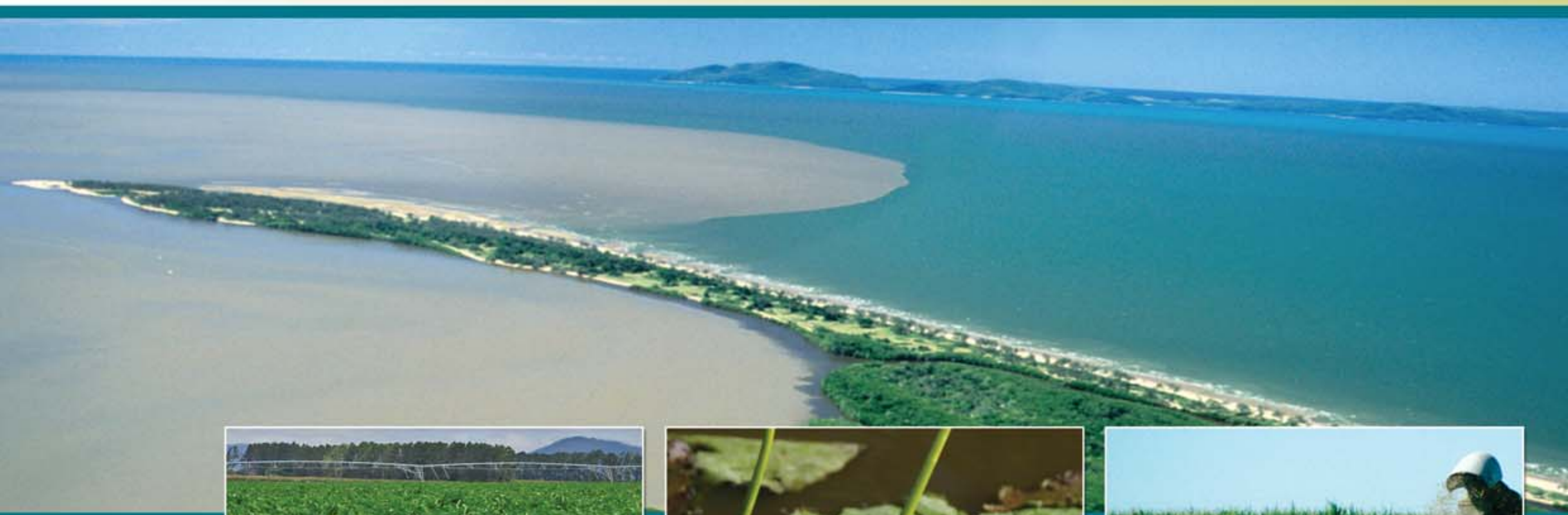
Synthesis Report

Marine and Tropical Sciences Research Facility

Advancing our understanding of the source, transport and impacts of pesticides on the Great Barrier Reef and in associated ecosystems

A Review of MTSRF Research Outputs, 2006-2010



Compiled by
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Australian Government
Department of Sustainability, Environment, Water, Population and Communities

Reef & Rainforest RESEARCH CENTRE

Advancing our understanding of the source, transport and impacts of pesticides on the Great Barrier Reef and in associated ecological systems

A Review of MTSRF Research Outputs, 2006-2010

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The Australian Government's Marine and Tropical Sciences Research Facility (MTSRF) supports world-class, public good research. The MTSRF is a major initiative of the Australian Government, designed to ensure that Australia's environmental challenges are addressed in an innovative, collaborative and sustainable way. The MTSRF investment is managed by the Department of Sustainability, Environment, Water, Population and Communities, and is supplemented by substantial cash and in-kind investments from research providers and interested third parties. The Reef and Rainforest Research Centre Limited (RRRC) is contracted by the Department to provide program management and communications services for the MTSRF.

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Reef & Rainforest
RESEARCH CENTRE

July 2011

Executive Summary

Research funded by the Marine and Tropical Sciences Research Facility (MTSRF) sought to quantify the source, transport and impact of agricultural pesticides on Queensland's aquatic and marine ecosystems. This summary report presents the details of the science outputs from this research over the period 2006 to 2010, which has advanced our knowledge of pesticides in North Queensland. This knowledge will allow for better decision making and appropriate prioritisation of pesticide management as part of an ongoing water quality improvement process being undertaken as part of the Reef Water Quality Protection Plan[1].

The report presents these findings for the Great Barrier Reef (GBR) and its catchments under four main headings, capturing the detection and movement of pesticides off agricultural lands into GBR marine waters as well as potential impacts. The four categories linking pesticides through this 'catchment to reef' continuum are:

- Key sources of pesticides;
- Transport of pesticides;
- Exposure and risk associated with pesticides; and
- Potential ecological impacts from pesticides.

The primary points related to these categories are summarised below.

Key sources of pesticides

- Concentrations of pesticides in rivers and streams are highest in areas of intensive agricultural activity, including sugarcane, but can also be sourced to grazing lands (tebuthiuron). Concentrations of pesticides in marine waters are likely to be highest from rivers that drain large areas of intensive agriculture.
- The loss of herbicide residues from sugarcane cultivation – particularly the photosystem-II inhibiting (PS-II) herbicides diuron, atrazine, hexazinone and ametryn – has been firmly established.
- The greatest proportion of PS-II herbicides is generated from sugarcane areas in the Wet Tropics region.
- Within the Wet Tropics region, diuron is the PS-II herbicide discharged in the highest amounts, followed by atrazine and hexazinone. The Herbert, Russell Mulgrave, Johnstone and Tully basins also deliver substantial exports of diuron.
- Grazing lands are the primary source of tebuthiuron. Monitoring carried out to date indicates that the Fitzroy Basin exports the highest loads of tebuthiuron.

Transport of pesticides

- Prior to the MTSRF, herbicide loads had only been reported for certain catchments in the Mackay-Whitsunday regions and their mode of transport (dissolved versus particulate) was not well known or quantified.
- Research within and outside the MTSRF measured pesticide loads from other catchments. These load data were used to model herbicide loads across the GBR

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[1] http://www.environment.gov.au/coasts/pollution/reef/

catchments, and suggests that the mean annual load of six key PS-II herbicides delivered to the GBR is approaching 30,000 kg/yr.

- It is likely that pesticide loads (herbicides, insecticides and fungicides) delivered to the GBR are larger than 30,000 kg/yr as not all land uses known to leak pesticides into GBR catchment waterways could be modeled. The model is based on the six key PS-II inhibiting herbicides only (diuron, atrazine, hexazinone, ametryn, simazine and tebuthiuron).
- Atrazine, and its degradation products, and diuron contribute a large proportion of herbicide load (up to 90%) to the GBR with early 'first flush' events accounting for the majority of herbicide loads leaving the catchment.
- Assessment of herbicide water-sediment partitioning in flood run-off highlighted that the majority of herbicides were transported in predominantly dissolved form, although a considerable fraction of diuron may also be transported in particulate-bound form (ca. 33%).
- Monitoring data suggest that PS-II herbicides behave conservatively in flood plumes (i.e. become diluted with seawater mixing but not removed by other processes) which allow them to be transported large distances in the GBR lagoon.

Exposure and risk associated with pesticides

- The presence of pesticide residues, particularly herbicides, is widespread in waterbodies of the GBR region, including streams, wetlands, estuaries, coastal and reef waters. Residues commonly detected include atrazine, diuron, ametryn, hexazinone and tebuthiuron. On occasions, residues of some of these herbicides exceed ecosystem guideline values and/or laboratory derived 'inhibition-effect' concentrations for freshwater, estuarine and marine ecosystems.
- Recent work on pesticide monitoring in paddocks, rivers and the marine environment has progressed our understanding of the extent and persistence of pesticides in freshwater and marine areas.
- When herbicides are detected in the GBR lagoon, 80% of the time more than one herbicide is present. The main herbicides detected in monitoring programs act in an additive manner in regards to PS-II inhibition. Therefore exposure and risk studies should not only consider herbicides individually but also as an additive herbicide mixture. The area of risk increases when herbicides are considered as a mixture.
- Diuron is one of the more potent PS-II herbicides in photosynthesis suppression of non-target marine and estuarine plants.
- Monitoring using a combination of passive and grab sampling has revealed pesticide contamination throughout the GBR, including detection in the relatively pristine Cape York region. The frequency of detection through passive sampling shows ubiquitous concentrations over time and space, with detection in both the wet and dry seasons.
- The area where herbicides occur at concentrations high enough to cause at least some inhibition of photosynthesis during certain times of the year (predominately wet season) may cover much of the inner GBR while exposure times (>1 month) may be long enough to cause potential chronic effects.
- Concentrations of pesticides are variable over time and space and thus it can be difficult to define the full impact of pesticide concentrations at any given sampling point. The complex transport mechanisms and variability within receiving waters can make it difficult to define the overall risk area within GBR waters.

