

Reef Rescue Research & Development

Technical Report

Pesticide dynamics in the Great Barrier Reef catchment and lagoon: management practices (sugar, grazing, bananas) and risk assessments: Overview report for project number RRRD037 and RRRD038



Stephen Lewis, Jon Brodie, Jenny Andersen, John Armour, Craig Baillie, Aaron Davis, Geoff Eaglesham, Amanda E Elledge, Emilie Fillols, Florita Flores, Christie Gallen, Rai Kookana, Jack McHugh, Bronwyn Masters, Phil Mercurio, Christina Mortimore, Jochen F Mueller, Andrew P Negri, Dominique O'Brien, Danni Oliver, Bob Packett, Chris Paxman, Samuel Rojas-Ponce, Melanie Shaw, David Mark Silburn, Rachael Smith, Ryan Turner, Craig M Thornton and Michael Warne

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Overview report for project number RRRD037 and RRRD038

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The Reef Rescue Research and Development Program (Reef Rescue R&D) was funded under the Australian Government's Caring for our Country program, and consisted of 18 projects. The Reef Rescue R&D is designed to improve our understanding of the link between land management practices and environmental impacts, and improve water quality across the Great Barrier Reef by informing on-ground projects to reduce the amounts of nutrients, pesticides and sediments reaching the Reef from agricultural lands.

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Cover photographs: Top Left – Banana Pesticide trails in South Johnstone; Top Right – Passive sampling in the Barrata Creek System; Bottom Left – Banded herbicide application trials in the Burdekin Bottom Right – Rainfall simulation and spot spay trials in the Burdekin. Images supplied by TropWater, James Cook University and Department of Natural Resources and Mines, Queensland.

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

Executive Summary

Pesticide runoff from agricultural lands has been recognised as a serious threat to the health and productivity of the Great Barrier Reef (GBR) (e.g. Lewis et al., 2009) and is considered a priority pollutant for management in the GBR catchment area. Pesticide residues have been detected in marine waters, sediments, seagrass meadows and in freshwater plumes in the GBR lagoon. Water quality targets have been introduced to reduce the runoff of pesticides with the aim of improving ecosystem resilience in the GBR, although it was not known if the adoption of best management practices in agriculture will meet these immediate targets. While it is clear that some pesticides have higher runoff potential than others due to their individual properties (i.e. persistence, solubility), a meticulous mass balance approach for individual pesticide chemicals was required to better parameterise/validate predictive models such as APSIM, HowLeaky? and Source Catchments to improve the accuracy of load calculations. This link is critical in the management of application rates of certain pesticides in the GBR catchments and to develop improved risk assessments for better management of the GBR. Moreover, the benefits of purported improved management practices to reduce the amount of pesticide runoff are largely unquantified. These links are critical in the management of application rates of certain pesticides in the GBR catchments and to inform/validate the modelling process within the RR monitoring and evaluation (M&E) program. This project fostered collaborations between research scientists, growers and industry stakeholders to address the major unknowns of pesticide dynamics in the GBR catchment area. The project package incorporated a range of key science providers with expertise in the management, transport and fate of pesticides and the projects were conducted across several regions of the GBR catchment area. This package included a series seven sub-projects:

- Determine the half lives in soils (and other key properties) of key pesticides used in the Great Barrier Reef catchment area for use directly in modelling for the RR M&E program
- Investigate the potential water quality and agronomic benefits of alternative herbicide products (to those currently used) used in sugarcane including Balance, Flame, Soccer and Krismat
- Determine the water quality benefits of improved practices to reduce pesticide runoff (Shielded sprayers, banded sprayers etc.)
- Ascertain the half lives in water and the exposure of key pesticides in the Great Barrier Reef catchment area and lagoon
- Tebuthiuron management in grazing lands
- Partitioning of pesticides in agricultural lands
- Pesticide management in bananas

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Acronyms Used In This Report

DSITIA	Department of Science, Information Technology, Innovation and the Arts (Queensland)
GBR	Great Barrier Reef
GBRWHA	Great Barrier Reef World Heritage Area

