes technology transfer, education, communication and demonstrations.

[9] Positive incentives comprise of landholder payments.

[10] Technology change refers to strategic and participatory research and development to optimise outcomes.

Table 6-5: Socio-economic research gaps in sugarcane and bananas.

Research Gap	Details
The efficiency of management practices that improve water quality	There is a paucity of economic studies that evaluate a change in individual practices as part of a broad system and how this affects the farm business at both an operational and economic level. Past studies have not examined improved pesticide management as being independent of the whole farming system, which raises the question of how pesticide management changes affect farm profitability in isolation. Examining the economic implications of pesticide management and improved management practices more broadly is critical for adoption and validation in a commercial setting. The intergration of economic, water quality and social data enables the prioritization of management practices to better inform policy decisions and investment in natural resource management programs. It is thus critical to identify specific management practices that are most likely to lead to both water quality improvement and increased profitability.
Targeted case studies	A targeted analysis focused on specific case studies would serve to confirm the findings from studies undertaken using stylised scenarios, especially in light of the heterogeneous nature of each region. Accordingly, this would necessarily involve continuing to work together with agronomists, extension officers and individual growers to demonstrate the practical implications of these management practices in a commercial setting. Furthermore, this would assist with the communication efforts to increase adoption and to verify the bio-physical, economic, and water quality results.
Emphasis on new and innovative practices with low adoption	Management practices are continually being improved as new information comes to light (e.g. Best Management Practices); therefore future research will need to evaluate the most current practices. The degree of risk associated with new practices plays an essential role in the adoption decision. If a new practice has limited adoption on a commercial basis and the efficacy of the new practice is uncertain then growers may be unwilling to adopt or require a high rate of return in order to outweigh the possibility of negative outcomes. Consequently, evidence validating the efficacy of A-Class herbicide management is crucial before the extensive adoption of A-Class herbicide management is likely to occur.
Recycle pits	Recycling pits are an area that needs particular research attention. Work undertaken by Poggio et al. (2014) acknowledges that there is a lack of knowledge about the water quality and economic implications of irrigation recycling pits. Addressing this information gap would increase the accuracy of the water quality results in the Burdekin region and provide a better understanding of the economic implications.
Implications for achieving ecological targets	There is a need to better understand the economic implications for achieving concrete ecological targets to achieve the environmental aims set out in Reef Plan. The recent economic work undertaken in the cane industry provides a very solid foundation for this work to occur.
Communication and extension of information	The extension of relevant and up-to-date information to growers is considered an essential function to help improve on-farm decision-making and boost the adoption of best management practices.

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APPENDICES

A.1 Chapter 1 Annexes

Appendix A: Results from three groundwater pesticide monitoring studies in the Lower Burdekin and Wet Tropics between 2011 and 2013.

Study location and date	Pesticides detected	No. detections (% of samples)	Concentration($\mu g\ L^{-1}$) Max	Mean of > LOR
Lower Burdekin August 2011 (Shaw et al. 2012)	atrazine	7 (13)	0.031	0.019
	desethylatrazine [a]	17 (32)	0.254	0.07
	desisopropylatrazine [a]	11 (21)	0.044	0.021
	diuron	2 (3.8)	0.125	0.072
	hexazinone	4 (7.5)	0.03	0.019
	metolachlor	1 (1.9)	0.009	0.009
	chlorpyrifos	2 (3.8)	0.4*	0.3*
Lower Burdekin Nov 2011 - April 2013 (Vardy et al. 2015)	<u>ametryn</u>	2 (1.6)	0.001	0.001
	atrazine	22 (20)	0.018	0.003
	desethylatrazine	98 (80)	0.327	0.077
	desisopropylatrazine	83 (68)	0.029	0.01
	<u>metsulfuron-methyl</u>,	1 (1.2)	0.003	0.003
	<u>propazin-2-hydroxy</u> (from propazine)	2 (2.2)	0.002	0.002
	<u>simazine</u>	2 (1.6)	0.002	0.002
Tully-Murray and Johnstone August 2012, December 2012 & April 2013 (Masters et al. 2014b)	atrazine [L]	7 (41)	0.027	0.011
	bromacil	3 (18)	0.007	0.004
	desethylatrazine	12 (71)	0.051	0.009
	desisopropylatrazine	8 (47)	0.017	0.006
	diuron [L]	10 (59)	0.310*	0.058
	glyphosate [L]	1 (8)	0.5	0.5050
	hexazinone [L]	14 (82)	0.76	0.074
	metsulfuron methyl	1 (6)	0.005	0.005
	propazin-2-hydroxy [L]	12 (71)	0.005	0.005
	simazine [L]	2 (12)	0.012	0.008
	imidacloprid [L]	6 (35)	1.5	0.405