Potential ecological impacts from pesticides

- An innovative multiple biomarker approach has linked patterns in land use with patterns of contamination observed in North Queensland's riverine ecosystems. Apparently healthy barramundi caught from five far northern Queensland rivers – the Herbert, Johnstone, Endeavour, Lockhart and Pascoe Rivers – were tested for exposure to a range of anthropogenic chemicals (results published in Humphrey *et al.* 2007) and showed reduced cholinesterase activity in muscle tissues, an increase in EROD activity and increased rates of DNA damage. All of these indicators are highly suggestive of exposure to pesticides.
- The herbicides most commonly detected in the GBR lagoon are PS-II inhibitors and include diuron, atrazine, hexazinone, ametryn, simazine and tebuthiuron.
- Herbicide concentrations in riverine flood plumes that extend into the marine environment can exceed concentrations shown to have negative effects (i.e. reduced photosynthesis) on certain species of coral, seagrass and microalgae.
- Atrazine and diuron herbicide residues persist in the lagoon at low concentrations even during non-flooding seasons.
- Laboratory-based research suggests the likelihood of negative effects to some plant species (such as seagrass and the algal symbionts of coral – zooxanthellae) from herbicide exposure in the GBR lagoon.
- Diuron, atrazine and hexazinone affected a key reef building species of crustose coralline algae at higher concentrations than affect coral, and symbiont type also affected the sensitivity of foraminifera to these herbicides.
- While the possible long-term effects of this chronic low-level exposure on the GBR ecosystem are uncertain, laboratory tests have indicated that sublethal concentrations of diuron can negatively affect the reproductive capacity of corals and reduce the rate of energy acquisition for young (recruit) corals.
- Growth rate and photosynthesis of two tropical microalgae species are negatively affected by diuron at concentrations that have been detected in inshore areas of the GBR.
- Laboratory studies revealed that reducing herbicide concentrations can protect corals and foraminifera from increases in sea surface temperatures projected under future climate change scenarios.

Contents

Acronyms and Abbreviations

ACTFR .... Australian Centre for Tropical Freshwater Research

AIMS .... Australian Institute of Marine Science

CSIRO .... Commonwealth Scientific and Industrial Research Organisation

DDT .... Dichlorodiphenyltrichloroethane

DERM .... Queensland Department of Environment and Resource Management

DEWHA .... Commonwealth Department of the Environment, Water, Heritage and the Arts (now Sustainability, Environment, Water, Population and Communities)

DPC .... Queensland Department of the Premier and Cabinet

EROD .... Ethoxyresorufin-O-deethylase

GBR .... Great Barrier Reef

GBRMPA .... Great Barrier Reef Marine Park Authority

JCU .... James Cook University

MTSRF .... Marine and Tropical Sciences Research Facility

NRM .... Natural Resource Management

PAH .... Polycyclic aromatic hydrocarbons

PCBs .... Polychlorobyphenols

PS-II .... Photosystem II

RRRC .... Reef and Rainforest Research Centre

UQ .... University of Queensland

WWF .... World Wide Fund for Nature

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The authors gratefully acknowledge the researchers who contributed to the pesticide research undertaken as part of the Marine and Tropical Sciences Research Facility (MTSRF). Outstanding work by Andrew Negri, Karen Kennedy, Jon Brodie, Zoe Bainbridge, Aaron Davis, Melanie Shaw and Katherine Martin and their research teams has been instrumental in advancing our knowledge of pesticide source, transport and impact in the Great Barrier Reef region.

Thank you to the then Department of the Environment, Water, Heritage and the Arts (DEWHA) (now Department of Sustainability, Environment, Water, Population and Communities) for funding the MTSRF, and the Reef and Rainforest Research Centre (RRRC) for supporting this program over the past four years. The involvement of primary end users in this research, including the Great Barrier Reef Marine Park Authority (GBRMPA), DEWHA, WWF, the Queensland Department of the Premier and Cabinet (DPC), Queensland Department of Environment and Research Management (DERM) and regional NRM groups, has ensured that the findings are useful.

About this Report

This report provides an overview of the key findings of research conducted under the Australian Government's Marine and Tropical Sciences Research Facility (MTSRF) relevant to pesticide sources, transport and impacts in the Great Barrier Reef (GBR). The MTSRF research theme *Halting and Reversing the Decline in Water Quality* (Program 7) was comprised of five major projects undertaken collaboratively by researchers from the Australian Institute of Marine Science (AIMS), James Cook University (JCU), the Australian Centre for Tropical Freshwater Research (at JCU), the CSIRO and Griffith University.

This report is one of several in a series of information products that summarise MTSRF research findings relevant to managing water quality in the GBR. Other products include:

- 'Managing water quality on the Great Barrier Reef: an overview of MTSRF research outputs, 2006-2010', compiled by Jane Waterhouse and Michelle Devlin (Waterhouse and Devlin, 2011);
- 'Improved understanding of biophysical and socio-economic connections between catchment and reef ecosystems: Wet and Dry Tropics case studies', compiled by M. Devlin and J. Waterhouse (Devlin and Waterhouse, 2010);
- 'Optimising water quality and impact monitoring, evaluation and reporting', compiled by J. Waterhouse (Waterhouse, 2010a).
- 'Thresholds of major pollutants with regard to impacts on instream and marine ecosystems', compiled by J. Waterhouse (Waterhouse, 2010b);
- 'Identification of priority pollutants and priority areas in the Great Barrier Reef Catchment', compiled by J. Waterhouse and J. Brodie (Waterhouse and Brodie, 2011);
- 'Water quality and climate change: managing for resilience', compiled by J. Johnson and K. Martin (Johnson and Martin, 2011a); and
- 'Managing for resilience of the Great Barrier Reef: Socio-economic influences', compiled by J. Johnson and K. Martin (Johnson and Martin, 2011b).

Visit http://www.rrrc.org.au/publications/synthesis_products.html to access and download these documents.

1. Introduction

In any discussion of reef health, the concept of ecosystem resilience is fundamental. A healthy, resilient ecosystem is one that can absorb shocks and recover from stress without loss of biodiversity or complexity. As the changing climate causes global environmental stress levels to increase, only healthy, resilient reefs and seagrass beds are likely to survive. Therefore successful conservation management of the Great Barrier Reef (GBR) in the era of climate change requires building and maintaining ecosystem resilience by reducing environmental stress wherever feasible. The management of pesticides and their potential impacts is essential for reef resilience and the long term health of the GBR.

To date, the weight of scientific evidence indicates that inshore reef health is negatively affected by pollutants, including pesticides, flowing out of rivers and into the GBR lagoon (see for example the Brodie *et al.* 2008). This accumulated evidence is sufficiently strong that governments and managing agencies have developed the Reef Water Quality Protection Plan ('Reef Plan'), which aims to build reef resilience by decreasing environmental stress caused by agricultural pollutants.

Pesticides represent a useful marker for the distribution of dissolved agricultural pollutants since there are no natural or pre-development levels to distinguish with current levels, as is the case with nutrients. Prior to the establishment of the Australian Government's Marine and Tropical Sciences Research Facility (MTSRF) and recent monitoring work, there was a general consensus that pesticides could potentially be a problem but limited information on the transport process and the levels of contamination in freshwater and marine systems, with almost no information on the potential impacts of pesticides on GBR ecosystems.

Sporadic monitoring of sediments, surface waters and groundwaters in the 1990s uncovered that a particular suite of herbicides in common use in the sugarcane industry such as diuron, atrazine, hexazinone and ametryn were regularly above analytical detection limits across several regions of the GBR catchment area (Müller *et al.* 2000; Hunter *et al.* 2001). These herbicides are all designed to inhibit photosynthesis via the photosystem-II (PS-II) apparatus of the target plant and provide residual control of broad leaf weeds and grasses. However, it has been difficult to place the concentrations of the herbicides detected in these initial monitoring programs into an environmental context until recently, when research revealed that concentrations of diuron as low as $1.0 \mu g L^{-1}$ had negative effects on the photosynthesis of certain seagrass species commonly found within the GBR (Haynes *et al.* 2000a).

A survey of sediments and seagrass along the Queensland coast (1997-1998) identified pesticide residues of the herbicide diuron and the insecticide dieldrin (deregistered in the 1990s) in the nearshore environment off the Wet Tropics region (Haynes *et al.* 2000b). Several organic pollutants were also detected in local crustaceans and marine mammals in the late 1990s (Mortimer, 2000; Haynes *et al.* 2005).