Abbreviations Used In This Report

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The authors would like to thank Ken Rohde who provided assistance with logistics to collect and prepare the soils for this study;. Michael Widderick and Andrew McClean from the Leslie Research Centre, DAFF, provided assistance with herbicide application. Peer Shenk and his research staff from the University of Queensland provided the analysis of microbial activity in soils. Thanks also to those who helped with preparation or collection of soil samples in the glasshouse including Kaela McDuffie (DNRM), Monia Anzooman (USQ) and Kevin Kodur (DNRM) with special acknowledgement of the contribution by Maria Harris (DNRM). This project was jointly funded through the rainfall simulation and paddock modelling components of the Paddock to Reef Integrated Monitoring, Modelling and Reporting program, the Reef R&D program and through a Reef Protection Program grant to include analyses for 'emerging' herbicides. Valuable technical advice was received from Dow AgroSciences staff Colin Sharpe and Graham Fossett, along with the provision and application of tebuthiuron products. Assistance with fieldwork was received from Department of Natural Resources and Mines staff Bruce Cowie, Luke Davison, Wendy Tang, Dale Heiner, Adrian Osborne and Warren Andrews. We are also grateful to Bruce Cowie, Luke Davison and Wendy Tang for assistance with project administration and data management. We thank David Reid from the Queensland Department of Agriculture, Fisheries and Forestry who conducted statistical analysis in GenStat. We thank Tim Staier and Dave Olsen from BSES for their assistance in the rainfall simulation trial. The assistance of the growers who participated in the shielded sprayer field trial is gratefully acknowledged. We are grateful to Cassie Thompson for assistance in the laboratory.

Key Research findings

1. Determine the half lives in soils (and other key properties) of key pesticides used in the Great Barrier Reef catchment area for use directly in modelling for the P2R program

Nine different soils from the Great Barrier Reef catchment area that represented differences in texture (i.e. particle size), organic content and pH were used to develop half-lives of 14 key herbicides (PSII, knockdown and emerging) used in cropping. Overall, the results from this study 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 outcomes of this research are now being incorporated into the latest Source Catchments model run to more accurately predict herbicide loads from croplands in the Great Barrier Reef catchment area.

2. Investigate the potential water quality and agronomic benefits of alternative herbicide products (to those currently used) used in sugarcane including Balance, Flame, Soccer and Krismat

Several rainfall simulation trials were conducted that examined the runoff potential of key herbicides used in the sugar industry so that direct comparisons could be made between each product (i.e. normalised for soil type, application of standard rates etc). Hence with the inclusion of toxicity data combined with our runoff data, a relative risk between the current PSII herbicides, knockdown herbicides and the alternative herbicides could be performed. Our preliminary data suggests that, provided that the alternative herbicides which are used for residual control in place of diuron are applied via a banded method, these alternatives pose no more of a risk than diuron. In addition, the findings for Objective 3 (below) suggest that if diuron was exclusively applied via banded spraying then it would be unlikely to exceed ecological protection guidelines in the Great Barrier Reef lagoon.

3. Determine the water quality benefits of improved practices to reduce pesticide runoff (shielded sprayers, banded sprayers etc.)

A trial conducted on an irrigated sugar paddock in the lower Burdekin showed that diuron and atrazine losses in drainage water could be reduced by 90% when they were applied to the raised beds only via the banded spraying technique. Previous studies using rainfall simulation methods suggested that losses of PSII herbicides in drainage water could be reduced by 50-60% when banded spraying was applied in rain-fed sugar cane systems. Further, spot spray trials showed that the losses of herbicides from a paddock reduced in proportion to the area sprayed. Our analysis suggests that if banded spraying technique was applied across the Great Barrier Reef catchment then ecological protection guidelines for PSII herbicides in the Great Barrier Reef lagoon would unlikely be exceeded at any time.

4. Ascertain the half lives in water and the exposure of key pesticides in the Great Barrier Reef catchment area and lagoon

The degradation half-lives of 8 common herbicides used in the Great Barrier Reef catchment area, which have been detected in the lagoon, were measured in seawater using standard procedures. The results show that the herbicides tested (the 6 common PSIs, as well as metolachlor and 2,4-D) have half-lives in seawater ranging from months to years, which explains the findings from monitoring programs that have detected herbicides in the Great Barrier Reef throughout the year. Furthermore the results show there is little potential for herbicide degradation in flood plumes that typically occur over a few weeks of the year. This finding is important for herbicide risk modelling of as it supports the application of a simple linear relationship where herbicide concentrations measured at the end of rivers can be 'projected' into the Great Barrier Reef lagoon assuming dilution with seawater mixing.

