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MARINE MONITORING PROGRAM

Annual Report for **inshore pesticide** monitoring

2015 - 2016

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Front cover image: View south towards the Russell River National Park and the junction of the Russell and Mulgrave Rivers over flooded sugar fields © Dieter Tracey, 2015.

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Acronyms

Acronym	Detail
2,4-D	2,4-dichlorophenoxyacetic acid
ANZECC	Australian and New Zealand Environment and Conservation Council
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
%CV	per cent coefficient of variation
C_W	Concentration in water
DSITI	Department of Science, Information Technology and Innovation
EC_x	x per cent maximal effective concentration is observed
ED	Empore Disk™ passive sampler
GBRCLMP	Great Barrier Reef Catchment Loads Monitoring Program
GBRMPA	Great Barrier Reef Marine Park Authority
GC-MS	Gas Chromatography-Mass Spectrometry
GPC	Gel Permeation Chromatography
GV	Guideline value
IC_x	x per cent of the maximal inhibitory concentration is observed
IWL	Interim working level
K_{OW}	Octanol-water partition coefficient
LC_x	x per cent of the lethal concentration is observed
LC-MS/MS	Liquid Chromatography-tandem Mass Spectrometry
LOD	Limit of Detection
LOR	Limit of Reporting
MCPA	2-methyl-4-chlorophenoxyacetic acid
MMP	Marine Monitoring Program
ms-PAF	Multisubstance - potentially affected fraction
NOEC	No Observed Effect Concentration
PDMS	Polydimethylsiloxane passive sampler
PFM	Passive/Plaster Flow Monitor
PSII-HEq	Photosystem II Herbicide Equivalent Concentration
PTFE	Polytetrafluoroethylene : Common brand name - Teflon
PWG	Pesticide Working Group
QAEHS	Queensland Alliance for Environmental Health Sciences (formerly Entox)
QA/QC	Quality Assurance/Quality Control
QHFSS	Queensland Health Forensic & Scientific Services
RPF	Relative Potency Factor
RWQPP	Reef Water Quality Protection Plan
SDB-RPS	Poly(styrenedivinylbenzene) copolymer – reverse phase sulfonated
SOP	Standard Operation Procedure
SSD	Species sensitivity distribution
TEF	Toxic Equivalency Factor

Note that throughout this report the term **pesticide** is used to refer collectively to the group of **insecticides, herbicides and fungicides**.

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About the MMP: The MMP is a water quality and ecosystem health long-term monitoring program in the Reef lagoon to track the effectiveness of the Reef Plan. This project is supported by the Great Barrier Reef Marine Park Authority (GBRMPA), through funding from the Australian Government's Caring for Our Country.

1. Executive Summary

Declining water quality as a result of land-based activities and run-off from adjacent catchments has been identified as one of the key threats to the long-term health and resilience of the Great Barrier Reef (the Reef). Sediment, nutrients and pesticides in run-off plumes reaching nearshore marine ecosystems, which are home to sensitive seagrass beds and coral reefs, may have adverse effects on the viability of marine plants and animals in these systems. The Reef Water Quality Protection Plan (Reef Plan, 2013) is a collaborative program designed to improve water quality in the Reef though improved land management practises in the adjacent catchments. In 2015-16, QAEHS carried out water quality monitoring in the nearshore marine environment of the Great Barrier Reef Marine Park as part of the Marine Monitoring Program (MMP) under Reef Plan (2013). The key objectives of the project were to monitor and assess trends in water quality (i.e. concentrations of pesticides) against water quality guidelines, and link nearshore pesticide concentrations with end-of-catchment pesticide loads discharged from rivers into the Reef lagoon.

In 2015-16, a combination of two different sampling techniques (passive and grab sampling) were utilised to monitor spatial and temporal trends in pesticide concentrations. Pesticides in these monitoring activities included photosystem II (PSII) inhibiting herbicides (such as ametryn, atrazine, diuron, hexazinone and tebuthiuron), which are commonly detected in catchment monitoring due to their heavy usage in Reef catchments in the sugar cane, horticulture and grazing industries. In recent years, other pesticides in addition to the traditional five high-usage PSII herbicides (which include pre- and post-emergent 'knockdown' herbicides) are being increasingly adopted by industry, and subsequently are also commonly detected in monitoring activities. Pesticide levels are reported here as concentrations detected (ng L^{-1}), and as PSII herbicide equivalent concentrations (PSII-HEq) (ng L^{-1}) (a measure of the ecotoxicity of PSII herbicide mixtures). PSII-HEq concentrations are assessed against an index from Category 5 (no reported effects) to Category 1 (demonstrated empirical effects on the growth and death of aquatic plants and animals exposed to the pesticide). An alternative ecotoxicity measure, the multisubstance – potentially affected fraction (ms-PAF), was assessed as part of a case study.

Passive samplers, which provide a time-averaged estimate of pesticide concentration over one to two month periods, were deployed at eleven fixed monitoring sites located in four Natural Resource Management regions (the Wet Tropics, Burdekin, Mackay Whitsunday and Fitzroy). Five of these sites have been continuously monitored for between seven to eleven years. To build direct linkages between land-based activities and marine ecosystem health, as well as identify the potential exposure risks in regions of known high pesticide use, five new monitoring sites were established in the previous monitoring year and one new site in the current year. These recent sites provide pesticide concentration information in areas where seagrass, coral reef and catchment monitoring activities are also being conducted. To assess potential exposure to terrestrial run-off entering the Reef lagoon, grab sampling was also conducted during periods of high freshwater river discharge. Grab samples provide a point-in-time snapshot of concentrations. Samples were collected during the wet season along transects extending from two rivers in the Wet Tropics region and at two adjacent river mouth areas within the Mackay Whitsunday.

As part of the Driver-Pressure-State-Impact-Response (DPSIR) framework, a range of pressures have been identified that influence the levels of pesticides discharged to the Reef lagoon. These include total runoff (quantified as end-of-catchment pesticide loads), annual rainfall, river discharge and cyclonic activity. 2015-16 was generally a 'low-pressure' year for pesticide discharge, with rainfall and river discharges generally below the long-term annual averages (rainfall ranged from average to well below average across all catchments and there was no cyclone activity). Catchment pesticide loads were similar to 2014-15 levels across most catchments and were generally at the lower end of reported annual loads since monitoring began. Consistent with low level pressures in 2014-15 and 2015-16, time-averaged pesticide concentrations

at fixed marine monitoring sites were, at most sites, similar to the previous monitoring year. Overall, concentrations were lower than levels during past 'high' pressure La Niña years when rainfall and cyclonic activity were considerably above long-term averages. There was one notable exception to this trend at Round Top Island in the Mackay Whitsunday region. Pesticide concentrations at Round Top Island were elevated across most of the wet season and the maximum concentrations were the highest since monitoring began (2005). Concomitant with these high levels, there were minor guideline value (GV) exceedances for three pesticides, diuron, imidacloprid and chlorpyrifos. Diuron and imidacloprid exceeded the proposed marine GVs developed by the Department of Science, Information Technology and Innovation, (DSITI) (430 and 33 ng L^{-1}, respectively). Chlorpyrifos exceeded the ANZECC trigger value (0.5 ng L^{-1}). Only incomplete historical monitoring data are available for Round Top Island from one previous year (2014-15) for comparison purposes. Further monitoring is required to establish whether this is an ongoing pattern at this site.

A range of PSII herbicides and other pesticides were detected at all monitoring sites in 2015-16. In line with previous monitoring years, diuron, atrazine and hexazinone were the most frequently detected and abundant of the pesticides at most sites. Maximum concentrations of these three herbicides (462, 245 and 72 ng L^{-1}, respectively) occurred at Round Top Island, and this profile is consistent with pesticide usage by the sugar cane industry in the adjacent catchment. Whilst diuron dominated the pesticide profile at most sites, atrazine was the most abundant pesticide at Barratta Creek (Burdekin region) and Repulse Bay (Mackay Whitsunday). Tebuthiuron was almost exclusively detected at North Keppel Island (released from Fitzroy catchment). In response to increasing usage, the prevalence and loads of other (non-PSII) pesticides are being monitored alongside the PSII herbicides. The proportion of other pesticides in the total load released to the Reef lagoon is increasing. For example, in 2015-16, the load of other pesticides ranged between 26 – 181 per cent of the PSII load, compared to 12 – 21 per cent in 2012-13. Of the other pesticides, metolachlor, 2,4-dichlorophenoxyacetic acid (2,4-D), 2-methyl-4-chlorophenoxyacetic acid (MCPA), imidacloprid, chlorpyrifos and pendimethalin were frequently detected in passive samplers at fixed sites. Compared to PSII herbicides, detected concentrations of other pesticides at the monitoring sites were very low (typically sub ng L^{-1}).

In both the current year and historically, monitoring sites located in the Mackay Whitsunday region have encountered the highest risk of PSII herbicide exposure, reaching concentrations known to cause photosynthetic inhibition in some coral and seagrass species (Category 2 and 3 on the PSII Herbicide Index). At the other end of the scale, the Wet Tropics have consistently been at the low end of exposure risk. Grab sampling within both these regions indicated that elevated PSII herbicide concentrations were localised near river mouths and, through dissipation, decreased towards the fixed monitoring sites. This indicates a lower risk of exposure with increasing distance from the river mouth.

At present, only the PSII herbicides are included in risk assessments for the MMP using the PSII-HEq index. The PSII-HEq index, which is based on a limited number of species, estimates the cumulative toxicity of contaminants with the same mode of action, and has historically been used in the MMP for estimating the toxicity of PSII herbicide mixtures. Given the uncertainty of the risks posed by the other (non-PSII) pesticides, their inclusion in the MMP pesticide risk assessment is becoming increasingly important. The multisubstance - potentially affected fraction (ms-PAF) approach has the capacity to assess mixture toxicity of contaminants with both similar and different modes of action. The currently available ms-PAF model is a concentration addition (CA) model which estimates the cumulative toxicity for contaminants with the same mode of action; therefore, a case study comparing results of the PSII-HEq index and the ms-PAF CA model using the current year's monitoring data was undertaken. Both marine and freshwater species are included in the model's underlying SSDs for the current ms-PAF model. This reflects the intended application of the model for estuarine (mixed marine and freshwater) systems. Given a current paucity of marine ecotoxicity data, combining fresh and marine species data also ensures that sufficient data are included in the SSDs to meet statistical requirements.

The GVs proposed by DSITI for marine and freshwater ecosystems (which are based on the same species data as for the ms-PAF model) indicate that there are different toxicological responses of aquatic species between fresh and marine ecosystems. Of the most commonly detected PSII herbicides detected at the fixed (marine) monitoring sites, i.e. diuron, atrazine and hexazinone, proposed GVs are available for diuron and hexazinone. For these two herbicides, the marine GV is approximately 5-fold higher than the freshwater GV. This suggests that inclusion of freshwater species in the SSD may be a conservative approach (i.e. more protective of the Reef). At present, no SSD (and hence no proposed GV) is available for atrazine.

Based on the investigations in the case study, further consideration of the risk categories is warranted to capture the most ecologically relevant, reasonable and protective tipping points. At present, the ms-PAF CA model predicts a PC99 concentration for diuron, the most prevalent PSII herbicide measured in the near-shore Reef marine environment, of 46 ng L^{-1} which is an order of magnitude lower than the proposed marine PC99 guideline value (430 ng L^{-1}). Adoption of an ms-PAF model based on SSDs for marine-only species for the MMP would bring greater consistency between the mixture model and the individual SSDs from which proposed marine GVs are determined. An on-going (2016-2019) National Environmental Science Programme (NESP) project aims to generate marine species ecotoxicity data for this and other risk assessment purposes. Before adopting ms-PAF to assess overall ecological risk as part of the MMP's annual reporting, the value of waiting until a marine ms-PAF model can be established should be considered or a decision should be taken to adopt a lower, but therefore more conservative, PC99 value for MMP reporting. Furthermore, it would be pertinent to wait until proposed GVs have been approved, SSDs for all chemicals earmarked for inclusion have been constructed and the response addition (RA) model to assess pesticides with different modes of action is available, to prevent any retrospective adjustments and a more accurate assessment of risk of the environmental mixtures present. While the ms-PAF RA model has not been examined here (currently being tested by DSITI), the application of the RA and CA models together will be highly valuable for assessing the combined toxicity of both PSII herbicides and other pesticides in the future.

Conclusions and directions for future monitoring. In conclusion, overall, the DPSIR framework is an effective approach to understand the complexity of pressures that may result in pesticides reaching sensitive Reef ecosystems. In 2015-16, trends in the pesticide monitoring data could be broadly interpreted in terms of high level pressure data, mainly related to hydrological conditions; i.e. the relatively low pesticide concentrations observed at most fixed monitoring sites were consistent with the relatively low pressures affecting pesticide discharge to the Reef lagoon throughout the year. Spatially, consistent with previous years and land-usage in the adjacent catchments, highest pesticide concentrations were detected at the Mackay Whitsunday region sites. The longer-term change in nearshore marine pesticide levels attributable to changed catchment land management practices, which is the focus of the Reef Plan, is, however, statistically challenging to elucidate. Whether the predicted 34 per cent reduction in total pesticide loads across the Reef catchments is reflected in the nearshore monitoring data is unknown.

Given the high inter- and intra-annual climatic and other pressure variability, meaningful trend comparisons require long term and complete monitoring data. A particular focus for future years will be on finding new ways to minimise passive sampler losses and/or damage to achieve successful, consecutive deployments. Changes to the fixed sampling sites were introduced in 2014-15 following a review of the MMP programs. This means that over half of the current sites have only one or two years of continuous data. Pressures over the last two monitoring years have been relatively stable and longer-term data are required for these sites to understand how changes in pressures affect the observed pesticide concentrations. Temporal concentration data for catchment pesticide discharge to the Reef lagoon should also be considered, where possible, in future reports. This will allow a more direct, temporal comparison between end-of-catchment pesticide data for major flow events and the levels of pesticides reaching fixed monitoring sites.

The current pesticide metric, the PSII-HEq Index, was identified as a suitable interim risk indicator in the 2013/4 pesticide MMP review. However, the limitations with this metric are well recognised and ultimately, a pesticide metric that can assess ecological risk to marine Reef organisms from mixtures of pesticides with different modes of action is paramount. The current ms-PAF CA model is a step towards this goal and when development of the response addition model has been completed by DSITI, this will be a highly valuable and the recommended risk assessment tool. In the meantime, to avoid retrospective adjustments and maintain consistency in MMP pesticide risk assessment, it is proposed that the PSII-HEq Index continue to be used.

Future directions for monitoring activities under the MMP program include: continued advances in pesticide monitoring through new analytical methods and calibration of passive samplers to detect new and emerging pesticides; the use of statistical models to elucidate underlying trends in pesticide usage, independent of variability in river flow that can also cause spatial and temporal changes in pesticide levels; and preliminary investigations into a 'whole-of-system' approach to predict pesticide exposure using the eReefs framework.

2. Introduction

The World Heritage Great Barrier Reef covers an area of 348,000 km^2, extending 2,000 kilometres along Queensland's coast and from the low water mark along the mainland coast up to 250 kilometres offshore (UNESCO, 1981). Thirty-five major rivers within a combined coastal catchment area of over 400,000 km^2 discharge into the Great Barrier Reef lagoon (Brodie et al., 2003). As the largest living structure on Earth, the Reef supports a rich and diverse ecosystem of marine organisms including many endangered species and is recognised as having outstanding universal value (UNESCO, 1981, GBRMPA, 2014). The declining quality of water entering the Reef lagoon as run-off from activities on adjacent catchments has, however, been identified as a key pressure on the Reef's long-term health and resilience (Reef Plan, 2013). Poor water quality is one of several key pressures to the future resilience of the Reef that have been identified, which include climate change, crown of thorns starfish (COTS), coastal development, shipping and fishing (GBRMPA, 2014). The cumulative impacts from multiple pressures has the potential to further weaken the Reef's resilience which may affect its ability to recover from major disturbances, such as cyclones, COTS outbreaks, and the increasing number of significant coral bleaching events (Thompson and Dolman, 2010, De'ath et al., 2012).

Land use in the Reef's discharging catchments varies, being largely undeveloped in the far north, with agriculture, mining, shipping and urban development predominant in the central and southern regions. Approximately 76 per cent of the land is used for agriculture (including sugar cane, beef grazing, horticulture, cropping, pastures and cotton) (Smith et al., 2012). The range of land uses in this region results in point and diffuse sources of nutrients and pesticides from activities such as pest control (i.e. application of pesticides, including herbicides, insecticides and fungicides), sewage management, aquaculture, earthworks and fertiliser application. Run-off from these lands contribute to suspended sediments, nutrients and pesticides in rivers and other waterways which are released to the Reef lagoon during the wet season (Brodie et al., 2013, Waterhouse et al., 2013). The magnitude of releases is highly influenced by weather conditions and most run-off is delivered in short-lived flood events during the wet season, forming distinct flood plumes that sometimes disperse far into the lagoon (Devlin and Schaffelke, 2009).

Systematic monitoring has identified that pesticide contamination in the rivers, streams and estuaries that drain into the Reef marine environment has been widespread (Brodie et al., 2012), with the highest levels around Mackay (Brodie et al., 2013). In some cases, pesticide concentrations have been elevated above Australian and New Zealand Water Quality Guideline (2000) trigger values in catchments adjacent to intensive agricultural activity (Smith et al., 2012, DSITI, 2015, O'Brien et al., 2016). Modelling estimates in 2013 suggested that over 12 tons of pesticides may be introduced into the Reef annually (Waters et al., 2014) which can be distributed through the marine environment in the flood plumes (Devlin and Schaffelke, 2009). Overall, concentrations of pesticides in the marine environment compared to rivers are generally low (Devlin et al., 2015), due to processes such as dilution and degradation (Lewis et al., 2009). However, the chronic effects of low level pesticide exposure to corals and seagrass, especially in combination with other local and global pressures, remain poorly understood on the Reef (Brodie et al., 2013).

In response to concerns about the impact of land-based run-off on water quality, the 2003 Reef Water Quality Protection Plan (Reef Plan) was implemented by the Australian and Queensland governments (Reef Plan, 2003) and further updated in 2009 and 2013 (Reef Plan, 2009, 2013). Reef Plan's single long-term goal for the marine environment is "*to ensure that by 2020 the quality of water entering the reef from broadscale land use has no detrimental impact on the health and resilience of the Great Barrier Reef*" (Reef Plan, 2013). In 2015, a long-term sustainability plan for protecting and managing the Reef until 2050 was introduced (Commonwealth of Australia, 2015), of which Reef Plan is a key component. The Reef 2050 Long Term Sustainability Plan (LTSP; (Commonwealth of Australia, 2015)) is the overarching framework for integrated

management of the Reef which "*firmly responds to the pressures facing the Reef and will address cumulative impacts and increase the Reef's resilience to longer term threats such as climate change*".

Under Reef Plan (2013), governments are working with farmers and graziers to halt and reverse the decline in the quality of water entering the Reef by setting specific land and catchment management targets as well as water quality targets by 2018. These targets include a minimum reduction in end-of-catchment pesticide loads of 60 per cent (Reef Plan, 2013). The implementation of agricultural best management practice (BMPs) aims to reduce nutrient, sediment and pesticide runoff from agricultural land use; for example, based on the current estimates of BMP uptake in the GBR catchment area, the Source Catchment models indicate that a 34 per cent reduction in total pesticide loads across the Marine Park catchments should occur. This includes a 44 per cent load reduction in the Mackay region (Reef Water Quality Protection Plan Secretariat, 2016) where the highest pesticide exposure has been reported (Brodie et al., 2013, Reef Water Quality Protection Plan Secretariat, 2016).

To monitor the progress towards Reef Plan's (2013) and the 2050 LTSP's goals and targets, the Paddock to Reef Integrated Monitoring, Modelling and Reporting Program (Paddock to Reef Program) collects and integrates data and information on the paddock-catchment-marine environments adjacent to and within the Marine Park (Paddock to Reef, 2013). Progress is reported through annual Report Cards. One of the 10 inter-related components of the Paddock to Reef program is the Marine Monitoring Program (MMP), formerly Reef Plan MMP. The MMP covers the Reef inshore environment and is a collaborative effort between the Australian Government and several research groups. The program aims to assess long-term changes (trends) in the condition of inshore water quality, and link this to changes in the health of key inshore environments (coral reefs and seagrass) (GBRMPA, 2011). There are several indicators of inshore water quality, including sediment, nutrient and pesticide levels, and this current report provides information about the temporal/spatial trends in pesticide levels in the inshore Reef zone as well as in flood plumes. Separate reports under the MMP provide an assessment of other inshore marine water quality indicators and linkages between river discharge and pollutant concentrations to end-of-catchment loads (Waterhouse et al., 2017b), the coral cover and composition (Thompson et al., 2017) and seagrass health and extent (McKenzie et al., 2017).

The specific objectives of the pesticide monitoring component of the MMP are to:

- Monitor and assess trends in inshore concentrations of pesticides against water quality guideline values relevant to the Marine Park, and
- Link inshore concentrations of pesticides and their end-of-catchment loads.

The program methods and results in 2015-16 are presented in this report with temporal (historical monitoring data since 2005) and spatial (regional and Reef-wide) interpretation.

3. Methodology

3.1 Overview

Water quality monitoring was conducted at fixed (long-term) monitoring sites using passive sampling techniques: a time-integrated sampling technique that provides a time-averaged estimated concentration. These samplers accumulate chemicals into a sorbing material from water via passive diffusion. The passive sampling techniques which are utilized in this component of the MMP include:

- SDB-RPS Empore™ Disk (ED) polar passive samplers for relatively hydrophilic organic chemicals with relatively low octanol-water partition coefficients (log K_{OW}) such as the PSII herbicides (e.g. diuron).
- Polydimethylsiloxane (PDMS) non-polar passive samplers for organic chemicals which are relatively more hydrophobic (higher log K_{OW}) such as chlorpyrifos.

In addition to the long-term pesticide levels assessment, flood plume monitoring was conducted during the wet season using grab sampling techniques and incorporated relevant passive sampling data from the fixed monitoring sites. Full details regarding these methodologies have been described in the *Marine monitoring program quality assurance and quality control manual 2015/2016* (GBRMPA, 2016) and in previous reports (Kennedy et al., 2012, Gallen et al., 2013, Gallen et al., 2014, Gallen et al., 2016).

3.2 Study area and sampling sites

3.2.1 Fixed monitoring sites (passive samplers)

The scientific criteria for selection of sampling sites were updated following a review of the program in 2013 and 2014 (Kuhnert et al., 2015) and include:

- The site must be representative of an inshore reef location;
- The site is co-located in proximity to sites used by other MMP monitoring activities such as seagrass monitoring, as well as other agencies conducting related monitoring (e.g. GBR Catchment Loads Monitoring Program, DSITI);
- The site should not be impacted by specific local point sources such as anti-foulants from boats or inlets of treated or untreated wastewater;
- The sampling site is logistically feasible and can be maintained for a long period;
- The site is located adjacent to catchments that have been identified as high risk for exposure to pesticides (Brodie et al., 2013);
- The site must have adequate statistical power to detect trends in pesticide concentrations.

Based on these criteria, 11 inshore Reef sites were selected for the 2014-15 and subsequent monitoring programs, including five continuing long-term monitoring sites (Table 1). Passive samplers were deployed at all 11 sites in 2015-16, with five sites located in the Wet Tropics region, one site in the Burdekin region, four sites in the Mackay Whitsunday region and one site in the Fitzroy region (Figure 1). Sites were located within the extent of flood plumes from rivers that drain a variety of land uses on the adjacent catchment areas and discharge into the Reef lagoon (Table 1, Figure 1). Of the 11 sites monitored for pesticides, three (Low Isles, Dunk Island, and Sarina Inlet) are also seagrass monitoring sites within the MMP (McKenzie et al., 2017). Five sites (Low Isles, High Island, Normanby Island, Dunk Island and North Keppel Island) are in the vicinity of coral reefs that are monitored under the MMP (Thompson et al., 2017).

Table 1: Location of fixed passive sampling sites, closest influencing river and date that MMP sampling first commenced

NRM region	Basin	Major River/ Creek	Fixed site name	Sampled since
Wet Tropics	Mossman	Mossman River	Low Isles	Aug-2005
	Mulgrave-Russell	Mulgrave River/ Russell River	High Island	May-2015*
			Normanby Island	Jul-2005
	Tully	Tully River	Dunk Island	Sep-2008
	Herbert	Herbert River	Lucinda	Jul-2014
Burdekin	Burdekin	Barratta Creek	Barratta Creek mouth	Mar-2014
Mackay Whitsunday	Proserpine/ O'Connell	Proserpine River/ O'Connell River	Repulse Bay	Sep-2014
	Pioneer/ Plane	Pioneer River/ Sandy Creek	Round Top Island	Sep-2014
	Plane	Sandy Creek	Sandy Creek	Sep-2014
		Plane Creek	Sarina Inlet	May-2009
Fitzroy	Fitzroy	Fitzroy River	North Keppel Island	Aug-2005

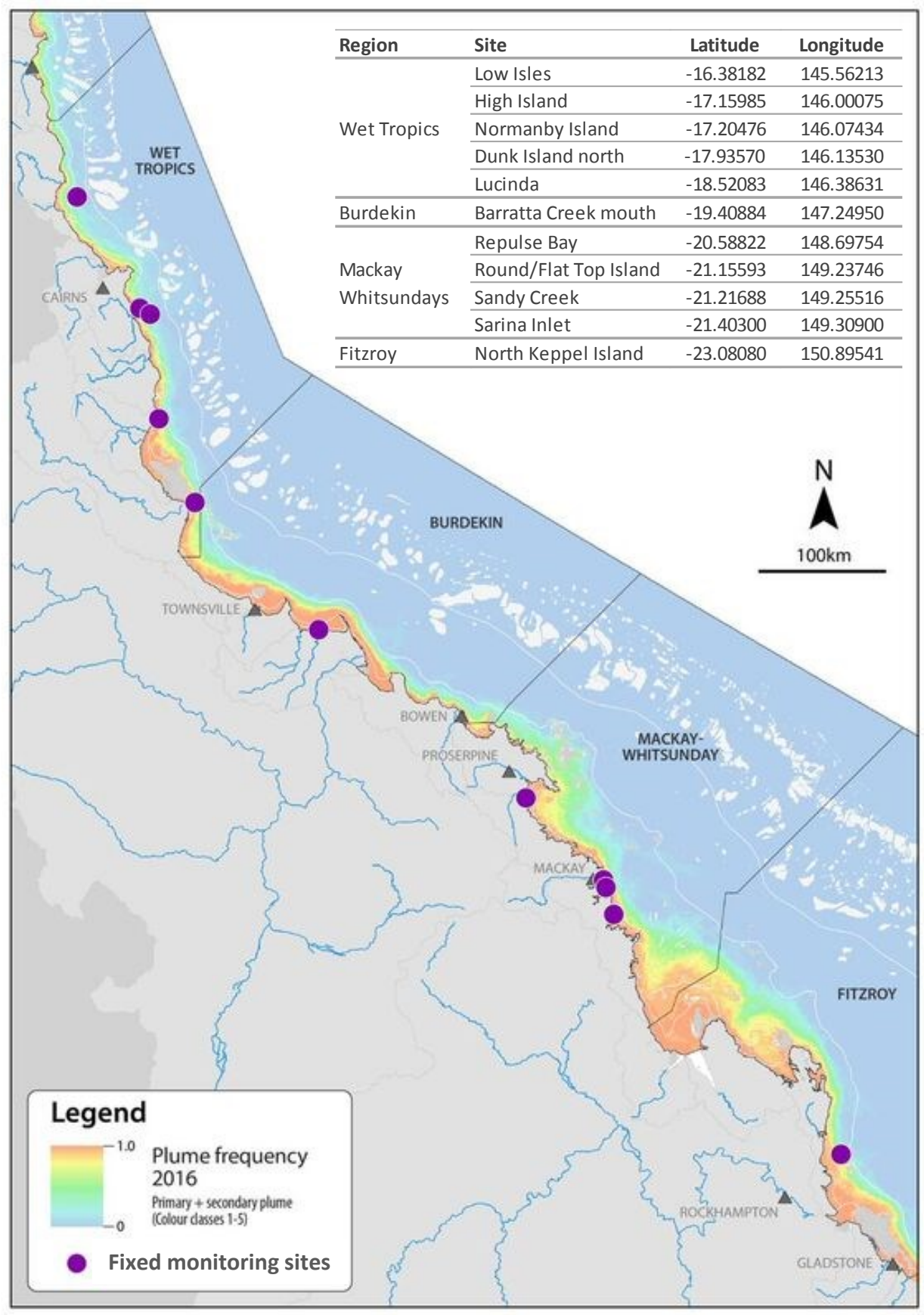
* High Island was reintroduced to the sampling program this year after its discontinuation in 2008.

The **Wet Tropics** region encompasses eight catchment areas, covering approximately 2.2 million hectares (ABS, 2010). Approximately 44 per cent of land is set aside as conservation and natural environment areas, however beef cattle grazing (30 per cent of total land use) and sugar cane (seven per cent of total land use) are the primary agricultural activities (DSITI, 2012b). Fixed sampling sites in the Wet Tropics region in 2015-16 were at Low Isles, High Island, Normanby Island, Dunk Island and Lucinda (Figure 1). Low Isles and Normanby Island have been monitored since 2005, Dunk Island since 2008 (once in 2007), and Lucinda since 2014. High Island was monitored in 2006-2008 and then discontinued until recommencing as part of the MMP pesticide program in the current year.

The **Burdekin** region spans five catchments and covers 14 million hectares, of which 90 per cent is used for agricultural purposes, with grazing primarily inland and some sugar cane and horticulture along the coast (ABS, 2010, DSITI, 2012c). The one sampling site in the Burdekin region in 2015-16 was at Barratta Creek mouth (Figure 2) which was established in 2014.

The **Mackay Whitsunday** region is the smallest NRM region, spanning four catchments with an area of approximately 900,000 hectares (ABS, 2010). This region is dominated by grazing, which comprises 30 – 60 per cent of the region's land use depending on the catchment basin, and the sugar cane industry, which comprises 6 – 50 per cent of the region's land use (DSITI, 2012e). Sampling sites in the Mackay Whitsunday region in 2015-16 were Repulse Bay, Round Top Island, Sandy Creek and Sarina Inlet (Figure 1). The Sarina Inlet site was established in 2009 and the remaining sites were established in 2014.

The **Fitzroy** region spans six catchments and covers an area of 15.6 million hectares (ABS, 2010). Cattle grazing is the most prevalent industry (78 per cent of the land use), with broad acre cropping (five per cent of the land use) and cotton farming also present (DSITI, 2012a). The only monitoring site in the Fitzroy region is at North Keppel Island (Figure 1). This site has been monitored since 2005 although it has had broken periods of sampling throughout some years.



Region	Site	Latitude	Longitude
Wet Tropics	Low Isles	-16.38182	145.56213
	High Island	-17.15985	146.00075
	Normanby Island	-17.20476	146.07434
	Dunk Island north	-17.93570	146.13530
	Lucinda	-18.52083	146.38631
Burdekin	Barratta Creek mouth	-19.40884	147.24950
Mackay Whitsundays	Repulse Bay	-20.58822	148.69754
	Round/Flat Top Island	-21.15593	149.23746
	Sandy Creek	-21.21688	149.25516
	Sarina Inlet	-21.40300	149.30900
Fitzroy	North Keppel Island	-23.08080	150.89541

Figure 1: Locations of current inshore Reef fixed monitoring sites where time-integrated sampling of pesticides occurred in 2015-16. Sites are overlaid on the 2015-16 flood plume frequency map (for more information see Section 3.5.5). Grey triangles indicate towns. (Source – Dieter Tracy, James Cook University)

3.2.2 Flood plume monitoring (grab sampling)

Terrestrial run-off assessments, i.e. flood plume monitoring, have been conducted in past monitoring years along transects extending from river mouths during discharge events in two or three NRM regions with a high risk from pesticide exposure. The locations and timing of the flood plume sampling changes annually, as it is largely event-driven and requires a rapid response. Flood plume sampling is also subject to sampling personnel safety and the availability of sampling vessels.

In 2015-16, flood plume monitoring was undertaken along transects extending from the mouths of two rivers in the Wet Tropics region – the Tully River and Russell-Mulgrave rivers (Table 2 and Figure 2). Both transects have been sampled in previous monitoring years, with the Russell-Mulgrave transect first sampled in 2013 and the Tully transect first sampled in 2010. In addition to the transects, grab samples were collected from two river mouths within the Burdekin focus area (Burdekin River and Barratta Creek) during two early season discharge events (Table 2 and Figure 2). These sampling sites are flood-response monitoring sites established by the JCU Inshore Marine Water Quality team.

Table 2: Sampling locations of grab samples for flood plume monitoring and relevant fixed (passive sampler) monitoring sites in the plume vicinity.