Pesticide use in the grazing and sugarcane industries (the main agricultural industries in the GBR catchment) has evolved over the last few decades. The main 'problems' controlled by pesticide application are listed in Table 1. During the 1940s and 50s both industries mainly used organochlorine insecticides (such as DDT, dieldrin, lindane) to control insect pests until these were widely banned/restricted in the late 1980s due to significant levels measured in beef exports and other environmental concerns. A number of alternative chemicals are now available for the treatment of ticks and fleas on cattle including pyrethroids, biopesticides (such as abamectin) and benzoylphenyl urea (such as fluazuron). Herbicides to control woody vegetation regrowth and weeds (particularly tebuthiuron) are also used in the grazing industry. Changing practices in the sugarcane industry to reduce soil erosion (such as minimal tillage) has caused an increased reliance on herbicide application particularly since the 1980s-90s (Johnson and Ebert, 2000). Some of the key herbicides used include paraquat, diuron, atrazine, glyphosate, hexazinone and ametryn, while organophosphates (such as chlorpyrifos) and chloronicotinyls (such as imidacloprid) are used to control the greyback grub in the sugarcane industry (Table 1).

Table 1: Common problems and pesticide use for grazing and sugarcane activities.

Agricultural industry	Problem	Typical pesticide application
Grazing	Ticks and fleas on cattle	Various insecticides
	Regrowth vegetation and weeds	Generally tebuthiuron, but can be others
Sugarcane	Greyback cane grub/beetle	Various insecticides
	Broad leaf weeds, grasses and vines	Predominantly paraquat, diuron, atrazine, glyphosate, hexazinone, ametryn 2, 4-D plus others

MTSRF research, working in conjunction with the Reef Rescue Marine Monitoring Program, has focused on improved estimation of pesticide loads delivered to the GBR (Brodie and Waterhouse, 2009; Kroon *et al.* 2010, in review; Waterhouse *et al.* in review), the examination of the sources, transport and exposure of PS-II inhibiting (PS-II) herbicides in different catchments of the GBR (Davis *et al.* 2008, in review-a, b; Bainbridge *et al.* 2006, 2008, 2009; Lewis *et al.* 2009, in review; Johnson *et al.* 2011), better reporting of pesticide exceedances in the GBR (Lewis *et al.* in review; Kennedy *et al.* in press) and laboratory based exposure-impact work identifying threshold values and the ecosystems likely to be impacted by pesticides (Negri *et al.* 2011).

Laboratory projects run by MTSRF-funded researchers have tested the effects of exposure of corals, crustose coralline algae and foraminiferans (Negri *et al*. 2011; van Dam *et al.* in review) to concentrations of atrazine, diuron and hexazinone that are known to occur on the GBR. The potential for synergistic effects have also been investigated with the combination of relatively high seawater temperature and herbicides being particularly stressful for coral symbionts (Negri *et al.* 2011).

Outside of the MTSRF, other scientists in the region have produced important recent publications on pesticide loads in the Fitzroy River (Packett *et al*. 2004; Packett *et al.* 2005; Packett *et al.* 2009) and other catchments of the GBR (Smith *et al.* in review), herbicides losses from sugarcane crops in the Burnett region (Stork *et al.* 2008) and pesticide residues in marine and freshwaters of the Mackay Whitsunday Region (Galea *et al.* 2008; Rohde *et al.* 2006, 2008). The outputs of these research programs have also been a key component of the ongoing research synthesis and the value of these additional programs are recognised in the continuing development of our pesticide understanding.

This report presents the latest findings from MTSRF research, with additional work cited where appropriate. The work has been carried out primarily by scientists at JCU, AIMS, CSIRO and UQ and has contributed significantly to a much greater understanding of the detection, transport and impact of pesticides on the GBR.

2. Research outputs

The MTSRF was a key funding agency for a number of research programs which examined the sources, transport and exposure of herbicides in the GBR catchment area and lagoon over the last four years and has advanced our understanding of the potential impacts of herbicides on GBR ecosystems. These research publications can be identified to a particular part of the pesticide research outcomes for the MTSRF, illustrated in Figure 1.

This report is presented in four sections related to pesticides in the GBR:

1. Key sources of pesticides;
2. Transport of pesticides;
3. Monitoring and measurement of pesticides; and
4. Exposure and risk associated with pesticides and potential ecological impacts.

Each section is presented as key messages, a summary of the research outputs and suggestions for future directions.

It is important to recognise some of the important work prior to the MTSRF which focused on the detection of pesticides in various GBR catchments (Hunter *et al.* 2001; Müller *et al.* 2000) estimates of loads in a few key catchments (Mitchell *et al.* 2005; Rodhe *et al.* 2006, 2008; Packett *et al.* 2009), and identification of pesticide residues incorporated into the sediments and biota of the GBR lagoon (Haynes *et al.* 2000a, 2005; Mortimer, 2000). However, in the lead up to the MTSRF, it was recognised that there was a substantive lack of information on pesticides in the GBR. International work had identified the movement and dispersion of pesticides as areas of concern with long term ecological monitoring in place to identify potential impacts and the work that was carried out under the MTSRF looked to address these research gaps. Our understanding of each step varies due to the degree of work that has been carried out within each area. In recent times, a large proportion of work has focused on the estimation of pesticide loads and the impact of pesticides on GBR systems through intensive laboratory based research.

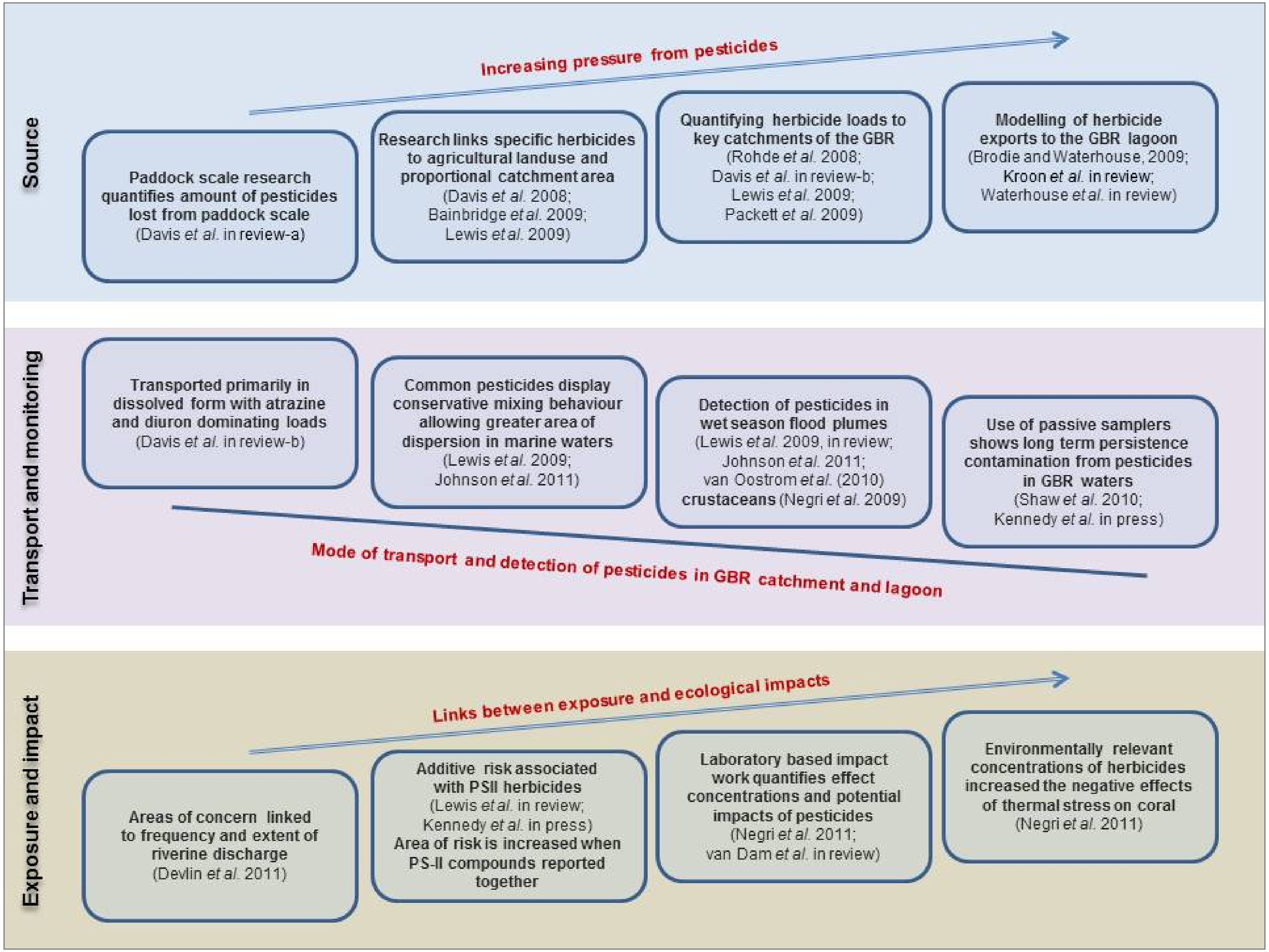

Figure 1: Contributions to pesticide knowledge since the commencement of the MTSRF Research Programme, also incorporating other relevant publications.