Four sites along the Barratta Creek drainage system were monitored continuously for pesticide residues over a 2 year period. Barratta Creek constitutes one of the major upstream catchments and drainage lines in the watershed of the Bowling Green Bay Ramsar wetland. During this study period, two changes in the regulated use of diuron by the sugarcane industry were introduced by the Australian Pesticides and Veterinary Medicines Authority (AVPMA). This included (1) an announcement in November 2011 that diuron is not to be applied after December 2011 and (2) an announcement in November 2012 of a diuron 'no spray window' for the coming wet season. The program provided valuable data on the spatial and temporal trends in pesticide usage, concentrations of pesticides in the creek over the long term and responses to the regulation of diuron that occurred during the monitoring program. A total of 37 different pesticide residues (not including metabolites/degradation compounds) were detected in the Barratta Creek Complex during the 2 year research program, although a number of these residues were detected infrequently (< 5 occasions of the 27 deployments of passive samplers) and at seemingly low levels (i.e. below available ecological guidelines). While concentrations of diuron and atrazine residues decreased as they moved towards and into the estuary, they remained above ecological guideline values for approximately 6 months of the year even at the Ramsar wetland/estuarine site. The findings suggest that the second regulation of diuron (i.e. a no spray window) was much more effective than the first regulation.

5. Tebuthiuron management in grazing lands

This project examined the movement of tebuthiuron in runoff and in soil from Brigalow lands at the plot (1.7 m²) and paddock (127,000 m²) scales. The results show that while no runoff event lost more than > 0.5% of the total applied tebuthiuron, mean concentrations in runoff up to 472 days after application always exceeded the current ecological protection guidelines (95% guideline = 2.2 µg.L⁻¹). The greatest event mean concentration detected was 105 µg.L⁻¹, which occurred 100 days after application. These data also indicate that tebuthiuron was largely transported in the dissolved phase. The research at the plot scale indicated how tebuthiuron moved through the soil profile driven by rainfall, with consistent decrease in soil concentrations from ~98 days after application. The results from this study could be up-scaled to estimate tebuthiuron loads from the Fitzroy River catchment which showed that there was reasonable agreement between monitoring and modeling of loads for this catchment.

6. Partitioning of pesticides in agricultural lands

The partitioning of pesticide residues in runoff (i.e. dissolved versus particle phases) were examined at a range of spatial scales from rainfall simulator plots ($< 3 \text{ m}^2$) up to catchment (14,700,000 ha) scale. At the plot scale, the results agreed with literature mobility values where pesticides with high mobility properties were largely transported in the dissolved phase while those with relatively low mobility were transported predominately attached to particulate matter. The findings at the larger sub-catchment and catchment scale sites showed that the pesticides detected were mainly transported in the dissolved phase. These results will allow improved modelling of pesticides throughout the Great Barrier Reef catchment and have provided valuable information to predict the fate of pesticides in the Great Barrier Reef lagoon.

7. Pesticide management in bananas

The surface runoff and deep drainage loss potential of three pesticides in common use in the Banana industry were examined at a banana plot at the South Johnstone Research Station over three years. The findings showed that the two herbicides analysed (glyphosate and glufosinate) could be detected in surface runoff and glyphosate was also occasionally detected in deep drainage. Indeed, glyphosate could be detected in both surface runoff and deep drainage following application 6 months earlier. The fungicide mancozeb was below detection limits throughout the monitoring program in both surface runoff and deep drainage samples. This research provided valuable data on the runoff potential of pesticides used the banana industry and an indication of their offsite risk to receiving waters.

Conclusions and future work

The collected work from this research package on pesticides in the Great Barrier Reef has delivered key outcomes relating to our understanding of their properties (i.e. half-lives, partitioning between dissolved and particulate phases); their potential to be lost in surface runoff and deep drainage; their ability to be managed on farm to reduce losses and; their overall risk in the Great Barrier Reef catchment and lagoon. Collectively, the outcomes allow improved modelling of several pesticides used in the Great Barrier Reef under the Paddock to Reef Integrated Monitoring, Modelling and Reporting Program. The projects examined sites within the main agricultural lands in the Great Barrier Reef catchment area including sugar cane, bananas, grazing and broadacre crops.