Transect	Sampling site	Sample type	Latitude	Longtitude
Russell-Mulgrave River	Russell-Mulgrave mouth	Grab	-17.2231	145.9688
	Normanby Island	Passive sampler	-17.2048	146.0743
	High Island	Grab	-17.1599	146.0008
	High Island	Passive sampler	-17.1599	146.0008
Tully River	Tully River mouth mooring	Grab	-18.0295	146.0609
	Bedarra Island	Grab	-18.0020	146.1414
	Dunk Island north	Grab	-17.9272	146.1416
	Dunk Island north	Passive sampler	-17.9272	146.1416
Burdekin River	Barratta Creek mouth	Grab	-19.4088	147.2495
	Barratta Creek mouth	Passive sampler	-19.4088	147.2495
	Burdekin River mouth 2	Grab	-19.6366	147.5973
	Burdekin River mouth 3	Grab	-19.7185	147.6226
	Burdekin River mouth mooring	Grab	-19.6440	147.6068

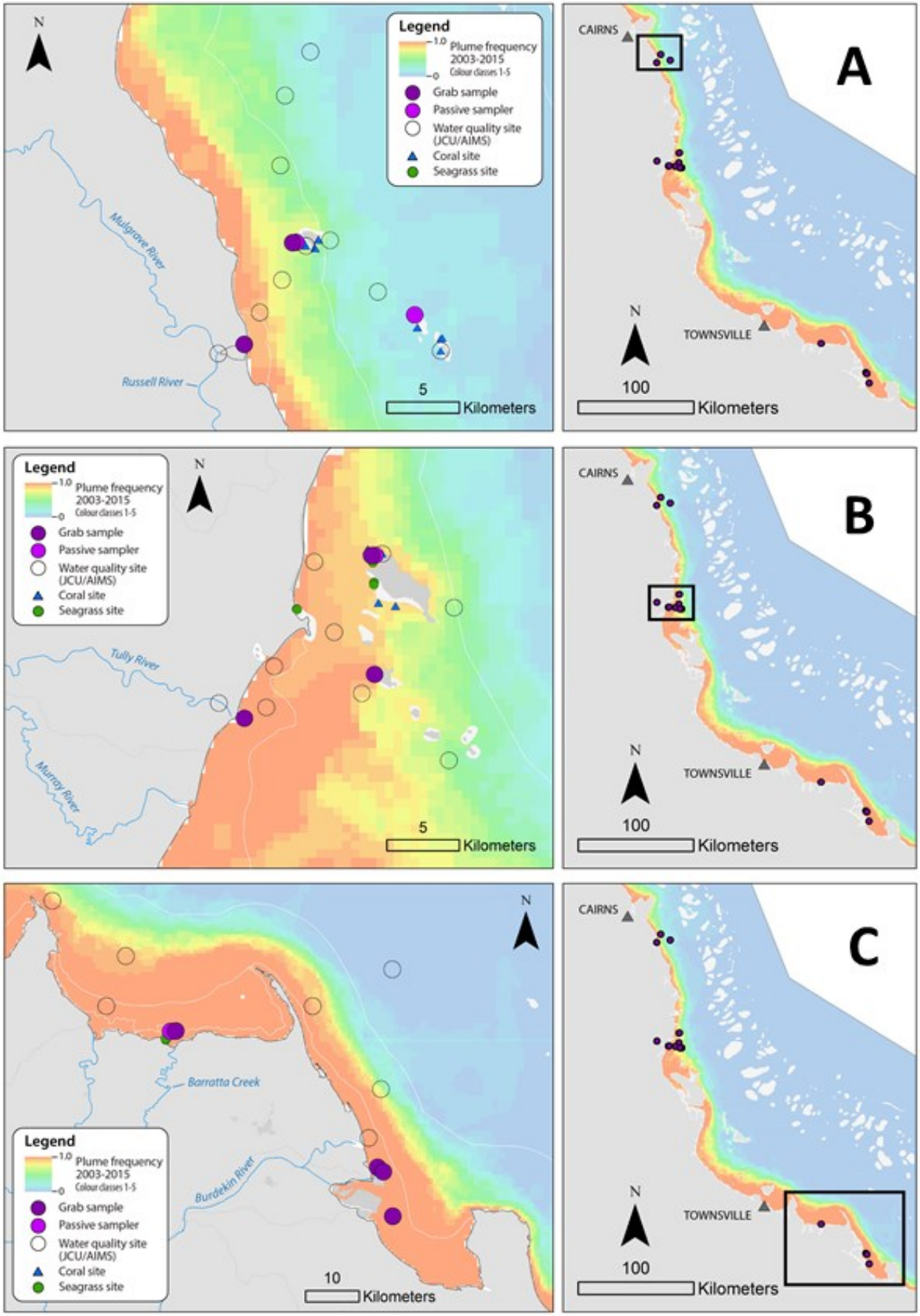


Figure 2: Locations of grab (flood plume monitoring) and passive samplers (fixed monitoring) collected on the (A) Russell-Mulgrave River transect, (B) Tully River transect, and (C) Barratta Creek/Burdekin River region. Sampling sites are overlaid on a colour-scale representing the frequency of flood plumes for 2003-2016. The water quality/coral/seagrass sites relate to other MMP program monitoring sites (see (McKenzie et al., 2017, Thompson et al., 2017, Waterhouse et al., 2017b). Maps provided by Dieter Tracey, James Cook University (JCU).

3.3 Sampling approaches

Full details of the techniques for passive and grab sampling are given in the *Marine monitoring program quality assurance and quality control manual 2015/2016* (GBRMPA, 2016). An overview of the sampling periods and types of samples collected is given below.

3.3.1 Passive sampling (fixed monitoring sites) to establish long-term trends

Pesticide monitoring at fixed monitoring sites is reported for the year to 30 April 2016. The year is divided into "Dry 2015" (May 2015 to October 2015) and "Wet 2015-16" (November 2015 to April 2016) sampling periods for reporting purposes. During dry sampling periods, passive samplers are typically deployed for two months at a time (maximum of three deployment periods each monitoring year), and for one month at a time during wet sampling periods (maximum of six deployment periods within each monitoring year). The maximum number of samples obtained from each location in the monitoring year is nine.

All eleven fixed sites were monitored in both the Dry 2015 and Wet 2015-16 sampling periods using EDs (Table **3**), targeting polar pesticides (see Appendix A Table A-2 for a list of the polar pesticides in the passive sampler analysis suite). Four sites also had PDMS samplers deployed during the Wet 2015-16 sampling period (Table **3**), targeting non-polar pesticides (see Appendix A Table A-3 for a list of the non-polar pesticides in the passive sampler analysis suite). PDMS samplers were co-deployed with the EDs in the Lower Burdekin region (one site) and the Mackay Whitsunday region (three sites) (Table **3**). These two regions were chosen for targeting non-polar pesticides based on their high proportions of sugar cane land use relative to other NRM regions, and the high pesticide risk assigned to these regions (Brodie et al., 2013). The deployment dates and results for each fixed monitoring site are provided in Appendix F Table F-2 to Table F-12.

Table 3: The types of passive samplers deployed at each fixed monitoring site in 2015-16.

Region	Site	EDs (polar)		PDMS (non-polar)	
		Dry	Wet	Dry	Wet
Wet Tropics	Low Isles	✓	✓	✗	✗
	High Island	✓	✓	✗	✗
	Normanby Island	✓	✗	✗	✗
	Dunk Island	✓	✓	✗	✗
	Lucinda	✓	✓	✗	✗
Burdekin	Barratta Creek Mouth	✓	✓	✗	✓
Mackay Whitsunday	Repulse Bay	✓	✓	✗	✓
	Round Top Island	✓	✓	✗	✓
	Sandy Creek	✓	✓	✗	✓
	Sarina Inlet	✓	✓	✗	✗
Fitzroy	North Keppel Island	✓	✓	✗	✗

3.3.2 Grab sampling to assess flood plume profiles

Sampling activities targeting discharge events from major Reef catchment rivers occurred during the Wet 2015-16 sampling period, and typically coincided with large rainfall events in the adjacent catchment area. Grab samples (250 mL) were collected along transects extending from river mouths to capture peak concentrations, assess the extent and gradient of pesticide concentrations in flood plumes, and establish the presence of any pesticides not adequately sampled by passive samplers (e.g. due to their high water solubility). In some cases, the transects coincided with fixed monitoring locations (Figure 2) to provide a complete pesticide profile over the discharge period that may be useful to compare against pesticide loads data.

A total of 24 grab samples were collected to monitor terrestrial run-off from the two river transects (the Tully and Russell-Mulgrave rivers) during five separate flood plume events between January and April 2016. A further nine grab samples were collected from the Burdekin focus area during both major discharge events in the Wet 2015-16 season. Further details for these samples including the date of collection and results for individual pesticides detected are provided in Appendix G Table G-1.

3.3.3 Sampler deployment and approaches for missing data

Samplers are cleaned, assembled and calibrated by QAEHS but are deployed in the field by a team of volunteers. The participation of volunteers from various community groups, agencies and tourist operations is a key feature of the long-term pesticide monitoring program and integral to the success of maintaining the program in often remote locations. Volunteers receive, deploy, retrieve and return the passive samplers to QAEHS for subsequent extraction and analysis. Volunteers are trained by the Great Barrier Reef Marine Park Authority (GBRMPA) and/or QAEHS staff in the Standard Operating Procedures (SOPs) for deploying and retrieving the passive samplers, ensuring high quality usable data.

Whilst every effort is made to deploy samplers in accordance with the proposed sampling schedule, there are circumstances every year where this is not possible. This may result in periods where passive samplers are not deployed (for example, during bad weather) or samplers are under- or over-deployed, i.e. the period the sampler is left in the water is less than or greater than the preferred period (2 months in dry season, 1 month in wet season). In addition, samplers are regularly lost in extreme weather events or are stolen or otherwise damaged. For periods of non-deployment, gaps between successful deployments are often up to 1-2 weeks at most and have minimum impact on the long-term trends. Longer periods of non-deployment or when samplers are lost can result in uncertainty in the representivity of the pesticide concentration data for that deployment season and, therefore, may affect the long-term trends (for example, when only one wet season sampler is successfully deployed in one year, but all 6 are deployed for previous years). This can make interpretation of long term trends challenging. Actual dates of deployment are given in Appendix F and average concentrations where only one sampler was received for that season are highlighted in the summary statistics tables in the Results section. Passive samplers are calibrated for an optimum deployment period and if they are over- or under-deployed, this reduces the confidence in the reported concentrations. If under-deployed, the amount of pesticide taken up into the sampler may be too low to be detected on the analytical instruments, resulting in a non-detect result when in fact the pesticide was present in the ecosystem. If over-deployed, the samplers may become saturated, violate the assumptions of pesticide uptake dynamics or become bio-fouled or otherwise contaminated in the field. In these cases, samplers are excluded from the analysis.

Passive samplers that show evidence of inappropriate storage during transportation that may lead to contamination (such as transport lids not attached or EDs returned dry) or damage during deployment (mud underneath membrane or severe biofilm that impedes water flow) are also excluded from analysis.

3.4 Pesticide analyses and reporting QA/QC (GC-MS and LC-MS/MS)

3.4.1 Target pesticides

The list of target chemicals originally derived at the commencement of the MMP through consultation with GBRMPA was based on the following criteria:

- pesticides detected in recent studies;
- those recognised as a potential risk;
- analytical affordability;
- pesticides within the analytical capabilities of Queensland Health and Forensic Scientific Services (QHFSS, who formerly conducted all analysis); and
- those likely to be accumulated using one of the passive sampling techniques (i.e. that exist as neutral species and are not too polar).

In 2015 in consultation with the Pesticide Working Group (PWG) and GBRMPA, the list of target chemicals was further expanded to include several other pre- and post-emergent herbicides (Appendix A Table A-4). The criteria by which these new target chemicals have been included are:

- registered for use in Reef catchments to supplement or replace the use of some traditional Photosystem II (PSII) herbicides;
- included in the suite for PSII end-of-catchment loads monitoring and catchment pesticide modelling programs conducted by other agencies (and thus better harmonisation across complimentary monitoring programs); and
- detected in recent studies and monitoring programs.

3.4.2 Instrument analyses and analytical quality assurance quality control (QA/QC)

Analysis of non-polar pesticides using Gas Chromatography-Mass Spectrometry (GC-MS) and polar herbicides using Liquid Chromatography-tandem Mass Spectrometry (LC-MS/MS) in passive samplers (PDMS and EDs) and grab samples was conducted at QAEHS. Further details are given in Appendix A Sample analysis was previously conducted by QHFSS. Inter-laboratory comparisons between QAEHS and QHFSS were conducted for two years for LC-MS analysis and one year for GC-MS analysis. No inconsistencies or bias emerged in the detection/non-detection and quantification of chemicals between the two laboratories (for details see Gallen et al. (2014), Gallen et al. (2016)).

QA/QC: Blanks were extracted and analysed with every batch of 12 samples. Most pesticides were below the limit of detection (LOD) in batch blanks. Where blank values were detected, sample concentrations in that batch that were less than 3 times the blank value were excluded from summary statistics and the PSII-HEq calculations and are shown with a "<" in the data tables in Fixed monitoring sites – sampler returns and individual site results. Analytical variability was tested by quadruplicate injections of 1 ppb calibration standard, and the median coefficient of variation for these replicates was 5.1% across all pesticides.

The LOD for the LC-MS/MS instrument data are defined as follows: the LODs are determined by adding a very low level of analyte to a matrix and injecting 9 times into the analytical instrument. The standard deviation of the resultant signals is obtained and a multiplication factor of 3 is applied to obtain the LOD. Values below the LOD are defined as non-detects (n.d.) in all tables in this report. The limit of reporting (LOR) is defined as 3 times the LOD. Values above 3 times the blank concentration are shown in the tables in this report in italics. Whilst there is some uncertainty regarding the accuracy of these relatively low concentrations, to be conservative, these values are included in summary statistics and PSII-HEq values and thus represent the worst-case scenario.

Variability in the overall performance (chemical uptake) of the EDs was tested by duplicate analysis of 16 ED samplers, and the mean coefficients of variation for these replicates ranged from 1.7% to 33%. Further details on QA/QC measures are summarised in the *Marine monitoring program quality assurance and quality control manual 2015/2016* (GBRMPA, 2016) and Appendix A Table A-1.

3.5 Data analyses and reporting metrics

3.5.1 Water quality guideline values (GVs)

A key aim of this program is to compare measured concentrations of pesticides and herbicides to current limits for chemicals in marine waters. Water quality in Australia is currently managed in accordance with the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ, 2000a). Trigger values are defined for a range of pesticides and an indication of the reliability of the value (low, moderate, high) is given (Appendix B Table B-1). The 2000 guidelines paid considerable attention to values derived using the assessment factor approach (Batley et al., 2014). For some pesticides, only freshwater guidelines or low reliability marine “interim working levels” (IWLs), e.g. for diuron, are available (ANZECC and ARMCANZ, 2000a). For several of the pesticides detected in this current monitoring year, no trigger values were available.

The use of species sensitivity distributions (SSDs) is the preferred method of deriving water quality guidelines (Warne et al., 2015). A SSD is a model of the variation in sensitivity of species in an ecosystem to a particular stressor and allows prediction of the percentage of species that is expected to be adversely affected at a given environmental stressor level (e.g. pesticide concentration). Under this approach, protective concentrations can be defined that typically offer four levels of protection: 99, 95, 90 and 80 per cent of species in the ecosystem being protected, referred to as PC99, PC95, PC90 and PC80, respectively (Batley et al., 2014). Using this approach, marine protective concentrations were derived by the Great Barrier Reef Marine Park Authority (GBRMPA, 2010) for tropical species (Appendix B Table B-1). These values were not proposed to be adopted as guidelines, but rather were published to provide concentrations to compare with ongoing monitoring data as part of Reef Plan (2009 and 2013). The Great Barrier Reef is considered as a high ecological value (HEV) ecosystem and, therefore, afforded the highest water quality protection level, i.e. protection of at least 99 per cent of species (PC99). This level of protection is judged the most suitable for this World Heritage Area, which is classified as having outstanding universal value and no change in the indicators of biological diversity beyond the natural variation is recommended.

The Australian and New Zealand water quality guidelines for freshwater and marine ecosystems are currently being revised to provide new guideline values (GVs) (previously termed trigger values) (Warne et al., 2015, DoE, 2016). Proposed GVs for 28 pesticides for freshwater and marine ecosystems, determined using SSDs, are being derived by the Department of Science, Information Technology and Innovation (DSITI) and will be submitted for consideration, national endorsement and inclusion into the Australian and New Zealand water quality guidelines (DSITI, 2017). If they are endorsed they will supersede the Water Quality Guidelines for the Great Barrier Reef Marine Park (GBRMPA, 2017).The proposed GVs for diuron in marine water (PC99, 95, 90, 80) have recently been announced based on ecotoxicity data for 20 marine phototrophic species belonging to six phyla and 11 classes and have been classified as very high reliability (King et al., 2017a) (Table B-1). Proposed GVs for 27 other pesticides, relevant to the current monitoring period, have also been derived and will be submitted for endorsement (Appendix B Table B-1).

For the purposes of this report, proposed GVs, trigger values and GBRMPA PC values are tabled in Appendix B and monitoring data are compared against the proposed GVs. Whilst these proposed values are still undergoing endorsement, adopting these proposed GVs is recommended in preference to any of the GVs or protective concentration values derived prior to 2017 (DSITI, 2017).

3.5.2 Comparison to end-of-catchment annual loads

One of the aims of this program is to link inshore concentrations of pesticides and their end-of-catchment loads. One approach to achieve this is to assess gradients in concentrations during flood plume events extending out from a river mouth into the Reef lagoon where fixed monitoring sites are located adjacent to sensitive coral reefs and seagrass beds (see flood plume monitoring, Section 3.2.2).

Annual pesticide loads are determined and reported through an ongoing monitoring program for major catchments discharging to the Reef under the Great Barrier Reef Catchment Loads Monitoring Program (GBRCLMP). Due to the timing of the MMP reporting cycle, the GBRCLMP information available to the MMP is a single annual load per catchment. In contrast, temporal (time integrated) pesticide concentrations are measured at the near-shore monitoring sites. Quantitative comparisons between the GBRCLMP load data and the pesticide concentration data at the monitoring sites are, therefore, not meaningful. Temporal end-of-catchment concentration data, reflecting the concentrations of pesticides being discharged with individual flow events, would allow correlations with the temporal marine monitoring data (also expressed as concentrations) to be investigated. In the absence of end-of-catchment temporal data, for the purposes of this report, qualitative comparisons of the types of pesticides discharge from catchments and observed at monitoring sites are performed (see Section 4.1.3).

3.5.3 Risk assessment metric – PSII herbicide equivalent concentrations

The risk of PSII inhibition to Reef species may be underestimated when concentrations of herbicides are considered individually rather than as part of a more complex mixture. In this report, PSII herbicide concentrations (ng L^{-1}) are also expressed as PSII herbicide equivalent concentrations (PSII-HEq) (ng L^{-1}). PSII-HEq concentrations are derived using relative potency factors (RPF) for each individual PSII herbicide with respect to a reference PSII herbicide, diuron (Appendix C Table C-3). The PSII-HEq concentration is the sum of the individual RPF-corrected concentrations of each individual PSII herbicide detected in each sample (either grab sample or passive sampler). RPF values for 8 PSII herbicides and 2 metabolites of atrazine have been previously determined based on the ecotoxicity response of five microalgal marine species (including zooxanthellae) and one freshwater microalgal species (see Appendix C). Also reported are the PSII-HEq Max values (the maximum PSII-HEq concentration detected at a given fixed monitoring site in a monitoring year) and PSII-HEq Wet Avg and PSII-HEq Dry Avg values (the average PSII-HEq concentration detected at a given fixed monitoring site during the wet and dry season, respectively). These values allow an assessment of the worst-case scenario of PSII herbicide exposure encountered during a monitoring year, the seasonal variation in the risk of PSII inhibition, and their trends over time.

To interpret data reported as PSII-HEq, the “PSII Herbicide Index” has been compiled (with GBRMPA). This Index defines ranges of PSII-HEq that equate with different levels of PSII inhibition (based on published toxicity data using Reef relevant species) (Appendix C Table C-4). Classifying the data generated in this MMP report based on these index categories provides an indication of the additive effects of PSII herbicides on marine flora, including sea grasses and algae, and coral zooxanthellae (see Appendix C for further information). The Index can quickly indicate the extent of PSII inhibition encountered at a given site (and its potential consequences), and provides a rapid indication of the duration and/or frequency that a site is exposed to elevated cumulative levels of PSII herbicides. A Category 1 classification (≥900 ng L^{-1}) is equivalent to exceeding the GBRMPA PC99 value for diuron (GBRMPA, 2010). It should be noted that the proposed marine GV for diuron for 99% species protection is 430 ng L^{-1} (King et al., 2017a) and so under the new guidelines, guideline exceedances may occur for both Category 2 (250-900 ng L^{-1}) and Category 1 PSII-HEq concentrations.

The PSII-HEq index was identified as a suitable indicator to detect changes in inshore pesticide levels over time based on a bootstrap simulation study using historical MMP data (Kuhnert et al., 2015). As part of this

review of the MMP, the authors recommended incorporation of this metric into the annual Reef Plan report card to assess progress against water quality targets (Kuhnert et al., 2015). Recently, Smith et al. (2016a) derived an alternative method to calculate RPF values (also referred to as toxic equivalency factors, TEFs) for calculating toxicity-based pesticide loads, which were calculated using matched datasets[1] and tests to maximize the environmental relevance and robustness of the TEFs. This approach was applied to derive Reef-specific TEFs for five priority PSII herbicides discharged to the Reef lagoon (ametryn, atrazine, diuron, hexazinone, and tebuthiuron) (Smith et al., 2016b). Despite being widely used and simple to calculate, a limitation of the current PSII-HEq method of risk assessment is that matched data sets should ideally be used to derive the relative potencies to a reference chemical (i.e. for each species tested, all PSII herbicides should be included in the same study to assess their toxicity relative to diuron). However, this seldom occurs and typically datasets are limited to only a few select compounds. This requirement for matched datasets dramatically reduces the amount of data suitable to derive relative potencies.

For consistency, the PSII-HEq values presented in this report are calculated using the RPF values used in previous years' reports. A comparison of the TEF values of Smith et al. (2016b) and our previously derived RPF values, and the concomitant PSII herbicide equivalent concentrations for the current year using the two different factors, is presented as part of the case study (Section 8).

3.5.4 Risk assessment metric – multisubstance-potentially affected fraction (ms-PAF)

The multisubstance-potentially affected fraction (ms-PAF) method (Traas et al., 2002) has been proposed as a more robust approach to quantify the overall ecological risk of mixtures of pollutants for ecological communities. The ms-PAF approach uses species sensitivity distributions (SSDs) from peer-reviewed ecotoxicity data published in the scientific literature or in reputable ecotoxicity databases such as the database published by the USEPA Office of Pesticide Program. SSDs are a well-documented method for estimating the adverse effects a concentration of a contaminant may have on an aquatic ecosystem, and are used in deriving water quality GVs. The approach is based on SSDs for all chemicals in a mixture and thus aligns more closely with the revised methods for proposed individual GV derivation, as well as the risk-based approach adopted by the Paddock to Reef program. The potentially affected fraction of species, i.e. percent of species in an ecosystem that will theoretically be affected at a given environmental mixture concentration, is considered an ecologically relevant assessment end point which better suits the goals of Reef Plan.

Unlike the HEq method, ms-PAF can account for both additive and non-additive interactions; i.e. it can determine a cumulative toxicity for a mixture of chemicals with the same toxic mode of action (e.g. for PSII inhibition, effects are assumed additive for all PSII-inhibiting herbicides in a mixture), but also for a mixture of chemicals with different modes of action (non-additive model). Non-additive interactions are an important consideration given the use of other pesticides with different modes of action in the Reef catchments.

In the previous monitoring year 2014-15, a case study reported interim ms-PAF values and ms-PAF Max values (the maximum ms-PAF value detected at a fixed monitoring site in a given monitoring year) for five priority PSII herbicides using SSDs provided by DSITI. Since then, the ms-PAF approach has been refined and SSDs for 28 pesticides have been determined by DSITI and will be published in the coming year (see Section 8 for more information). The SSDs of each PSII herbicide, used in the ms-PAF calculation, are composed of five to 45 phototrophic species (depending on the availability of ecotoxicity data), with a total of 90 species used to calculate the PSII herbicide mixtures, almost one-third of which were marine species, and included microalgal, seagrass, macrophyte and macroalgal species (King et al., 2017a). The use of freshwater and estuarine species in the development of the SSDs may affect their representivity and relevance to the Reef marine environment and requires further investigation. However, the inclusion of new

[1] Matched datasets are defined by Smith et al. (2016a) as "toxicity data from studies conducted within the same laboratory where multiple chemicals are tested under the same test conditions to a consistent set of organisms."

chronic data (Negri et al., 2015) (excluded from previous GVs but of demonstrated local relevance), are likely to improve representivity of the SSDs. Work to develop the non-additive model for a wider range of pesticides, many relevant to the Reef, which have different modes of action is on-going. The ultimate aim is to report a single assessment end point (PAF) for all monitored pesticides detected in the MMP program.

The SSDs used in the ms-PAF approach (both additive and non-additive) are also the basis for the proposed GVs that will be submitted for national endorsement and inclusion into the Australian and New Zealand water quality guidelines (see Section 3.5.1). Until endorsed, the SSDs are considered interim. For the current report, to avoid retrospective adjustment to reported ms-PAF data, the ms-PAF values for the current year only are given in a Case Study reported in Section 8 together with a comparison of the ms-PAF method compared to the PSII Herbicide Index for the current year's results to assess ecological risk.

3.5.5 Mapping the frequency and extent of flood plumes (frequency maps)

River flood plumes are the primary vehicles that deliver catchment-derived pollutants to the Reef lagoon. Mapping the frequency, spatial extent and duration of these flood events can inform management about the areas that may be the most at risk from acute or chronic effects of pollutant exposure resulting from river discharge. It should be noted that whilst flood plumes are a major contributor to the movement of pesticide loads from catchments to the Reef lagoon, the amount of pesticides released with an individual flood plume will depend on many factors in addition to water flow, e.g. timing of pesticide applications relative to rainfall events, degradation rates etc. For many catchments, the highest concentrations of pesticides are released at the beginning of the wet season with the first 'flush'. Flood plumes later in the year may deliver little or no pesticides to the marine environment. In this report, we present the plume maps and frequencies with the intention to inform the likelihood of a fixed (passive sampling) monitoring site to be located within a flood plume and how often and for how long it may be impacted by plume waters. Information on colour dissolved organic matter (CDOM) and total suspended solids (TSS) in flood plumes (which are the basis of the flood plume maps – see below) cannot be used to predict expected levels of pesticides reaching a monitoring site.

The Marine Water Quality component of the MMP maps the frequency and extent of (surface) flood plumes (Waterhouse et al., 2017b). This is achieved using ocean colour (corresponding to different water types) collected via satellite imagery that exploits differences in colour of plume waters from ambient marine waters in 1km^2 'pixels' (Devlin et al., 2012). Plumes are classified into three water types:

- Primary – very high turbidity, low salinity (0 to 10 ppt), and very high values of CDOM and TSS;
- Secondary – intermediate salinity, elevated CDOM concentrations, and reduced TSS due to sedimentation, where phytoplankton growth is prompted by the increased light (due to lower TSS) and high nutrient availability delivered by the river plume;
- Tertiary – exhibits no or low TSS associated with the river plume, and above-ambient concentrations of chlorophyll *a* and CDOM.

It should be noted that plume exposure mapping may be complicated by the resuspension of fine sediments during periods of high winds and waves (rather than periods of actual river discharge) as well as cloud cover.

Weekly flood plume colour class data was recorded for each of the fixed monitoring sites for the wet season (details provided in Appendix E Table E2). Reef-wide, annual and multi-annual frequency maps were also obtained (all plume frequency maps were prepared by Dieter Tracy (JCU)). Site maps presented in this report overlay the plume frequency maps to indicate sampling site positions relative to (primary and secondary) flood plume occurrences.

4. Results

The design of the MMP and the structure of this report follows a Driver-Pressure-State-Impact-Response framework (Figure 3) derived from Great Barrier Reef Outlook reporting. Agricultural activities (particularly sugar cane cultivation) are the major diffuse source of pesticides in run-off and the focus of Reef Plan initiatives. Other sources of pesticide run-off may, however, also result from urban and industrial activities (GBRMPA, 2013). The drivers and pressures influencing pollutant release to the Reef lagoon from diffuse agricultural activities include factors relating to the amount of pesticide usage in the catchments (e.g. type and application rates of pesticides, agricultural land use area, adoption of best management practices for land management), as well as factors related to the transport potential of pesticides from the catchments to the Reef lagoon (e.g. rainfall, cyclones, timing and method of herbicide application, herbicide run-off behavior, herbicide persistence, volume of water discharged from rivers, frequency of flood plumes).

This results section addresses the Driver-Pressure-State results for pesticide water quality. The key 2015-16 drivers/pressures are presented in Section 4.1 and include agricultural land use, rainfall, cyclones and freshwater river discharge, as well as multiple paddock-scale pressures relating to pesticide usage and transport potential into the riverine system which are reflected collectively in the end-of-catchment pesticide loads discharged to the Reef lagoon (Figure 3). The state, or condition, of water quality with respect to pesticides is presented in summary in Section 4.2 with further details in the supporting Appendices.

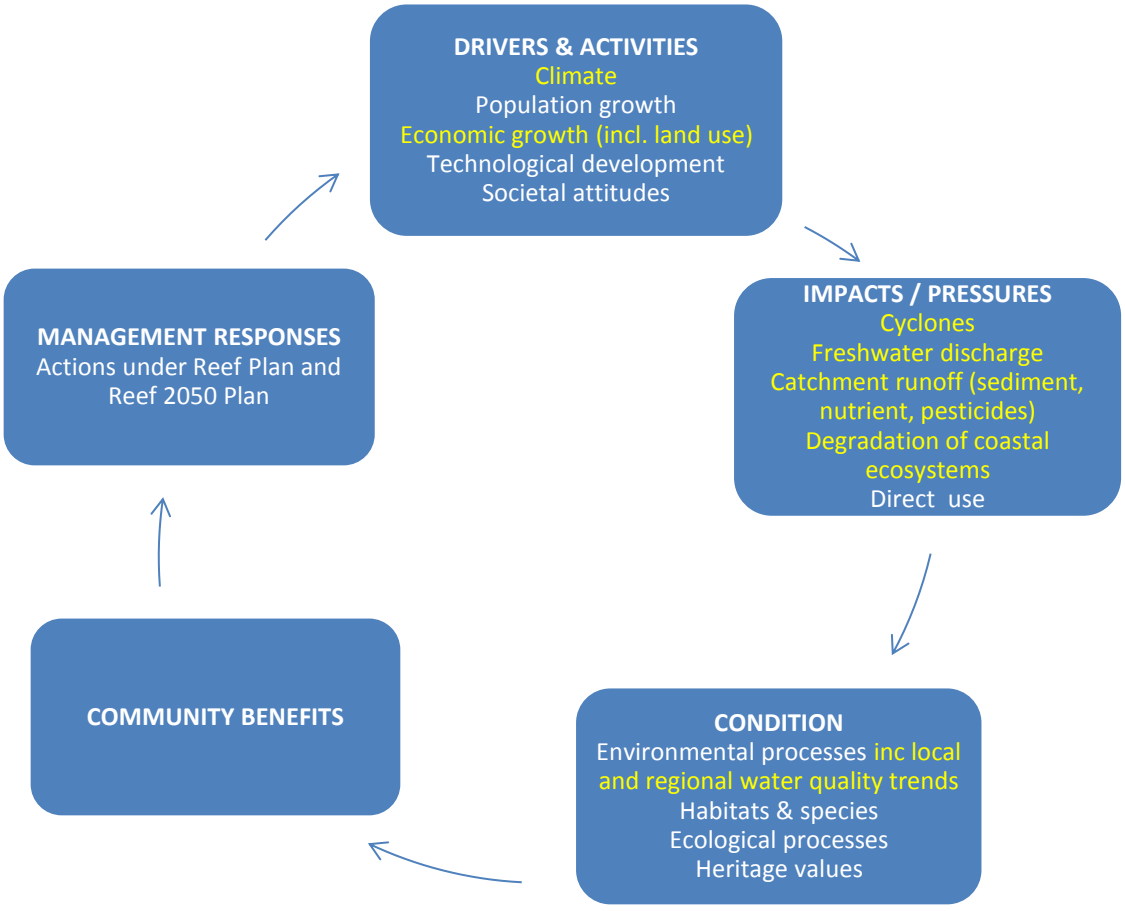


Figure 3: DPSIR framework used to guide the structure of the MMP, derived from the 2015 Great Barrier Reef Strategic Assessment (figure modified from Waterhouse et al. (2017b)). The aspects highlighted in yellow are included in this report.