<u>Underlined</u> – pesticides not detected by Shaw et al. (2012); [a] - breakdown product of atrazine; LOR = Limit of report; [b] – only detected at the Northcote riparian bore on the Barratta Creek site; L – also detected in lysimeter leachate in sugarcane or bananas; *Exceeds the Australian and New Zealand trigger value for freshwater ecosystem protection (ANZECC & ARMCANZ, 2000).

Appendix B: Monitoring Sites: Spatial and temporal extent of pesticide monitoring in creeks and rivers undertaken since 2009.

NRM Region	Catchment	River/Creek	Years of monitoring	Program and/or Reference
Wet Tropics	Daintree	Daintree	2013 – 2014	GBRCLMP
	Mossman		2012 – 2013	GBRCLMP
	Russell-Mulgrave	Mulgrave	2013 – 2015	GBRCLMP
		Russell	2013 – 2015	GBRCLMP
	Johnstone	Sth Johnstone River Nth Johnstone River	2009 – 2010 2010 – 2015	GBRCLMP GBRCLMP
	Tully	Tully River	2009 – 2015	GBRCLMP
	Herbert	Herbert River Blunder Creek Mill Creek Millstream Wild River Nettle Creek Rudd Creek Cashmere Crossing Nash's Crossing Waterfall Creek Boundary Creek Hawkins Creek John Row Bridge Forresthome Drain Waterview Creek Seymour River	2010 – 2015 2011 – 2014 2011 – 2014 2011 – 2014 2011 – 2014 2011 – 2014 2011 – 2014 2011 – 2014 2011 – 2014 2011 – 2014 2011 – 2014 2011 – 2014 2011 – 2014 2011 – 2014 2011 – 2014 2011 – 2014	GBRCLMP HWQMP HWQMP HWQMP HWQMP HWQMP HWQMP HWQMP HWQMP HWQMP HWQMP HWQMP HWQMP HWQMP HWQMP HWQMP
Burdekin	Haughton	Haughton River Barratta Creek Barratta Creek East Barratta Creek West	2013 – 2015 2009 – 2015 2011 – 2013 2011 – 2013	GBRCLMP GBRCLMP O'Brien et al 2013a O'Brien et al 2013a
	Burdekin	Burdekin River Belyando River Suttor River	2009 – 2015 2009 – 2011 2009 – 2011	GBRCLMP GBRCLMP GBRCLMP
Mackay-Whitsundays	O'Connell	O'Connell River	2013 – 2015	GBRCLMP
	Pioneer	Pioneer River	2009 – 2015	GBRCLMP
	Plane	Sandy River	2009 – 2015	GBRCLMP
Fitzroy	Fitzroy	Fitzroy River	2009 – 2015	GBRCLMP
		Comet River	2009 – 2015	GBRCLMP
		Dawson River	2009 – 2014	GBRCLMP
Burnett- Mary	Burnett	Burnett River	2009 – 2015	GBRCLMP
	Mary	Mary	2013 – 2015	GBRCLMP
		Tinana	2013 – 2015	GBRCLMP