Opportunities for further work include improving our assessment of toxicity to better understand the relative risks of different pesticides in the Great Barrier Reef; conducting further paddock-scale trials to examine pesticides that were not examined during these studies and to better understand changes in relative risk with timing between application and rainfall/runoff; testing of half-lives of other key pesticides in seawater; follow-up monitoring of the Barratta Creek system to examine if the pesticide profiles change over time; replicating the tebuthiuron research and examining its runoff behaviour in other soil types and catchments; examining the partitioning (dissolved versus particulate) of pesticides across a range of different soil types and; further examination of pesticide losses in banana lands under different application scenarios and for different products.

Objective 1: Soil half lives

Executive summary extracted from Shaw, M., Silburn, D.M., Rojas-Ponce, S., Lewis, S.E., Davis, A., (2013). Herbicide degradation on Queensland cropping soils and crop residue

Half-lives measured in a controlled environment. Report to the Department of National Resources and Mine.

Herbicides applied in the cropping industries in Queensland are regularly detected in waters flowing to the Great Barrier Reef (GBR) and Reef Plan (Anon, 2013) sets targets for the reduction in loads of 'priority' herbicides by 2018. Progress towards these targets is assessed through the Paddock to Reef Integrated Monitoring, Modelling and Reporting Program (P2R) which includes modelling from farm scale to end of system loads. 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, however, there are currently limited data available to inform prediction of the fate of herbicides in a tropical environment. The objective of this study was to provide measured half-lives for herbicides on Queensland cropping soils and crop residue to improve modelling of herbicide fate in the GBR catchment.

Half-lives of commonly applied herbicides in cane, grains and grazing industries in Queensland have been compared in a controlled environment on common cropping soils. Cropping soils were collected from the tilled layer (0-0.1 m) from nine sites in Queensland to represent a range in textural properties and pH. Cane crop residues (trash) were also collected. Soils were kept moist using capillary rise from a hanging water column and were placed in a temperature controlled glasshouse. Following herbicide application, surface samples were collected over a period of 100 days to track dissipation of the herbicides. Half-lives have been calculated for fourteen herbicides including those considered to be high 'priority' under Reef Plan (Anon, 2013) (atrazine, ametryn, diuron, hexazinone and tebuthiuron) and alternative residual products which are being used with increasing frequency in Queensland (isoxaflutole, imazapic, pendimethalin, trifloxysulfuron, S-metolachlor, metribuzin). Three commonly applied knockdown herbicides, 2,4-D, glyphosate and paraquat, were also included in the study. Preliminary results from this study are reported here.

Half-lives were found to range from 12 days for atrazine on the Ferrosol (WAK) to >744 days for paraquat on a heavy Vertosol (MAK). The half-life values were comparable to international database and literature values from tropical field studies for well-studied herbicides including atrazine and ametryn. However, half-lives for several herbicides that have not previously been reported under local conditions (imazapic, pendimethalin, trifloxysulfuron) were on average 2.5-6 fold faster than international database values (PPDB, University of Hertfordshire). For example, the mean half-life of imazapic was 37 days (ranging from 20-81) which is approximately 6 fold shorter than reported in the PPDB. In contrast, the degradation rate of isoxaflutole was >10 fold slower than PPDB values. Half-lives for all herbicides on cane residues were slower than has been previously reported, which may be due to the effects of herbicide washoff in field studies and to limited photodegradation in the current study.

Half-lives varied by less than a factor of 2 between soils for the herbicides atrazine, 2,4-D and isoxaflutole whereas half-lives for diuron varied by a factor of 14. Total organic carbon

was found to be a significant explanatory variable for predicting degradation rates for many of the herbicides in this study. Further analysis of the data is required to investigate the relationship between measured half-lives and soil properties to extend prediction of spatial variability in herbicide degradation for all soils in the GBR catchment.