4.1 Drivers and pressures influencing pesticide concentrations

Consistent with the reporting structure for all MMP projects, this section outlines the 2015-16 drivers and pressures potentially impacting pesticide levels in the near-shore marine environment.

4.1.1 Land use

A wide range of land uses occur in the Reef catchments, with great diversity between NRM regions (Figure 4, Appendix D Figure D-1).

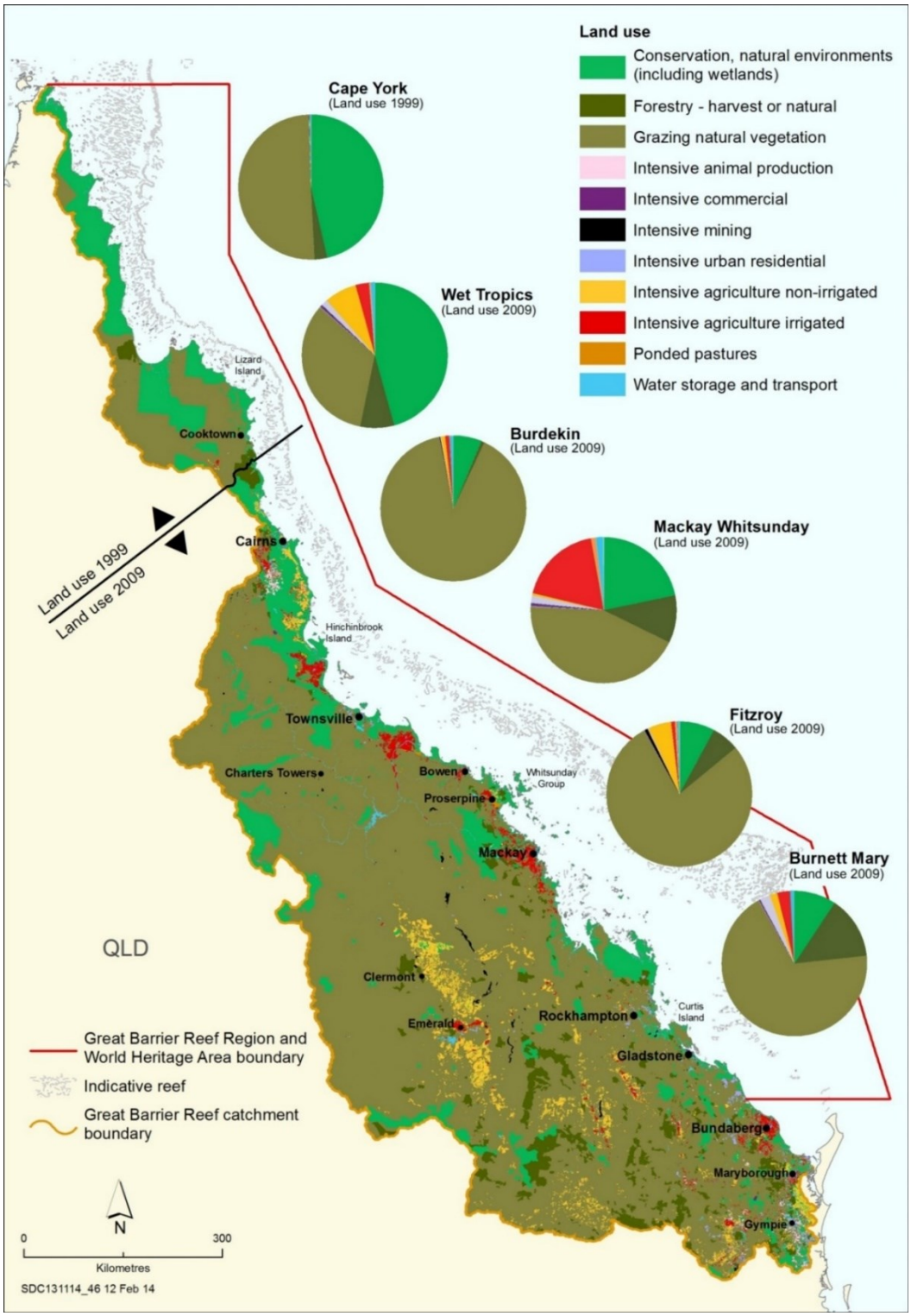


Figure 4: Land use in the Reef catchments. Sourced from GBRMPA (2014)

Certain regions and/or smaller coastal catchments may represent areas of higher localised risk of pesticide run-off due to the intensity and nature of agricultural activities (such as sugar cane cropping) occurring in coastal areas (Brodie et al., 2013). In total, 80 per cent of the Reef catchments support agricultural activities with cattle grazing the most extensive land use, particularly in the drier Burdekin and Fitzroy regions of which 90 per cent and 77 per cent, respectively, are utilised for this purpose (DSITI, 2012c, a). The Wet Tropics and Mackay Whitsunday regions also have grazing activities (31 per cent and 42 per cent, respectively); however other uses such as nature conservation (33 per cent of land use in the Wet Tropics) and irrigated cropping (sugarcane) (18 per cent of land use in the Mackay Whitsunday) are also significant (DSITI, 2012e, b). Although land-use is well characterised in the Reef catchments, limited data on pesticide usage are available and models are used to extrapolate from the relatively small experimental database for run-off of pesticides from the different land use areas to a wider range of catchment conditions and to also investigate the impact of management options (Shaw et al., 2011). For the purposes of this report, monitored end-of-catchment pesticide loads that enter the Reef lagoon (see Section 4.1.3) are used to inform the pesticide profiles observed at fixed and other monitoring sites.

4.1.2 Hydrological conditions in the Reef catchments

An overview of the rainfall and cyclonic activity, and associated river discharge, for the Reef region is given in the following three sections. These data are intended to provide a high-level understanding of the climatic and flow conditions experienced in Reef catchments in 2015-16 and allow broad comparisons with previous years. In Section 4.3 below, regional monitoring data are presented in the context of individual rivers' hydrographs (river flow rates over time).

4.1.2.1 Rainfall

The neutral conditions following the peak of the 2014-2016 El Niño event in December 2014 remained for the 2015-16 monitoring year (BOM, 2016). The first significant rainfall event occurred in the coastal areas in December 2015 and persisted until March 2016 (Appendix E Figure E-1, Table 4). Overall in 2015-16, rainfall in most Reef catchments was below the long-term average (Figure 5, Appendix E Figure E-2). Normanby catchment was the exception, although the increase compared to average was marginal. Whilst rainfall overall was lower than the long-term annual average, in the northern and central Reef coastal zone, total rainfall in the wet season was higher than in the previous monitoring year (2014-15) (Appendix E Figure E-3).

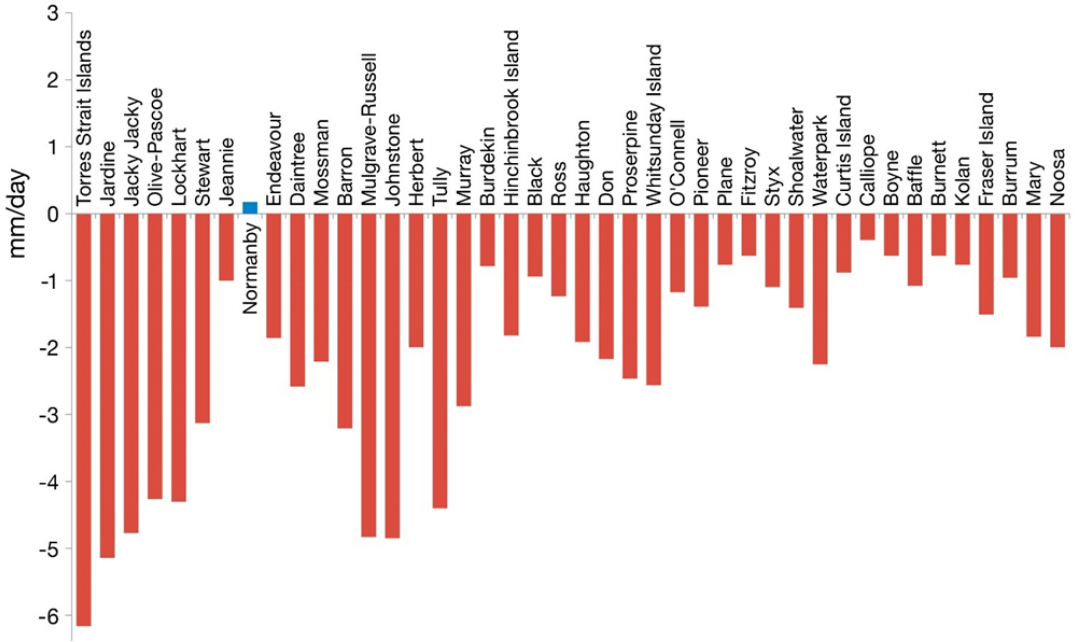
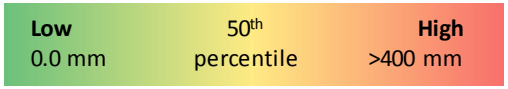


Figure 5: Annual average wet season rainfall (December 2015 - April 2016), as compared to the long-term wet season rainfall average (1961 – 1990). Red bars denote catchments with rainfall below the long-term average, blue above the long-term average. Source Waterhouse et al. (2017b)

Table 4: Weekly mean catchment rainfall (mm) in catchments adjacent to fixed passive sampler sites during the 2015-16 wet season (beginning 1 December 2015). Table provided by Dieter Tracey, JCU

		w1	w2	w3	w4	w5	w6	w7	w8	w9	w10	w11	w12	w13	w14	w15	w16	w17	w18	w19	w20	w21	w22
Region	**Catchment**	01-Dec-15	08-Dec-15	15-Dec-15	22-Dec-15	29-Dec-15	05-Jan-16	12-Jan-16	19-Jan-16	26-Jan-16	02-Feb-16	09-Feb-16	16-Feb-16	23-Feb-16	01-Mar-16	08-Mar-16	15-Mar-16	22-Mar-16	29-Mar-16	05-Apr-16	12-Apr-16	19-Apr-16	26-Apr-16
Wet Tropics	Mossman	33	45	59	261	144	30	20	23	79	19	25	18	43	107	83	155	14	1.6	30	37	17	22
	Mulgrave-Russell	34	24	73	203	114	6.6	7.8	48	43	26	82	2.0	102	122	162	116	40	1.4	65	101	71	87
	Herbert	4.6	6.1	11	71	54	9.2	3.7	17	50	29	21	5.7	12	117	110	100	3.1	0.1	23	31	15	9.6
	Tully	13	15	35	102	95	6.2	8.0	22	52	29	50	1.8	34	186	190	159	14	0.5	68	126	73	53
Burdekin	Burdekin	5.2	2.7	1.2	25	57	11	8.6	2.9	60	84	3.5	1.3	5.3	47	19	18	11	0.2	0.7	4.7	0.3	0.5
	Haughton	5.5	1.9	0.3	6.7	122	12	6.1	1.7	12	83	20	2.8	4.3	89	27	46	11	0.0	1.4	12	0.1	0.5
Mackay Whitsunday	Proserpine	1.6	8.3	0.8	8.8	129	21	28	3.9	13	104	4.7	16	14	217	45	19	15	0.1	11.6	93	2.0	14
	O'Connell	1.6	15	3.4	9.1	98	41	42	4.8	22	195	6.3	16	19	407	71	16	8.3	0.0	5.2	87	0.8	12
	Pioneer	1.9	9.5	3.1	13	52	47	44	3.9	24	226	5.0	12	22	354	47	7.4	11	0.0	4.3	32	0.9	11
	Plane	8.0	6.6	2.5	13	42	53	68	2.3	35	288	8.1	19	30	363	53	7.5	26	0.0	6.0	23	2.4	16
Fitzroy	Fitzroy	13	11	1.1	15	32	10	8.8	4.7	62	106	0.9	6.4	4.2	20	4.0	13	19	1.0	0.2	2.2	0.1	0.9



Colour gradient: Red indicates the highest value, yellow represents the 50th percentile and green represents the lowest value.

4.1.2.2 Cyclones

The 2015-16 Australian cyclone season was the least active tropical cyclone season since reliable records started in 1969 (Bureau of Meteorology, 2017). There is a strong relationship with eastern Australian tropical cyclone impacts and the El Niño-Southern Oscillation phenomenon, with almost twice as many impacts during La Niña than during El Niño. Only three named tropical cyclones developed in the wider Australian region and only one of these systems was in Queensland - Tropical Cyclone Tatiana. Tatiana, a category 2 cyclone, developed in the Coral Sea approximately 1,000 km northeast of Mackay in February 2016, but posed no threat to the Queensland or Reef coast. For information on cyclonic activity in the Reef region since 2006, see Waterhouse et al. (2017b).

4.1.2.3 River discharge

Total annual discharge of freshwater (based on corrected gauge values for the hydrological year, see Waterhouse et al. (2017b)) into the Reef lagoon in 2015-16 (35.2 x 10^6 ML) was comparable to 2014-15 levels (36.2 x 10^6 ML) (Figure 6) and for two consecutive years has remained below the long-term median discharge (60.3 x 10^6 ML). Rivers located in the northern catchments typically flow year-round, whereas rivers located in the southern drier catchments only flood periodically following large rain events during summer (Lewis et al., 2006, Larson et al., 2013). Overall, higher river discharges are associated with the northern catchments (Figure 7), although in 2015-16 all of the major rivers adjacent to fixed passive sampler sites had a total wet season discharge less than 1.5 times their long-term median (Table 5). This monitoring year, gauged rivers in the Wet Tropics contributed 44 per cent of the total volume of freshwater discharge into the Reef, compared to 6.5, 5.8 and 16 per cent in the Burdekin, Mackay Whitsunday and Fitzroy regions, respectively. The differences in the timing, duration and intensity of rainfall between the northern and southern Reef catchments drive river flow and contribute to the pattern of pesticide discharge to the marine environment.

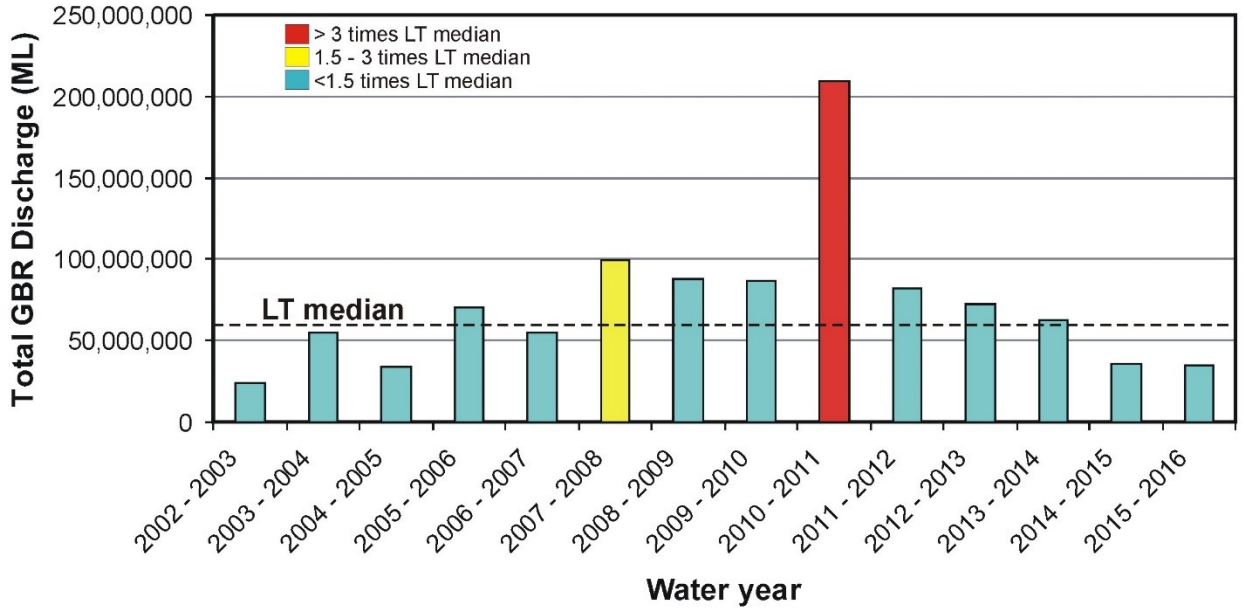


Figure 6: Long-term total annual discharge in mega litres (ML) (hydrological year: 1 October to 30 September) for the 35 main Reef river catchments. Data derived from DNRM http://watermonitoring.dnrm.qld.gov.au/host.htm and raw gauge discharge data were corrected by Waterhouse et al. (2017b) to account for different placement position of gauges within each catchment. Figure reproduced from Waterhouse et al. (2017b).

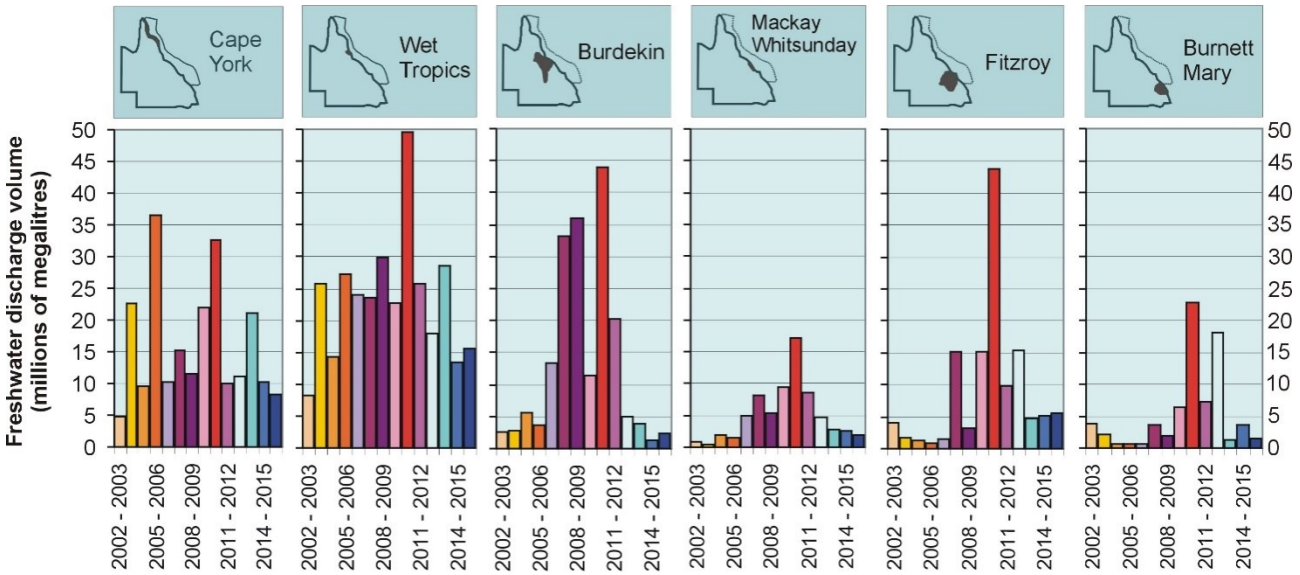


Figure 7: Corrected annual discharge from each NRM region for 2002-2003 to 2015-16 in millions of megalitres (ML) per year. Data derived from DNRM http://watermonitoring.dnrm.qld.gov.au/host.htm and figure reproduced from Waterhouse et al. (2017b).

4.1.3 End-of-catchment annual pesticide loads

The end-of-catchment annual pesticide loads monitored under the GBRCLMP reflect the entirety of paddock-scale drivers and pressures resulting in pesticide losses into waterways and subsequent detection in marine environments. Thirty-six pesticides and metabolites were monitored in 17 catchments (comprising ten end-of-catchment and seven sub-catchment sites) under GBRCLMP in 2015-16 (Huggins et al., *in prep*). Samples were collected at regular intervals throughout the year (typically monthly) during low-flow (ambient) conditions and higher frequency sampling during high-flow (event) conditions. Monitoring data were extrapolated to calculate annual pesticide loads entering the Reef lagoon from these catchments. Three rivers adjacent to passive sampling sites were not monitored during 2015-16: Mossman River (Low Isles site), Proserpine River (Repulse Bay site) and Plane Creek (Sarina Inlet) (Table 6).

In the current monitoring year, each PSII herbicide and major metabolite detected in the marine monitoring program was also detected at the end of at least one catchment adjacent to passive samplers' locations (Table 6). Atrazine, diuron and hexazinone were detected at all sites, and except for the Fitzroy River catchment, these three herbicides dominated the PSII herbicide load profile across all catchments (Appendix E Figure E-4). Fluometuron and prometryn loads were very low and were only at detectable levels at one/two sites, respectively. The PSII herbicide load profiles reflect the land use in a monitored catchment (e.g. tebuthiuron loads reflect the grazing land use in the central and southern NRM regions) (Table 6).

An expanded suite of other (non-PSII) pesticides were also monitored as part of the GBRCLMP program. A total of eight additional pesticides were monitored at both the fixed monitoring sites (this report) and as part of the GBRCLMP. All or most of these other pesticides were discharged from catchments adjacent to fixed monitoring sites in this program (Table 6). The exception was the Fitzroy River catchment where only three of the eight pesticides were detected.

Table 5: 2015-16 wet season discharge (ML) of the major Reef catchment rivers adjacent to passive sampling sites (c.a., November 2015 to April 2016, inclusive) compared to the long term (LT) median discharge (1970 to 2000). Relative wet season discharge (fraction of long-term median) for the current wet season and previous 5 years are shown.

Region	Site	2015–16 wet season discharge (ML)	LT median wet season discharge (ML)	Relative wet season discharge (fraction of long-term median)					
				2010 - 2011	2011 - 2012	2012 - 2013	2013 - 2014	2014 - 2015	2015 - 2016
Wet Tropics	Mossman	1,245,275	1,207,012	1.7	1.3	1.0	1.6	0.7	1.0
	Mulgrave-Russell	3,253,825	4,457,940	1.8	1.3	0.8	1.2	0.7	0.7
	Tully	2,942,770	3,536,054	2.1	1.0	0.9	1.2	0.8	0.8
	Herbert	1,895,526	3,556,376	3.5	1.3	0.9	1.2	0.3	0.5
Burdekin	Burdekin	1,807,104	4,406,780	7.9	3.5	0.8	0.3	0.2	0.4
Mackay Whitsunday	Proserpine	316,648	887,771	5.2	2.4	1.0	0.8	0.2	0.4
	O'Connell	284,171	796,718	5.2	2.4	1.0	0.8	0.2	0.4
	Pioneer	597,117	776,984	4.7	2.0	1.5	0.8	2.6	0.8
	Plane	832,508	1,052,831	4.6	2.7	1.9	0.7	0.2	0.8
Fitzroy	Fitzroy	3,589,342	2,852,307	13.3	2.8	3.0	0.6	0.9	1.3

Colours highlight years for which river flow exceeded the median annual flow as estimated from available long-term time series for each river: yellow = 1.5 to 2-times LT median, orange = 2 to 3-times LT median, red= >3-times LT median. Discharge data were supplied by DNRM and corrected by Waterhouse et al. (2017b) for different placements of gauges within each catchment. The full dataset from which these data were derived is given in **Appendix E** Table E-1.

Table 6: Annual end-of-catchment pesticide loads from monitored Reef catchments relevant to passive sampling sites (1 July 2015 – 30 June 2016). PSII-HEq loads are derived using PSII RPFs for this report, consistent with previous MMP reports (see Section A-4, Appendix A). GBRCLMP data from Huggins et al. (*in prep*).

CATCHMENT ANNUAL LOADS		Annual load PSII herbicides (and metabolites) (kg) (* included in PSII-HEq Index)														Annual load other (non-PSII) pesticides (kg)												
River and site name	Passive sampling sites	Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine†	Simazine*	Tebuthiuron*	*Terbutryn*	PSII-HEq (kg)	Metolachlor	2,4 D	*2,4 DB*	Haloxyfop	MCPA	*Fluazifop*	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	*Tebuconazole*	*Chlorpyrifos*	*Pendimethalin*	*Propiconazole*	*Trifluralin*
Lowest – 50th percentile – Highest																														
Mossman River	*Low Isles*																													
Mulgrave River at Deeral	High Island &	0.77	12	2.3	0.60	0.31	14	0.043	9.2	1.4	n.d.	n.d.	0.043	n.d.		21	1.2	13		0.82	5.2		13	1.3	6.2	0.62					
Russell River at East Russell	Normanby Island	2.5	23	4.9	n.d.	0.16	81	n.d.	36	2.1	n.d.	n.d.	n.d.	n.d.		102	1.3	23		1.7	3		6.1	6.9	62	0.85					
Tully River at Euramo	Dunk Island	n.d.	38	11	0.44	n.d.	140	n.d.	77	5.0	n.d.	n.d.	4.4	n.d.		177	0.42	170		15	n.d.		6.5	6.9	150	6.0					
Herbert River at Ingham	Lucinda	n.d.	20	6	4.2	n.d.	58	n.d.	32	4.9	n.d.	n.d.	n.d.	n.d.		74	8	59		5.4	n.d.		56	11	88	n.d.					
Barratta Creek at Northcote	Barratta Creek	0.67	110	11	4.3	3.3	9.3	n.d.	1.5	4.4	0.002	0.098	0.24	0.53		30	7.3	41		0.65	4.2		4.4	1.1	2.3	0.012					
Proserpine River																														
O'Connell River at Caravan Park	Repulse Bay	0.001	14	2.4	0.74	n.d.	4.1	n.d.	2.7	0.36	n.d.	0.016	0.008	1.2		8	2.8	10		0.016	0.51		1.7	1.2	8.3	0.044					
Pioneer River at Dumbleton PS	Round Top Island	0.72	150	17	7.5	0.077	170	n.d.	42	2.6	n.d.	0.04	0.5	n.d.		213	14	44		n.d.	9.7		28	11	76	0.11					
Sandy Creek at Homebush	Sandy Creek	1.4	46	7.6	3.5	0.005	54	n.d.	19	7.8	0.013	0.014	0.16	0.3		71	10	31		0.023	9.6		17	14	23	0.52					
Plane Creek	*Sarina Inlet*																													
Fitzroy River at Rockhampton	N. Keppel Island	n.d.	100	23	13	0.27	58	n.d.	17	n.d.	n.d.	n.d.	n.d.	1000		163	270	11		n.d.	n.d.		36	n.d.	n.d.	n.d.					

† Measured as Propazin-2-hydroxy

n.d. pesticide not measured at any sampling point above the pratical quantification limit

Colour coding reflects lowest (green) to highest (red) values for each pesticide across the catchments (yellow is the 50th percentile). Grey shading indicates no data are available.

4.2 Reef-wide results

4.2.1 Fixed monitoring site passive sampler return record

This monitoring year, 73 per cent of fixed site passive sampler sets sent to volunteers were successfully deployed, returned (undamaged) and analysed (Appendix F Table F-1,). In comparison, successful sampler returns for the two previous years were 83 and 84 per cent. The remainder of samplers were unsuccessful for several reasons, but were typically because of a lost mooring following bad weather or *in situ* damage (e.g. membrane lost or fouled). Four sites (Dunk Island, High Island, Lucinda, and North Keppel Island) had complete sampling records in 2015-16, with no missed deployments. Due to a changeover in the local volunteer organisation, Normanby Island had only one successful deployment in the dry season and none in the wet season. As in the previous year, only two successful deployments of samplers occurred at Sarina Inlet (both exceeding the recommended deployment period) and none in the wet season. For sites with lower deployment rates, trend comparisons with previous years are generally not possible, and care needs to be taken when comparing between the monitoring sites.

4.2.2 Reef-wide summary pesticide results

4.2.2.1 Frequency of pesticide detections

Twelve PSII herbicides and two metabolites of atrazine (DE atrazine and DI atrazine) were included in the sample analysis suite of the passive sampler extracts. Of these, eleven were detected at one or more of the marine monitoring sites (Figure 8). The most commonly detected PSII herbicides were atrazine, diuron and hexazinone. Fluometuron, prometryn and terbutryn were not detected at any site. Of the fifteen other pesticides in the analysis suite (eleven polar and four non-polar), nine were detected at measurable levels in ED samplers and all three non-polar pesticides were detected in the PDMS samplers (Figure 8). 2,4-DB and fluazifop were not detected at any site. Of the non-polar pesticides, chlorpyrifos and pendimethalin were frequently detected at all sites where samplers were deployed. Propiconazole and trifluralin were both detected only twice at a single site.

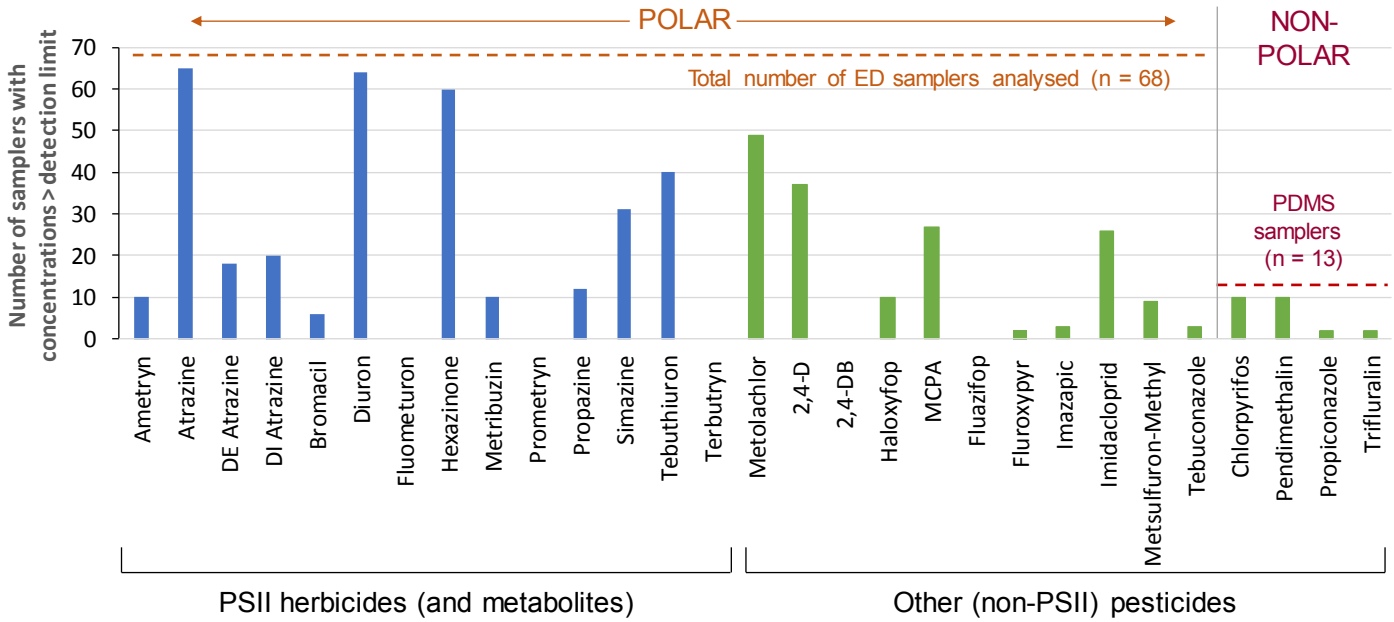


Figure 8: Number of ED and PDMS samplers that had measurable pesticide levels (i.e. above the limit of detection, LOD) for each pesticide included in this study, out of a total of 68 ED samplers and 13 PDMS samplers returned in 2015-16 (Table F-1, Appendix F).

4.2.2.2 Summary of pesticide concentrations in 2015-16

The PSII herbicides detected at the highest concentrations in 2015-16, which were also the most frequently detected, were diuron (maximum concentration (C_{max}) 460 ng L^{-1}), atrazine (C_{max} 250 ng L^{-1}) and hexazinone (C_{max} 72 ng L^{-1}), all detected at Round Top Island in the Mackay Whitsunday region (Table 7). Other pesticides 2,4-D, imidacloprid, MCPA and metolachlor were also frequently detected although at relatively lower concentrations at most sites (typically <1 ng L^{-1}) (Table 7). The exception was Round Top Island, where comparatively higher concentrations of these four other pesticides were observed (see regional report below).

In the current monitoring year, the PSII-HEq Max across all sites ranged from 0.12 – 530 ng L^{-1}. Most of the sites (eight out of eleven) had maximum PSII-HEq concentrations in the Category 5 risk category (no reported ecosystem effects). Barratta Creek reached a Category 4, Sandy Creek a Category 3 and Round Top Island a Category 2. At a Category 2 concentration on the PSII-HEq Index, there may be a risk of reduced photosynthesis capacity for diatom, seagrass and coral species.

Diuron was generally the dominant contributor to the PSII-HEq Max at the fixed monitoring sites due to its potency as a PSII inhibitor and its relatively higher concentrations (Figure 9). The diuron per cent contribution to total PSII-HEq Max varied between sites, ranging from 36 per cent (Repulse Bay) to 87 per cent (Round Top Island), and was consistently high in the Wet Tropics (77 to 86 per cent across the five sites). In contrast to the previous monitoring year when diuron dominated PSII-HEq Max at all sites, in 2015-16 at Barratta Creek and Repulse Bay, atrazine's contribution was similar to or greater than diuron (35 and 53 per cent, respectively).