3. Key sources of pesticides

3.1 Key messages

- Pesticides concentrations in rivers and the inshore GBR lagoon are highest in adjacent catchments that drain intensive agricultural activity, including sugarcane, but can also be sourced to grazing lands (tebuthiuron).
- The loss of herbicide residues – particularly diuron, atrazine, hexazinone and ametryn – from sugarcane cultivation has been firmly established.
- The greatest proportion of PS-II herbicides is generated from sugarcane areas in the Wet Tropics region.
- In the Wet Tropics region, diuron is the PS-II herbicide discharged in the highest amounts, followed by atrazine and hexazinone. The Herbert, Russell-Mulgrave, Johnstone and Tully basins deliver substantial exports of diuron.
- Grazing lands are the primary source of tebuthiuron in the GBR catchments. The Fitzroy Basin exports the highest loads of this herbicide.

3.2 Research outputs

While a broad range of pesticides have been detected in the GBR catchment area and lagoon, herbicide detections predominate, and in many cases, are attributable to specific land uses in the upstream catchments (Mitchell *et al.* 2005; Davis *et al.* 2008; Lewis *et al.* 2007; 2009; Packett *et al.* 2009). Diuron, atrazine, hexazinone and ametryn are sourced to the sugarcane industry (Bainbridge *et al.* 2009; Lewis *et al.* 2009), atrazine can also be sourced to grain crops (Packett *et al.* 2009), tebuthiuron is used in the beef grazing industry (Lewis *et al.* 2009; Packett *et al.* 2009) and simazine is linked to plantation forestry (Bainbridge *et al.* 2009; Lewis *et al.* 2009).

Sugarcane cultivation is second only to pastoral cattle grazing as the dominant agricultural land use in the GBR catchment area, with the industry concentrated almost exclusively along the coastal zone. While pesticide usage is a significant and integral component in Australian sugarcane production, the environmental implications of pesticide usage have proved an ongoing issue for the industry, whether driven by human health or ecosystem health considerations (Cavanagh, 1999). Australian sugar production is particularly reliant on a wide variety of herbicidal applications, and a more restricted range of insecticidal controls (Johnson and Ebert 2000; Cavanagh, 1999). Recent changes in farming practices within the sugar industry, particularly minimum or zero tillage systems, has exacerbated this reliance on herbicides (Hargreaves *et al.* 1999; Johnson and Ebert, 2000) and a number of the PS-II herbicides widely used in the industry (atrazine, ametryn, diuron, hexazinone) have been identified as a particular concern for GBR ecosystems (Brodie *et al.* 2008; Jones, 2005). Use of these herbicides in sugarcane areas, particularly in Wet Tropics, lower Burdekin and Mackay Whitsunday, is associated with elevated herbicide concentrations in the adjacent GBR waters (Bainbridge *et al.* 2009; Davis *et al.* 2008; Lewis *et al.* 2009).

Significant losses of herbicides occur during wet season rainfall run-off events, particularly from paddocks with recent pesticide applications (Davis *et al.* in review-a). In addition, there can be substantial off-site pesticide movement from fully irrigated sugarcane farms during the dry season with high losses (loads and event concentrations) reported from dry-season irrigation events following pesticide application (Davis *et al.* 2008, in review-a). Pesticide losses associated with irrigation tailwater is more likely to affect local freshwater wetlands, whereas run-off during the wet season is more likely to impact downstream estuarine-marine environments. This seasonal dichotomy in pesticide run-off dynamics results in two distinct phases for pesticide movement. As concluded by Davis *et al.* (in review-a) this leads to different management approaches to reduce ecological risk from the impacts of pesticide losses from irrigated cane farms. The first is during the dry season when farmers can exert high levels of management to control pesticide inputs and outputs to minimize risk of impact. The second is when losses are more rainfall driven and these climatic constraints limit farmers' options to reduce risks. Reducing pesticide use in this second phase is especially important for reducing risk of ecological impacts to the GBR.

3.3 Future directions

Research is continuing to further refine the annual loads of pesticides exported to the GBR lagoon and to understand pesticide movement and dispersion within GBR catchments and lagoon, particularly in relation to specific land uses. Future monitoring efforts also need to focus on other agricultural industries known to use pesticides such as bananas, grain crops and tree plantations.

3.4 Primary references

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4. Transport of pesticides

4.1 Key messages

- Prior to MTSRF, herbicide loads had only been reported for certain catchments in the Mackay-Whitsunday regions and their mode of transport (dissolved versus particulate) was not well unknown or quantified.
- Research within and outside MTSRF measured loads from other catchments. These load data were used to model herbicide loads across the GBR catchment area which suggests that the mean annual load of the six key PS-II herbicides delivered to the GBR is approaching 30,000 kg/yr.
- It is likely that pesticide loads (herbicides, insecticides and fungicides) delivered to the GBR are larger than 30,000 kg/yr as not all land uses known to leak pesticides into GBR catchment waterways could be modeled. The current model is based on the six key PS-II herbicides only (diuron, atrazine, hexazinone, ametryn, simazine and tebuthiuron).
- Atrazine, and its degradation products, and diuron contribute a large proportion of herbicide load (up to 90%) with early 'first-flush' events accounting for the majority of herbicide loads leaving the catchment.
- Assessment of herbicide water-sediment partitioning in flood run-off highlighted that the majority of herbicides were transported in predominantly dissolved form, although a considerable fraction of diuron may also be transported in particulate-bound form (ca. 33%).
- Monitoring data suggest that PS-II herbicides behave conservatively in flood plumes (i.e. become diluted with seawater mixing but not removed by other processes) which allow them to be transported large distances in the GBR lagoon.

4.2 Research outputs

PS-II herbicides are a priority contaminant because they are residual, relatively soluble and mobile and hence have a higher propensity to reach the marine environment at detectable concentrations. They have relatively longer half-lives than many other herbicides and are widely used in agricultural practices throughout the GBR catchment area. Recent MTSRF-supported work on pesticide monitoring in paddocks, rivers and the marine environment has progressed our understanding of the extent and persistence of pesticides in freshwater and marine areas (e.g. Lewis *et al.* 2009; Bainbridge *et al.* 2009; Shaw *et al.* 2010).

Pesticide residues have been detected across virtually the entire continuum of GBR associated environments including: catchment irrigation drainage systems and waterways (Müller *et al.* 1999; Davis *et al.* 2008, in review-a; Hunter *et al.* 1996, 1998, 2001; Mitchell *et al.* 2005; Müller *et al.* 2000; Packett *et al.* 2009; Stork *et al.* 2008); estuaries (Duke *et al.* 2005); nearshore marine habitats (Haynes *et al.* 2000a); and coastal marine environments (Kennedy *et al.* in press; Lewis *et al.* 2009, in review; Shaw and Müller, 2005; Shaw *et al.* 2010).

Pesticide loads exported to the GBR are highly seasonal and can be variable from year to year and thus are difficult to estimate, especially with the limited available monitoring datasets. Maughan and others (2008) provided the first GBR-wide load estimates of PS-II herbicides exported to the GBR lagoon using a simple model to provide loads for a GBR Exposure Model. These preliminary estimates have since been improved through the efforts of the MTSRF researchers to inform Reef Rescue investment in 2009 (Brodie *et al.* 2009a) and the definition of priority areas under the *Great Barrier Reef Protection Amendment Act 2009* (Reef Protection Package). Lewis and others (see Brodie *et al.* 2009b; Waterhouse *et al.* in review) established an improved method to estimate end-of-catchment pesticide loads for the GBR which incorporates a range of land uses and types of herbicides, resulting in considerable differences (increases) in the estimated PS-II herbicide loads for the GBR catchments. Existing herbicide load data were used to develop runoff coefficients ($kg.ha^{-1}$) for the six key herbicides designed to inhibit PS-II in plants and commonly detected in the GBR lagoon, including diuron, atrazine, hexazinone, ametryn, simazine and tebuthiuron for sugarcane, grazing and cropping lands. The latest models suggest that the mean annual load of these six herbicides in total is around 28,000 kg (Brodie *et al.* 2009b; Waterhouse *et al.* in review; Kroon *et al.* 2010). Further refinements to this original model are currently being completed by Lewis and colleagues (in review). Figure 2 shows the estimated PS-II herbicide load from each of the GBR catchments. The modeling data suggest that PS-II herbicide loads are highest in the catchments south of Cairns, extending to the Fitzroy River. Studies in the lower Burdekin floodplain indicate that the majority (>50%) of the annual herbicide loads is delivered in the early 'first flush' flows (Davis *et al.* in review-b).