Half-lives of herbicides in the controlled environment were compared to dissipation measured on several of these same soils in field trials. The lack of consistent trends between herbicide degradation rates observed in the field and those observed in the controlled glasshouse environment highlights the difficulty in isolating factors contributing to dissipation in a field scenario. Values derived in the current study can be considered to provide conservative estimates for the tested soil temperature and moisture conditions since loss processes including leaching, runoff, plant uptake and to some degree photodegradation have been excluded. Further, the half-lives derived in this study relate to the surface 2.5 cm of soil which is the depth relevant to extraction of herbicides into runoff. These values are more appropriate for use in agricultural soil water balance models where losses due to degradation are considered as a separate process to loss through runoff/leaching/plant uptake. Adoption of the half-life values from this study in the paddock to reef modelling program will improve prediction of herbicide losses under various management scenarios and therefore improve the prediction of loads of herbicides entering the GBR lagoon.

Objectives 2&3: Pesticides in sugar

Executive summary extracted from Lewis, S.E., Silburn, D.M., Shaw, M., Davis, A., O'Brien, D.S., Oliver, D., Brodie, J.E., Andersen, J.S., Kookana, R. Fillols, E., Rojas-Ponce, S., McHugh, J., Baillie, C. (2013) Pesticides in the sugarcane industry: an evaluation of improved management practices. Report to the Reef Rescue Water Quality Research & Development Program. Reef and Rainforest Research Centre Limited, Cairns (28pp.).

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

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

The relative risk analysis suggests that, for the herbicides examined in the rainfall simulation trials, the alternative/new herbicides have a generally lower risk than diuron. However, trifloxysulfuron sodium (Krismat), s-metolachlor (Dual Gold, more toxic than metolachlor) and the metabolite of isoxaflutole (Balance) (DKN) need further analysis before we can have full confidence in these results. Additional Great Barrier Reef toxicity data would also help confirm our model. This preliminary analysis suggests that provided the residual herbicides are applied with banded/shielded sprayers on the raised bed or hill (50 to 60% less than what would be applied as a broadcast application), residual herbicides can be adequately managed in the sugarcane industry with far less impact on the Great Barrier Reef.

Objective 4: Water half-lives and Barratta Creek exposure study

Executive summaries extracted from

- Negri, A.P., Mercurio, P., Flores, F., Mueller, J.F. (2013) *Pesticide dynamics in the Great Barrier Reef catchment and lagoon: grazing, bananas and grain. Herbicide persistence in the marine environment. Report to the Reef Rescue Water Quality Research & Development Program. Reef and Rainforest Research Centre Limited, Cairns (18pp.) and*
- O'Brien, D.S, Lewis, S.E., Davis, A., Gallen, C., Paxman, C., Smith, R., Warne, M., Mueller, J., Brodie, J.E., (2013) *Pesticide exposure within the Barratta Creek*

Catchment. Report to the Reef Rescue Water Quality Research & Development Program. Reef and Rainforest Research Centre Limited, Cairns)

Runoff containing pesticides from agricultural land is recognised as a potential threat to inshore habitats of the Great Barrier Reef (GBR), with the photosystem II (PS) herbicides, including Diuron and Atrazine being the most frequently detected pesticides marine waters of the GBR. These herbicides act by inhibiting photosynthesis in terrestrial weeds and can impact non-target marine species including corals and seagrass in the same way. The potential for pesticides to move from paddock to the reef depends on their individual properties, including their persistence and solubility. Understanding the persistence of herbicides is critical to better parameterize and validate predictive risk models and to better inform the management of application methods and rates of pesticides in the GBR catchments to reduce runoff.

This was the first study to quantify the seawater persistence of priority herbicides detected in the GBR lagoon. Standard Flask Experiment 1A revealed extremely slow degradation of Diuron, Atrazine, Hexazinone, Tebuthiuron, Simazine, and Ametryn in the absence of light and sediments, with all herbicides exhibiting half-lives of between 657 and 1016 days. Experiment 2 was conducted in outdoor ponds with unfiltered coastal water and treatments included the presence and absence of light and sediments. These conditions more closely mimic coastal habitats in the GBR lagoon than flask experiments in incubators. Under the most environmentally relevant conditions (light + sediments) the order of persistence was Metolachlor (half-life, $t_{1/2}$ = 32 d) < Atrazine (107 d) < Diuron (139 d) < Hexazinone (201 d) < 2,4-D (288 d) < Tebuthiuron (944 d). The presence of coastal sediments consistently reduced the persistence (1.1 – 6.3-fold) of herbicides, especially in moderate sunlight. Moderate sunlight also reduced the persistence of Diuron, Atrazine, Hexazinone, Tebuthiuron and Metolachlor in the presence of sediments. 2,4-D was a notable exception and was far more persistent in the light. Changes in persistence were most likely due to the influence of light and sediments on microbial populations.