4.2.2.3 Comparison to guideline values

At the fixed monitoring sites, three exceedances of guideline values (GVs) occurred in 2015-16. All occurrences were at the Round Top Island site and were within 9 per cent of the relevant GV. The three exceedances were:

- diuron (C_{max} 462 ng L^{-1}, compared to the proposed marine PC99 GV of 430 ng L^{-1} (Table B-1))
- imidacloprid (C_{max} 36 ng L^{-1}, compared to the proposed marine PC99 GV of 33 ng L^{-1} (Table B-1))
- chlorpyrifos (C_{max} 0.52 ng L^{-1}, compared to the ANZECC and ARMCANZ (2000) marine PC99 value of 0.50 ng L^{-1} (Table B-1)).

It should be noted that the existing ANZECC and ARMCANZ trigger value for diuron is 1,800 ng L^{-1} (which is a low reliability interim working value) and the GMRMPA PC99 is currently 900 ng L^{-1} (Table B-1); under both these guidelines, the Round Top Island maximum diuron value would not be an exceedance. The proposed GV is, however, high reliability (King et al., 2017a) and therefore comparisons with this proposed value are more meaningful and recommended. There are no existing PC99 or trigger values for imidacloprid, nor a proposed GV for chlorpyrifos.

4.2.2.4 Comparison to previous years: trends in pesticide concentrations

For many sites, the 2015-16 maximum pesticide concentrations did not show any notable change from 2014-15 and, where historical records are available to compare, overall levels remained lower than the extremely wet years of the last La Niña cycle (Figure 9). The PSII-HEq Max values follow similar trend patterns (Figure 10).

Trend comparisons will become more meaningful in future years as more historical data become available for the five sites in the program for which monitoring began in 2014-15 (Lucina, Barratta Creek, and three of the four sites in the Mackay Whitsunday regions, Repulse Bay, Round Top Island and Sandy Creek). Likewise, for trends at High Island which was re-introduced to the monitoring program in the current year. A focus on finding ways to increase sampler returns wherever possible, particularly in the wet season, will also be important.

Table 7: Maximum detected pesticide concentrations at each fixed passive sampling site. Colour coding reflects lowest (green) to highest (red) values for each pesticide across the catchments (yellow is the 50th percentile).

MAXIMUM CONCENTRATION		Maximum concentration PSII herbicides and their metabolites (ng/L) (* included in PSII-HEq Index)														PSII-HEq (ng/L)	Maximum concentration other non-PSII pesticides (ng/L)														
Region	Passive sampling site	Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	2,4 D	2,4 DB	Haloxyfop	MCPA	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole	Chlorpyrifos	Pendimethalin	Propiconazole	Trifluralin
Wet Tropics	Low Isles	n.d.	0.22	n.d.	n.d.	n.d.	1.4	n.d.	0.65	n.d.	n.d.	n.d.	0.02	0.05	n.d.	**1.7**	0.04	0.05	n.d.	0.01	0.01	n.d.	n.d.	n.d.	0.03	n.d.	0.01				
	High Island	n.d.	0.49	0.14	0.02	n.d.	2.8	n.d.	1.2	0.07	n.d.	n.d.	0.02	0.04	n.d.	**3.3**	0.07	0.27	n.d.	0.02	0.02	n.d.	n.d.	n.d.	0.24	n.d.	0.03				
	Normanby Island	n.d.	0.08	n.d.	n.d.	n.d.	0.09	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.12**	0.01	0.02	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	0.01	n.d.	n.d.				
	Dunk Island	n.d.	0.39	n.d.	n.d.	n.d.	1.5	n.d.	0.94	n.d.	n.d.	n.d.	0.01	0.04	n.d.	**2.0**	0.05	0.00	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.16	n.d.	n.d.				
	Lucinda	n.d.	0.78	n.d.	0.05	0.03	2.7	n.d.	0.85	n.d.	n.d.	n.d.	0.10	0.15	n.d.	**3.2**	0.08	0.25	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	0.47	n.d.	n.d.				
Burdekin	Barratta Creek	0.77	52	9.7	1.1	0.39	7.0	n.d.	1.1	1.0	n.d.	0.48	0.26	0.31	n.d.	**18**	0.76	0.36	n.d.	0.05	0.10	n.d.	0.17	n.d.	0.07	0.03	n.d.	0.16	0.16	n.d.	n.d.
Mackay Whitsunday	Repulse Bay	n.d.	8.8	0.19	0.02	n.d.	0.95	n.d.	0.65	0.18	n.d.	0.06	0.09	0.26	n.d.	**2.6**	0.15	0.07	n.d.	n.d.	0.004	n.d.	n.d.	n.d.	0.13	n.d.	n.d.	0.004	0.002	n.d.	n.d.
	Round Top Island	1.4	250	28	4.8	n.d.	460	n.d.	72	2.0	n.d.	1.0	n.d.	n.d.	n.d.	**530**	6.4	19	n.d.	0.02	5.2	n.d.	1.4	1.2	36	0.59	n.d.	0.52	0.22	2.1	0.01
	Sandy Creek	0.21	26	1.3	0.34	n.d.	45	n.d.	15	0.44	n.d.	0.13	0.06	0.74	n.d.	**55**	0.42	0.14	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	0.39	0.10	n.d.	0.01	n.d.	n.d.	n.d.
	Sarina Inlet	n.d.	0.59	n.d.	0.07	n.d.	0.90	n.d.	0.56	n.d.	n.d.	n.d.	0.04	0.18	n.d.	**1.2**	0.04	0.21	n.d.	n.d.	0.03	n.d.	n.d.	n.d.	0.01	0.08	n.d.				
Fitzroy	N. Keppel Island	n.d.	0.46	0.04	0.02	n.d.	0.51	n.d.	0.13	n.d.	n.d.	n.d.	0.03	2.6	n.d.	**0.8**	0.34	0.15	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.				

n.d. maximum pesticide concentration below limit of detection

Lowest — **50th percentile** — **Highest**

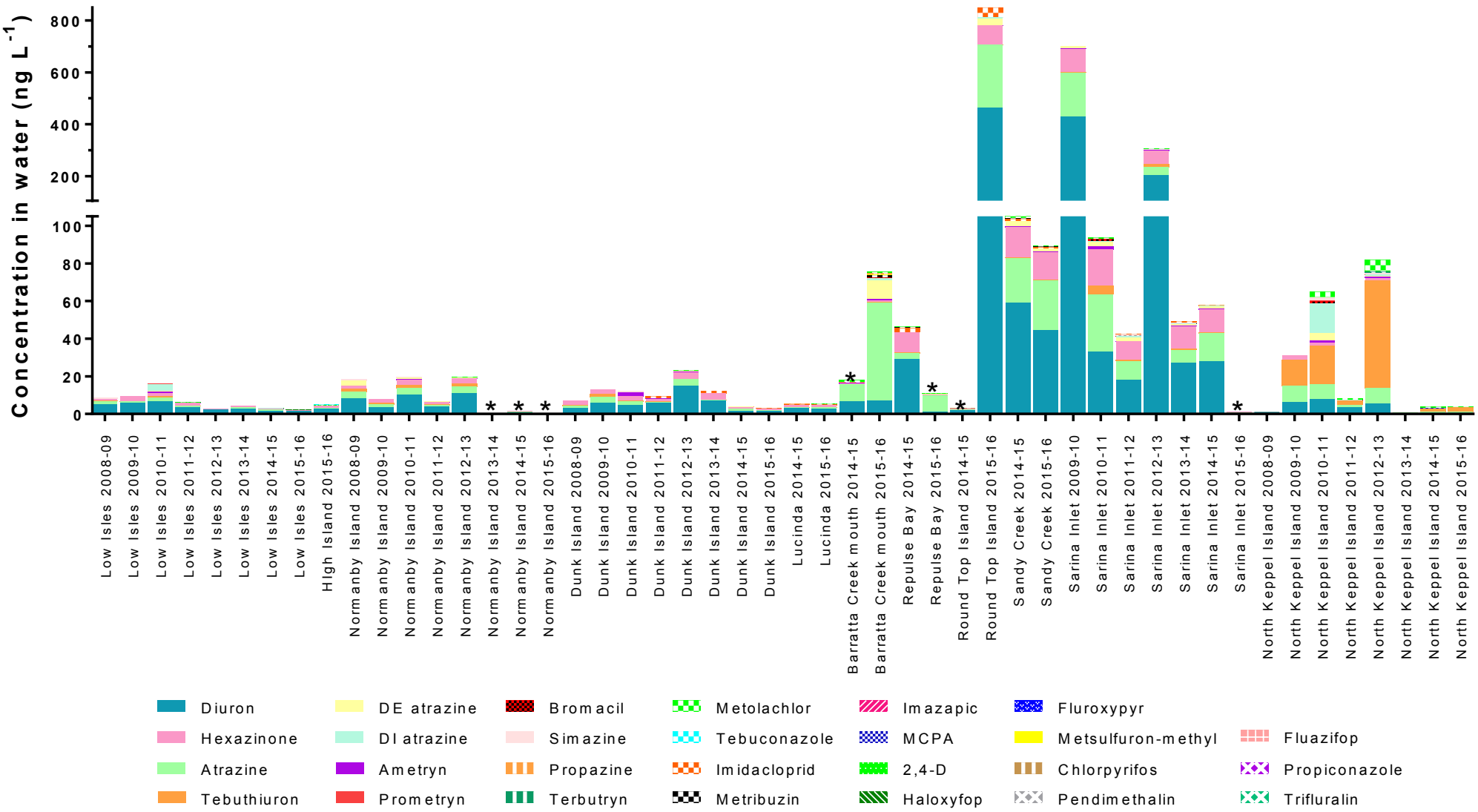


Figure 9: Maximum concentrations of individual pesticides at all sites monitored in 2015–16 compared to previous years (2008-09 onwards). Diuron dominated the profile at most sites, the exceptions being Barratta Creek mouth (atrazine was the highest contributor) and North Keppel Island (tebuthiuron was the highest contributor). Several pesticides were recently added to the analysis suite and are only included in the relevant years (2014-15 and 2015-16). 2,4-DB and fluometuron are not shown as values were <LOD for all sites. * Values with an asterisk are not representative values due to wet season sampling being incomplete and should be interpreted with caution. At Normanby Island and Sarina Inlet, the 2015-16 maximum is a dry season value as no wet season samplers were successfully deployed. At Barratta Creek no samplers were deployed during the period of highest rainfall in 2014-15. At Repulse Bay, the 2015-16 maximum may be understated as no samplers were deployed from January-April 2016 when the highest rainfall occurred. At Round Top Island, the prior year, 2014-15, maximum concentration is likely understated due to gaps in wet season deployments in that year.

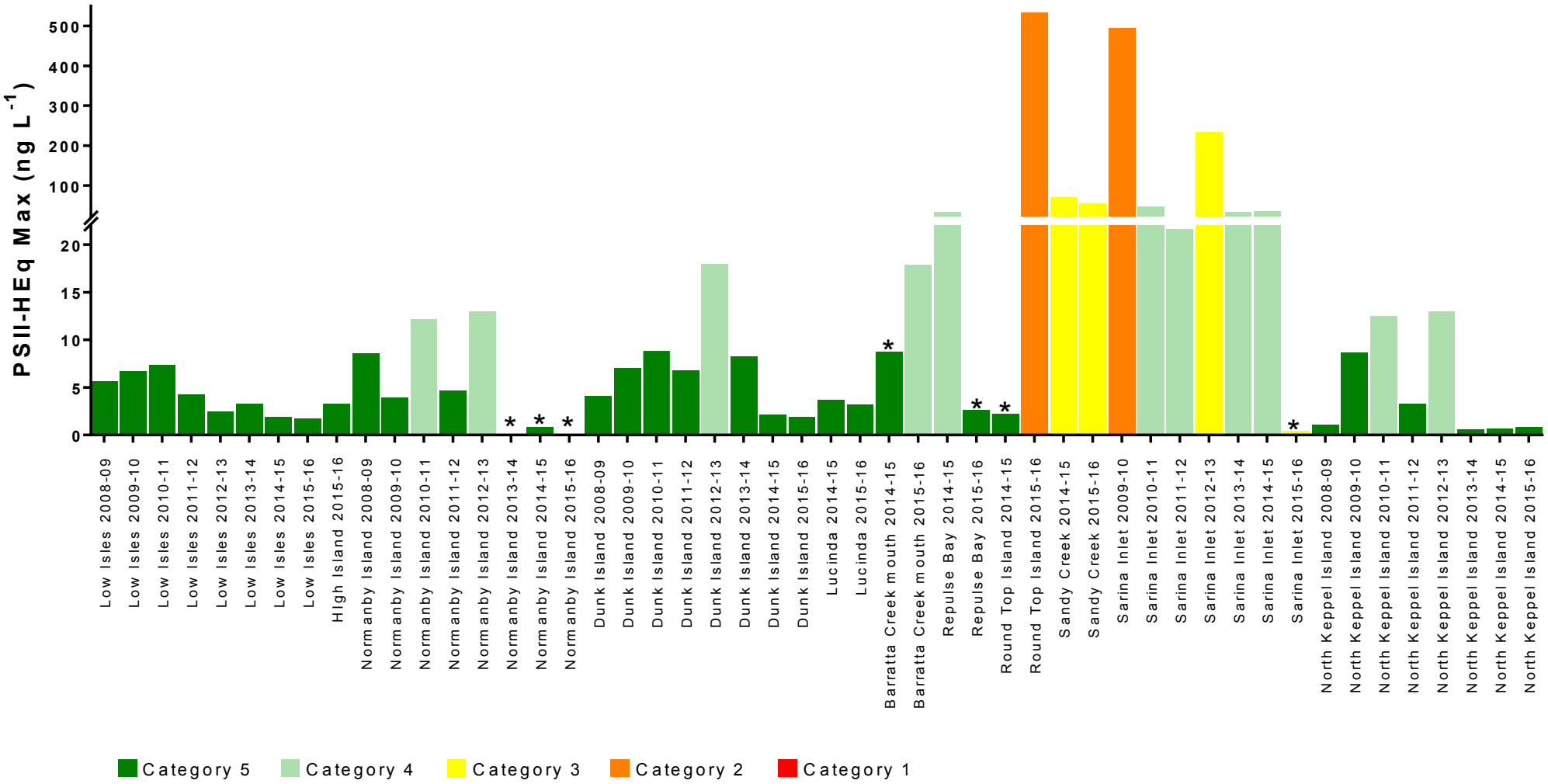


Figure 10: Maximum PSII herbicide equivalent concentrations at all sites monitored in 2015–16 compared to previous years (2008-09 onwards). The five categories of the PSII index reflect published effects on photosynthesis, where Category 5 is no impact and Category 1 is the equivalent to the 99 per cent species protection GBRMPA guideline value for diuron. Values with an asterisk are not representative values (refer to caption for Figure 9) and should be interpreted with caution.

4.3 Regional results

4.3.1 Wet Tropics Region

The current monitoring year was a dry year for the Wet Tropics, with a maximum weekly rainfall of 260 mm across all wet season weeks and all catchments (highest rainfall occurred in the Mossman River catchment in late December; Table 4). River discharge across the region was generally lower than the long-term average (range 50-100%; Table 5), which was consistent with the previous monitoring year. The overall climatic conditions in this region contributed to reduced flood plume frequencies at all fixed monitoring sites (i.e. the proportion of wet season weeks that a site was exposed to primary or secondary plume waters as determined by ocean colour class, see Appendix E Table E2 and explanatory text; frequencies ranged from 0.09 to 1). Wet Tropics flood plume frequencies were the lowest of all regions included in this program and for over a third of the weeks during the wet season, the Wet Tropics sites and particularly sites further north were impacted by only tertiary plume waters.

Concentrations of PSII herbicides during the current wet season were almost identical to the low concentrations detected across all Wet Tropics sites in the previous monitoring year (Table 8; for historical data, see Appendix I Figure I-1 to Figure I-5), and pesticide levels were low overall compared to longer term data (for historical data, see Appendix H Figure H-1 to Figure H-5). In 2015-16, the Wet Tropics rivers generally flowed year-round with flow events occurring regularly throughout the year (Figure 11 A-C and E). The exception was the Herbert River (adjacent to Lucinda monitoring site) in the south of the region, which had only one main flow event in March 2016 (Figure 11 G). At all the Wet Tropics monitoring sites, maximum PSII HEq concentrations were associated with the March 2016 flow event (Figure 11 A-D, E, G). The relatively lower concentrations observed earlier in the wet season during the first major river discharge of the season (e.g. at Low Isles associated with the December 2015 high flow event), may be a result of dilution by the high water volumes or timing of pesticide applications.

Table 8: Summary statistics for the maximum and Wet and Dry Season average PSII-HEq concentrations (ng L^{-1}) since monitoring commenced in the Wet Tropics. Block colours indicate the maximum PSII-HEq Index category for that year

Site		Routine sampling commenced	Risk category										Plume Frequency 2015-16
			2015-16	2014-15	2013-14	2012-13	2011-12	2010-11	2009-10	2008-09	2007-08	2006-07	2005-06	
Low Isles	PSII-HEq Wet Avg	2005-06	0.72	0.97	1.5	1.6	2.1	4.4	1.9	2.1	3.9	2.5	5.6	0.30
	PSII-HEq Dry Avg		0.10	0.10	1.58	*0.45*	0.82	0.73	0.88	1.89	0.64	0.56	1.20	
	PSII-HEq Max		**1.7**	**1.9**	**3.3**	**2.5**	**4.2**	**7.4**	**6.7**	**5.7**	**6.6**	**6.0**	**14**	
High Island	PSII-HEq Wet Avg	Re-started 2015-16	1.6								8.8	10.4		0.71
	PSII-HEq Dry Avg		0.11								4.5	3.4		
	PSII-HEq Max		**3.3**								**9.8**	**12**		
Normanby Island	PSII-HEq Wet Avg	2005-06	*0.12*†	0.69	-	5.3	1.8	6.2	1.9	2.6	11	3.7	*5.0*	0.09
	PSII-HEq Dry Avg		-	-	-	2.1	0.6	0.7	0	2.6	3.3	0.53	0.2	
	PSII-HEq Max		***0.12†***	**0.88**	-	**13**	**4.7**	**12**	**4.0**	**8.6**	**17**	**6.4**	***5.0***	
Dunk Island	PSII-HEq Wet Avg	2008-09	0.61	1.3	4.4	8.9	3.4	8.8	4.4	3.0		*4.7*		0.90
	PSII-HEq Dry Avg		0.04	0.8	2.2	2.3	*0.1*	2.2	1.1	*0*		-		
	PSII-HEq Max		**2.0**	**2.1**	**8.3**	**18**	**6.8**	**8.8**	**7.1**	**4.1**		***4.7***		
Lucinda	PSII-HEq Wet Avg	2014-15	1.1	1.3										1.00
	PSII-HEq Dry Avg		0.19	1.7										
	PSII-HEq Max		**3.2**	**3.7**										

†*Unreliable: only 1 successful sampling period in the season*

- no data available for this season (EDs overdeployed, not sent or lost)

PSII herbicides (and metabolites) detected using EDs in the Wet Tropics region in 2015-16 were almost exclusively atrazine, diuron and hexazinone and all three were detected in all wet season samplers returned from the Wet Tropics monitoring sites (note that no wet season monitoring data were available for Normanby

Island) (Appendix F Table F2 to Table F-6). Tebuthiuron was detected late in the wet season at the four sites for which samples were available. Other pesticides, 2,4-D, imidacloprid, MCPA and metolachlor, were also detected in the region (in 13 to 78 per cent of samplers), with the most frequent detections at High Island for all four (78, 78, 44 and 67 per cent, respectively).

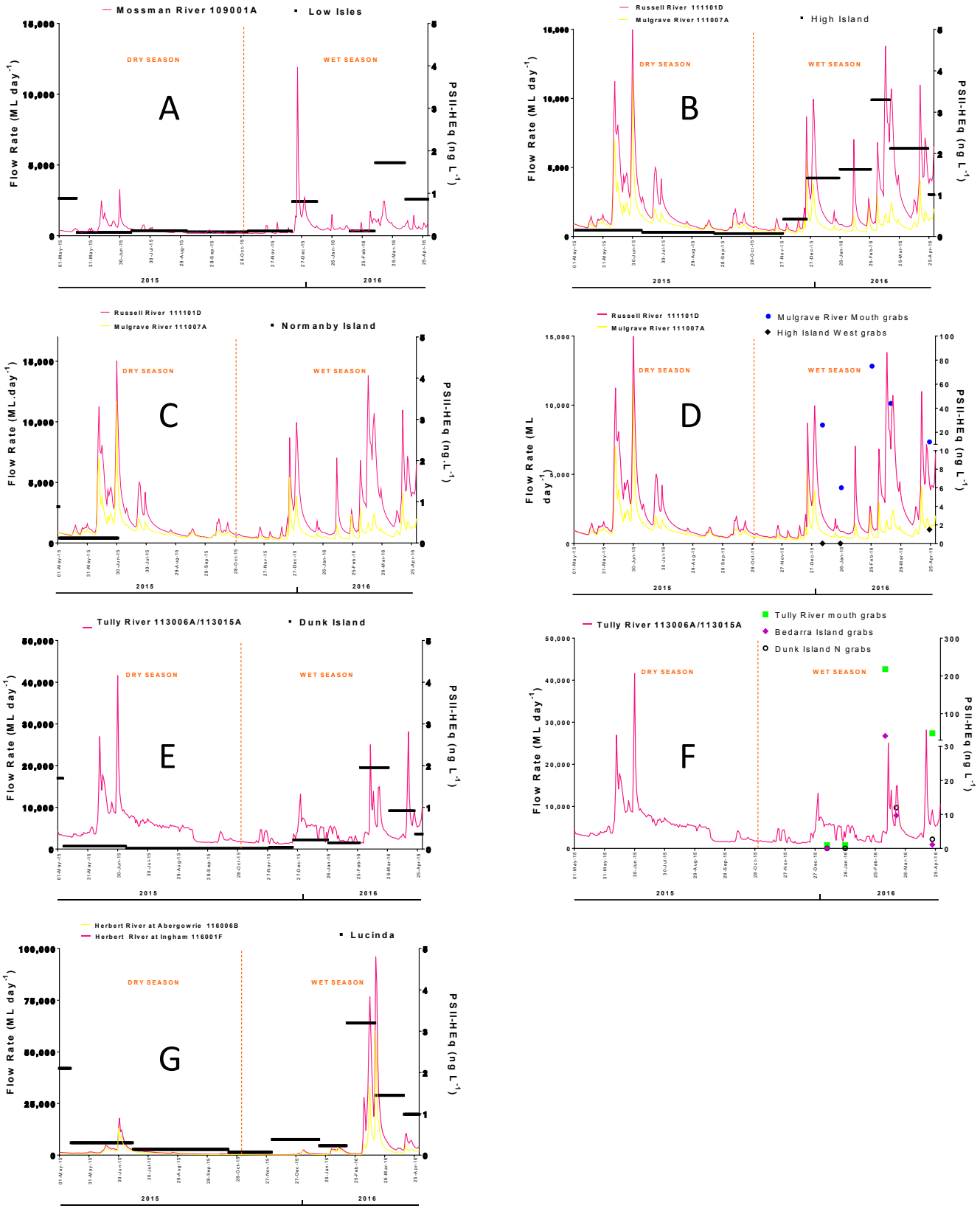


Figure 11: Temporal trends in PSII-HEq at fixed passive sampling sites (A-C, E, G) and PSII-HEq levels in grab samples (D, F) in 2015-16, relative to the flow rate of rivers influencing the Wet Tropics sampling sites. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network.

Land use in the Wet Tropics differs between its northern and southern catchments with the northern Daintree and Mossman River catchments largely comprised of national parks and state forests. Large areas of land are used for sugarcane growing in the southern catchments clustered around Cairns, Innisfail, Tully and Ingham (ABS, 2013). The PSII herbicide profiles (Appendix I Figure I-1 to Figure I-5) and PSII-HEq Max values (Table 8) did not, however, differ significantly between the Wet Tropics monitoring sites and remained low overall. Diuron generally contributed around half the total pesticide concentration at all sites, and represented just over 70 per cent of the average PSII-HEq concentration.

Since monitoring commenced, 85 per cent of PSII-HEq Max values in the Wet Tropics have been Category 5, and the remainder have been low Category 4 (Table 8). The PSII-HEq Max and wet/dry season average values in 2015-16 were all Category 5 on the PSII-HEq Index, with no clear trends apparent over time (Table 8). It should be noted that the concentrations of 2,4-D, imidacloprid, MCPA and metolachlor were not included in the calculation of the risk category, and therefore the risk from all pesticides could be higher in this region than what is reported here.

In 2015-16, grab samples were collected in two regions in the Wet Tropics, adjacent to the river mouths of the Russell/Musgrave River and the Tully River. Pairs of grab samples were collected from the Russell/Musgrave River mouth and High Island (fixed monitoring site) on five occasions throughout the wet season which coincided with three major flow events of the year (Figure 11 D). Two of the samples from High Island were destroyed in transit, leaving five river mouth samples and three High Island samples. The highest PSII herbicide concentrations were associated with samples collected in the river mouth during the second flow event in late February/early March. PSII-HEq concentrations reached 75 ng L^{-1} (Category 3 on the PSII-HEq Index) in February and 44 ng L^{-1} in March (Category 4). These levels, were however, relatively low by comparison to 2014-15 grab sampling from the same river mouth (maximum PSII-HEq concentrations of 339 ng L^{-1}, Appendix F Figure F-1). The profile of the major pesticides in the grab samples was highly consistent with the previous year, dominated by diuron, hexazinone, atrazine, imazapic and imidacloprid (Appendix G Table G-1). In the current year, low levels of several other pesticides were also detected in some grab samples, including 2,4-D, haloxyfop and fluroxypyr (Appendix G Table G-1). There were no pesticides other than diuron in the grab samples from High Island, and diuron was only detected in one of the three samples at low levels (1.5 ng L^{-1}). This is consistent with the relatively low pesticides levels measured in the ED passive samplers from High Island in the current monitoring year (Table 8). No passive sampling was undertaken at High Island in the previous monitoring year, so it is not known whether the higher pesticide levels in the river mouth in 2014-15 were also reflected at High Island in that year.

In the Tully region, a similar repeated grab sampling program was undertaken throughout the wet season, with samples collected on five occasions from three sites (Tully River mouth, Bedarra Island directly offshore from the Tully River and Dunk Island which lies to the north of the Tully). As for the Russell/Musgrave sampling, samples were collected to coincide with major flow events (Figure 11 F). Although the first rain of the year fell in late December, pesticides were first detected at measurable quantities in the grab samples following the high flow event in March 2016 (Figure 11 F). The highest March 2016 PSII-HEq concentration was 218 ng L^{-1} (Category 3) at the Tully river mouth, with a very similar profile to the Russell/Mulgrave river mouth grab samples (Table G-1). The Bedarra Island grab sample from the same high flow event in March 2016 had a very similar pesticide profile but lower concentrations than at the river mouth, although it was a notably high concentration considering its distance offshore (41 ng L^{-1}). Whilst no pesticides were at detectable levels in two grab samples from the river mouth in 2014-15, PSII-HEq concentrations reached Category 2 levels in the 2013-14 monitoring year (Appendix F Figure F-2) when both diuron and metolachlor exceeded the low reliability IWLs for marine waters (ANZECC and ARMCANZ, 2000a, Gallen et al., 2014). Concentrations in the later months of the 2015-16 wet season remained elevated at all sites, although lower than during the first major flow event, and pesticide levels were similar at both Dunk and Bedarra Islands at both subsequent sampling events (Table G-1). Diuron, atrazine, hexazinone and imidacloprid were the most frequently detected pesticides in all the grab samples.

4.3.2 Burdekin Region

The Burdekin River is historically the river with the highest long-term median discharge volume, however above median discharge is intermittent and highly reliant on large rainfall events in the catchment. In 2015-16, discharge from the Burdekin River to the Reef lagoon was double the previous year but still very low compared to the long-term average (0.4 times average, Table 5). Following a first flush in November 2015, two main flow events occurred in early January and early February 2016 and river flow was minimal for the remainder of the year (Figure 12). Sampling data were not available for the first flush event, and peak concentrations of PSII herbicides at Barratta Creek monitoring site were associated with the January high flow event (Figure 12 A). The current year PSII-HEq Max was higher than the previous year (which was the first year monitored; Table 9), but as discussed above, comparisons to previous years are complicated by missing samplers during the heaviest rain period in 2014-15 (for historical data see Appendix H Figure H-6).

Table 9: Summary statistics for the maximum and Wet and Dry Season average PSII-HEq concentrations (ng L^{-1}) since monitoring commenced in the Burdekin region. Block colours indicate the maximum PSII-HEq Index category for that year

Site		Routine sampling commenced	Risk category										Plume Frequency 2015-16
			2015-16	2014-15	2013-14	2012-13	2011-12	2010-11	2009-10	2008-09	2007-08	2006-07	2005-06	
Barratta Creek Mouth	PSII-HEq Wet Avg	2014-15	6.1	5.0										1.0
	PSII-HEq Dry Avg		*0.16*†	-										
	PSII-HEq Max		18	8.8										

†*Unreliable: only 1 successful sampling period in the season*

- no data available for this season (EDs overdeployed, not sent or lost)

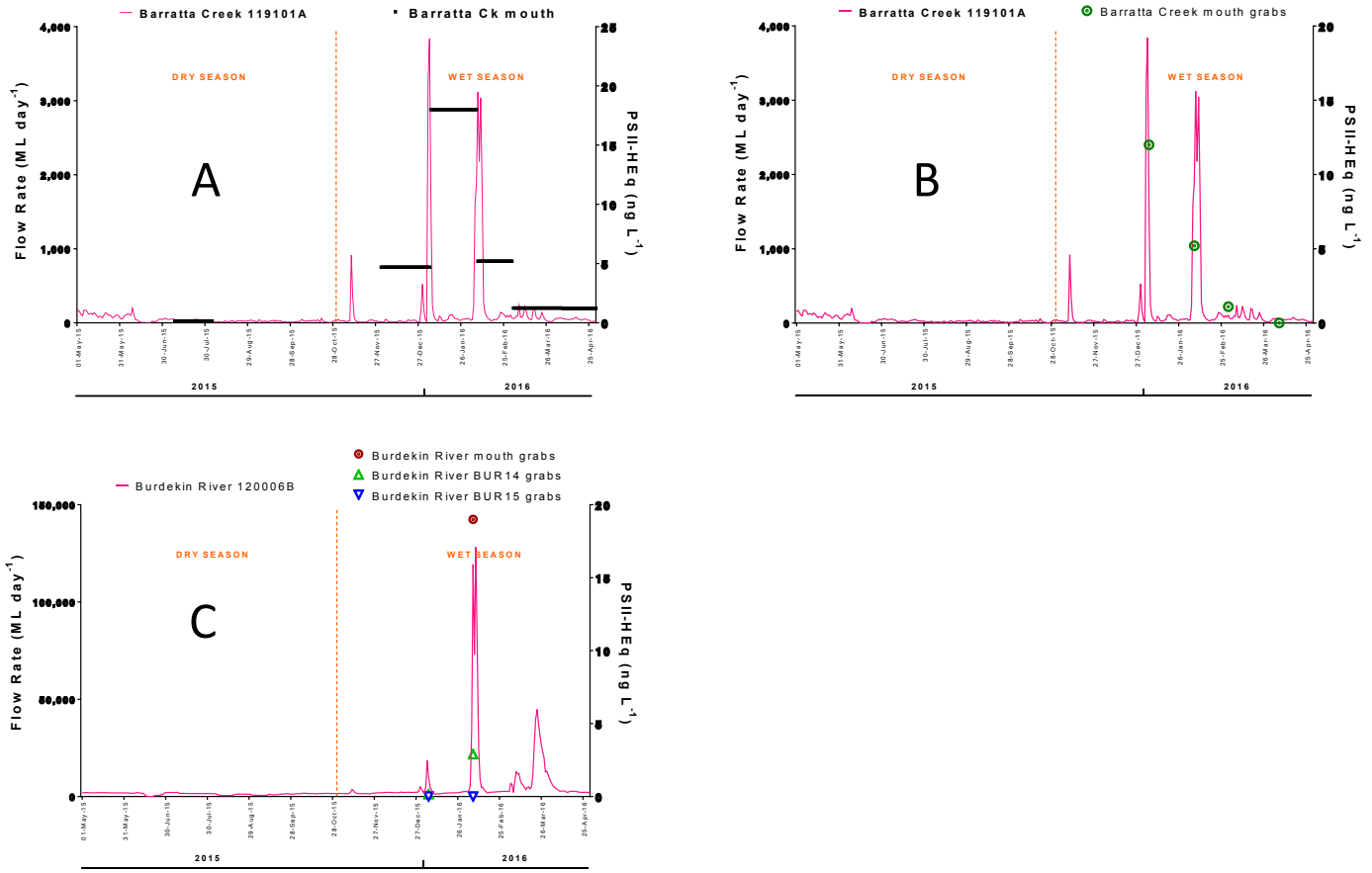


Figure 12: Temporal trends in PSII-HEq at Barratta Creek mouth fixed passive sampling site (A) and PSII-HEq levels in grab samples from (B) Barratta Creek mouth and (C) Burdekin River mouth in 2015-16, relative to the flow rate of the rivers influencing the sampling sites. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network.