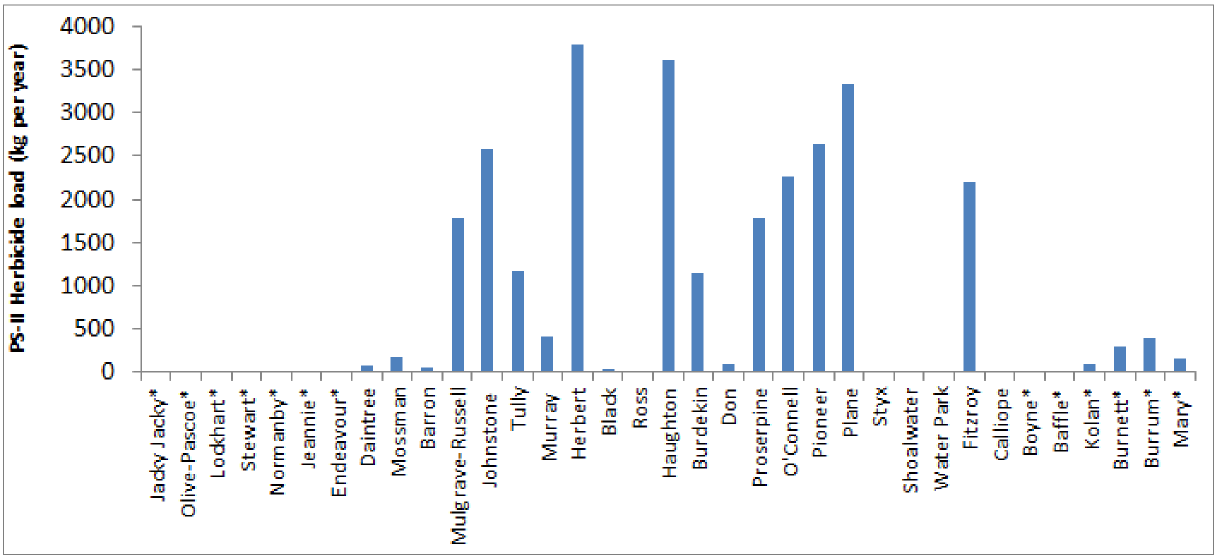

Figure 2: Summary of the current best estimates of PS-II herbicide loads discharged to the GBR. Source: *Brodie *et al.* 2009a, 2009b; # Reported as the Lower Burdekin in Brodie *et al.* 2009b.

There have been limited studies of the dynamics of pesticides in the transport from the catchments to the GBR. However, MTSRF research has shown that at least initially, PS-II herbicides are transported in the dissolved (or colloidal) phase, as they displayed conservative mixing behavior in river plumes and were not removed via sediment deposition, biological uptake or chemical degradation (Lewis *et al.* 2009; Johnson *et al.* 2011). This finding supports the results of Davis and others (in press-b) from filtered and unfiltered river water samples collected during high flowevents where typically >90% of herbicides were associated with the dissolved phase, apart from diuron, where ~30% resided in the particulate phase. However, PS-II herbicides (predominately diuron) have also been detected in benthic sediments and plants (Duke *et al.* 2005; Haynes *et al.* 2000a) which suggests that herbicides can eventually be removed from the water column via biological uptake or adsorption onto organic materials.

4.3 Future directions

MTSRF researchers have considerably advanced the knowledge of the annual loads of PS-II herbicides delivered to the GBR lagoon, identified the timing of when the highest proportion of loads are delivered and examined their mode of transport in rivers and in flood plumes. Considerable knowledge gaps still exist regarding aspects of pesticide delivery to the GBR such as the transport pathways and partitioning of particular pesticides (i.e. dissolved versus particulate), and temporal variability in loads associated with the relatively high climatic (hydrologic) variability that characterise many GBR catchments (Brodie *et al.* 2011; Bainbridge *et al.* 2009).

Future studies should examine the mode of transport and calculate loads of other key herbicides used in the GBR catchment area (e.g. 2,4-D, metolachlor). Despite being regularly detected in streams, 2,4-D has never been analysed in flood plumes in the GBR lagoon due to budget constraints. Moreover, the mode of transport for the key pesticides (partitioning between dissolved and particulates and 'first flush') need to be examined further in other catchments of the GBR (other than the lower Burdekin). Finally, additional monitoring data targeting other key agricultural land uses (plantation forestry, horticulture, bananas) in the GBR catchment area will allow runoff coefficients to be developed in these lands to further refine the estimates of pesticide export to the GBR.

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5. Exposure and risk associated with pesticides

5.1 Key messages

- The presence of pesticide residues, especially herbicides, is widespread in waterbodies of the GBR region, including streams, wetlands, estuaries, coastal and reef waters. Residues commonly detected include atrazine, diuron, ametryn, hexazinone and tebuthiuron. On occasions, residues of some of these herbicides exceed ecosystem guideline values and/or laboratory derived ‘inhibition-effect’ concentrations for freshwater, estuarine and marine ecosystems.
- Recent work on pesticide monitoring in paddocks, rivers and the marine environment has progressed our understanding of the extent and persistence of pesticides in freshwater and marine areas.
- The main herbicides detected in monitoring programs act in an additive manner in regards to PS-II inhibition and 80% of time when herbicides are detected in the GBR lagoon, more than one herbicide is present. Therefore exposure and risk studies shouldnot only considerherbicides individually but also as an additive herbicide mixture. As such the area of risk increaseswhen herbicides are considered as a mixture.
- Diuron is one of the more potent PS-II herbicides in photosynthesis suppression of non-target marine and estuarine plants.
- Monitoring using a combination of passive and grab sampling has revealed pesticide contamination throughout the GBR, including detection in the relatively pristine Cape York Region. The frequency of detection through passive sampling shows ubiquitous concentrations over time and space, with detectable concentrations present in both the wet and dry seasons.
- The area where herbicides occur at concentrations high enough to cause at least some inhibition of photosynthesis during certain times of the year (predominately wet season) may cover much of the inner GBR while exposure times (>1 month) may be long enough to cause potential chronic effects.
- Concentrations of pesticides are variable over time and space and thus it can be difficult to define the full impact of pesticide concentrations at any given sampling point. The complex transport mechanisms and variability within receiving waters can make it difficult to define the overall risk area within GBR waters.

5.2 Research outputs

Novel monitoring techniques

The monitoring studies responsible for detection of pesticides in GBR waters (for example, refer to Kennedy *et al.* in press) have used two separate techniques: grab samples taken in river water plumes where the highest concentrations of pesticides are detected, and passive samplers which can be deployed for a period of a few days up to one month. The combination of direct water and passive monitoring in the GBR lagoon is the best available approach to assess the acute and chronic risks of PS-II herbicides. Direct water samples collected during river runoff events typically provide a short-term ‘snap shot’ concentration and may be directly compared to laboratory-measured acute toxicity or ‘effects-based’ concentrations, while passive samplers provide an understanding of the longer-term herbicide exposure in marine ecosystems.

Over the last decade passive samplers have gained wide acceptance as effective tools for monitoring organic pollutants in aquatic environments (Seethapathy *et al.* 2008). The passive samplers accumulate residues and an ‘average’ pesticide concentration may be calculated over the period of deployment (Shaw and Mueller, 2009; Kennedy *et al.* in press). Uptake of pesticides into the passive samplers is initially governed by linear first order kinetics, providing a time weighted average of the exposure concentration incorporating fluctuations in the environmental concentration, as opposed to grab samples which provide information on environmental pollutant concentrations for only one point in time (Shaw and Mueller, 2009).

Their robust, simple designs which do not require maintenance or intervention allow the samplers to be deployed for extended periods in remote locations such as areas in the GBR. The passive samplers also provide much lower detection limits (0.1 ngL^{-1}) for the herbicides of concern compared to those currently available in grab samples (10 ngL^{-1}). Long in-situ accumulation periods (relative to grab samples) enable low concentrations of analytes to be detected. In some cases, passive samplers detected herbicides that were below present detection levels in direct water samples (e.g. diuron and simazine in the Fitzroy River plume) providing a more complete picture of the extent of individual herbicide transport due to the improved detection limits. These characteristics of passive samplers can represent considerable advantages over grab sampling techniques for monitoring in the GBR environment where low pollutant concentrations are the norm and waterways are characterized by episodic flows associated with monsoonal rainfall events during which pesticide concentrations may fluctuate dramatically (Mitchell *et al.* 2005).

Monitoring data from passive samplers deployed throughout the GBR lagoon show that herbicide residues at some inshore sites persist at very low concentrations (~1-10 ngL^{-1}) throughout the year (Johnson *et al.* 2011; Kennedy *et al.* in press). Residues of the herbicides diuron, atrazine, hexazinone, ametryn, simazine and tebuthiuron have all been detected in passive samplers deployed in the GBR lagoon with time-averaged concentrations between 1-120 ngL^{-1}.

Passive sampler-derived results have also detected herbicides in nearshore waters adjacent to Cape York (Johnson *et al.* 2011), an area virtually undeveloped compared to other regions of the GBR catchment area. This highlights the need to better characterise both the usage patterns and the fate of these compounds in tropical marine environments. Potential impacts to ecosystems of the GBR from chronic exposure to the complex mixtures of contaminants present are not clear and require further investigation.