The long persistence of herbicides in seawater in the pond, Experiment 2, demonstrates that negligible herbicide degradation is likely in flood plumes lasting for weeks and that herbicides reaching the GBR lagoon may persist there for many months to years. These results help explain the year-round detection of herbicides in the GBR lagoon. This reliable persistence data for priority herbicides detected in the GBR lagoon is now available to managers, regulators and industry to enable (in combination with exposure and toxicity data) more effective and targeted management of these agricultural contaminants and develop more accurate spatial risk assessment models for coral reefs and seagrass beds of the GBR. Further work is needed to quantify the fate of dozens of other herbicides, fungicides and insecticides, as well urban and industrial contaminants detected in the GBR lagoon.

Barratta Creek constitutes one of the major upstream catchments and drainage lines in the watershed of the Bowling Green Bay Ramsar wetland. The Barratta Creek catchment has been considerably altered following the development of the Burdekin-Haughton Water Supply Scheme (BHWSS) in the late 1980s, which led to the establishment of perennial flow within the creek after it became the main distributary channel for irrigation tailwater runoff. As such, pesticide concentrations within the creek prior to the undertaking of this project were elevated compared to most streams of the Great Barrier Reef catchment area. This project initially proposed a 12 month monitoring program at four sites within the Barratta

creek system. Additional resources were obtained and the project was continued for an additional twelve months so that at the conclusion of the monitoring program, 24 months of continuous monthly pesticide monitoring had been undertaken. During this study period, two changes in the regulated use of diuron by the sugarcane industry were introduced by the Australian Pesticides and Veterinary Medicines Authority (AVPMA).

A total of 37 different pesticide residues (which does not include metabolites of some of these pesticides) were detected in the Barratta Creek Catchment during the two year research program, although a number of these residues were detected infrequently (< 5 occasions of the 27 deployments) and at low concentrations (i.e. below available ecological guidelines). Since pesticide usage data are unavailable in the upstream catchment area, this research program provides valuable insights on the pesticides in common use in this region. Moreover, long-term programs provide insights into changing patterns in pesticide usage. This study found increasing levels of metribuzin and metolachlor in Barratta Creek which likely reflects the wider adoption of these 'alternative' herbicides to diuron and atrazine in the lower Burdekin region. The herbicides diuron and atrazine regularly exceeded ANZECC and ARMCANZ (2000) ecological protection guidelines for several months (five to seven months of the year) at all four sites including in the Ramsar wetland in Bowling Green Bay. While concentrations of both atrazine and diuron progressively decrease towards the lower reaches of the Creek system (e.g. in the Ramsar wetland site concentrations were approximately a third to a half of the values measured at the upper site), they still exceeded the 99% species protection value for six months of the year.

The change in the types of pesticides and their concentrations detected throughout this monitoring program has provided a valuable record of the pesticides employed by the local industry and how the usage of pesticides by the industry has changed in response to regulatory action. As such it is advisable that the monitoring of pesticide residues within the Barratta Creek is continued. This monitoring program will ensure that any future changes in pesticide usage are captured so that pesticides used by local industries are not being transported into the receiving environments at concentrations likely to put valuable species or ecosystems at risk.

Objective 5: Tebuthiuron in grazing

Executive summary extracted from Thornton, C. M. and Elledge, A.E. (2013) Pesticide Dynamics in the Great Barrier Reef Catchment and Lagoon: Management Practices (Grazing, Bananas and Grain Crops) and Risk Assessments (Project RRRD038). Tebuthiuron Management in Grazing Lands (Subproject 2). Report to the Reef Rescue Water Quality Research and Development Program. Reef and Rainforest Research Centre Limited, Cairns (25 pp).

The Brigalow Belt Bioregion of Queensland has been extensively cleared for agriculture, with the majority of cleared areas being utilised for grazing (Thornton and Elledge 2013). If left uncontrolled, the proportion of woody species in grazed pastures increases over time, leading to a decrease in pasture productivity (Burrows 2002, Scanlan 2002). This productivity decline has negative implications for both the environment and the viability of grazing enterprises. In order to avert productivity decline, the regrowth of woody species in grazed

pastures is typically controlled by either mechanical intervention, such as blade ploughing or stick raking, or by the use of herbicides, such as tebuthiuron (Partridge *et al.* 1994).