Almost all the PSII herbicides (and metabolites) monitored in this program were identified in the samplers from Barratta Creek and were, for most of these (including ametryn, atrazine, bromacil, diuron, hexazinone, simazine and tebuthiuron; Appendix F Table F-7), detected in 100 per cent of the samplers over the wet season. Only fluometuron, prometryn and terbutryn were not above detection limits in any sampler. The other pesticides MCPA and metolachlor were also frequently detected. Using PDMS samplers, chlorpyrifos and pendimethalin were often detected but at very low concentrations in the wet season (Appendix F Table F-7).

Historically, atrazine and atrazine metabolites have typically dominated the pesticide profile at Burdekin sites, including those sites monitored in previous years but no longer in the current program (e.g. Cape Cleveland; (Gallen et al., 2016)). The same atrazine-dominated profile was observed at Barratta Creek in 2015-16. In January 2016, when the highest concentrations were measured, atrazine made up 70 per cent of the total PSII herbicide concentration (Figure I-6) and represented 47 per cent of the PSII-HEq concentration.

A review of the extent of the Burdekin flood plume indicated that average flood events could reach a northward distance of approximately 200 km, and the maximum for extreme large flood events could be approximately 500 km (Lewis et al., 2006). In previous dry years, sites located within this region have remained Category 5 on the PSII Index suggesting minimal northwards transport of pesticide loads (Gallen et al., 2016). In 2015-16, although generally a dry year, the main rain events in early 2016 resulted in a PSII-HEq Max value in the low Category 4 range (Table 9).

In addition to deploying passive samplers at the Barratta Creek mouth, grab samples were also collected from this location, as well as from several locations within the Burdekin River mouth (to the south of Barratta Creek). The Burdekin River is a large river system, with river flow rates approximately two orders of magnitude higher than Barratta Creek and a different flow event pattern (Figure 12 B vs C).

Whilst the 2015-16 annual load of pesticides discharged from the Burdekin River was around one third of that for Barratta Creek, the profile of pesticides was fairly similar, dominated by atrazine, diuron and 2,4-D (Huggins et al., *in prep*). Tebuthiuron was, however, only discharged from the Burdekin River, and was not present in the Barratta Creek. Consistent with the loads profiles and the passive sampling results from the Barratta Creek mouth, the profiles of pesticides in the grab samples at both river mouths were dominated by atrazine (and its breakdown products), diuron and 2,4-D, with tebuthiuron at detectable levels only in the Burdekin samples (Table G-1). The highest pesticide concentrations in passive samplers at Barratta Creek fixed monitoring site were measured in the deployment period 5 January to 6 February, which coincided with two high flow events that occurred in the first week of January and the first week of February. Grab samples were collected during each of these high flow events, and Category 4 PSII-HEq Max values in the grab samples were reached at Barratta Creek mouth on 5 January (12 ng L^{-1}) and at the Burdekin River mouth on 6 February (19 ng L^{-1}). The Burdekin River mouth sample also contained tebuthiuron at detectable levels (7.7 ng L^{-1}, Table G-1). The levels of pesticide measured in the Burdekin River mouth were quite localised as grab samples from two other positions (BUR14 and BUR15, to the south of the main discharge channel) had considerably lower levels (Figure 12 C). At present, a fixed passive sampling site is located within the Barratta Creek mouth but no ongoing monitoring of the Burdekin River outflow is taking place. The comparable pesticide levels in the Burdekin River and Barratta Creek grab samples, suggests that future assessments of passive sampling site locations should consider the optimal positioning of the fixed monitoring site in this area, particularly if there is overlap in the typical flood plume paths from these two river systems.

4.3.3 Mackay Whitsunday Region

The Mackay Whitsunday region had the highest rainfall of all the Reef discharge catchments in 2015-16, with the maximum weekly rainfall of 400 mm falling in the O'Connell catchment in early March 2016 (Table 4). Despite this, the annual discharge from the major rivers in the region were all well below the long-term (LT) median (0.4 – 0.8 times the LT average; Table 5). Distinct wet season high flow events characterised the river flow across the region (two main events in February and March 2016), with low or no flow typically

through the rest of the year (Figure 13). At all the fixed monitoring sites, where continuous monitoring data were available, highest pesticide concentrations were observed during the first of these high flow events. The first flush events of the wet season, although typically at lower flow rates than the high flows later in the season, were also associated with elevated pesticide concentrations (Figure 13).

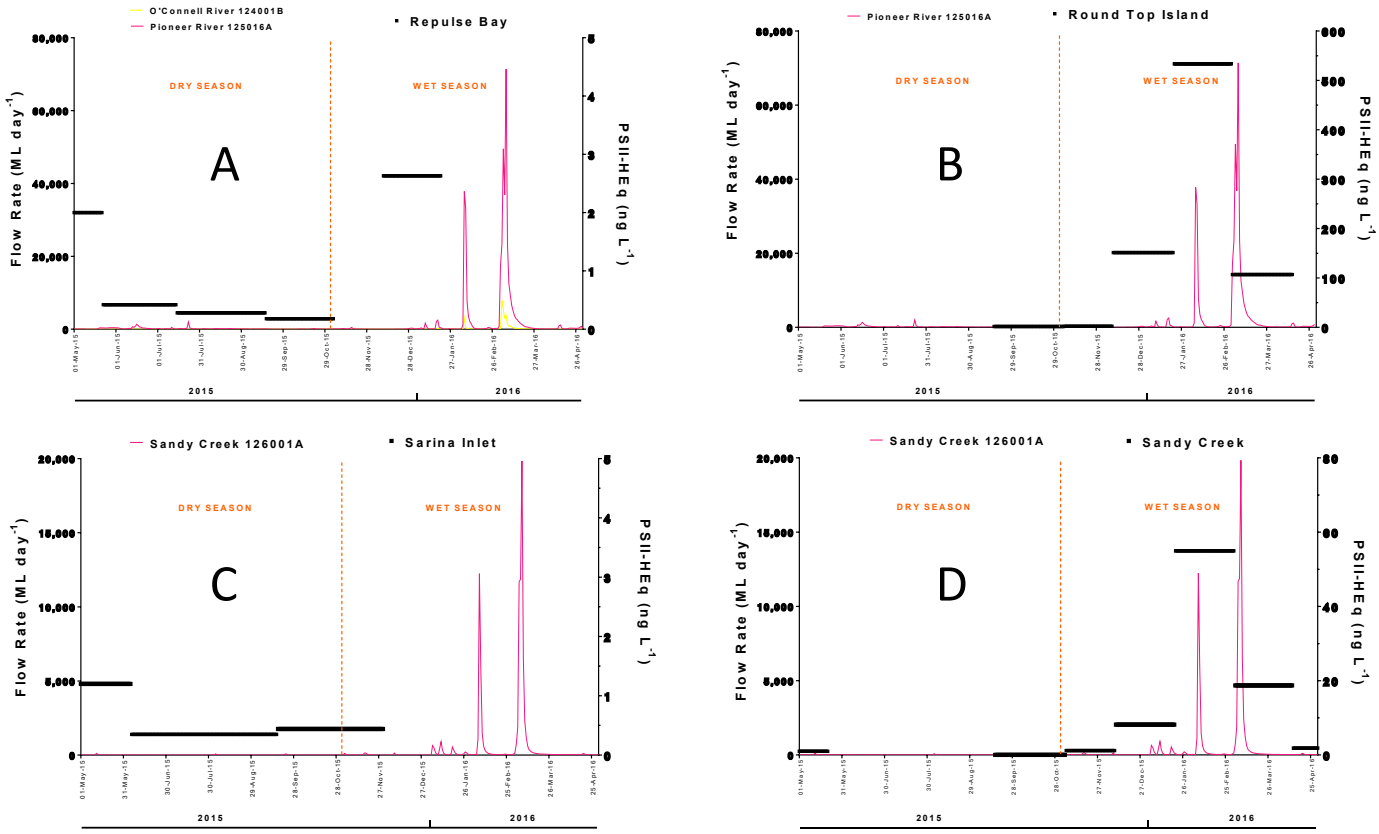


Figure 13: Temporal trends in PSII-HEq in 2015-16, relative to the flow rate of rivers influencing the four Mackay Whitsunday fixed passive sampler sites. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network.

Concentrations of PSII herbicides during the wet season at Round Top Island were the highest reported in ED samplers at the sites currently being monitored, compared to both current year and all historically reported levels. Elevated pesticide levels at Round Top were associated with a small first flush event at the beginning of the wet season and two high flow events in the Pioneer River (Figure 13 B). Pesticide levels in the available samples at the other fixed monitoring sites in this region were not as elevated as at Round Top; for example, levels at Sandy Creek were almost identical to 2014-15 with a PSII-HEq Max value at a low Category 3 (Table 10). Trend comparisons at the other two sites (Sarina Inlet and Repulse Bay) were not possible as only one wet season sampler was successfully deployed in the 2015-16 wet season at both these sites (Table 10; for historical data, see Appendix I Figure I-7 to Figure I-10).

PSII-HEq Max values at sites located in this region have been consistently higher than sites located in other regions (Table 7). This is the seventh consecutive year that the Mackay Whitsunday region had the site with the highest PSII-HEq Max concentration. Since monitoring commenced, 24 per cent of PSII-HEq Max values in the Mackay Whitsunday region have been classified as Category 5, 38 per cent of values have been Category 4 and a further 38 per cent as either Category 2 or 3 (Table 10). These comparatively higher concentrations may reflect both the land use, pesticide usage and land management practices of the adjacent catchment. as well as the ideal positioning of the monitoring sites to intercept flood plumes from nearby rivers.

PSII herbicides (and metabolites) detected at sites in this region include ametryn, atrazine (and DE/DI atrazine), diuron, hexazinone, simazine and tebuthiuron, as well as trace levels of metribuzin and propazine (Table F-8 to Table F-11). Atrazine, diuron, hexazinone and tebuthiuron were detected in every sample from this region. Other herbicides imidacloprid, 2,4-D and metolachlor were regularly detected, and metsulfuron-

methyl and metribuzin were detected in this region only. Using PDMS samplers, propazine and pendimethalin were detected at low concentrations, whilst chlorpyrifos (marginally) exceeded the marine guideline value for one sampling period at Round Top Island. It should be noted that the concentrations of 2,4-D, imidacloprid, metolachlor, metsulfuron-methyl, metribuzin and chlorpyrifos were not included in the calculation of the risk category, and therefore the risk from all pesticides could be higher in this region than what is reported here.

Table 10: Summary statistics for the maximum and Wet and Dry Season average PSII-HEq concentrations (ng L^{-1}) since monitoring commenced in the Mackay Whitsunday region. Block colours indicate the maximum PSII-HEq Index category for that year.

Site		Routiine sampling commenced	Risk category										Plume Frequency 2015-16
			2015-16	2014-15	2013-14	2012-13	2011-12	2010-11	2009-10	2008-09	2007-08	2006-07	2005-06	
Repulse Bay	PSII-HEq Wet Avg	2014-15	*2.6†*	11										1.0
	PSII-HEq Dry Avg		0.29	-										
	PSII-HEq Max		***2.6†***	**34**										
Round Top Island	PSII-HEq Wet Avg	2014-15	198	1.6										1.0
	PSII-HEq Dry Avg		1.7†	-										
	PSII-HEq Max		**533**	**2.2**										
Sandy Creek	PSII-HEq Wet Avg	2014-15	17	17										1.0
	PSII-HEq Dry Avg		-	-										
	PSII-HEq Max		**55**	**70**										
Sarina Inlet	PSII-HEq Wet Avg	2009-10	-	18	14	85	12	22	114					1.0
	PSII-HEq Dry Avg		0.39	1.7	2.3	3.6	1.4	2.4	0.88					
	PSII-HEq Max		**0.44**	**36**	**34**	**234**	**22**	**47**	**495**					

†Unreliable: only 1 successful sampling period in the season

- no data available for this season (EDs overdeployed, not sent or lost)

Round Top Island site had the highest concentration of diuron compared to any other site and consequently, it also had the highest PSII-HEq Max of 533 ng L^{-1}, which is a Category 2 risk of herbicide exposure on the PSII-HEq Index (Table 10). The current year maximum concentrations were of a similar magnitude to levels measured at Sarina Creek in 2009-10. As the samplers record a time-averaged concentration, it is not known exactly how long these elevated concentrations were maintained at Round Top. However, Category 2 concentrations were experienced for, at most, one month (consistent with the sampler deployment period), after which the time-average concentrations dropped to Category 3. A minimum Category 3 risk was maintained at Round Top for a four-consecutive month period (early December 2015 to mid-April 2016) and this could increase the risk of reduced photosynthesis in diatom and seagrass species during this period. Round Top Island is not currently a monitoring site for either coral or seagrass under the MMP.

As discussed above, consistent with the high pesticide concentrations observed at Round Top Island (Figure 13; Appendix F Table F-9), there were three (minor) GV exceedances in 2015-16 (diuron, imidacloprid and chlorpyrifos). Comparative historical data are lacking for this site as sampling only commenced in 2014-15, and the maximum concentration in that year is likely understated due to gaps in wet season deployments. Thus, ongoing monitoring at this site is necessary to understand whether these exceedances are an isolated incidence or will be regular occurrences. Historical data from all MMP monitoring sites (see Appendix H) indicate that high pesticide concentrations (and guideline exceedances) are not necessarily correlated with large flow events possibly due to dilution effects associated with the high volume of water discharged during these events. Pesticide concentrations in river discharges may therefore be higher in drier years because there is less dilution. However, in dry years, sufficient discharge is required for pesticides to reach monitoring sites that are not close to the river mouth. The Round Top Island monitoring site is approximately 5 km off-shore from the Pioneer River mouth and has a flood plume frequency of 1 (Appendix E Table E-2), suggesting a high potential for plume waters to reach this monitoring site. The low dilution effects associated with drier years may explain the high pesticide concentrations observed at Round Top Island in 2015-16, although longer-term data to include wetter years would be necessary to confirm this. Modelling the pesticide

movement from the Pioneer River into the nearshore environment would also be an option to better understand the observed high levels. This may be achieved in the future using the eReefs hydrodynamic model using the temporal end-of-catchment pesticide levels as input data.

4.3.4 Fitzroy Region

Although discharge from the Fitzroy River was slightly higher in 2015-16 than the long term average (1.3 times the LT average; Table 5), river flow was relatively low for most of the wet season with one major high flow event occurring in January/February 2016 followed by a smaller event in March (Figure 16). Flow conditions were similar to those during the previous two monitoring years (Figure H-11), and concentrations of PSII herbicides during the wet season at North Keppel Island were low and consistent with concentrations detected in 2013-14 and 2014-15 (Table 11:; for historical data see Appendix I Figure I-11).

PSII herbicides detected at North Keppel Island in 2015-16 included atrazine, diuron, hexazinone and tebuthiuron (Table F-12). Atrazine (maximum concentration 0.46 ng L^{-1}) and diuron (maximum concentration 0.11 ng L^{-1}) were detected most frequently at this site (89 and 78 per cent of samplers, respectively) but at very low concentrations. Tebuthiuron typically dominates the PSII herbicide profile at North Keppel Island (Appendix I Figure I-11) and elevated concentrations (2.0 – 2.6 ng L^{-1}) were observed in the January/February 2016 samplers when the first and only significant rain of the year fell (Figure 16; Table F-12).

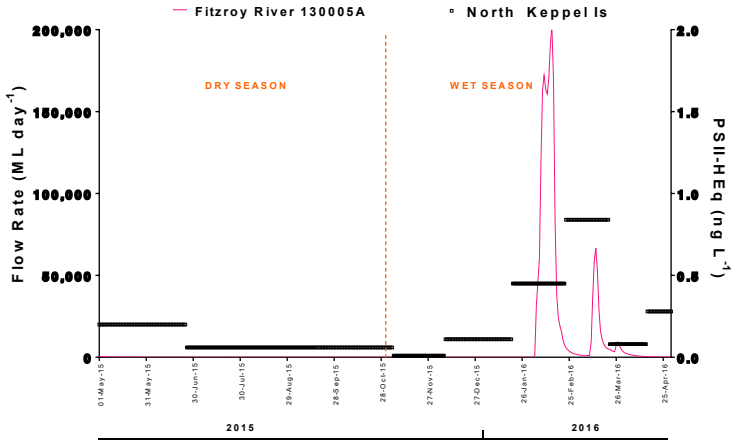


Figure 14: Temporal trends in PSII-HEq in 2015-16, relative to the flow rate of the Fitzroy River influencing N Keppel Island's fixed passive sampler site. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network.

Table 11**:** Summary statistics for the maximum and Wet and Dry Season average PSII-HEq concentrations (ng L^{-1}) since monitoring commenced in the Fitzroy region. Block colours indicate the maximum PSII-HEq Index category for that year

Site		Routiine sampling commenced	Risk category											Plume Frequency 2015-16
			2015-16	2014-15	2013-14	2012-13	2011-12	2010-11	2009-10	2008-09	2007-08	2006-07	2005-06	
North Keppel Island	PSII-HEq Wet Avg	2005-06	0.30	0.26	0.18	4.4	1.7	4.0	4.1	0.73‡	1.9	0.94	1.7	0.95
	PSII-HEq Dry Avg		0.11	0.07	0.38	0.88	0.42	0.69	-	0.86	-	0.45	0.07	
	PSII-HEq Max		0.84	0.66	0.60	13	3.4	12	8.7	1.1	2.6	1.9	1.9	

‡*Only 2 successful sampling periods in the season*

The PSII-HEq Max value at North Keppel Island in the Fitzroy region has been consistently a low Category 4 or 5 since monitoring commenced in 2005 (Table 11), with the majority (eight out of the eleven years or 85 per cent) being Category 5 on the PSII-HEq Index. The 2015-16 PSII-HEq Max at this site was the second lowest of all fixed monitoring sites. The seasonal differences in maximum concentrations between wet and dry seasons are consistently small at this site (Table 11; Figure 16).

5. Discussion

Pressures and overall trends in pesticide levels at fixed monitoring sites. The current monitoring year experienced relatively low-level pressures governing the release of pesticides into the Reef lagoon. Overall, 2015-16 was a dry year compared to long term averages (rainfall ranged from average to well below average across all catchments and there was no cyclone activity) and river discharges were generally lower than their long-term averages. Although there were some minor exceptions, total catchment runoff, quantified as pesticide end-of-catchment loads, was similar to 2014-15 levels across most catchments and were generally at the lower end of reported annual runoff since monitoring began. Likewise, the profiles of pesticides in the discharged loads were broadly in line with recent years with no major changes except a marginal shift in profile towards higher tebuthiuron loads in the Fitzroy catchment in the current monitoring year compared to the previous two years.

Consistent with low level pressures, pesticide concentrations at fixed monitoring sites were, at most sites, similar to the previous monitoring year, and overall were lower than levels during past 'high' pressure La Niña years when rainfall and cyclonic activity were considerably above long-term averages. There was one significant exception to this trend and at Round Top Island in the Mackay Whitsunday region, pesticide levels were elevated across most of the wet season and the maximum concentrations were the highest since monitoring began for the sites currently monitored. Concomitant with these high pesticide levels, there were minor guideline value exceedances for three pesticides, diuron, imidacloprid and chlorpyrifos. Comparative data are lacking for this site (sampling commenced 2014-15), and ongoing monitoring is necessary to understand whether these exceedances were isolated incidences or are typical of this catchment and this is a higher risk site. The interpretation of these high 2015-16 pesticide levels was complicated by incomplete comparative monitoring data from the previous year. A particular focus going forward will be to develop strategies to reduce sampler thefts, damage and other avoidable losses to improve trend analyses.

Even when complete monitoring data sets are available, it can still be challenging to elucidate the reasons behind observed trends in monitored offshore pesticide data, especially when changes to pressures occur simultaneously. Whether a reduction in pesticide detections at offshore monitoring sites is due to, for example, climatic variabilities influencing pesticide transport potential from catchment to Reef or better land management practices reducing pesticide usage and runoff, or both, requires a detailed understanding of all the factors driving these changes. Quite often, the necessary data needed to interpret these changes (particularly pesticide usage and application rates) are either not available or only updated periodically. All these factors, as well as the overall small number of fixed passive sampling sites, make it difficult to quantitatively assess the link between improved land management practices as a direct result of Reef Plan initiatives and changes in nearshore marine water quality. Since pesticides are principally exported during runoff events in the wet season, river discharge is expected to be a key driver of pesticide concentrations reaching offshore monitoring sites. To assess the success of Reef Plan initiatives, an approach to identify long term trends in pesticide levels at strategic monitoring sites due to changes in pesticide runoff rather than a result of inter-annual changes in river flow is required. Statistical models to achieve this, for example, a generalised additive modelling framework (Kuhnert et al., 2015), will be considered in future reports.

PSII herbicide profiles. Consistent with previous monitoring years, diuron, atrazine and hexazinone were the most frequently detected and abundant PSII herbicides at most sites (Kennedy et al., 2010a, Bentley et al., 2012, Kennedy et al., 2012, Gallen et al., 2013, Gallen et al., 2014, Gallen et al., 2016). These herbicide residues reflect land-use applications primarily in the sugar cane, horticulture and grain cropping industries (Bainbridge et al., 2009, Lewis et al., 2009, Kroon et al., 2013, Devlin et al., 2015). A comparison between end-of-catchment load data and maximum pesticide concentrations at each site indicated that the profile of PSII herbicides detected at the fixed monitoring sites are almost identical to those in the discharged loads and appear consistent with the land use in the adjacent catchment areas. The major land uses within the

Reef catchments are agricultural cropping, livestock grazing and other primary production (such as forestry) (ABS, 2010, DSITI, 2012d). Sugar cane farming is clustered heavily along many rivers in NRM region, for example, throughout the Wet Tropics region, Barratta Creek (Lower Burdekin) region and Proserpine and Pioneer Rivers (Mackay-Whitsunday region), with 18 per cent of the Mackay Whitsunday region alone used for sugar cane farming (Lewis et al., 2009, DSITI, 2012b, c, e). Modelling estimates have suggested that sugar cane contributes >90 per cent of the annual load of PSII herbicides transported into waterways and marine areas from Reef catchments (Kroon et al., 2012).

Diuron is typically associated with the intensive sugar caning activity in the coastal area of the Tully River, Herbert River, Pioneer River and Sandy Creek catchments, and high loads were discharged from these catchments in 2015-16. Consistent with previous years, PSII herbicide profiles at many fixed passive sampling sites were also dominated by diuron. Atrazine, also registered for use in sugarcane, has historically been used extensively in the Barratta and Burdekin catchments, and as found during recent passive sampling activities in these catchments (O'Brien et al., 2016), this herbicide continues to represent the highest proportion of PSII herbicides at the monitoring sites in this region.

Tebuthiuron loads have been, and continue to be, associated almost exclusively with the Burdekin and Fitzroy River catchments where land use is predominantly grazing. The North Keppel Island site in the Fitzroy region has in the past been characterised by relatively high concentrations of tebuthiuron, including an exceedance of the GBRMPA guidelines in 2013 (Gallen et al., 2013). In the current monitoring year, the maximum tebuthiuron concentration across all the sites was again measured at North Keppel. Following the large loads of tebuthiuron discharged from the Fitzroy (a total of 11890 kg) and Burdekin Rivers (a total of 1070 kg) between 2010 – 2013, tebuthiuron levels dropped considerably but as of 2015-16 were increasing again. This PSII herbicide is only discharged at trace levels from catchments other than the Fitzroy but is consistently detected up and down the Reef coastline at low levels. This suggests tebuthiuron has long-range transport potential reaching as far as the Wet Tropics region, which is consistent with its long half-life (under Reef relevant conditions) of over 900 days (Negri et al., 2014). Despite its widespread usage in grazing areas, there is little data relating to tebuthiuron application in Reef catchments and its movement in catchment run-off (Devlin et al., 2015).

Other pesticide profiles. Farming best management practice of Reef-based agricultural industries (particularly sugar cane cultivation) endorses the use of alternative herbicides (such as 2,4-D, glyphosate) (Reef Plan, 2013, Smith et al., 2015). In addition, a large number of other pesticides are also now known to be used and transported in catchments discharging to the Reef (Devlin et al., 2015), including other herbicides (i.e. herbicides that are not used as a PSII herbicide alternative weed control e.g. metsulfuron-methyl), insecticides and fungicides. The prevalence and loads of other pesticides are now being monitored as part of GBRCLMP alongside the five PSII herbicides targeted as a priority for reduction in Reef Plan (2009 and 2013). The contribution of the PSII herbicides (in sum total) to the annual load of all pesticides has decreased: for example, in 2015-16, the load of non-PSII inhibiting pesticides ranged between 26 – 181 per cent of the total PSII herbicide load across the monitoring sites, compared to 12 – 21 per cent in 2012-13 (Gallen et al., 2013). In three catchments (Mulgrave, Tully and Herbert Rivers, all in the Wet Tropics), total loads of other pesticides were higher than the total for PSII herbicides. Metolachlor had the highest total load of non-PSII inhibiting pesticides, with the Fitzroy River the largest contributor, followed by 2,4-D which had increased substantially from the 2014-15 maximum (Wallace et al., 2016).

2,4-D, imazapic, imidacloprid, metolachlor, MCPA and metsulfuron-methyl were routinely detected in passive samplers in the current monitoring year. Consistent with the previous year when routine analysis of these other pesticides in both passive and grab samples was initiated, 2,4-D, MCPA (both auxin growth inhibitors) and metolachlor (a long chain fatty acid inhibitor) were detected in the ED (polar) passive samplers at most sites. In addition, in 2015-16, imidacloprid was also detected at all monitoring sites except for North Keppel Island in the Fitzroy region. Compared to PSII herbicides, however, detected concentrations of other

pesticides at the monitoring sites were consistently very low (except at Round Top Island, other pesticide concentrations at all sites were <1 ng/L).

Although typically monitored at low concentrations, the frequency of detection of these other pesticides combined with end-of-catchment loads that are (in many cases) comparable to those of the priority PSII herbicide's and increasing, reinforces the importance of continued monitoring of these chemicals. It is evident that rivers are delivering diverse mixtures of pesticides with multiple modes of action into the marine environment, and this presents a combined toxicity risk to aquatic life. At present, there are limited passive sampler calibration data available for many of the other pesticides now in use in Reef catchments. Some pesticides (e.g. the herbicide asulam) are highly water soluble and unlikely to accumulate in passive samplers, and therefore a combination of both grab and passive sampling will likely be necessary to increase the probability of detecting them in the marine environment. Calibration studies in the field are labour intensive, however they may need to be considered in the future to better understand the uptake of these chemicals into passive samplers, and more accurately estimate water concentrations.

Pesticide metric for risk categorisation. The PSII-HEq index was identified as a suitable indicator to detect changes in inshore pesticide levels over time based on a review by Kuhnert et al. (2015). In both the current year and historically, monitoring sites located in the Mackay Whitsunday region have encountered the highest risk of exposure to PSII herbicides, with PSII herbicide concentrations that have been shown to inhibit photosynthesis in some species of coral and seagrass (Category 2 and 3 on the PSII Herbicide Index) (Flores et al., 2013). Round Top Island, which had the highest recorded pesticide levels (both on a concentration and a toxic equivalence basis) for currently monitored sites to date, is located within this region and, together with Sarina Inlet in previous years, are the sites where highest risk has been identified. Based on a previous risk assessment of the priority PSII herbicides, the Mackay Whitsunday region was also identified as having the highest risk of toxic effects to coral reefs and seagrasses and the reduction of pesticides in this region is a management priority (Brodie et al., 2013). It should be noted that the locations of the passive samplers, which are in close proximity to river and creek mouths in the Mackay Whitsunday region, likely skew the data towards a higher number of herbicide detections (and at higher concentrations) at sites located in this region, compared to other regions.

At present, only the PSII herbicides are included in exposure risk assessments (using PSII-HEq concentrations). The use, run-off potential, transport, fate and ecotoxicity of alternative herbicides (and other pesticides) are not well understood, despite their already extensive use, and it is essential to determine whether they may have negative effects on the health and resilience of the Reef. A desktop assessment of the relative risk of alternative herbicides (considering the risks of off-site run-off and toxicity across a range of indicative trophic levels) found that several of the proposed alternatives presented a risk comparable to those of the priority PSII herbicides they were replacing (Davis et al., 2014). It should be noted however that in the same assessment 2,4-D and MCPA (two of the most frequently detected alternatives in passives samplers in 2015-16) were predicted to have lower environmental risks than the priority PSII herbicides. It appears that care must be taken when restricting or prohibiting the use of certain problematic pesticides as alternatives may not be having the desired result of reducing off-site environmental impacts. Rather than shifting usage to pesticides with potentially similar risk profiles, improved management practices to reduce pesticide run-off with an emphasis on those that are the most cost effective may prove more useful in reaching Reef Plan targets by 2018 (Lewis et al., 2013, Davis et al., 2014, Lewis et al., 2014).

Given the uncertainty over the risk profile of some non-PSII inhibiting pesticides, including other pesticides in the exposure risk assessment under the MMP is becoming increasingly important. The multisubstance – potentially affected fraction (ms-PAF) approach to assess mixture toxicity of pesticides (Traas et al., 2002) is an alternative approach to the PSII-HEq index used in this program that can assess the cumulative risk for a suite of pesticides that have different modes of action. The additive model (for PSII herbicides with the same mode of action) was applied to the current year's monitoring data as a case study (see Section 8). When the

non-additive model has been developed (in progress by DSITI), this will be a highly valuable and the recommended tool to assess the combined toxicity of both PSII and other pesticides.

Concentration gradients with distance from river mouths. The sampling conducted as part of the terrestrial run-off component of this program since 2010 enables a direct comparison of pesticide levels at sampling locations close to river discharge points (within river mouths) compared to levels further offshore at fixed monitoring sites. Decreasing concentration gradients with distance offshore are indicative of dilution, degradation and other effects following dispersal of pesticide loads into the wider Reef lagoon water body. Historically, localised areas of highly elevated PSII herbicide concentrations have occurred near river mouths within the Wet Tropics whereas samples collected kilometres into the Reef lagoon at fixed monitoring sites indicate a lower risk of exposure. In 2015-16, paired grab samples between river mouths and offshore monitoring sites collected during high river flow events showed a clear dilution effect with distance from a river mouth. PSII HEq concentrations at river mouths reached Category 3 levels for some grabs samples and whilst concentrations were observed to decrease with distance from the river mouth, concentrations at distant sampling sites (e.g. up to 14 km in the case of Dunk Island on the Tully River transect) were still elevated when compared to pre-event concentrations. The profiles of pesticides were highly similar between the river mouths and the offshore locations, consistent with the adjacent river catchment being the primary source of the pesticides observed in the nearshore environment.

In some catchments, the concentrations of pesticides are more constantly elevated, such as at Barratta Creek where flow is less seasonally driven. In 2015-16, pesticides were not detected at either the Barratta Creek or Burdekin River mouths until very high flow events later in the wet season, and no distinctive first flush with the first high flow of the year was evident. This is consistent with a more constant flow and related discharge throughout the year. The pesticide levels in grab samples from both these river mouths were similar (low category 4), despite lower annual loads discharged from the Burdekin River catchment, and were highly localised to the main flow channels in the river mouth.

Whilst the frequency and intensity of concentration pulses associated with high flow river events are reduced with distance from river sources, low-level chronic exposure of herbicides in nearshore marine areas as demonstrated in this MMP may still have significant impacts at the receiving environments. Effects may include changes in microbial communities (Magnusson et al., 2012), negative effects on seagrass energetics and growth (Negri et al., 2015), as well as reduced photosynthesis and reproductive output of corals (Negri et al., 2005, Cantin et al., 2007) and other Reef/tropical photosynthetic species. Furthermore, cumulative impacts of herbicide exposure and other external stressors (such as rising sea surface temperature) have been demonstrated and are likely to increase in the future based on current climate trends (Negri et al., 2011, van Dam, 2012, van Dam et al., 2012). These interactions reemphasise the importance of programs such as Reef Plan and the MMP in implementing effective land management practices and measuring the resulting trends in water quality to protect sensitive marine organisms against the consequences of global stressors such as climate change.