As the pool of ecotoxicological studies expand, these monitoring approaches will become increasingly important to help understand the impacts and risks of herbicide exposure in the GBR lagoon. Ongoing monitoring of pesticides in the GBR is required to assess the effectiveness, or otherwise, of land management strategies aimed at reducing pollutant loads and the combination of passive sampling tools and direct sampling can provide a sensitive tool with which to inform this monitoring.

Freshwater systems

MTSRF-supported research has detected herbicide residues within and surrounding high value (Ramsar and ANCA recognised, internationally and nationally significant) coastal wetlands and freshwater ecosystems within the GBR catchment area and, at times, concentrations of atrazine and diuron residues exceed Australian freshwater ecological protection guidelines (Davis *et al.* 2008, in review-a, in review-b; Smith *et al.* in review). Preliminary desktop modeling analysis suggests that the combination of PS-II herbicides detected in the Barratta Creek complex of the lower Burdekin region are at concentrations that are likely to negatively affect (acute and chronic) components of these highly valued ecosystems (Davis *et al.* in review-a).

Marine waters of the Great Barrier Reef

Direct water ‘grab samples’ for pesticide analysis at end-of-system river sites and in flood plume waters has been undertaken in the Burdekin (Lewis *et al.* 2007, 2009; Davis *et al.* 2008; in review-b), Mackay-Whitsunday (Mitchell *et al.* 2005; Rohde *et al.* 2006, 2008; Masters *et al.* 2008; Lewis *et al.* 2009), Tully-Murray (Bainbridge *et al.* 2009; Lewis *et al.* 2009), Fitzroy (Packett *et al.* 2009; Lewis *et al.* in review) and Burnett-Mary (McMahon *et al.* 2005) regions of the GBR catchment. Herbicides have been detected in each instance of monitoring and are frequently detected in inshore waters of the GBR. The highest concentrations occur during flood plumes associated with the monsoon season (austral summer) (Lewis *et al.* 2009), coinciding with rising surface temperatures in GBR waters. These flood plumes also transport elevated levels of suspended solids and dissolved nutrients and can significantly reduce salinity, all of which may interact with high sea surface temperatures to threaten corals and other sensitive organisms (Fabricius, 2005).

Diuron and atrazine are the most commonly detected herbicides in GBR waters and concentrations in flood plumes exceed, at times, laboratory-based lowest observable effect concentrations for marine plants and/or ecological protection guidelines for the GBR Marine Park (Lewis *et al.* 2009, in review; Magnusson *et al.* 2010). Data generated from time-averaged (typically over 15 to 30 days) passive sampler deployments indicate that the highest concentrations of the most frequently detected herbicide diuron occur in the Mackay Whitsunday region which supports the direct water ‘grab’ sample data (Kennedy *et al.* in press). Other herbicides detected in the GBR lagoon waters include hexazinone, ametryn, simazine, tebuthiuron, bromacil and metolachlor while residues of the insecticide imidacloprid have also been detected in some parts of the GBR (Davis *et al.* 2008; Kapernick *et al.* 2006, 2007; Kennedy *et al.* in press; Lewis *et al.* 2009, in review; Shaw and Müller, 2005; Shaw *et al.* 2010). Thus, herbicide residues have been measured in inshore parts of the GBR lagoon at concentrations that have the potential to harm marine plant communities.

The passive sampler data show that herbicide residues can be detected in the GBR lagoon throughout the year with the highest concentrations coinciding with river discharge events. The data also allow for estimations of herbicide exposure times in the GBR lagoon. Herbicide residues in some parts of the GBR lagoon can persist at concentrations above GBR PS-II thresholds for at least one month of the year which suggests potential for chronic effects (Lewis *et al.* in review).

Monitoring on the GBR lagoon following wet season discharge show that 80% of the time when herbicides are detected, more than one is present. These herbicides have been shown to act in an additive manner with regards to PS-II inhibition. MTSRF-funded research (Lewis *et al.* in review) developed two normalisation indices for herbicide mixtures that were calculated based on current guidelines and PS-II inhibition thresholds developed by the GBR Marine Park Authority (GBRMPA, 2009). The results show that the area of risk increases under the proposed additive PS-II inhibition threshold and that the resilience of this important ecosystem could be reduced by exposure to these herbicides (Lewis *et al.* in review).

The method of combining pesticides can vary between researchers with methods suggesting normalisation based on threshold limits/guideline values (Lewis *et al.* in review) and toxic equivalency factors based on EC_{50} concentrations (Smith *et al.* in review). The appropriateness of each method is currently being discussed, although each method identifies that the area of risk is far greater when reporting as a combined value and not a single pesticide threshold or concentration. Use of additive indices in the assessment of PS-II risk increased the area of risk for all GBR regions, and in particular, the Mackay-Whitsundays area (Figure 3). A combination of grab and passive sampling was used in this risk analysis and highlights the area likely to see an impact from PS-II herbicide exposure (Lewis *et al.* in review).

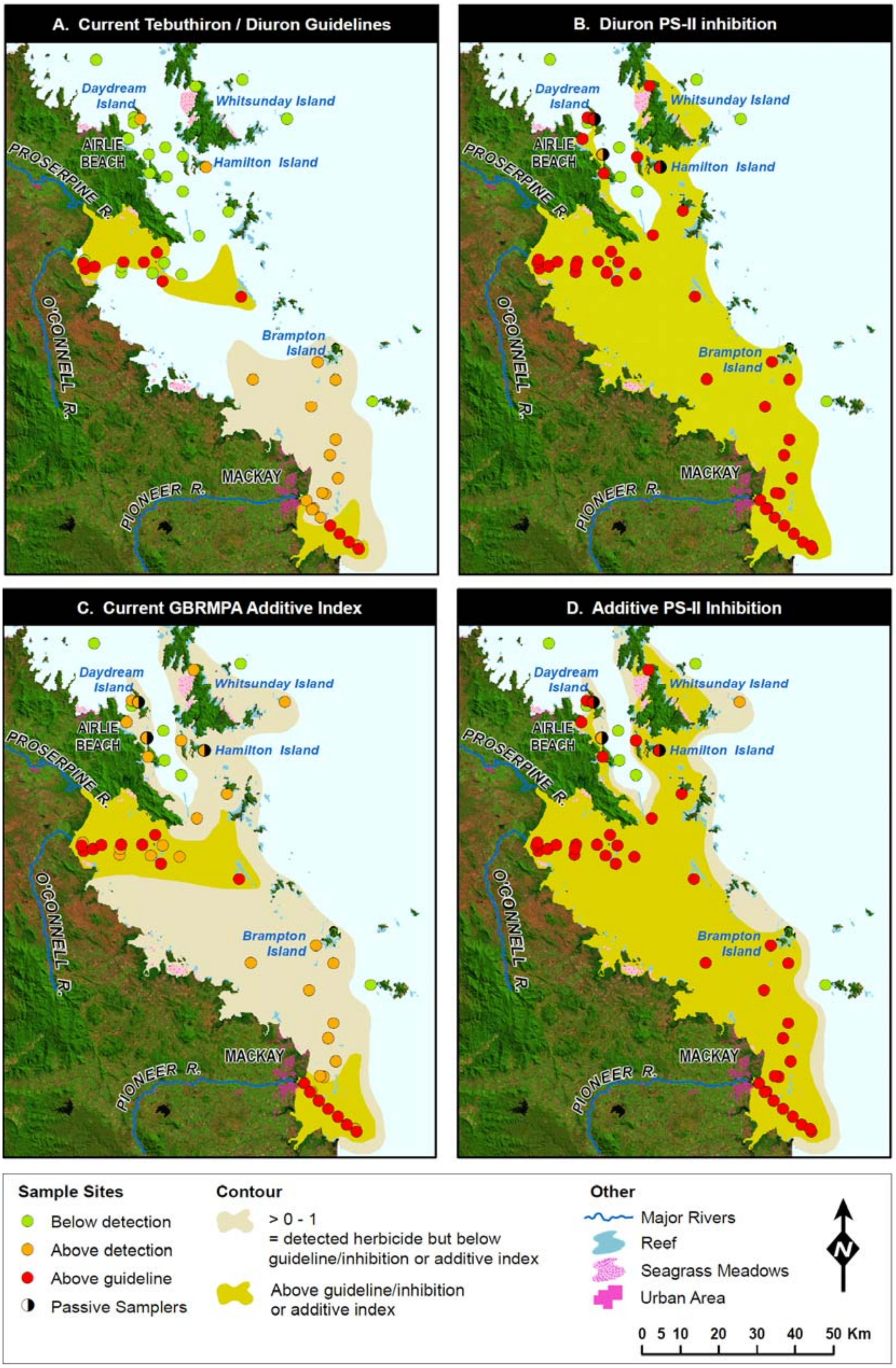

Figure 3: Area of PS-II herbicide risk for Mackay-Whitsundays using additive risk analysis using the two normalization indices based on current guidelines and PS-II thresholds.