Under Objective 1 of Reef Plan 2009 (Department of the Premier and Cabinet 2009), tebuthiuron is one of the five priority herbicides identified as main pollutants in water entering the Great Barrier Reef lagoon. A literature review of tebuthiuron research in Australia found 12 published papers; six of which focused on end of system water quality loads and concentrations at the basin scale (>10,000 km²) with little focus on process understanding. Thus, this study sought to examine the movement of tebuthiuron in runoff at both the plot (1.7 m²) and paddock (12.7 ha) scales, in addition to movement in soil.

At the paddock scale, runoff 100 days after application showed high concentrations of tebuthiuron (mean 103 µg/L); 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%. The highest loss was associated with the highest discharge runoff event. Comparison of individual event hydrographs showed that tebuthiuron concentrations declined exponentially with time. Furthermore, results indicated that tebuthiuron movement in runoff was in a dissolved form rather than being transported adsorbed to suspended sediments.

At the plot scale, maximum load of tebuthiuron in the soil from 0 to 5 cm deep occurred 28 days after application. This is likely due to the movement of tebuthiuron from trash into the soil following rainfall. Maximum loads in the soil from 5 to 20 cm deep occurred between 56 and 98 days after application. After 98 days tebuthiuron concentrations at all depths tended to decrease over time. Losses of tebuthiuron in runoff were greater from Vertosols than Sodosols.

This study has filled a significant knowledge gap about the behaviour of tebuthiuron at the plot and paddock scale, and provides data where none previously existed. The data also improves understanding of tebuthiuron behaviour from predominantly grazed catchments that discharge into the Great Barrier Reef lagoon. Limitations of this study are: (1) data were sourced solely from the Fitzroy Basin; (2) only Vertosol and Sodosol soil types were investigated; (3) investigation of persistence in soil was limited to particular profile depths and time intervals; and (4) runoff at the paddock scale was limited to 17 months data with only small runoff events immediately after application. These limitations could be easily addressed by replicating the plot components of this study on additional soil types in other Great Barrier Reef catchments. Opportunities also exist for replicating the paddock scale work in additional catchments of the Brigalow Catchment Study.

Objective 6: Partitioning of pesticides in agricultural lands

(Executive summary extracted from Packett, R., (2013) Project RRRD038 Pesticide dynamics in the Great Barrier Reef catchment and lagoon: management practices (grazing, bananas and grain) and risk assessments. Dissolved and particulate herbicide transport in central Great Barrier Reef catchments (Subproject 3). Report to the Reef Rescue Water Quality

Research & Development Program. Reef and Rainforest Research Centre Limited, Cairns (21 pp.))

Current best management practice in agriculture often involves reducing mechanical soil disturbance and increased use of chemicals to control weed growth. However, offsite transport of herbicides to the marine environment can impact on non-target species and ecosystems (Haynes et al. 2000; Jones et al 2003). In response to declining water quality in the Great Barrier Reef (GBR) lagoon the Reef Water Quality Protection Plan has been implemented (Reef Water Quality Protection Plan Secretariat, 2009). Major components of the plan are the GBR catchment event monitoring and modelling programs (Joo et al., 2012). The monitoring program does not currently differentiate between dissolved and particulate transport of herbicides and the modelling program is constrained by a lack of data for simulating exports of particulate bound fractions of herbicides to the reef lagoon.

A range of pesticides are used on agricultural lands in the Central Queensland region which includes the Fitzroy, Burdekin and Mackay Whitsunday, Great Barrier Reef catchments (Bainbridge et al., 2009a). The objectives of this project were to collect and analyse water runoff samples from agricultural lands at various scales to determine the percentage of herbicides transported in the dissolved and particulate phase. Sampling was undertaken at a range of scales from rainfall simulator plots (<3m²), farm, sub catchment and catchment (14,700,000 ha) scale. Water samples were collected during 2012 and 2013 specifically for partitioning analysis. Thirty six samples were collected from rain simulation trials on sugar cane plots in the Burdekin and Mackay Whitsunday catchments, and from rainfall simulation trials on grazing plots in the Fitzroy Catchment. Fifty eight runoff event samples were collected at farm, sub catchment and whole of catchment scales from cropping and grazing lands in the Fitzroy basin. Samples were analysed to determine the types of chemicals transported and the percentage of herbicide concentration being transported in the dissolved and particulate phase.