Future directions. Land use in the Reef catchments continues to change, and thus the impacts of these activities on the surrounding environment are dynamic. With changing land use, it is likely that changes in both the amounts and types of agricultural pesticides being used, as well as the timing and methods of application, will influence environmental levels and the level of risk to aquatic marine life. There are no data available for the current local-scale usage of pesticides in the Reef catchments, apart from limited estimates in the 1990's and more general estimates from 2008-2009 that are unlikely be relevant to current pesticide usage (ABS, 2010, Devlin et al., 2015). This lack of data severely limits assessments of pesticide losses (relative to the amount applied) as well as accurate modelling of pesticide loads at the catchment scale. Pesticide usage is seasonal, crop-specific and can fluctuate yearly based on specific pest pressures, climatic conditions, regulatory action (such as the restriction on diuron use in 2012), use of resistant crop varieties or the development of herbicide resistance in weeds (Devlin et al., 2015). The currently available information

allows only comparison of the types of pesticides being released in catchment runoff (i.e. end-of-catchment loads) and those pesticides monitored in near shore areas. To understand the underlying factors driving the trends in pesticide levels in catchment runoff, longer term data are likely to be required. In the meantime, industry extension staff and updated land use maps would be a useful resource to identify changes in pesticide usage and relating these changes to monitored pesticides under the MMP.

Relatively low levels of PSII herbicides were detected at most sites in 2015-16 and for prior years (for which monitoring data are available). Whilst PSII herbicide exposure is not expected to be a high-risk factor for adverse impacts on Reef health, it is important to understand the cumulative impacts of low level chronic exposure to PSII herbicides and other pesticides in conjunction with other stressors, e.g. light and/or higher sea temperatures. In particular, the compound effects of simultaneous stressors on key organisms on the Reef including the effects of global climate change (increasing sea temperatures, ocean acidification), an increase in the severity and frequency of damaging weather events such as cyclones, and increases in the frequency of flood events are not fully understood. In view of these multiple driving factors for change, interpreting trends remains challenging, but is essential when ascertaining whether improving or declining water quality is driven by land management practices and success of Reef Plan initiatives or is an artefact of climatic conditions. Statistical models to elucidate underlying trends, where possible, are an important consideration for future assessments. However, for these models to be statistically robust, long-term monitoring data are required. This allows the variability due to seasonal climatic changes to be differentiated from other factors, such as land management practices. Following changes to the sampling sites as a result of the 2013/2014 MMP review, six of the current 11 fixed monitoring sites have at most two years of monitoring data. For these sites, additional years of data are necessary for robust trend analyses.

Ultimately, a whole-of-system pesticide exposure assessment may become possible through the eReefs framework, a hydrodynamic model developed for the Reef system. Recent changes to the framework have opened opportunities to potentially apply this model to end-of-catchment pesticide loads and predict the distribution of discharged loads from each catchment into the near-shore environment. Monitoring data generated through the current MMP program could provide necessary field data for model validation both spatially and temporally. The eReefs framework was recently applied to a case study to assess PSII herbicide risk in the Inshore Water Quality 2015-16 MMP report (Waterhouse et al., 2017b) and recent changes to the framework may address limitations that were identified through the case study. This framework would provide three-dimensional capability to predict pesticide concentrations at any point within the Reef lagoon, which increases spatial coverage of pesticide ‘monitoring’ to the whole-of-Reef, as well as generating information that can inform the optimal placement of passive samplers to capture and measure key pesticide pulses released from adjacent catchments. This information will facilitate insight into impacts on ecosystem health and assist in prioritising management action. Whilst monitoring an area as vast and complex as the Reef remains a challenge, long-term monitoring programs such as the MMP are valuable and sensitive tools that can assist in protecting such a significant ecosystem.

6. Conclusions and Directions for Monitoring

In conclusion, overall, the DPSIR framework is an effective approach to understand the complexity of pressures that may result in pesticides reaching sensitive Reef ecosystems. In 2015-16, trends in the pesticide monitoring data could be broadly interpreted in terms of high level pressure data, mainly related to hydrological conditions; i.e. the relatively low pesticide concentrations observed at most fixed monitoring sites were consistent with the relatively low pressures affecting the Reef region throughout the year. Spatially, consistent with previous years and land-usage in the adjacent catchments, highest pesticide concentrations were detected at the Mackay Whitsunday sites. The longer-term change in nearshore marine pesticide levels attributable to changed catchment land management practices, which is the focus of the Reef Plan, however, is statistically challenging to elucidate. Whether the predicted 34 per cent reduction in total pesticide loads across the Reef catchments is reflected in the nearshore monitoring data is unknown.

Given the high inter- and intra-annual climatic and other pressure variability, meaningful trend comparisons require long term and complete monitoring data. A particular focus for future years will be on finding new ways to minimise passive sampler losses and/or damage to achieve successful, consecutive deployments. Changes to the fixed sampling sites were introduced in 2014-15 following a review of the MMP programs. This means that over half of the current sites have only one or two years of continuous data. Pressures over the last two monitoring years have been relatively stable and longer-term data are required for these sites to understand how changes in pressures affect the observed pesticide concentrations. Temporal concentration data for catchment pesticide discharge to the Reef lagoon should also be considered, where possible, in future reports. This will allow a more direct, temporal comparison between end-of-catchment pesticide data for major flow events and the levels reaching fixed monitoring sites.

The current pesticide metric, the PSII-HEq index, was identified as a suitable interim risk indicator in the 2013/4 review of the pesticide MMP. However, the limitations with this metric are well recognised and ultimately, a pesticide metric that can assess ecological risk to marine Reef organisms from mixtures of pesticides with different modes of action is paramount. The current ms-PAF model is a step towards this goal (see case study in Section 8) and when development of the non-additive model has been completed by DSITI, this will be a highly valuable and the recommended risk assessment tool. In the meantime, to avoid retrospective adjustments and consistent risk assessment, the PSII-HEq Index will continue to be used.

Going forward, continued efforts will be made to seek opportunities to collaborate with other Reef Plan programs (such as GBRCLMP) to provide a more integrated view of management practice adoption, paddock scale monitoring, catchment monitoring and marine monitoring that will improve information on the temporal pressures driving pesticide exposure of critical ecosystems. Other areas of potential focus will be to:

- Continue to develop analytical methods to quantify the concentrations of other pesticides which are likely to have an increasing contribution to pesticide loads discharged into the Reef lagoon;
- Consider conducting further field calibration studies to measure the uptake of other pesticides and provide better estimates of water concentrations;
- Develop statistical approaches to separate inter-annual and inter-event effects of flow variability on long-term trends in pesticide levels, to better assess changes in pesticide levels that are attributable to improved land management practices in the adjacent catchments;
- Work with the Inshore Water Quality MMP team to further assess the eReefs framework as a tool to predict spatial and temporal trends in pesticide concentrations in the Reef lagoon and undertake a preliminary model investigation of a specific catchment region to compare predicted pesticide concentrations with historic monitoring data.

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8. CASE STUDY: Comparison of the multisubstance - potentially affected fraction (ms-PAF) and PSII-HEq methods

Introduction

The multisubstance - potentially affected fraction (ms-PAF) method allows the effect of multiple pesticides on an ecosystem to be estimated. The potentially affected fraction of species is determined, i.e. percentage of species in an ecosystem that will theoretically be affected when exposed to a given mixture concentration. This approach has been proposed as a more robust approach to quantify the overall ecological risk of mixtures of pollutants for ecological communities compared to the PSII-HEq approach historically reported for the MMP pesticide monitoring program. Background information on the current state of development of the ms-PAF approach for Reef ecosystem species is given in the methods section above (see section 3.5.4).

For this case study, the ms-PAF for each sample in the monitoring data set reported for the current year was determined based on thirteen PSII herbicides (see Table 12; note that terbuthylazine is included in the model but was not monitored in the current year). The PSII herbicides have been shown to have the same mode of action (PSII inhibition) and follow a concentration addition (CA) model (Faust et al., 2001, Backhaus et al., 2004, Magnusson et al., 2010). The overall approach and the species sensitivity distributions (SSDs) for each of the PSII herbicides were developed by Rachael Smith, Olivia King and co-workers at DSITI. The relevant data are the basis of the pesticide risk assessment component of the 2017 Update Scientific Consensus Statement (Waterhouse et al., 2017a). The two methods of assessing environmental risk of additive herbicide mixtures (the PSII-HEq Index and ms-PAF method) were compared for the current monitoring year, together with the toxic equivalence approach developed by Smith et al. (2016a) and used in the GBRCLMP.

Methodology for ms-PAF approach

The ms-PAF CA model approach was first described by Traas et al. (2002). In brief, to determine the ms-PAF of a field sample that contains a mixture of PSII herbicides, a global[2] PSII herbicide SSD, SSD_G, that represents the percentage of species affected by a mixture of PSII herbicides is determined. To determine SSD_G for a PSII herbicide mix, individual SSDs for each herbicide were normalised to a common dimensionless scale based on hazard units (HU) so that each re-scaled SSD had a PC50 (concentration at which 50% of species are affected) of 1 HU (Figure 15). To do this, for each data point in an individual SSD, the concentration was divided by its PC50 value (also referred to as its α (alpha) value which is the mid-point of a logistic cumulative frequency distribution (CFD) fitted to the SSD; Table 12) and replotted. An 'averaged' logistic CFD was then fitted to the individual HU-scaled SSDs (Figure 15, right graph) to determine a single SSD_G for the mixture defined by an average midpoint of the global distribution (α_G) and an average slope (β_G) (Table 12). To determine the ms-PAF for a field sample using the SSD_G, the concentration of each PSII herbicide in the sample was converted to hazard units (by dividing each concentration by the herbicide's SSD α value (PC50)) and then summed for all PSII herbicides. This gave the total hazard units for all PSII herbicides in the sample, $HU_{ms} = \sum_i HU_i$ for each herbicide, i. The ms-PAF could then be determined from:

$$ms - PAF = \frac{1}{1+\left(\frac{\sum HU}{\alpha_G}\right)^{-\beta_G}} \qquad \text{Equation (1)}$$

The ms-PAF method used here had three modifications from the CA method of Traas et al. (2002): (1) a logistic CFD, rather than a log-logistic CFD, was fitted to the ecotoxicity data of individual herbicides in order to generate the individual SSDs; (2) the midpoint of the curve (α) when PAF equals 50% was used rather

[2] A global regression model fits one model to the cumulative distribution of multiple variables. In this case a logistic model was fitted to the species ecotoxicity data of all 13 PSII herbicides. This global SSD thus provided the representative SSD for all PSII herbicides.

than the median to calculate the HUs; and (3) the parameters, α_G and β_G, were determined by fitting a global CFD using SigmaPlot 13.0 (Systat) rather than assuming $\alpha_G = 1$ and then determining β_G as the average of the β's from the individual SSDs..

The SSDs for which α values are reported in Table 12, as well as the overall ms-PAF approach developed by DSITI, are currently undergoing external review and changes may be made in the future. In particular, the SSD for atrazine is being updated and the revised value was not available before the release of this report. Once completed, atrazine's α value, and therefore also α_G and β_G, reported in Table 12 will be revised. For this reason, only the current year's monitoring data were converted to ms-PAF to avoid retrospective changes to the historical data set.

Table 12: PSII herbicides included in the CA model for the ms-PAF calculations. Alpha and beta values, representing the mid-point and slope of best-fit logistic distributions, for individual herbicide and their mixture are given (where data available).

PSII herbicide	α value	β value
Ametryn	4.3	n.a.
Atrazine*	33	n.a.
Diuron	5.1	n.a.
Hexazinone	9.4	n.a.
Tebuthiuron	53	n.a.
Simazine	79	n.a.
Metribuzin	7.9	n.a.
Bromacil	12	n.a.
Fluometuron	126	n.a.
Prometryn	7.9	n.a.
Propazine	17	n.a.
Terbuthylazine†	*15*	n.a.
Terbutryn	6.0	n.a.
Mixture (SSD_G)	0.942	0.989

n.a. – data not provided (not necessary to calculations)

* Atrazine SSD is in the process of being updated, this α is for the 'old' SSD

† Terbuthylazine was not monitored for in this program, so no data are available

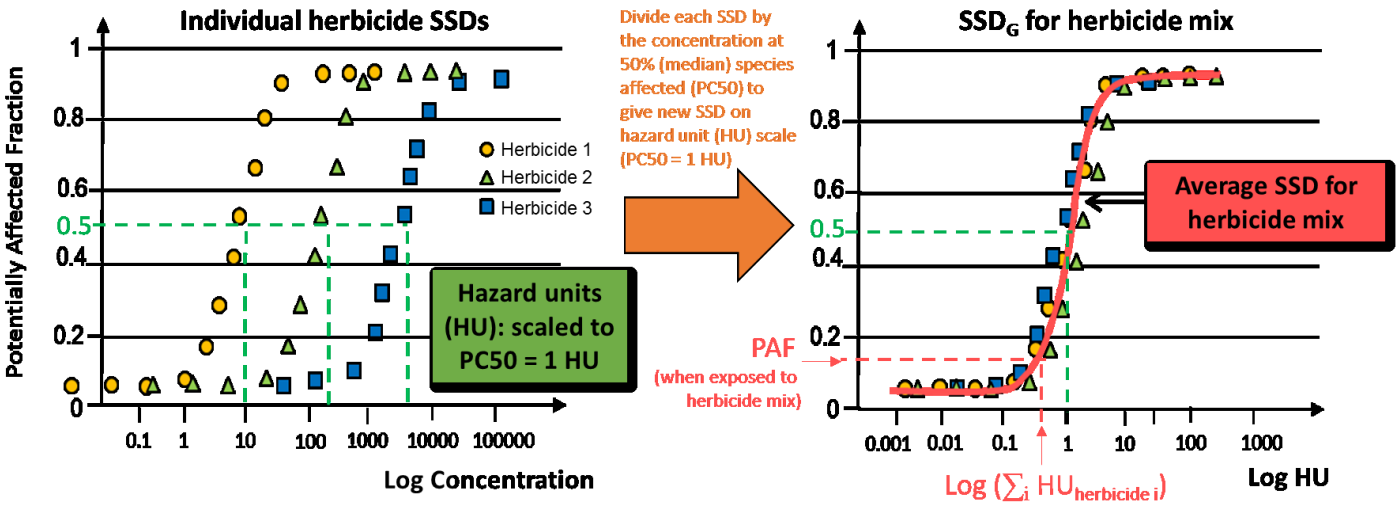

Figure 15: Overview of approach to determine a multi-substance species sensitivity distribution (SSD) for a mixture of herbicides with the same mode of action (concentration additive model). SSDs on a concentration basis for individual herbicides (left graph) are converted to a dimensionless hazard unit (HU) scale which normalizes all SSDs to have a PC50 value (concentration at which 50% of the species are affected) of 1 HU (right graph). An 'average' SSD is fitted to the individual HU scale-SSDs and the midpoint (α_G) and slope (β_G) of the global distribution are determined in order to calculate PAF for an environmental mixture.

Toxicity thresholds - marine versus freshwater species

Proposed guideline values (GVs) for diuron have been published for both freshwater and marine species (DSITI, 2017). The marine GV for protection of 99% of species, 430 ng L^{-1}, is based on an SSD including 20 marine species from six phyla and 11 classes (King et al., 2017a). The equivalent proposed freshwater guideline value, based on an SSD including 26 freshwater species from four phyla and seven classes, is approximately an order of magnitude lower than the marine value at 80 ng L^{-1} (King et al., 2017b). Amongst the other priority PSII herbicides, the proposed marine GVs for ametryn and hexazinone are both similarly higher than for freshwater species (Table 13). For tebuthiuron, the marine and freshwater proposed GVs are almost identical.

For the ms-PAF model, marine and freshwater species were combined to generate a single SSD for each chemical. Thus, for diuron, for example, the concentration determined using the ms-PAF model that would result in a PAF of 1% (i.e. PC99, 46 ng L^{-1}, Table 13) will be different to the marine GV of 430 ng L^{-1} (considered protective of 1% of marine species). For diuron, the ms-PAF model PC99 is lower than the marine GV as it includes more sensitive freshwater species. Inclusion of both marine and freshwater species generates more robust SSDs for the ms-PAF model as ecotoxicity data for marine species are often lacking. Furthermore, the ms-PAF approach developed to date is intended for risk assessment of annual end-of-catchment pesticide loads which relate to variably freshwater, mixed estuarine, and marine waters and therefore inclusion of fresh and marine species is considered relevant across these environments. If the current ms-PAF model is to be used to determine the ecological risk of pesticides in the nearshore marine environments, careful consideration of the PC99 (and other ANZECC and ARMCANZ risk categories, PC95, PC90 and PC80) between the marine GVs (based on marine species and used to identify guideline exceedances in this report, see section 4.2.2.3 above) and the ms-PAF model (based on fresh water and marine species and a lower, more conservative threshold value than for marine species alone (Table 13)) must be undertaken. This is discussed further below in the context of the results presented in this case study.

Table 13: Proposed guideline values compared to PC99 values using the ms-PAF model for the five priority PSII herbicides.

			Concentration determined using ms-PAF model (ng L^{-1})		**Converted ms-PAF PC99 to PSII-HEq and toxic equivalence****	
PSII herbicide	**Marine proposed GV (ng L^{-1})**	**Freshwater proposed GV (ng L^{-1})**	**Concentration to give PAF of 1% (ms-PAF PC99)**	**ms-PAF PC99 as % of marine proposed GV**	**PSII-HEq concentration (using RPFs in the current report)**	**Toxic equivalent (TE) concentration (using TEFs, Smith et al., 2016)**
SSD species:	***Marine***	***Freshwater***	***Marine/freshwater***		***Marine***	***Marine/freshwater***
Ametryn	100	74	**39**	39%	51	25
Atrazine*	n.a.	n.a.	**295**	-	47	11
Diuron	430	80	**46**	11%	**46**	**46**
Hexazinone	1,800	310	**85**	4.7%	32	18
Tebuthiuron	4,700	4,800	**474**	10%	38	9.0
			Coefficient of variation % (across five values)		**18%**	**69%**

* Insufficient ecotoxicological data are currently available to determine statistically robust marine and freshwater SSDs for atrazine. The ms-PAF model uses an alpha value of 32.7705, which is under revision.

** The ms-PAF PC99 was converted to toxic equivalence concentrations on two other risk scales. The concentration for each PSII herbicde should be the same as for diuron (i.e. 46 ng L^{-1}). The coefficient of variation is a measure of the variability of the calculated PSII-HEq and TE concentrations.

Results: Comparison of ms-PAF risk categories, PSII-HEq Index and Proposed GVs

The concentrations that would result in 1, 5, 10 and 20% potentially affected fraction of species, i.e. the PC99, PC95, PC90 and PC80 ANZECCARMCANZ risk category thresholds, were determined using the ms-PAF model for the five priority PSII herbicides (Table 13). This allows direct comparison between the PAF risk categories (PC99 is relevant to the Reef) and the PSII Herbicide Equivalence (HEq) Index (used in the current

and previous pesticide monitoring reports). Using the ms-PAF model, the PC99 concentrations were 46 ng L^{-1} (diuron), 39 ng L^{-1} (ametryn), 295 ng L^{-1} (atrazine), 85 ng L^{-1} (hexazinone), and 474 ng L^{-1} (tebuthiuron) (Table 13). These PC99 concentrations were all lower than the respective marine proposed GV (ranging from 5 to 39% of the GV), and also were lower than the freshwater proposed GV (10 to 57% of the GV) (Table 13). Whilst the species composition of the SSDs explains some of the differences between the ms-PAF and the marine guideline PC99 values, it is not theoretically expected that the ms-PAF PC99 values would be lower than the freshwater GV for these herbicides (note: since the same species are used for the SSDs for both the GVs and the ms-PAF model, and freshwater GV < marine GV for the five priority PSII herbicides, theoretically the PC99 for all species lies between the marine and freshwater PC99 guideline values). At low PAF values such as 1%, the fitted logistic distribution and therefore the determined PC99 are highly sensitive to changes in the fitted β value (slope), hence differences in β between the individual SSDs and the global SSD_G may also contribute to the relative differences in PC99 values.

The ms-PAF PC99 values were also converted to toxic equivalent concentrations using both relative potency factors (RPF) reported in this MMP report and toxic equivalent factors (TEF) reported by Smith et al. (2016b) (Table 13). By definition, the toxic equivalent concentration for each of the five herbicides to elicit the same effect (i.e. 1% of species affected) should be the same. Relative to diuron (46 ng L^{-1}) which is the recommended reference herbicide under both toxicity schemes (RPF = TEF = 1 for diuron), the calculated PSII-HEq for each ms-PAF PC99 concentration ranged from 32 – 51 ng L^{-1} (Table 13) for ametryn, atrazine, hexazinone and tebuthiuron, which represented a percent coefficient of variation (%CV) of 18%. By comparison, the toxic equivalent concentrations determined using TEFs ranged from 9 – 25 ng L^{-1} which was consistently lower than the diuron concentration of 46 ng L^{-1} (%CV of 69%). The relative differences in potency/toxicity factors is compared and discussed further below.

The ms-PAF risk categories (based on marine and freshwater species) for the five priority PSII herbicides are more conservative than for marine-only species (relevant to the Reef protection) and therefore adopting the ms-PAF approach affords a higher level of protection. It is of interest to further understand how risk categories under these two risk assessment approaches align if the ms-PAF model is to be applied to assess risk of pesticide exposure in nearshore marine environments in the future. Based on a calculated ms-PAF PC99 concentration for diuron of 46 ng L^{-1}, the PSII-HEq index categories 4 (effects reported for 2 diatom species but no corals or seagrasses) and 5 (no reported effects for any photosynthetic species) would be considered protective of 99% of Reef species (Table 14). A category 3 on the PSII-HEq index aligns with the ms-PAF PC95 values (240 ng L^{-1}), i.e. concentrations in category 3 would theoretically be expected to affect between 1 and 5% of species (Table 14).

As noted in the previous year's report, having two categories below the relevant threshold for the Reef (PC99) may be an advantage as it provides a pre-warning mechanism for concentrations that are approaching the trigger value. Category 5 also defines a lower limit to the toxic range of pesticide concentrations (i.e. there will be a theoretical concentration at which no ecosystem effects are experienced, and this is not necessarily only when pesticides are completely absent) which cannot be derived with an SSD approach. It should also be noted that PSII-HEq categories 3, 4 and 5 are all below the proposed marine GV of 430 ng L^{-1} to protect 99% of species, suggesting that even at concentrations when there are published scientific observations of reduced photosynthesis for two seagrass species and three diatoms (category 3), overall it is expected that only 1% of all marine ecosystem species will be adversely impacted.

Table 14: Comparison of risk categories for marine waters using the ms-PAF and the PSII-HEq methods (percentage of species potentially affected and the corresponding equivalent diuron concentration (ng L^{-1}), relative to the proposed marine PC99 GV.

PSII Risk Index	Diuron PSII equivalent Concentration	ms-PAF model: % species potentially affected	Diuron ms-PAF concentration	ANZECC and ARMCANZ Risk Category	Proposed PC99 marine guideline value for diuron
1	≥ 900 ng L^{-1}	**>20%**	>1,200 ng L^{-1}	<80% of species protected	
2	250 - 900 ng L^{-1}	**10 - 20%**	520 - 1,200 ng L^{-1}	80% of species protected (PC80)	
		5 - 10%	240 - 520 ng L^{-1}	90% of species protected (PC90)	**430 ng L^{-1}**
3	50 - 250 ng L^{-1}	**1 - 5%**	46 - 240 ng L^{-1}	95% of species protected (PC95)	
4	10 - 50 ng L^{-1}	**<1%**	≤46 ng L^{-1}	99% of species protected (PC99)	
5 (no effect)	≤ 10 ng L^{-1}				

In addition to the PC99 comparison discussed above, PC95, PC90 and PC80 diuron equivalent values were compared between the ms-PAF model and the recently released proposed diuron GVs (King et al., 2017a, King et al., 2017b) (Table 15). The greatest differences were observed for PC99, where the ms-PAF PC99 value was an order of magnitude lower than the marine GV and approximately half the freshwater GV. The relative difference decreased with increasing % of species effected (i.e. as you move 'up' the SSD to a higher PAF value). The ms-PAF model PC80 concentration, i.e. 20% effected species, was identical to the marine GV (Table 15). This suggests that any effects of species composition (freshwater/marine versus marine) and difference in slope (β) of the fitted logistic functions between individual and global SSDs, has most impact at the lower, most sensitive end of the species sensitivity distribution.

Table 15: Comparison of proposed diuron marine and freshwater guideline values and the ms-PAF model predicted equivalent diuron concentrations (as per Table 14) for 99, 95, 90 and 80% species protection

Risk category	Proposed diuron PC99 GV (King et al., 2017a, b) Marine ng L^{-1}	Proposed diuron PC99 GV (King et al., 2017a, b) Freshwater ng L^{-1}	ms-PAF model predicted diuron PC99 concentration ng L^{-1}
High conservation value systems (99% species protection)	430†	80	46
Slightly to moderately disturbed systems (95% species protection)	670	230	240
Highly disturbed systems (90% species protection)	860	420	520
Highly disturbed systems (80% species protection)	1,200	900	1,200

† Relevant to the Reef protection

The above comparisons focus on individual PSII herbicides, and it is important also to assess mixtures. Different mixture profiles of PSII herbicides with the same diuron-equivalent concentration (using the PSII index) return consistent PAF values using the ms-PAF model (Table 16); for example, for a range of theoretical mixtures dominated by diuron (consistent with the monitoring results in this report) each with a PSII-HEq of 46 ng L^{-1} (equivalent to 1% PAF), PAF values ranged from 1.04 – 1.09% PAF (%CV of 2.4%).

Table 16: Comparison of the ms-PAF values for seven hypothetical PSII herbicide mixtures

	Concentration (ng L^{-1})					PSII-Heq	PAF
	Ametryn	Atrazine	Diuron	Hexazinone	Tebuthiuron	(ng L^{-1})	(%)
Mix 1			46			46	1.00
Mix 2		17	38	13	4	46	1.05
Mix 3		30	35	16	2	46	1.06
Mix 4		5	35	23	18	46	1.09
Mix 5	7	15	28	16	4	46	1.04
Mix 6		19	36	19		46	1.07
Mix 7	0.6	14	38	13		46	1.05

Results: Comparison of ms-PAF (%) and PSII-HEq concentrations for 2015-16 samples

The predicted ms-PAF values from the current monitoring year data were plotted against the PSII-HEq concentrations for each sample Appendix F Table F-2 to Table F-12) (Figure 16). The scales of the two vertical axes in Figure 16 (left for PAF and right for PSII-HEq) were aligned based on the PC99, 95 and 90 values determined using the ms-PAF model above (Table 14) so that a direct comparison between the PSII-HEq values and the PAF could be made. The risk values determined under both approaches followed an almost identical pattern with the PAF values equal to or slightly lower than the equivalent PSII-HEq data. This suggests that, based on the SSDs currently available, the two risk approaches differ primarily only in their relative scales, i.e. that the relative potencies of the PSII herbicides that dominate the pesticide mixtures observed in this monitoring program under the two risk assessment approaches are relatively consistent.

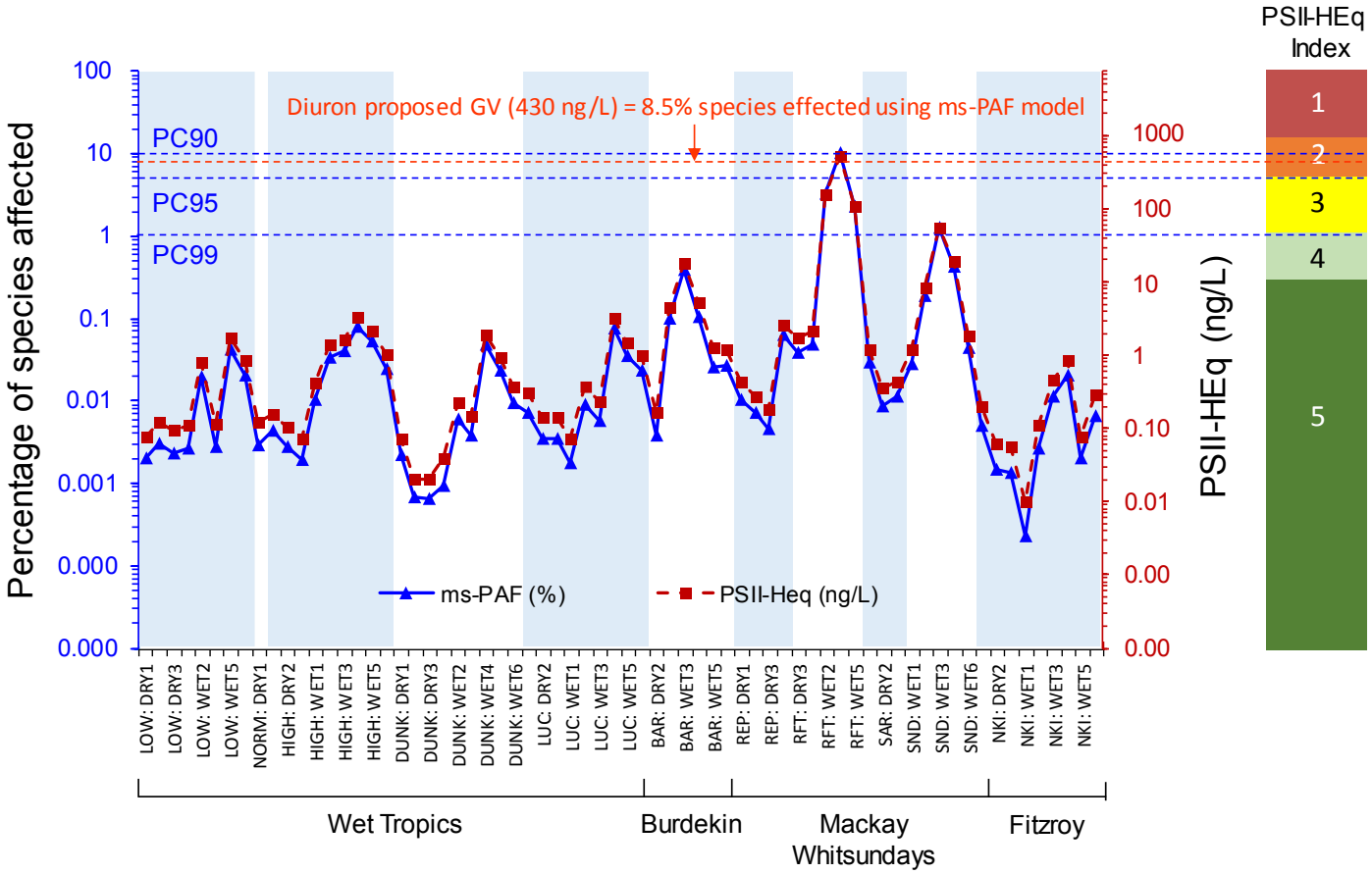

Figure 16: Comparison of all current monitoring data calculated as the PAF (%) and using the PSII- HEq approach. Axes were aligned assuming 1% PAF was equivalent to 46 ng/L PSII-HEq, 5% equivalent to 240 ng/L and 10% equivalent to 520 ng/L (see main text and Table 14). Both axes are shown on a log scale (for presentation purposes only). Site names are identified using the following codes: LOW (Low Isles), NORM (Normanby Island), DUNK (Dunk Island), LUC (Lucinda), BAR (Barratta Creek), REP (Repulse Bay), RFT (Round Top Island), SAR (Sarina Inlet), SND (Sandy Creek), NKI (North Keppel Island); WET and DRY are wet and dry season samples, respectively, which are chronologically numbered (dry season: 1 = May/June 2015; 2 = July/Aug 2016, 3 = Sep/Oct 2015; wet season: 1 = Nov 2015, 2 = Dec 2015, 3 = Jan 2016, 4 = Feb 2016, 5 = Mar 2016, 6 = Apr 2016)

The ms-PAF data for 2015-16 suggest that there were four exceedances of the targeted PAF for the Reef (≤1%), all occurring in the Mackay Whitsunday NRM region (Figure 16). These correspond to one category 2 and three category 3 occurrences on the PSII-HEq index. In line with the discussion above, there was, however, only one exceedance of the proposed diuron marine GV in the monitoring year (Figure 16).

Results: Relative potencies of PSII Herbicides

The similarity in patterns between the ms-PAF and PSII-HEq values prompted a comparison of the relative potencies of the thirteen PSII herbicides (and two atrazine metabolites) between the ms-PAF and the PSII-HEq methods. These were further compared to new toxic equivalency factors (TEFs) recently reported for the five priority PSII herbicides, ametryn, atrazine, diuron, hexazinone and tebuthiuron, which are used to quantify the toxicity of end-of-catchment loads under GBRCLMP (Smith et al., 2016b), as well as the relative toxicity suggested by the proposed marine and freshwater guideline values (comparing PC99 for each PSII herbicide). For the ms-PAF approach, the relative toxicity of the herbicides is related to the alpha value, i.e. how 'far' each herbicide's PC50 toxicity is from the normalised position on the HU scale (PC50 = 1 HU). The metric 1/alpha is directly correlated to the relative toxicity of each PSII herbicide (high alpha, low toxicity, and vice versa). To make a comparison with RPFs (used to calculate PSII-HEq) and TEFs, each herbicide was assigned a value of 1/alpha which was then normalised relative to an assumed potency of 1 for the reference herbicide diuron (as for RPFs and TEFs). A similar approach was adopted for the GVs. Each PC99 GV is the concentration to protect 99% of species in an aquatic ecosystem and a high GV indicates a low toxicity herbicide and vice versa. The relative potency of the herbicides is therefore correlated with 1/GV. As for ms-PAF, 1/GV was assigned to each pesticide and then normalised relative to diuron (assumed potency of 1).