5.3 Future directions

Research conducted during MTSRF and the Reef Rescue Marine Monitoring Program has greatly advanced our knowledge of the exposure and risk of herbicide residues in the GBR catchment area and lagoon. Future monitoring of herbicide residues in the GBR lagoon needs to further examine the exposure times of herbicides from different regions and also collect regular samples throughout the wet season to fully quantify the area and time of risk. This monitoring should be coupled with measurements of salinity, seawater temperature, light, suspended solid and nutrient concentrations so that these data may be used in future laboratory experiments that examine the effects of 'multiple stressors'. Future research efforts need to examine the most optimal technique (either out of the ones currently available or new) to quantify the risk of herbicides in the GBR lagoon so that these risks are reported consistently over coming years allowing comparisons to be drawn throughout the Reef Plan. Further research on better integrating data generated from grab and passive samples is also required.

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6. Potential ecological impacts

6.1 Key messages

- Herbicide concentrations in riverine flood plumes that extend into the marine environment can exceed concentrations shown to have negative effects (i.e. reduced photosynthesis) on certain species of coral, seagrass and microalgae.
- The herbicides most commonly detected in the GBR lagoon are PS-II inhibitors and include diuron, atrazine, hexazinone, ametryn, simazine and tebuthiuron.
- Laboratory-based research suggests that there are negative effects to some plant species (such as seagrass and the algal symbionts of coral – zooxanthellae) from herbicide exposure in the GBR lagoon, with potential longer-term effects.

6.2 Research outputs

Understanding the impacts from the increasing loads and concentrations of pesticides measured in the GBR is a crucial step in our understanding of the short and long term impacts of pesticides on GBR ecological systems. The groups of herbicides which are commonly detected have relatively well understood acute effects on marine plants in the GBR (reviewed and collated in GBRMPA, 2009). These impacts have been documented over the last 10 years with several laboratory-based studies on the acute (short term) effects of the commonly detected herbicides on species of seagrass (Haynes *et al.* 2000b), mangroves (Duke *et al.* 2005), microalgae (Bengston-Nash *et al.* 2005; Magnusson *et al.* 2010), coral-symbionts (Jones and Kerswell, 2003; Jones *et al.* 2003; Jones, 2005; Negri *et al.* 2005; Cantin *et al.* 2007) and foraminifera symbionts (van Dam *et al.* in review). Recent GBR based studies have begun to identify the potential impacts of the increasing loads of pesticides delivered from the GBR catchment to estuarine and coastal areas.

A summary of the detection of pesticides and the known impact of pesticides on GBR biota is provided in Table 2.

All of these studies use a technique known as pulse amplitude modulation chlorophyll fluorescence which measures the efficiency of photosynthesis in the target plant. This technique can identify the concentration of a particular herbicide that will have a ‘negative effect’ on the plant species (e.g. IC50 = concentration that inhibits 50% of photosynthesis). These studies have shown short term impacts from the exposure to the common herbicides detected on the reef. The effects include reduced photosynthesis, bleaching, reduced growth and mortality (Table 2). While the long-term effects of chronic low-level exposure on the GBR ecosystem are largely unknown, laboratory tests have indicated that sublethal concentrations of diuron can negatively affect the reproductive capacity of corals (Cantin *et al.* 2007), and reduce the rate of energy acquisition for young (recruit) corals (Cantin *et al.* 2009).

An overview of the current knowledge of the impacts of pesticides on freshwater and marine ecosystem health is presented below.

Table 2: Summary of the detection and known impact of pesticides detected for GBR biota.

GBR biota	Detection and known impact								
	Pesticides	Insecticides	Fungicides	PS-II herbicides					
				Inhibition of photosynthesis	Growth inhibition	Reduced energy acquisition	Reduced reproduction	Bleaching	Effects enhanced by:
Microalgae				Y	Y				
Crustose coralline algae				Y					Sediments
Seagrass				Y					
Foraminifera				Y					High temperatures
Coral (symbionts)				Y	Y			Y	High temperatures
Coral (host)		Inhibit larval settlement	Inhibit larval settlement			Y	Y	Y	
Crabs	Y	Multiple biomarkers for stress							
Fish		Multiple biomarkers for stress							
Turtles	Y								
Dugongs	Y								

Freshwater species

There are limited studies on the impact of herbicides in freshwater systems within the GBR catchment. However, an important study on barramundi in Wet Tropics Rivers has shown some significant first order impacts using indicators of pesticide contamination (Humphrey *et al.* 2007). An innovative multiple biomarker approach has linked patterns in land use with patterns of contamination observed in North Queensland's riverine ecosystems. For example, barramundi caught from five far northern Queensland rivers – the Herbert, Johnstone, Endeavour, Lockhart and Pascoe rivers – were tested for exposure to a range of anthropogenic chemicals (Humphrey *et al.* 2007). Analysis of muscle tissue in the Johnstone and Herbert rivers indicated exposure to pesticides, particularly insecticides of the organophosphorus and carbamate variety, both of which are difficult to detect in water samples. Barramundi collected in the Wet Tropics Rivers (Herbert and Johnstone Rivers) showed reduced cholinesterase activity in the muscle tissues, an increase in EROD activity and increased rates of DNA damagerelative to barramundi from other rivers with less modified catchments.

Assays of EROD activity in fish are widely used in contamination monitoring internationally, as increased activity of this enzyme is known to occur due to exposure to some kinds of hydrocarbons, polychlorobyphenols (PCBs), pesticides, dioxins and furans. While the observed increase in EROD activity in barramundi from the Johnstone and Herbert rivers would be considered only moderate by international standards, it is still a significant departure from the near 'natural' levels observed in the less heavily modified catchments of the Lockhart and Pascoe rivers. Many environmental contaminants can act as genotoxins, either directly or through the formation of reactive intermediates in the liver during metabolic breakdown, thus increasing the rates of DNA damage. Genotoxic concentrations of polycyclic aromatic hydrocarbons (PAH) were detected in water samples from the Johnstone River, and to a lesser degree in the Herbert River. By comparison, PAH concentrations were below detectable levels in the other three rivers (Humphrey *et al.* 2007).

Calcifying organisms (corals, crustose coralline algae and foraminifera)

The common PS-II herbicides detected in the GBR lagoon all reduce electron transport through the PS-II pathway in corals and other plants (Jones *et al.* 2003). This reduction in electron transport is correlated with diminished uptake of energy by the host corals (Cantin *et al.* 2009) and subsequent reductions in reproductive output (Cantin *et al.* 2007). The obstruction of electron transport through PS-II by herbicides such as diuron can also result in oxidative stress, leading eventually to photoinhibition, expulsion of symbionts and bleaching (Jones *et al.* 2003; Negri *et al.* 2005; Cantin *et al.* 2007).

Negri and colleagues (2005) found that two hours of exposure to 1 μgL^{-1} diuron caused reductions in photosynthetic efficiency, chronic photoinhibition and damage to PS-II for the symbionts of two-week-old coral colonies (see also Jones, 2005). Similarly, Harrington and others (2005) showed that even short-term exposure to trace concentrations of diuron (0.79 μgL^{-1}) in combination with sedimentation impaired the resilience of crustose coralline algae (an algal group that is very important in the ecology of coral reefs). In addition, very low concentrations of insecticides and a fungicide used in Great Barrier Reef catchments was found by Markey *et al.* (2007) to negatively affect settlement of larval corals.

Laboratory work by Magnusson and others has also shown impacts of pesticides on reef ecosystems from a cellular to system change within coral, seagrass and algal communities. For example, a shift in the community structure of benthic biofilms was observed following exposure to environmentally relevant concentrations of diuron over a four-week period, resulting in enhanced tolerance to herbicides over time (Magnusson *et al.* in review). These results strongly suggest that inter-species differences insensitivity to herbicides may alter the primary productivity or other functional characteristics of tropical ecosystems.

These effects of herbicides on corals is concerning since these are one of the primary reef-building and habitat forming organism on coral reefs. Herbicides can also affect other calcifying organisms such as foraminifera. These organisms host at least four different types of alga and all are affected by herbicides (van Dam *et al.* in review). While foraminifera do not seem as sensitive and react more slowly to herbicides than corals, their photosystems are damaged at low herbicide concentrations. Crustose coralline algae (CCA) is a key reef-building species and is a preferred substratum for corals and other organism to recruit on. Laboratory studies conducted as part of MTSRF showed that photosynthesis in CCA is reduced by diuron, atrazine and hexazinone (Negri *et al.* 2011). It is not known how coral recruitment onto CCA may be affected by prior exposure to herbicides.