Appendix C: Locations and characteristics of wetlands examined for pesticides and the dominant landuses of the surrounding land. (Source: unpublished data from the DSITI pilot Wetland Project)

NRM Region	River / creek system	Wetland location	Wetland type	Surrounding landuse (1 km)*
Burdekin	Haughton River	Horseshoe Lagoon, 4 km south west of Giru	Lacustrine	Conservation, Irrigated sugar, Irrigated perennial horticulture, Rural residential.
	Haughton River	1km west of Giru	Palustrine	Irrigated sugar, Livestock grazing.
Mackay-Whitsundays	Sandy Creek	DeMoylens Lagoon near Mirani	Palustrine	Irrigated sugar, Livestock grazing, Waste disposal.
	Sandy Creek	Sandy Creek Site 1 near Chelona	Palustrine	Conservation and natural environments, Irrigated sugar, Livestock grazing, Rural living
	Sandy Creek	Sandy Creek Site 2 near Chelona	Palustrine	Conservation and natural environments, Irrigated sugar, Livestock grazing, Rural living.
Burnett Mary	Cattle Camp Creek	Mon Repos	Palustrine	Conservation and natural environments, Livestock grazing, Irrigated sugar, Rural residential.
	Burnett River	Sharon	Palustrine	Conservation and natural environments, Irrigated sugar, Rural residential.
	Burnett River	Kolan	Palustrine	Conservation and natural environments, Irrigated sugar, Livestock grazing, Recreation and culture, Rural residential.
	Yellow Waterholes Creek	Yellow Waterholes Creek near Alloway	Palustrine	Irrigated perennial horticulture, Irrigated sugar, Livestock grazing, Residential.
	Yellow Waterholes Creek	Yellow Waterholes Creek near Calavos	Palustrine	Irrigated seasonal horticulture, Irrigated sugar, Livestock grazing.
	Un-named	Kinkuna (Burrum Coast National Park)	Palustrine	Conservation and natural environments.

*From Queensland Current Landuse (SIRQRY.QLD_LANDUSE_CURRENT_X)

Appendix D: Spatial and temporal extent of pesticide marine monitoring since 2009

NRM Region	Monitoring Site	Years of monitoring	Program and/or Reference
Cape York	Pixies Garden	2005/06 to 2009/10?	Kennedy et al. 2012a
Wet Tropics	Low Isles	2005/06 to 2013/14	Gallen et al. 2014
	Green Island	2009/10 to 2013/14	Gallen et al. 2014
	Fitzroy Island	2005/06 to 2010/11; 2012/13 to 2013/14	Gallen et al. 2014
	Normanby Island	2005/06 to 2012/13	Gallen et al. 2014
	Dunk Island	2006/07; 2008/09 to 2013/14	Gallen et al. 2014
	Tully River mouth to Sister Island transect[1]	2010/11	Kennedy et al. (2012b)
	Herbert River mouth[1]	2011/12	Devlin et al. 2012b
Burdekin	Orpheus Island	2005/06 to 2013/14	Gallen et al. 2014
	Magnetic Island	2005/06 to 2013/14	Gallen et al. 2014
	Cape Cleveland	2007/08 to 2013/14	Gallen et al. 2014
Mackay-Whitsundays	Pioneer Bay	2009/10 to 2012/13	Gallen et al. 2014
	Daydream Island	2006/07 to 2007/08	Kennedy et al. 2012a
	Whitsunday Island	2006/07 to 2013/14	Gallen et al. 2014
	O'Connell River mouth (since 2009?)		
	Pioneer River mouth (since 2009?)		
	Sarina Inlet	2009/10 to 2012/13	Gallen et al. 2014
Fitzroy	North Keppel Island	2005/06 to 2013/14	Gallen et al. 2014
	Great Keppel Island (since 2009?)		
	Fitzroy River mouth (since 2009?)		
Burnett- Mary			

[1] Flood plume monitoring