The relative potencies of diuron (equal to 1) and atrazine (two of the three dominant PSII herbicides in the current monitoring year as well as historically) were almost identical under the ms-PAF and the PSII-HEq approaches (Figure 17 A). It should be noted, however, that the alpha value for atrazine is being revised and therefore its relative potency compared to diuron is likely to change (the alpha value is expected to be lower and therefore ms-PAF overall toxicity may increase; R. Smith *(pers comm)*). The ms-PAF relative potency for hexazinone, the third most prevalent herbicide, was marginally lower than the RPF (Figure 17 A), which likely accounts for the slightly lower ms-PAF values for many samples through the year (Figure 16). For the other PSII herbicides, tebuthiuron, simazine, prometryn and fluometuron, the concentrations of these four PSII herbicides in all samples in the current monitoring year were low and therefore any differences in relative potencies had a low effect on the overall risk value.

There were five additional herbicides included in the ms-PAF model this year for which RPFs have not been determined (bromicil, metribuzin, propazine, terbuthyl and terbutryn); however, most of these herbicides are, at present, at trace levels in all samples in this report and so do not contribute to any notable difference in overall risk between the two approaches.

The TEF values reported in 2016 were consistently lower than the relative potencies of the PSII herbicides under the ms-PAF and PSII-HEq approaches, ranging from 22% to 55% of the PSII RPF values for the four major PSIIs (other than diuron which is the assumed reference herbicide for both methods (RPF = TEF = 1)) (Figure 17 A). The TEFs are not used to define toxicity in the MMP program (end-of-catchment diuron-equivalent loads were recalculated for Table 6 using the RPFs) and so further investigation was not undertaken at this stage. It is worth noting that the ms-PAF model and the TEFs were developed for use in estuarine (mixed freshwater/marine systems). Therefore, when comparing toxic loads reported elsewhere in Reef Plan, the differences in relative potency for the PSII herbicides under the ms-PAF approach compared to the TEFs should be taken into consideration.

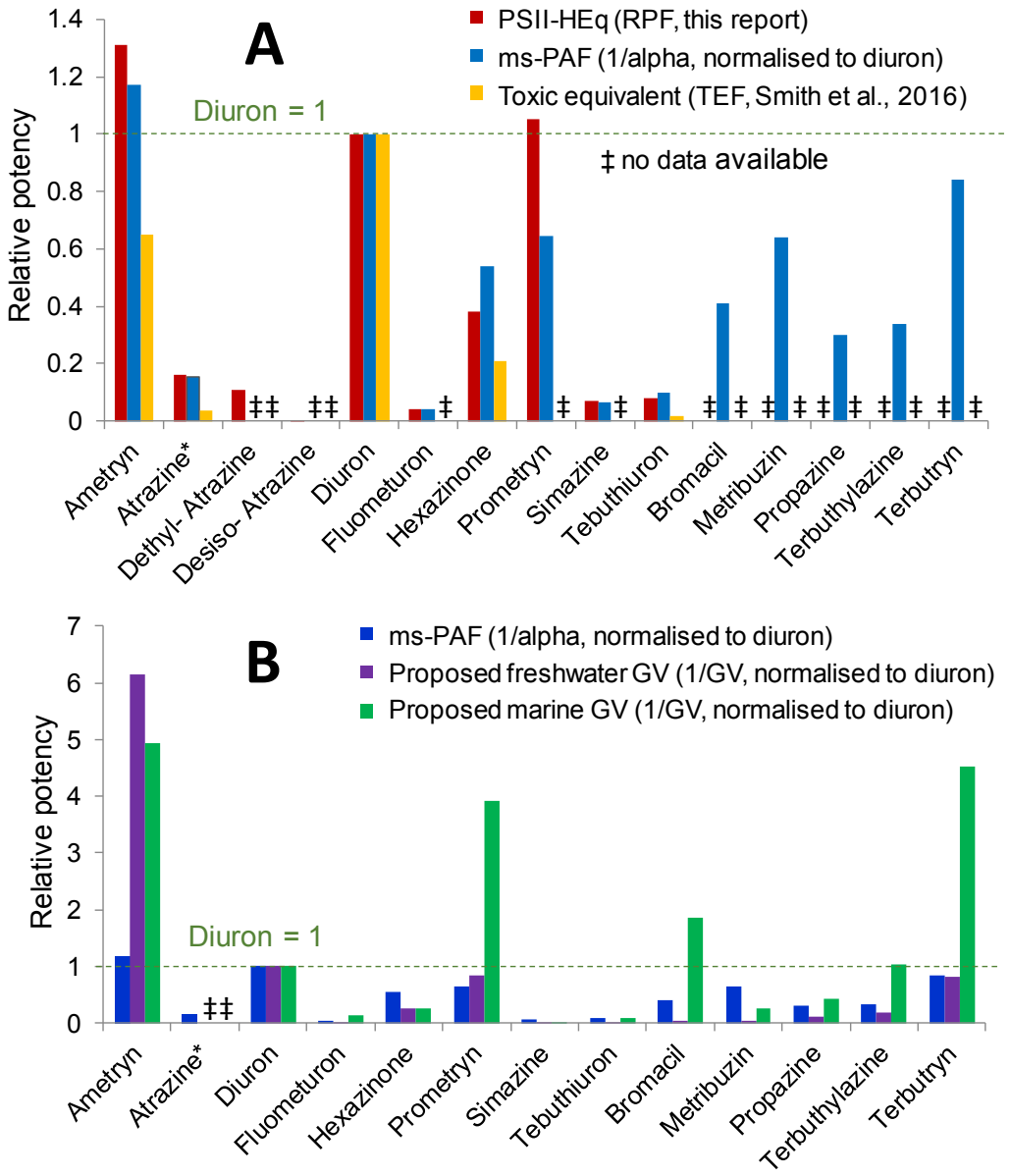

Figure 17: Comparison of relative toxicity of PSII herbicides (same mode of action) based on (A) potency factors (RPF, used to derive PSII-HEq concentration),1/alpha (normalised to 1 for diuron the reference herbicide, used to determine the percentage of species effected under the ms-PAF method) and toxic equivalency factor (TEF, used to determine toxic loads (Smith et al., 2016b)) and (B) 1/alpha (ms-PAF) compared to proposed guideline values for both freshwater and marine (derived as 1/GV and normalized to diuron = 1). *Relative potency of atrazine under the ms-PAF model is currently being revised and is presented here based on an old value. ‡ Values are not currently available.

Comparison of the relative potency of PSII herbicides under the freshwater and marine GVs with ms-PAF, indicated that for some herbicides, freshwater GVs and ms-PAF relative potencies were consistent (e.g. prometryn and terbutryn) whilst for others, marine GVs and ms-PAF were consistent (e.g. propazine) (Figure 17 B). This possibly reflects the inclusion of different freshwater and marine species in the ms-PAF for different herbicides. In other cases, both GV relative potencies differed notably from the ms-PAF values (e.g. ametryn and bromacil) and some GV relative potencies, especially for the marine values, were notably high (Figure 17 B).

The above comparisons suggest that in addition to understanding the PC99 and other risk threshold values across the various risk assessment approaches (proposed GVs, ms-PAF PC99 and PSII-HEq Index categories), it is also important to understand the relative potencies of the herbicides and elucidate the underlying reasons for any differences so that potency factors can be applied consistently throughout Reef Plan.

Conclusions

In conclusion, the ms-PAF model is a recognised and recommended approach to quantify the overall ecological risk of mixtures and will be a highly valuable risk assessment tool particularly when pesticides with other modes of action can be incorporated using the response addition (RA) model. Refinement of the SSDs underlying the ms-PAF model is on-going and a review of the overall approach is being undertaken by DSITI. The revised model will be revisited in 2016-17, if relevant.

Based on the investigations in this case study, further consideration of the risk categories is warranted to capture the most ecologically relevant, reasonable and protective tipping points. At present, the ms-PAF model predicts a PC99 concentration for diuron, the most prevalent PSII herbicide measured in the near-shore Reef marine environment, of 46 ng L^{-1} which is an order of magnitude lower than the proposed marine PC99 guideline value (430 ng L^{-1}). Adoption of an ms-PAF model based on SSDs for marine-only species for the pesticides MMP would bring greater consistency between the mixture model and the individual SSDs from which proposed marine GVs are determined. It is well recognised that over- or under-estimations of herbicide exposure risk can have considerable and opposing consequences, either imposing over-regulation and challenging the profitability of land use practices along the coastal catchments, or by threatening the health and resilience of a fragile ecosystem already subjected to multiple local and global stressors. An on-going National Environmental Science Programme (NESP) project (2016-2019), “Ecotoxicology of pesticides on the Great Barrier Reef for guideline development and risk assessments” (NESP, 2016), aims to generate marine ecotoxicity data specifically for this purpose.

Before adopting ms-PAF to assess overall ecological risk as part of the MMP’s annual reporting, the benefits of waiting until a marine ms-PAF model can be established should be considered or a decision should be taken to adopt a lower, but therefore more conservative, PC99 value for MMP reporting. Furthermore, it would be pertinent to wait until proposed GVs have been approved and SSDs for all chemicals earmarked for inclusion have been constructed to prevent any retrospective adjustments and a more accurate assessment of risk of the environmental mixtures present.

Appendix A Complete analyte list for LC-MS and GC-MS analysis

A-1 Sources of uncertainty

To interpret both trends in the long-term data and true changes in concentrations year to year, there must be an understanding of the inherent variability of the data. Possible sources of uncertainty when using the passive samplers may include (but are not limited to) the effects of salinity and water temperature on chemical uptake into the sampler, accurate measurement of exposure time, the integrity of the flow-limiting membrane over the deployment period, degree of biofouling on the surface of the sampler and its effect on the sampling area, analytical error and variability in the dissolution of the PFM used to approximate water flow (and sampling rates).

Salinity (ionic strength) has been found to have a very small effect on the solubility of the gypsum contained in the PFM, which is subsequently used to estimate sampling rates with respect to the water flow at a given site (O'Brien et al., 2011b). The effect of salinity on a hypothetical calculation of water concentration from an ED found that a change in salinity from 5 g L^{-1} (freshwater) to 35 g L^{-1} (marine water) did not change the estimated flow rate (to two significant figures) under either low or high dissolution rate conditions. The effect of water temperature on the dissolution of the PFM is not well understood, but as water temperature remains relatively constant between the wet and dry seasons (20-25°C) it is assumed to have a negligible effect.

Replicate PFMs are deployed at each passive sampler site, and the mass lost per day is used to estimate the sampling rate of chemicals. Normalised difference percentages between duplicate PFMs deployed at each site this monitoring year ranged between <1 and 22% (mean of 6.4%), showing good agreement (this excludes 32 sampler-sets where PFM duplicates were both empty upon retrieval).

Duplicate EDs are deployed at each sampling site and returned to QAEHS. One duplicate sampler is analysed for approximately every 10 samples to determine the variability in the overall performance (chemical uptake) of the EDs (Table A-1). This monitoring year, 16 ED sampler sets were analysed in duplicate, with 143 herbicide detections in both duplicates and 25 herbicide detections in only one of the duplicates. Mean coefficients of variation (%CVs) for chemicals (which includes detections in both duplicates only) ranged from 1.7% (fluroxypyr) to 33% (metsulfuron methyl). Variability in the estimated water concentrations of diuron, hexazinone and atrazine was 20%, 17% and 19%, respectively.

The objective of most passive sampling field studies is to derive an accurate estimate of the concentration of pollutants present in the environment. However, the environmental concentrations obtained from passive sampling can only be accurate when appropriate calibration data (i.e. sampling or chemical uptake rates usually in units of L day^{-1}) is used to derive these values. Sampling rates are influenced by the prevailing conditions at a sampling site and include temperature, water flow and the degree of sampler biofouling, and cannot be easily predicted based on a chemical's physico-chemical properties. Whilst there is an ever-increasing amount of calibration data available for commonly detected anthropogenic chemicals, calibration data is still lacking for many, particularly for new and emerging chemicals.

The sampling rates (R_s) of many polar chemicals relevant to the Reef have been reported in both field and laboratory calibration experiments throughout the literature (Booij et al., 2002, Stephens et al., 2005, Shaw et al., 2009, Shaw and Mueller, 2009, Stephens et al., 2009, Vermeirssen et al., 2009, O'Brien et al., 2011a, Kaserzon et al., 2014), although rates vary due to the conditions under which they were conducted. Atrazine was common to all of these studies and was chosen as a reference point to estimate compound specific sampling rates of other herbicides on a proportional basis (i.e. R_s of chemical X / R_s of atrazine).

The relationship between the sampling rate of atrazine and flow effects has been extensively investigated (O'Brien et al., 2011a). Using this relationship, a sampling rate for each herbicide was calculated, specific to the flow conditions encountered at a particular site during each deployment. By inserting the relevant water velocity (estimated from PFM loss rate) into the equation and adjusting the resulting sampling rate by their proportion relative to atrazine, compound specific sampling rates were estimated for other herbicides, to provide estimates of herbicide water concentrations. For herbicides where no calibration data is available, the sampling rate of atrazine has been assumed. Whilst there is always variability in calibration data, regardless of whether calibration data is available or has been assumed, the objectives of the pesticide monitoring component (to monitor trends in pesticide concentrations) of the MMP can be achieved, provided the same calibration data is used year-on-year.

Table A-1: Summary of variability (% coefficient of variation) of replicate ED analysis

Chemical	Detections in both duplicates (n)	Mean % CV	Min % CV	Max % CV
2,4-D	9	18	1.1	33
Ametryn	5	14	1.4	35
Atrazine	13	19	0.2	56
Bromacil	2	12	11	12
Desethyl atrazine	9	7.0	0.8	17
Desisopropyl atrazine	8	20	1.1	52
Diuron	15	20	1.6	94
Fluroxypyr	1	1.7	1.7	1.7
Haloxyfop	3	5.7	2.7	7.6
Hexazinone	15	17	0.5	63
Imazapic	2	2.4	2.0	2.8
Imidacloprid	9	15	0.2	34
MCPA	5	16	0.4	48
Metsulfuron methyl	5	33	0.9	48
Metolachlor	13	17	5.0	48
Metribuzin	3	10	4.8	15
Prometryn	1	22	22	22
Propazine	5	11	4.2	23
Simazine	9	7.4	0.8	19
Tebuthiuron	10	14	1.1	43
Tebuconazole	1	9.0	9.0	9.0

Note: Only instances where a chemical was detected in both replicates have been included

A-2. Target chemicals

Table A-2: QAEHS LC-MS/MS analyte list for positive and negative mode analysis

Positive Ion Mode	Negative Ion Mode
Ametryn	2,4-D
Asulam	2,4-DB
Atrazine	Fluroxypyr
Bromacil	Haloxyfop
Desethyl Atrazine	MCPA
Desisopropyl Atrazine	
Diuron	

Positive Ion Mode	Negative Ion Mode
Fluazifop	
Fluometuron	
Hexazinone	
Imazapic	
Imidacloprid	
Metolachlor	
Metribuzin	
Metsulfuron-methyl	
Prometryn	
Propazine	
Simazine	
Tebuconazole	
Tebuthiuron	
Terbutryn	

Table A-3: QAEHS GC-MS analyte list for PDMS extracts

Pesticide
Chlorpyifos
Pendimethalin
Propazine
Propiconazole
Trifluralin

Table A-4: Proposed priority pesticides and herbicides specified under the MMP (proposed by PWG 18 August 2015) and other pesticides of interest for potential inclusion in monitoring and reporting activities (feedback from the Paddock to the Reef program). Instrument limit of detection (LOD) and limit of reporting (LOR) are given (μg L^{-1}), where available.

Chemical	Description	Priority or of interest	LC-MS/MS		GC-MS
			LOD	LOR	LOR
2,4-D	Phenoxy-carboxylic-acid herbicide	Priority	0.03	0.10	
2,4-DB	Phenoxy-carboxylic-acid herbicide	Of interest	5.0	15	
Aciflurofen*	Herbicide: cell membrane disruptor	Of interest			
Ametryn	PSII herbicide – methylthiotriazine	Priority	0.56	1.69	
Asulam	Herbicide: inhibition of DHP – carbamate	Of interest			
Atrazine	PSII herbicide – chlorotriazine	Priority	0.05	0.15	
Atrazine – desethyl	PSII herbicide breakdown product (also active)	Priority	0.005	0.10	
Atrazine – desisopropyl	PSII herbicide breakdown product (also active)	Priority	0.02	0.10	
Bromacil	PSII herbicide – uracil	Of interest	0.02	0.10	
Chlorothalonil*	Organochlorine fungicide	Priority			
Chlorpyrifos	Organophosphate insecticide	Priority			0.5
Diazinon*	Insecticide: inhibits acetylcholinesterase	Of interest			
Diuron	PSII herbicide – pheynylurea	Priority	0.02	0.10	
Ethametsulfuron methyl*	Herbicide: acetolactate synthase (ALS) inhibition	Of interest			
Fipronil*	Phenylpyrazole insecticide	Priority			
Fluazifop	Herbicide: inhibition of acetyl CoA carboxylase	Of interest	0.02	0.10	

Chemical	Description	Priority or of interest	LC-MS/MS		GC-MS
			LOD	LOR	LOR
Fluometuron	PSII herbicide – urea	Of interest	0.01	0.10	
Fluroxypyr	Pyridine carboxylic acid herbicide	Priority	0.02	0.10	
Glyphosate*	Broad-spectrum systemic herbicide	Priority			
Haloxyfop	Aryloxyphenoxy-propionate herbicide	Priority	0.04	0.13	
Hexazinone	PSII herbicide – triazinone	Priority	0.01	0.10	
Imazapic	Imidazolinone herbicide	Priority	0.02	0.10	
Imidacloprid	Neonicotinoid insecticide	Priority	0.01	0.10	
Isoxaflutole and DKN*	Isoxazole herbicide	Priority			
MCPA	Phenoxy-carboxylic-acid herbicide	Priority	0.05	0.14	
Mesosulfuron methyl*	Herbicide: acetolactate synthase (ALS) inhibition	Of interest			
Metolachlor	Chloracetanilide herbicide	Priority	0.03	0.10	
Metribuzin	PSII herbicide – triazinone	Priority	0.03	0.11	
Metsulfuron methyl	Sulfonylurea herbicide	Priority	0.03	0.10	
MSMA*	Herbicide: inhibition of cell division	Of interest			
Paraquat*	Herbicide: photosystem-I-electron diversion	Of interest			
Pendimethalin	Dinitroaniline herbicide	Priority			1.0
Prometryn	PSII herbicide – methylthiotriazine	Priority	0.54	1.61	
Propazine	PSII herbicide – chlorotriazine	Priority	0.06	0.18	
Propiconazole*	Conazole fungicide	Priority			2.0
Prothiophos*	Insecticide: inhibits acetylcholinesterase	Of interest			
Simazine	PSII herbicide – chlorotriazine	Priority	0.08	0.24	
Tebuconazole	Conazole fungicide	Priority	0.10	0.31	
Tebuthiuron	PSII herbicide – thiadazolurea	Priority	0.01	0.10	
Terbuthylazine*	PSII herbicide – triazine	Priority			
Terbutryn	PSII herbicide – triazine	Of interest	0.55	1.7	
Triclopyr*	Pyridine carboxylic acid herbicide	Priority			
Trifloxysulfuron*	Herbicide: inhibition of ALS – sulfonyl urea	Of interest			
Trifluralin	Herbicide – dintiroaniline	Priority			0.2

* Not currently analysed by QAEHS
Shaded chemicals are included as part of the Paddock 2 Reef Integrated Monitoring, Modelling and Reporting Program
Red text indicates that the sampling rate of atrazine has been assumed.

A-3. Analytical details and quality assurance quality control (QA/QC)

QAEHS undertakes all herbicide analysis of passive and grab samples using Liquid Chromatography-tandem Mass Spectrometry (LC-MS/MS).

ED extracts and grab samples were analysed for herbicides using a Sciex QTRAP 6500+ mass spectrometer (Sciex, Concord, Ontario, Canada) equipped with an electrospray (TurboV) interface coupled to a Shimadzu Nexera HPLC system (Shimadzu Corp., Kyoto, Japan). Separation was achieved using a 2.6 micron 50 x

2.0mm Phenomenex Biphenyl column (Phenomenex, Torrance, CA) run at 45˚C, and a flow rate of 0.3 mL min^{-1} with a linear gradient starting at 5% B, ramped to 100% B in 5.2 minutes then held at 100% for 4.3 minutes followed by equilibration at 5% B for 3.5 minutes. (A = 1% methanol in HPLC grade water, B = 95% methanol in HPLC grade water, both containing 0.1% acetic acid). The mass spectrometer was operated in both positive and negative ion multiple reaction-monitoring mode, using nitrogen as the collision gas monitoring two transitions for each analyte.

Positive results were confirmed by retention time and by comparing transition intensity ratios between the sample and an appropriate concentration standard from the same run. Samples were reported as positive if the two transitions were present (with peaks having a signal to noise ratio greater than 3), retention time was within 0.15 minutes of the standard and the relative intensity of the confirmation transition was within 20% of the expected value. The value reported was that for the quantitation transition.

Analysis of PDMS extracts for non-polar pesticides was conducted on a Thermo Scientific TSQ Quantum XLS Triple Quadrupole GC-MS/MS. The mass spectrometer was operated in positive ion, multiple reaction monitoring mode, using argon as the collision gas. Prior to introduction into the mass spectrometer, compounds were separated on an Agilent J & W DB5-MS (25m; 0.25mm i.d.; 0.25µm film thickness) column. Samples were injected in splitless mode at 80°C. The GC oven was held at 80°C for 2 minutes and ramped to 180°C at 20°C/minute; held for 0.5 minutes and ramped to 300°C at 10°C/minute and held for 10.5 minutes. The transfer line and ion source were heated at 280°C and 270°C respectively. Helium was used as the carrier gas at a rate of 1.0 mL/minute. A quantitative and qualitative ion transition was monitored for each compound.

Appendix B Water quality guidelines

Table B-1: Water quality limits available for pesticides (protective concentration values, PC95 and PC99, will protect 95% and 99% of the species in the ecosystem, respectively) (ng L^{-1}).

Chemical	DSITI proposed guideline values (GV)[a]		ANZECC and ARMCANZ[c]		GBRMPA[e]	
	Proposed GV	Notes	Trigger Value	Notes	Protective Concentration	Notes
2,4-D	1,040,000	PC99; low reliability; Marine water				
Ametryn	100	PC99; moderate reliability; Marine water			500	PC99; Moderate reliability
					1,000	PC95; Moderate reliability
Atrazine	-		700	PC99; Fresh water	600	PC99; Moderate reliability
			1,300	PC95; Fresh water	1,400	PC95; Moderate reliability
			ID	PC99/95; Marine water		
Bromacil	230	PC99; moderate reliability; Marine water				
Chlorpyrifos	-		0.5	PC99; Marine water	0.5	PC99; High reliability
			9	PC95; Marine water	9	PC95; High reliability
			0.04	PC99; Freshwater		
Diuron	430[b]	PC99; very high reliability; Marine water	200[d]	IWL; low reliability; Freshwater	900	PC99; moderate reliability
			1,800[d]	IWL; low reliability; Marine water	1,600	PC95; moderate reliability
Fipronil	3.4	PC99; moderate reliability; Marine water				
Fluometuron	20,000	PC99; moderate reliability; Marine water				
Fluroxypyr	87,000	PC99; moderate reliability; Marine water				
Haloxyfop	589,000	PC99; low reliability; Marine water				
Hexazinone	1,800	PC99; low reliability; Marine water			1,200	Low reliability

Chemical	DSITI proposed guideline values (GV)[a]		ANZECC and ARMCANZ[c]		GBRMPA[e]	
	Proposed GV	Notes	Trigger Value	Notes	Protective Concentration	Notes
Imazapic	49	PC99; very low reliability; Marine water				
Imidacloprid	34	PC99; moderate reliability; Marine water				
MCPA	1,000	PC99; low reliability; Marine water				
Metolachlor	Marine data n.a.		20[d]	IWL, low reliability; Freshwater		
	Freshwater: 16		20[d]	IWL, low reliability; Marine water		
Metribuzin	2,000	PC99; moderate reliability; Marine water				
Metsulfuron methyl	Marine data n.a. Freshwater: 4.7					
Pendimethalin	240	PC99; moderate reliability; Marine water				
Prometryn	110	PC99; moderate reliability; Marine water				
Propazine	2,200	PC99; low reliability; Marine water				
Propiconazole	2,100	PC99; moderate reliability; Marine water				
Simazine	28,000	PC99; low reliability; Marine water	200	PC99; Freshwater	200	PC99; Low reliability
			3,200	PC95; Freshwater		
			ID	PC99/95: Marine water		
Tebuthiuron	4,700	PC99; moderate reliability; Marine water	20	PC99; Freshwater	20	PC99; low reliability
			2,200	PC95; Freshwater		
			ID	PC99/95: Marine water		
Terbuthylazine	400	PC99; moderate reliability; Marine water				
Terbutryn	79	PC99; moderate reliability; Marine water				

Chemical	DSITI proposed guideline values (GV)[a]		ANZECC and ARMCANZ[c]		GBRMPA[e]	
	Proposed GV	Notes	Trigger Value	Notes	Protective Concentration	Notes
Triclopyr	36	PC99; low reliability; Marine water				
Trifluralin	-		2,600	PC99; Freshwater		
			ID	PC99/95: Marine water		

[a] Reported in the 2017 Scientific Consensus Statement (Waterhouse et al., 2017a) as proposed ecotoxicity threshold values
[b] Sourced from King et al. (2017a) (PC99, PC95, PC90 and PC80 are derived, only PC99 relevant to the Reef reported in the table)
[c] Sourced from Table 3.4-1 of the ANZECC and ARMCANZ Guidelines, Volume 1 (ANZECC and ARMCANZ, 2000a)
[d] Interim Working Level (IWL) (rather than trigger value) as indicated in Volume 2, Chapter 8.3.7 of the ANZECC and ARMCANZ Guidelines (ANZECC and ARMCANZ, 2000b)
[e] Sourced from Table 26 & Table 27 of the Water Quality Guidelines for the Great Barrier Reef Marine Park (GBRMPA, 2010)
ID - insufficient data were available to determine a trigger value

Appendix C Supporting literature for PSII-HEq index

Table C-1: Scientific publications indicating the effect concentrations and the end-points for the reference PSII herbicide diuron used to define specific PSII-HEq Index categories as an indicator for reporting purposes

Category	PSII-HEq Range (ng L^{-1})	Description	Supporting Literature with Respect to the Reference Chemical Diuron				
			Species	Effects Concentration (ng L^{-1})	Endpoint	Toxicity measure	Reference (see footnotes)
5	HEq ≤ 10	No published scientific papers that demonstrate any effects on plants or animals based on toxicity or a reduction in photosynthesis. The upper limit of this category is also the detection limit for pesticide concentrations determined in field collected water samples.					
4	10 < HEq ≤ 50	Published scientific observations of reduced photosynthesis for two diatoms.	**Diatoms**				
			D. tertiolecta	50	↓photosynthesis	LOEC	Bengston Nash *et al* 2005
			N. closterium	50	Sensitivity	LOEC	Bengston Nash *et al* 2005
3	50 < HEq < 250	Published scientific observations of reduced photosynthesis for two seagrass species and three diatoms.	**Seagrass**				
			H. ovalis	100	↓photosynthesis	LOEC	Haynes et al 2000
			Z. capriconi	100	↓photosynthesis	LOEC	Haynes et al 2000
			Diatoms				
			N. closterium	100	Sensitivity	IC10	Bengston Nash *et al* 2005
			P. tricornutum	100	Sensitivity	IC10	Bengston Nash *et al* 2005
			D. tertiolecta	110	↓photosynthesis	IC10	Bengston Nash *et al* 2005
2	250≤ HEq ≤ 900	Published scientific observations of reduced photosynthesis for three coral species.	**Coral - Isolated zooxanthellae**				
			S. pistillata	250	↓photosynthesis	LOEC	Jones *et al* 2003
			Coral - Adult colonies				
			A. formosa	300	↓photosynthesis	LOEC	Jones & Kerswell, 2003
			S. hystrix	300	↓photosynthesis	LOEC	Jones *et al* 2003
			S. hystrix	300	↓photosynthesis	LOEC	Jones & Kerswell, 2003
1	HEq > 900	Published scientific papers that demonstrate effects on the growth and death of aquatic plants and animals exposed to the pesticide. This concentration represents a level at which 99 per cent of tropical marine plants and animals are protected, using diuron as the reference chemical.	**Seagrass**				
			Z. capriconi	1000	↓photosynthesis	LOEC	Chesworth *et al* 2004
			Z. capriconi	5000	↓growth	LOEC	Chesworth *et al* 2004

Category	PSII-HEq Range (ng L^{-1})	Description	Supporting Literature with Respect to the Reference Chemical Diuron				
			Species	Effects Concentration (ng L^{-1})	Endpoint	Toxicity measure	Reference (see footnotes)
			Z. capriconi	10000	↓photosynthesis	LOEC	Macinnis-Ng & Ralph, 2004
			C. serrulata	10000	↓photosynthesis	LOEC	Haynes *et al* 2000b
			Coral - Isolated zooxanthellae				
			M. mirabilis	1000	↓C^{14} incorporation	LOEC	Owen *et al* 2003
			F. fragum	2000	↓C^{14} incorporation	LOEC	Owen *et al* 2003
			D. strigosa	2000	↓C^{14} incorporation	LOEC	Owen *et al* 2003
			Larvae				
			A. millepora	300	↓ Metamorphosis	LOEC	Negri *et al* 2005
			Coral recruits				
			P. damicornis	1000	↓ photosynthesis	LOEC	Negri *et al* 2005
			P. damicornis	10000	Loss of algae	LOEC	Negri *et al* 2005
			Coral - Adult colonies				
			A. formosa	1000	↓ photosynthesis	LOEC	Jones *et al* 2003
			P. cylindrica	1000	↓ photosynthesis	LOEC	Jones *et al* 2003
			M. digitata	1000	↓ photosynthesis	LOEC	Jones *et al* 2003
			S. hystrix	1000	↓ photosynthesis	LOEC	Jones *et al* 2003, Jones 2004
			A. millepora	1000	↓ photosynthesis	LOEC	Negri *et al* 2005
			P. damicornis	1000	↓ photosynthesis	LOEC	Negri *et al* 2005
			S. hystrix	2300	↓ photosynthesis	EC50	Jones *et al* 2003
			A. formosa	2700	↓ photosynthesis	EC50	Jones & Kerswell, 2003
			M. digitata	10000	Loss of algae	LOEC	Jones *et al* 2003
			P. damicornis	10000	Loss of algae	LOEC	Negri *et al* 2005
			S. hystrix	10000	Loss of algae	LOEC	Jones 2004
			P. cylindrica	10000	GPP* rate, GPP to respiration ration, effective quantum yield	LOEC	Råberg *et al* 2003
			Macro Algae				
			H. banksia	1650	↓ photosynthesis	EC50	Seery *et al* 2006

Category	PSII-HEq Range (ng L^{-1})	Description	Supporting Literature with Respect to the Reference Chemical Diuron				
			Species	Effects Concentration (ng L^{-1})	Endpoint	Toxicity measure	Reference (see footnotes)
			Red Algae				
			P. onkodes	2900	↓ photosynthesis	LOEC	Harrington *et al* 2005
			Diatoms				
			Navicula sp	2900	↓ photosynthesis	IC50 Acute, 6 m	Magnusson *et al* 2006
			P. tricornutum	3300	↓ photosynthesis	I50	Schreiber *et al* 2002
			Mangroves				
			A. marina	1100	Health	NOEC	Duke *et al* 2003, 2005
			A. marina	1500	Reduced health	LOEC	Duke *et al* 2003, Bell & Duke 2005
			A. marina	2000	Dieback/ absence	Mortality	Duke et al 2003, Bell & Duke 2005
			A. marina	1500	Reduced health	LOEC	Duke *et al* 2003, Bell & Duke 2005

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In addition, the following marine data are from the Australian Pesticides and Veterinary Medicines Authority (APVMA, 2005), Volume I and II as preliminary findings for diuron (Table C-2). Effects concentrations are reported in µg L^{-1}. This data set has also been used in the derivation of Category 1 of the PSII-HEq Index.