Combined impacts

The effects of PS-II herbicides at relatively low concentrations and short exposure periods can be fully reversible; however extended exposure periods may significantly lengthen recovery periods and impact on ecosystem resilience (Jones, 2005). Longer term effects of herbicide exposure on marine ecosystems may drive the more sensitive species to become depleted and out-competed by less sensitive species (e.g. Magnusson *et al.* 2010; in review). Indeed, the overall impacts from long term exposure to ecosystem communities may be more subtle and include disruptions such as reproductive suppression, reduced resilience to disease/climate change and repressed recovery following disturbance (Cantin *et al.* 2007; Jones *et al.* 2003; Jones, 2005; Magnusson *et al.* in review). Conversely, it may be possible that some species (or communities) can adapt to pulsed herbicide exposure in the environment. Some studies on microalgal communities exposed to herbicides show increased tolerance (due to species composition changes) following repeated exposure (Tlili *et al.* 2008; Magnusson *et al.* in review), although this tolerance has not been tested observed for individual organisms in the tropical marine environment.

The threat to the GBR posed by climate change may be further exacerbated by the coincident input of elevated levels of nutrients, sediments, and pesticides in river discharge. Environmentally relevant concentrations of herbicides can increase the negative effects of thermal stress on coral (Negri *et al.* 2011). The effects of herbicide exposure can be further exacerbated in combination with other environmental influences such as seawater temperature, salinity, nutrients and sedimentation. For example, diuron attached to sediment particles can produce an enhanced effect on the sedimentation stress on crustose coralline algae (Harrington *et al.* 2005). Ongoing experiments (van Dam and colleagues) are testing the combined effects of herbicides and thermal stress on foraminifera and symbionts isolated from coral and foraminifera. The effect of either diuron or atrazine in combination with higher sea surface temperature on chronic photoinhibitionin corals was distinctly greater than the sum of the individual effects indicating a synergistic (greater than additive) effect of herbicides (diuron or atrazine) and temperature. Negri and colleagues (2011) suggests that reductions in herbicide runoff would potentially improve survival rate of the coral symbiont.

6.3 Future directions

The impacts of PS-II herbicides on certain components of GBR ecosystems is well reported by GBRMPA (2009), however the longer term chronic effects on e.g., coral reproduction (see Cantin *et al.* 2007); the ability of corals to recover from disturbance (Carilli *et al.* 2009); immune system functionality and long-term marine organism fitness (Eggen *et al.* 2004) are unclear. Short-term ecotoxicological studies on endpoints for growth and survival are insufficient to analyse these potential chronic effects and future studies may need to examine changes at the molecular level such as DNA damage and gene responses which may help to better quantify and understand sublethal stresses (Eggen *et al.* 2004).

Complex mixtures of pesticides can have unpredictable ecosystem effects (Relyea, 2009; Shaw and Muller, 2005, Shaw *et al.* 2010), especially if their individual effects on a variety of organisms are poorly understood. In addition to the commonly found herbicides, there are a number of pesticides less commonly detected in the GBR lagoon, e.g. bromacil, metolachlor (both herbicides) and imidacloprid, chlorpyrifos and prothiophos (insecticides). These pesticides all have different modes of action that require ecotoxicological investigation using different endpoints (i.e. other than PS-II inhibition). Herbicide degradation products such as 3,4-dichloroaniline (diuron degradation compound) and desethyl atrazine (atrazine degradation compound) can have some PS-II inhibition ability (Giacomazzi and Cochet, 2004) and inert or surfactant/wetting ingredients in pesticide formulations can also cause environmental harm (Cox and Surgan, 2006). These products should all be included into mixture toxicity assessments once data become available. Ecotoxicological studies on corals have noted complex interactions between herbicides and sea water temperature (Negri *et al.* 2011). Therefore physical (e.g. temperature, salinity) and chemical parameters may also need to be measured in monitoring programs to better understand pesticide toxicity.

Knowledge of the potential impacts to GBR ecosystems, particularly coral reefs, has been advanced considerably by MTSRF researchers as illustrated in Table 2. However our understanding of the full extent of impact and the potential interactions between other pollutants (sediments, nutrients, temperature stress, and freshwater stress) and pesticides is still developing and will be a major topic for future research. The next step is to also identify where actual impacts are occurring or likely to occur, both in the freshwater and coastal systems and the GBR ecosystems. Monitoring of pesticide impact within international waters focuses heavily on the detection of impact, with large ecotoxicological programs in place to identify the occurrence and frequency of these impacts. As our understanding of the potential impacts advances, our knowledge of what and where to monitor in the freshwater and marine environments will also advance, allowing the development of appropriate indicators that are responding to pesticides as a single pressure or as a combined pressure with other dominant pollutants.

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7. Conclusions

The scientific evidence summarised here, plus a large body of international research, indicates that there is a risk that the runoff agricultural chemical residues are negatively affecting the resilience of inshore coral reefs, and that this is especially likely during the wet season when floods deliver the highest concentrations and loads to the Great Barrier Reef lagoon (Lewis *et al.* 2009). These wet season floods deliver not only agricultural pollutants but also sediments and low-salinity conditions to these inshore reefs during the warmest part of the year, when coral reefs and seagrass meadows may already be suffering temperature stress, and corals may be attempting to spawn (sexual reproduction generally occurs in November/December each year). Pesticide runoff is therefore likely to be contributing to erosion of ecosystem resilience of inshore reefs in the Great Barrier Reef lagoon.

Research carried out though the MTSRF and other programs have all identified that the application, supply and exposure of ecosystems to pesticide contamination has the potential to impact on the freshwater and marine environment, and is a major management issue for the long term protection of the GBR. This report has highlighted the recent research, supported by MTSRF funding, has considerably advanced our understanding of the sources of pesticides from GBR catchments, the transport mechanisms of pesticides to marine waters, the level and extent of exposure from pesticides within the GBR lagoon and the potential impacts from the environmentally relevant pesticide concentrations which have been detected in the GBR. Our understanding has improved through these research programs as highlighted by the catchment to reef conceptual model presented in Figure 4 relating to the source, delivery and impact of pesticides on the GBR.

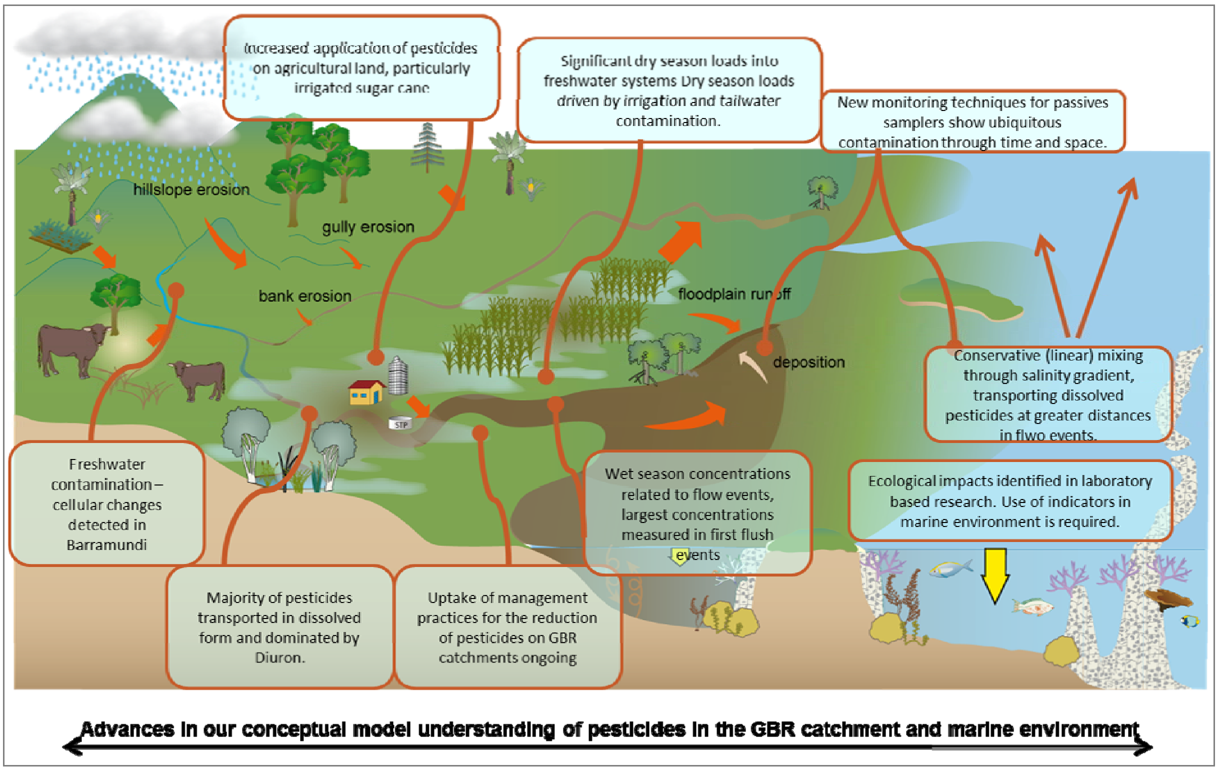

Figure 4: Illustration of the science advances in our understanding of pesticides in the GBR catchment and marine environment.

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