Results from rain simulation trials were in general agreement with data from the literature regarding mobility, a function of solubility and partitioning properties, for common herbicides. Those with low movement ratings tended to move off site with substantial percentages in the particulate phase, while those with high movement ratings were transported mainly in the dissolved phase. Catchment scale runoff events produced by natural rainfall resulted in minor particulate phase transport and major dissolved phase transport. The information gained will assist land managers to make informed decisions about the potential for offsite transport of different herbicide selections. The data produced by this study should also assist catchment modellers and model developers to more accurately represent the transport of herbicides from paddock scale through to the GBR lagoon. Future studies could investigate methods for collecting larger amounts of suspended sediments from flood waters for analysis. Filtering of larger (known) volumes of flood water would provide sufficient amounts of suspended sediments to help increase confidence in results from laboratory analysis. Further studies on half-lives and partitioning of chemicals in a range of soil types under controlled conditions are also suggested. This would allow for increased knowledge of *in-situ* partitioning of chemicals over time and the potential risk for runoff transport.

Objective 7: pesticides in bananas

(Executive summary extracted from Masters, B., Mortimore, C., Armour, J., and Lewis, S. (2013) Pesticide runoff and deep drainage in banana cropping. Report to the Reef Rescue Water Quality Research & Development Program. Reef and Rainforest Research Centre Limited, Cairns)

Pesticide runoff from agricultural lands has been recognised as a serious threat to the health and productivity of the Great Barrier Reef. In contrast to PSII herbicides (i.e. diuron, atrazine, hexazinone and ametryn) little is known about the rate and extent of movement of the herbicides commonly used in banana production (~11,000 ha). Two herbicides, glufosinate-ammonium (Basta) and glyphosate (and its breakdown product AMPA), and the fungicide Penncozeb 75DF (75% mancozeb), were monitored in runoff and deep drainage from a banana plot at South Johnstone from 2011-2013. Basta was applied to control weeds under the banana plant, and some inter-row grass control, whilst Glyphosate 450 was used to control grass cover in the inter-row only. Penncozeb 75 DF was applied for the control of yellow sigatoka. Surface water was collected during rainfall runoff events with an automated refrigerated pumping sampler, at an existing Paddock to Reef monitoring site. Deep drainage was collected on a weekly to fortnightly basis with a lysimeter system at a depth of 1 m beneath the banana rows.

Both herbicides were present in surface water runoff throughout both wet seasons. Event mean concentrations (EMC) of glufosinate (acid) in runoff in January 2012, one week after application, were 6.3 µg/L and then generally declined with time and rainfall to <0.5 µg/L by early March. They remained at <0.5 µg/L until the end of monitoring in late March. In next wet season, EMC values of glufosinate (acid) were 1.55 – 2.84 µg/L during a large runoff event that occurred 5 days after application. Glyphosate (EMC 0.1-2.5 µg/L) and its breakdown product, AMPA (EMC 1.3-6.3 µg/L) were detected in all runoff events. This was despite runoff occurring as long as 6 months after application. In deep drainage, glyphosate was detected (0.8-1.1 µg/L) on 2 occasions in the month following 700 mm of rainfall over 4 days in late January 2013. This was 6 months after application, and during this interval there was below average rainfall. The fungicide mancozeb was below detectable limits (< 5 µg/L) in runoff and deep drainage.

These findings have important implications to the management and use of these herbicides in banana cropping. The future direction of this research should consider continued monitoring of runoff and deep drainage over a range of seasons. Further information is required on:

- susceptibility glufosinate (acid) to runoff if applied outside the wet season;
- the release glyphosate into leachate;
- partitioning of glyphosate in runoff (dissolved vs particulate form); and
- whether the spray-out of crops with glyphosate (a common practice in many crops) results in losses in runoff.

Secondly, further research is needed on the dissipation of glyphosate in soils and plant matter, to understand the persistence of this herbicide, which was previously thought to be short-lived. This includes other industries that use glyphosate, e.g. sugarcane farming.