Table C-2: Preliminary effects of diuron in marine organisms

Organisms and comments	Toxicity (ug L^{-1}) test substance (95% CL)	Year reported	US EPA category
Fish			
M. cephalus (striped mullet) tech. (95%) static	6300 (NR), 48h, acute	1986	S
C. variegates (Sheephead minnow) 99% active constituent; static	6700 (NR), 96h, acute NOEC = 3600	1986	Core
Invertebrates			
M. bahia (Mysid shrimp) 99% active constituent; static	LC50 = 110, 96h, acute NOEC = 1000	1987	Core
M. bahia (Mysid shrimp) 96.8% active constituent; early life stage; static	28d LOEC = 110 NOEC = 270	1992	Core
P. aztecus (Brown shrimp) 95% active constituent; flow through	LC50 = 1000, 48h acute	1986	S
C. virginica (Eastern oyster) 96.8% active constituent; flow through	EC50 = 4800, 96h, acute NOEC = 2400	1991	Core
C. virginica (Eastern oyster) 96.8% active constituent; flow through	EC50 = 3200, 96h acute	1986	Core
Algae			
D. tertiolecta 95% active constituent; static	EC50 = 20, 240h chronic	1986	S
Platmonas sp 95% active constituent; static	EC50 = 17, 72h chronic	1986	S
P. cruentum (red algae) 95% active constituent; static	EC50 = 24, 72h chronic	1986	S
M. lutheri 95% active constituent; static	EC50 = 18, 72h chronic	1986	S
I. galbana 95% active constituent; static	EC50 = 10, 72h chronic	1986	S
Marine diatoms			
N. incerta 95% active constituent; static	EC50 = 93, 72h chronic	1986	S
N. closterium 95% active constituent; static	EC50 = 50, 72h chronic	1986	S
P. tricornutum 95% active constituent; static	EC50 = 10, 240h chronic	1986	S
S. amphoroides 95% active constituent; static	EC50 = 31, 72h chronic	1986	S
T. fluviatilis 95% active constituent; static	EC50 = 95, 72h chronic	1986	S
C.nana 95% active constituent; static	EC50 = 39, 72h chronic	1986	S
A. exigua 95% active constituent; static	EC50 = 31, 72h chronic	1986	S

C-1. Calculating PSII-HEq concentrations and assessing risk using the PSII Index

A given PSII herbicide with an RPF of 1 is equally as potent as diuron. If it is more potent than diuron it will have an RPF of >1, while if it is less potent than diuron it will have an RPF of <1. To calculate the PSII-HEq concentration of a given grab or passive sample, it is assumed that these herbicides act additively (Escher et al., 2006, Muller et al., 2008, Magnusson et al., 2010). The PSII-HEq (ng L^{-1}) is therefore the sum of the individual RPF-corrected concentrations of each individual PSII herbicide, i, with potency factor RPF_i and concentration C_i, (ng L^{-1}) detected in the sample using (Equation 2):

$$\mathbf{PSII-HEq} = \sum_{i=1}^{n} \mathbf{C_i \ x \ RPF_i} \qquad \text{Equation (2)}$$

RPF values for the chemicals of interest were obtained from relevant laboratory studies (Table A9). For the initial determination of RPF consensus values, average values from studies obtained using corals, Phaeodactylum and Chlorella were used (different organisms were not weighted). The PSII-HEq concentrations in this report were then predicted using these mean preliminary consensus RPF values giving equal weight to EC_{50} and EC_{20} values. These initial consensus values were developed and applied to determine PSII-HEq since the baseline reporting year 2008-09 and, for the sake of consistency, have not been updated. However, it should be acknowledged that as more data continue to be published (Magnusson et al., 2010), it is likely that these values would benefit from review and updating in the future to include not only more data for these chemicals but also additional PSII herbicides that are detected in the Reef lagoon.

Table C-3: Relative potency factors (RPF) for PSII herbicides and selected transformation products

PSII Herbicides	Relative potency (range)						Relative potency
	Zooxanthellae (Corals) [a]	Phaeodactylum tricornutum[bcd]	Chlorella vulgaris[bde]	Zooxanthellae (Corals) [a]	Phaeodactylum tricornutum[bcd]	Chlorella vulgaris[bde]	Mean/ Preliminary consensus [f] RPF
Diuron (reference)	**1**	**1**	**1**	**1**	**1**	**1**	**1**
Ametryn	1.2-1.35	0.94	0.9 -2.7	1.28	0.94	1.71	**1.31**
Atrazine	0.05-0.06	0.1-0.4	0.15 -0.3	0.05	0.22	0.21	**0.16**
Desethyl-atrazine			0.01-0.2			0.105	**0.11**
Desisopropyl-atrazine			0.003			0.003	**0.003**
Fluometuron			0.04			0.04	**0.04**
Hexazinone	0.2-0.26	0.27-0.82	0.17-0.95	0.23	0.46	0.44	**0.38**
Prometryn			1-1.1			1.05	**1.05**
Simazine	0.02	0.03-0.05	0.02-0.26	0.02	0.04	0.14	**0.07**
Tebuthiuron	0.01	0.07	0.11-0.2	0.01	0.07	0.15	**0.08**
Terbuthylazine			0.3			0.3	**0.3**

[a] (Jones and Kerswell, 2003); [b] (Muller et al., 2008); [c] (Nash et al., 2005); [d] (Schmidt, 2005); [e] Macova et al., unpublished data (Entox); [f] Based on a preliminary summary of available data when derived in 2009; it should be noted that bromacil (routinely analysed for since 2009-2010) and terbutryn (routinely analysed for from the end of 2010-2011) are also PSII herbicides and not currently incorporated into PSII-HEq estimates (no RPF).

This index uses published scientific evidence with respect to the effects of the reference PSII herbicide diuron (summarized for each index category Table C-1 and Table C-2). These index criteria have been slightly modified from those indicated in the baseline reporting year 2008-09 (Kennedy et al., 2010b). Note that the Index Category decreases as the concentrations (and associated PSII-HEq) of herbicides increases.

The Index consists of five Categories which range from Category 1 (> 900 ng L^{-1}), which represents the highest risk of exposure (above the 99 per cent species protection trigger value derived for the reference PSII herbicide diuron (GBRMPA, 2010), to Category 5 (≤10 ng L^{-1}), which represents concentrations below which no published PSII inhibition effects have been observed.

Table C-4: PSII-Herbicide Equivalent (PSII-HEq) Index developed as an indicator for reporting of PSII herbicides across the MMP

Category	Concentration (ng L^{-1})	Description
5	PSII-HEq ≤ 10	No published scientific papers that demonstrate any effects on plants or animals based on toxicity or a reduction in photosynthesis. The upper limit of this category is also the detection limit for pesticide concentrations determined in field collected water samples
4	10 < PSII-HEq ≤ 50	Published scientific observations of reduced photosynthesis for two diatoms
3	50 < PSII-HEq < 250	Published scientific observations of reduced photosynthesis for two seagrass species and three diatoms
2	250 ≤ PSII-HEq ≤ 900	Published scientific observations of reduced photosynthesis for three coral species
1	PSII-HEq > 900	Published scientific papers that demonstrate effects on the growth and death of aquatic plants and animals exposed to the pesticide

For categories 2 – 4:

- The published scientific papers indicate that this reduction in photosynthesis is reversible when the organism is no longer exposed to the pesticide;
- Detecting a pesticide at these concentrations does not necessarily mean that there will be an ecological effect on the plants and animals present;
- These categories have been included as they indicate an additional level of stress that plants and animals may be exposed to in the Marine Park. In combination with a range of other stressors (e.g. sediment, temperature, salinity, pH, storm damage, and elevated nutrient concentrations) the ability of these plant and animal species to recover from impacts may be reduced.

Appendix D Supplemental information on drivers

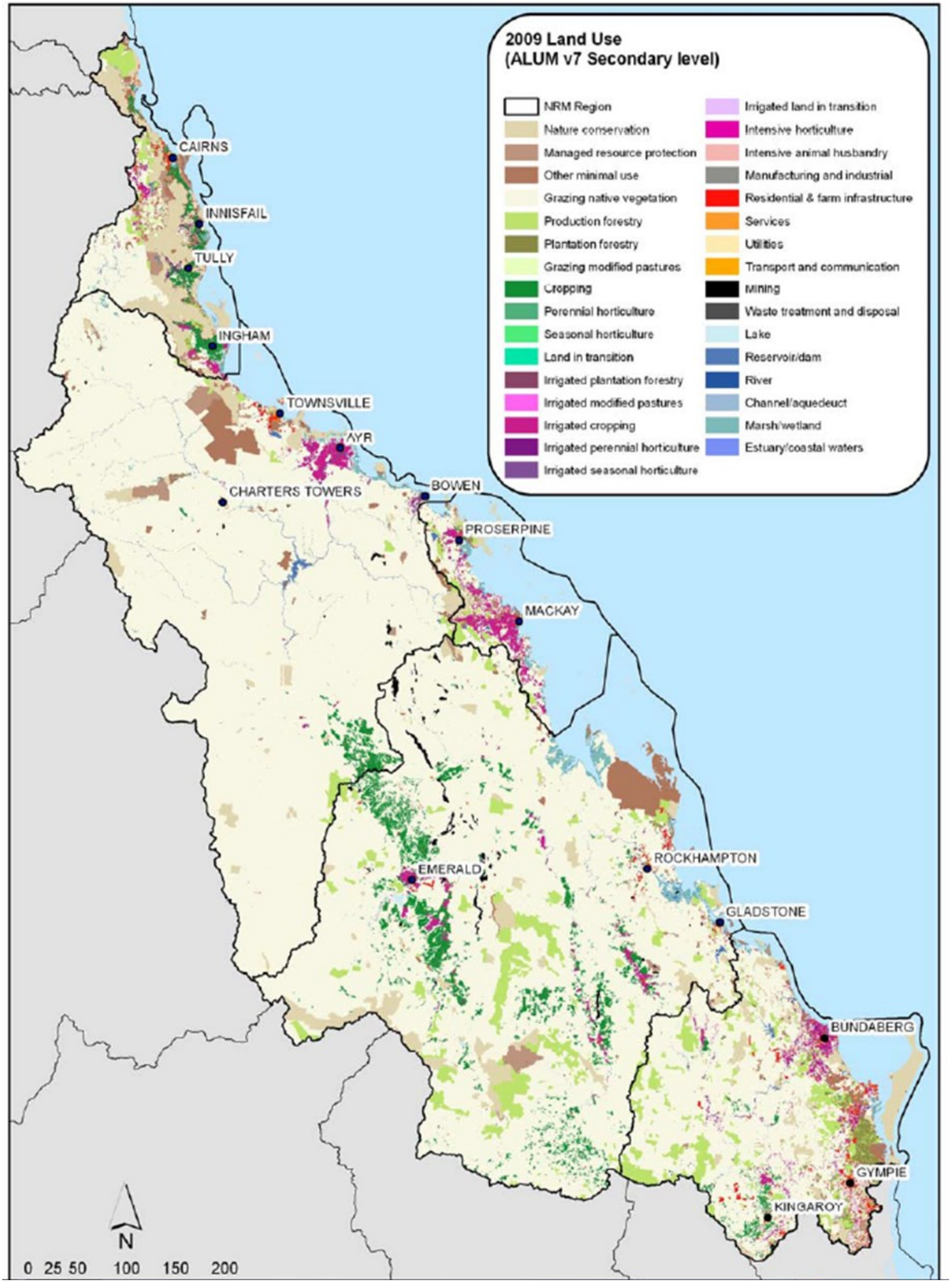


Figure D-1: Land Use map of the Reef catchment (2009).

Appendix E Supplemental information on pressures

Table E-1: Wet season discharge (ML) of the main Reef rivers (c.a., November 2015 to April 2016, inclusive), compared to the previous five wet seasons and long-term (LT) median discharge (1986-2016). Colours indicate levels above the long-term median: yellow for 1.5 to 2 times; orange for 2 to 3 times, and red for greater than 3 times. Data source: DNRM, table derived from Waterhouse et al. (2017b) (– = data not available).

Basin	LT median	2010 - 2011	2011 – 2012	2012 - 2013	2013 - 2014	2014 - 2015	2015 - 2016
Jacky Jacky Creek	2,021,488	4,735,197	1,820,422	1,986,825	3,790,832	1,498,138	630,787
Olive Pascoe River	2,526,860	5,918,996	2,275,527	2,483,531	4,738,541	1,872,672	788,484
Lockhart River	1,600,345	3,748,697	1,441,167	1,572,903	3,001,076	1,186,026	499,373
Stewart River	674,618	2,180,850	616,070	523,353	1,311,775	298,816	311,901
Normanby River	4,159,062	11,333,284	2,181,990	3,462,238	5,059,657	2,914,859	3,407,359
Jeannie River	1,263,328	2,824,817	1,048,269	695,195	1,869,982	1,434,447	1,581,015
Endeavour River	821,163	1,836,131	681,375	451,877	1,215,488	932,391	1,027,660
Daintree River	1,722,934	3,936,470	2,396,905	1,668,302	5,137,023	1,905,224	1,623,478
Mossman River	1,207,012	2,014,902	1,526,184	1,147,367	1,918,522	874,068	1,245,275
Barron River	526,686	2,119,801	852,055	328,260	663,966	380,395	182,999
Mulgrave-Russell River	4,457,940	7,892,713	5,696,594	3,529,862	5,420,678	3,145,787	3,253,825
Johnstone River	4,743,915	9,276,874	5,338,591	3,720,020	5,403,534	3,044,680	3,416,331
Tully River	3,536,054	7,442,768	3,425,096	3,341,887	4,322,496	2,659,775	2,942,770
Murray River	1,227,888	4,267,125	2,062,103	1,006,286	1,531,172	366,212	974,244
Herbert River	3,556,376	12,593,674	4,545,193	3,189,804	4,281,607	1,095,372	1,895,526
Black River	228,629	1,424,283	747,328	188,468	419,290	17,654	129,783
Ross River	445,106	2,092,684	1,324,707	276,584	1,177,255	-	-
Haughton River	553,292	2,415,758	1,755,712	517,069	573,976	120,674	267,986
Burdekin River	4,406,780	34,834,316	15,568,159	3,424,572	1,458,772	880,951	1,807,104
Don River	342,257	3,136,184	802,738	578,391	324,120	171,305	101,562
Proserpine River	887,771	4,582,697	2,171,287	851,504	720,427	157,123	316,648
O'Connell River	796,718	4,112,676	1,948,591	764,170	646,537	141,008	284,171
Pioneer River	776,984	3,630,422	1,567,684	1,162,871	635,315	2,028,936	597,117
Plane Creek	1,052,831	4,809,239	2,854,703	1,948,929	737,580	241,254	832,508
Styx River	187,756	906,144	275,219	968,106	544,155	376,009	343,877
Shoalwater Creek	213,653	1,031,129	313,180	1,101,638	619,211	427,872	391,308
Water Park Creek	563,267	2,718,432	825,657	2,904,319	1,632,466	1,128,027	1,031,630
Fitzroy River	2,852,307	37,942,149	7,993,273	8,530,491	1,578,610	2,681,949	3,589,342
Calliope River	152,965	1,000,032	345,703	1,558,380	283,790	479,868	148,547
Boyne River	38,691	252,949	87,443	394,178	71,782	121,378	37,574
Baffle Creek	367,525	3,650,093	1,775,749	2,030,545	275,517	710,352	257,093
Kolan River	47,866	779,168	307,837	810,411	45,304	213,857	111,172
Burnett River	234,463	9,421,517	643,137	7,581,543	218,087	853,349	381,054
Burrum River	63,918	114,492	117,762	90,921	62,188	150,113	334,681
Mary River	1,144,714	8,719,106	4,340,275	7,654,320	594,612	1,651,901	480,854

Missing values represent years for which >15% of daily flow estimates were not available. Daily discharge for Euramo site (Tully River) from July, 2011 to November, 2012 and from October, 2014 to August, 2015 were estimated from Gorge station (Tully River) using: Euramo Disch = Gorge Disch * 3.5941; Daily discharge for Pioneer river now includes Miriani station, allowing flow record since 1977-11-09. Dumbleton and Miriani stations are correlated by the following equation: Dumbleton Disch = Miriani Disch * 1.4276; All data from the Ross gauge station, which ceased in 2007-08-01 with no substitute in the same river, was replaced by Bohle gauge station; Boyne gauge station was ceased in 2012-06-30 with no substitute in the vicinities of the closed station; Endevour gauge station was ceased in 2015-05-10 with no substitute in the vicinities of the closed station Proserpine gauge station was ceased on 3.6.2014 with no substitute in the vicinities of the closed station. The full dataset does not exist for the Normanby gauging station.

Table E-2: Weekly flood plume colour class (1 – 6) for fixed site passive sampler locations during the 2015-16 wet season (beginning 1 December 2015)

Site	Longitude	Latitude	Region	Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
				Plume Frequency	30-Nov-15	07-Dec-15	14-Dec-15	21-Dec-15	28-Dec-15	04-Jan-16	11-Jan-16	18-Jan-16	25-Jan-16	01-Feb-16	08-Feb-16	15-Feb-16	22-Feb-16	29-Feb-16	07-Mar-16	14-Mar-16	21-Mar-16	28-Mar-16	04-Apr-16	11-Apr-16	18-Apr-16	25-Apr-16
Low Isles	145.56213	-16.38182	Wet Tropics	0.30	7	6	7	7	5	6	5	6	6	7	6	6	6	6	6	5	5	5	6	6	5	7
High Island West	146.00075	-17.15985	Wet Tropics	0.71	6	6	6	7	5	6	4	5	6	6	5	5	5	5	5	5	5	5	5	5	5	5
Frankland Group West	146.07434	-17.20476	Wet Tropics	0.09	7	6	7	6	6	6	6	6	6	7	6	6	6	6	6	5	5	6	6	6	6	6
Dunk Island North	146.13530	-17.93570	Wet Tropics	0.90	5	5	6	5	5	5	5	5	5	6	5	5	5	5	7	4	5	5	5	5	5	7
Lucinda	146.38631	-18.52083	Wet Tropics	1.00	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Barratta Creek mouth	147.24950	-19.40884	Burdekin	1.00	4	4	4	2	2	2	4	2	3	3	4	2	3	4	4	3	4	2	3	4	4	4
Repulse Bay	148.69754	-20.58822	Mackay Whitsunday	1.00	4	5	5	5	5	5	5	5	5	5	5	5	4	5	4	4	4	4	4	4	4	4
Round Top Island	149.23746	-21.15593	Mackay Whitsunday	1.00	4	5	5	5	5	5	4	5	5	5	4	5	5	5	4	5	5	5	5	5	5	5
Sarina Inlet	149.30900	-21.40300	Mackay Whitsunday	1.00	4	4	5	2	5	4	4	2	5	5	4	4	4	7	4	4	5	3	4	4	3	5
Sandy Creek	149.25516	-21.21688	Mackay Whitsunday	1.00	5	5	5	5	5	5	5	5	5	5	4	5	5	5	4	5	5	5	5	5	5	5
North Keppel Island	150.89541	-23.08080	Fitzroy	0.95	5	5	5	5	5	5	5	5	5	6	5	5	5	7	5	5	5	5	5	5	5	7

A value of 7 indicates no data available (e.g. due to cloud cover or the pixel was beyond the plume area). Weekly data comprises the minimum colour class at each pixel recorded for the week. Dark blue colour class (6) = tertiary plume water; light blue (colour class 5) = secondary plume water; green, yellow, orange and red (colour classes 4 to 1 respectively) = primary plume water.

E.1 Flood plume mapping

Six colour classes have been defined that correspond to three water types – primary, secondary and tertiary. Each water type is associated with different levels and combination of pollutants which potentially have different impacts on Reef ecosystems (Devlin et al., 2012, Álvarez-Romero et al., 2013). These impacts relate to turbidity and other effects of CDOM and are not the same as for pesticides, but water type is an indicator of the potential for a flood plume to reach a particular monitoring site. For each of the fixed monitoring sites, the weekly colour class (i.e. the minimum colour class at each pixel recorded for the week) was recorded, for 22 weeks of the wet season (beginning on 1 December 2015) (see table above). Weeks that have no data (a value of 7) indicate that the sites were beyond the plume extent for those weeks. The annual frequency of occurrence for primary and secondary water types (colour classes 1 – 5) were calculated for each fixed monitoring sites by dividing the number of weeks that a pixel was retrieved as either primary or secondary water types, by the maximum number of weeks (i.e. 22) in a wet season. The frequency of occurrence of flood plumes can then be aggregated into frequency classes of low risk of a flood plume reaching the site (frequency of 0.1) to high risk (frequency of 1) to create frequency maps for primary and secondary water types.

Annual plume frequency maps can then be prepared by overlaying weekly composite maps as the number of weeks that a pixel was retrieved as either primary, secondary or tertiary water type, divided by the maximum number of weeks in a wet season (as shown in Figure 1 and Figure 2). Annual exposure maps are useful to identify the year to year variation of the surface water types but can also be useful to develop a long-term surface exposure map that can identify areas that are at higher risk of exposure to surface pollutants over a longer temporal scale. To create multi-annual exposure maps, the annual frequency maps are overlaid and the water type category for each pixel reclassified using the median pixel value (all plume frequency maps were prepared by Dieter Tracy (JCU)).

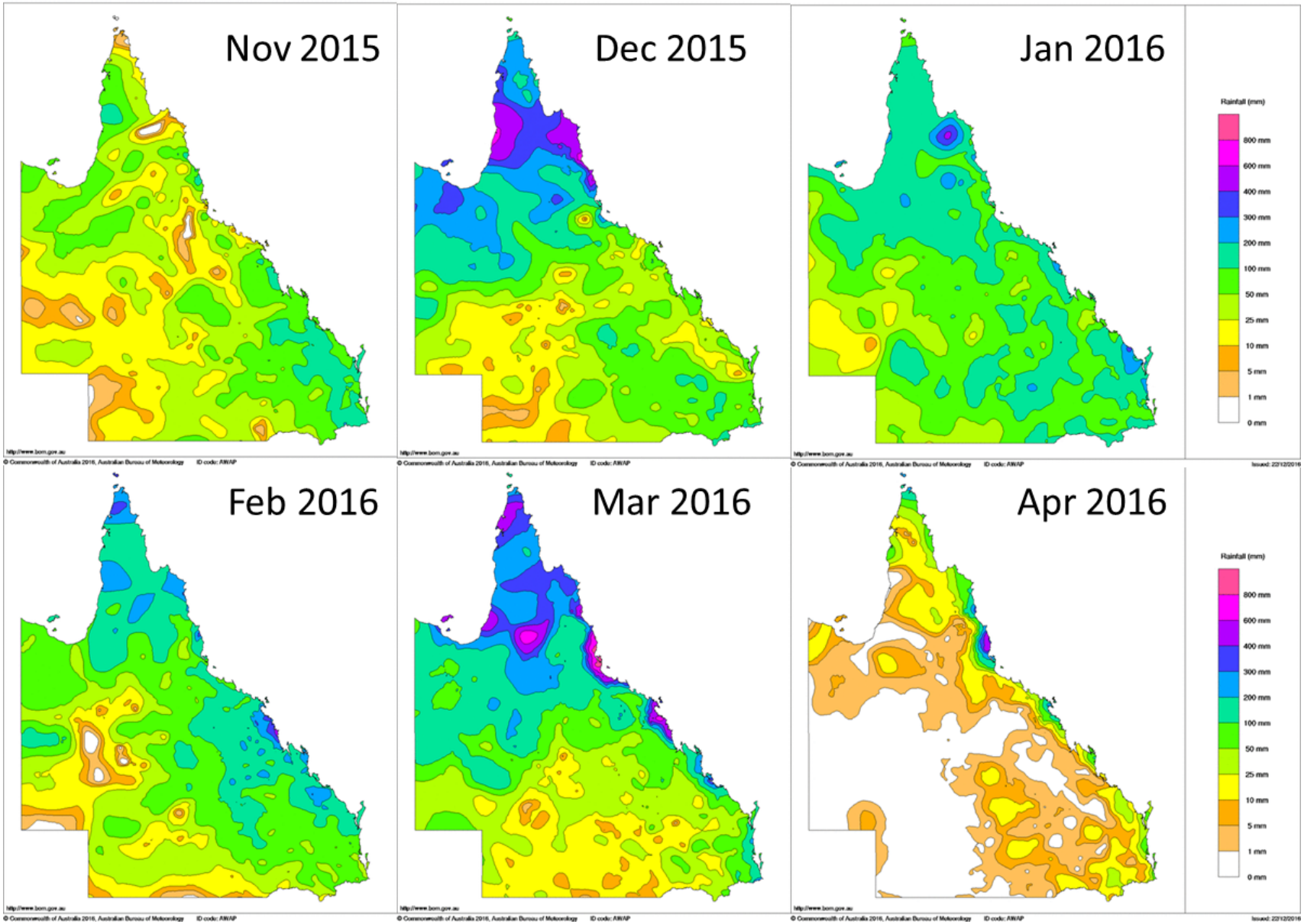


Figure E-1: Total monthly rainfall for the wet 2015-16 season across Queensland (Bureau of Meteorology, 2017)

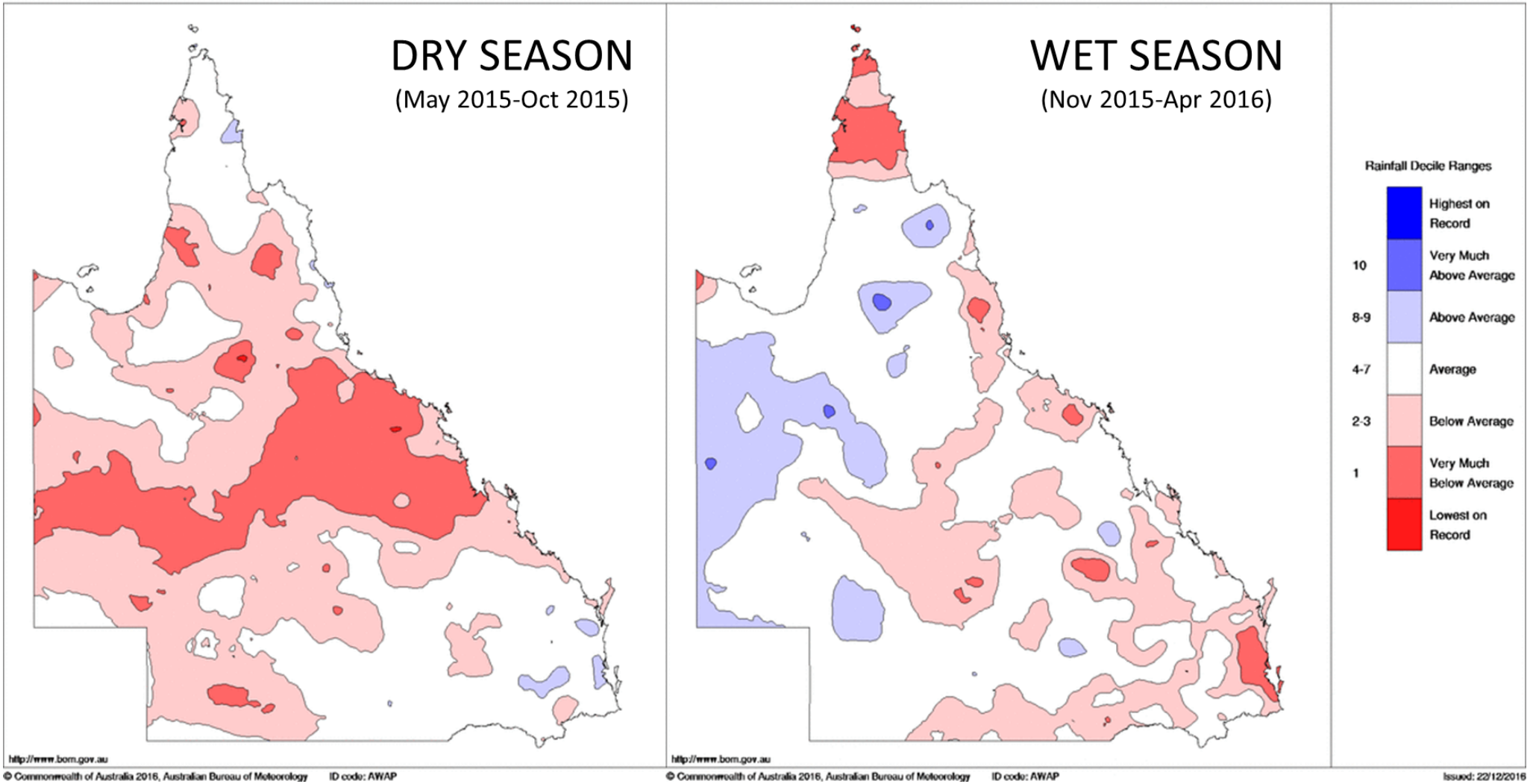


Figure E-2: Rainfall decile ranges (comparison of current period with long term average) for the dry season between May 2015- Oct 2015 (left) and wet season between Nov 2015 – 30 April 2016 (right). Figure sourced from Bureau of Meteorology

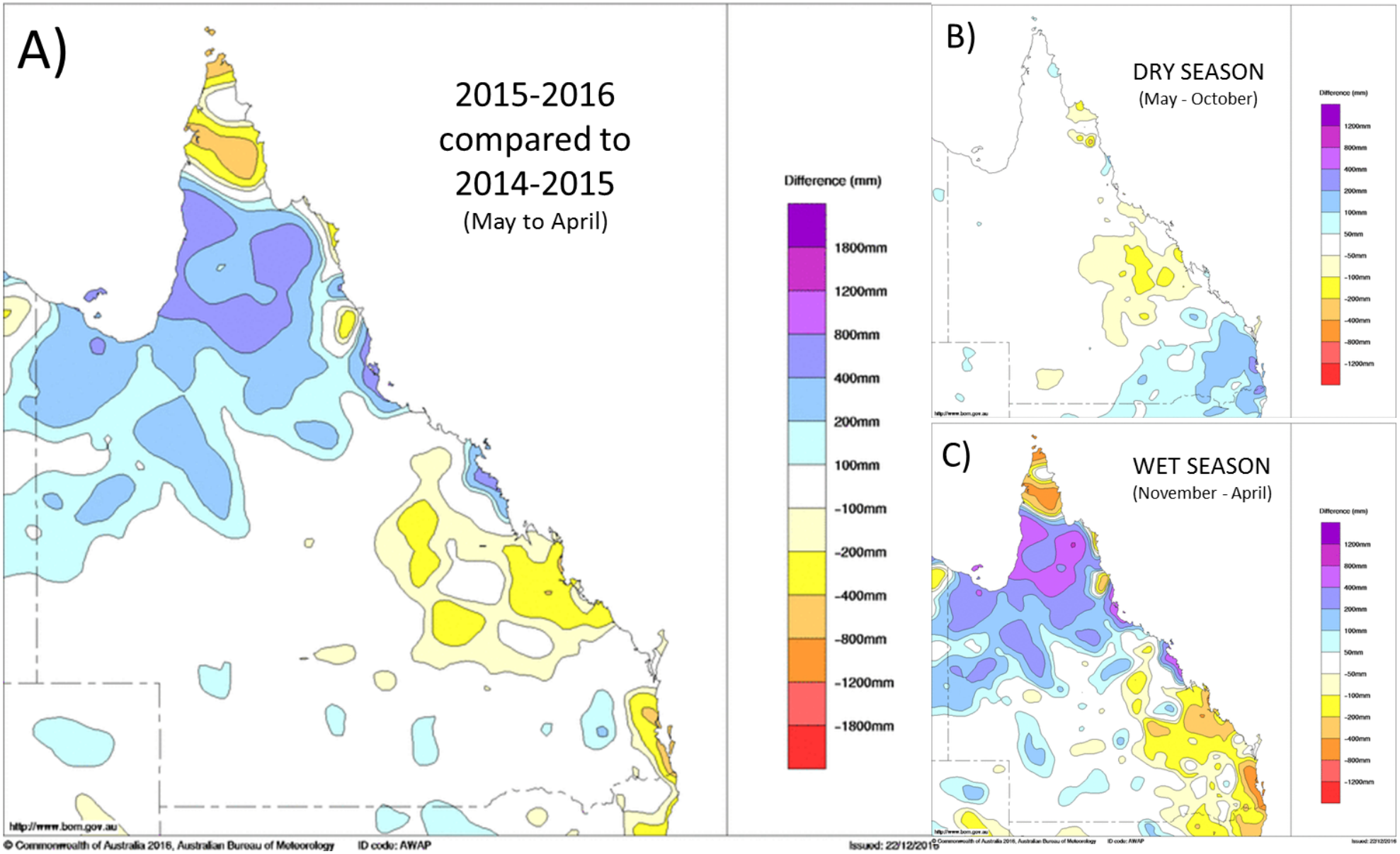


Figure E-3: A) Inter-annual rainfall difference between the previous monitoring year (2014-15) and the current monitoring year (2015-16). B) and C) show comparison between previous year and current year for dry and wet season, respectively. A negative value indicates that rainfall was lower this year compared to the previous year. Figure sourced from Bureau of Meteorology

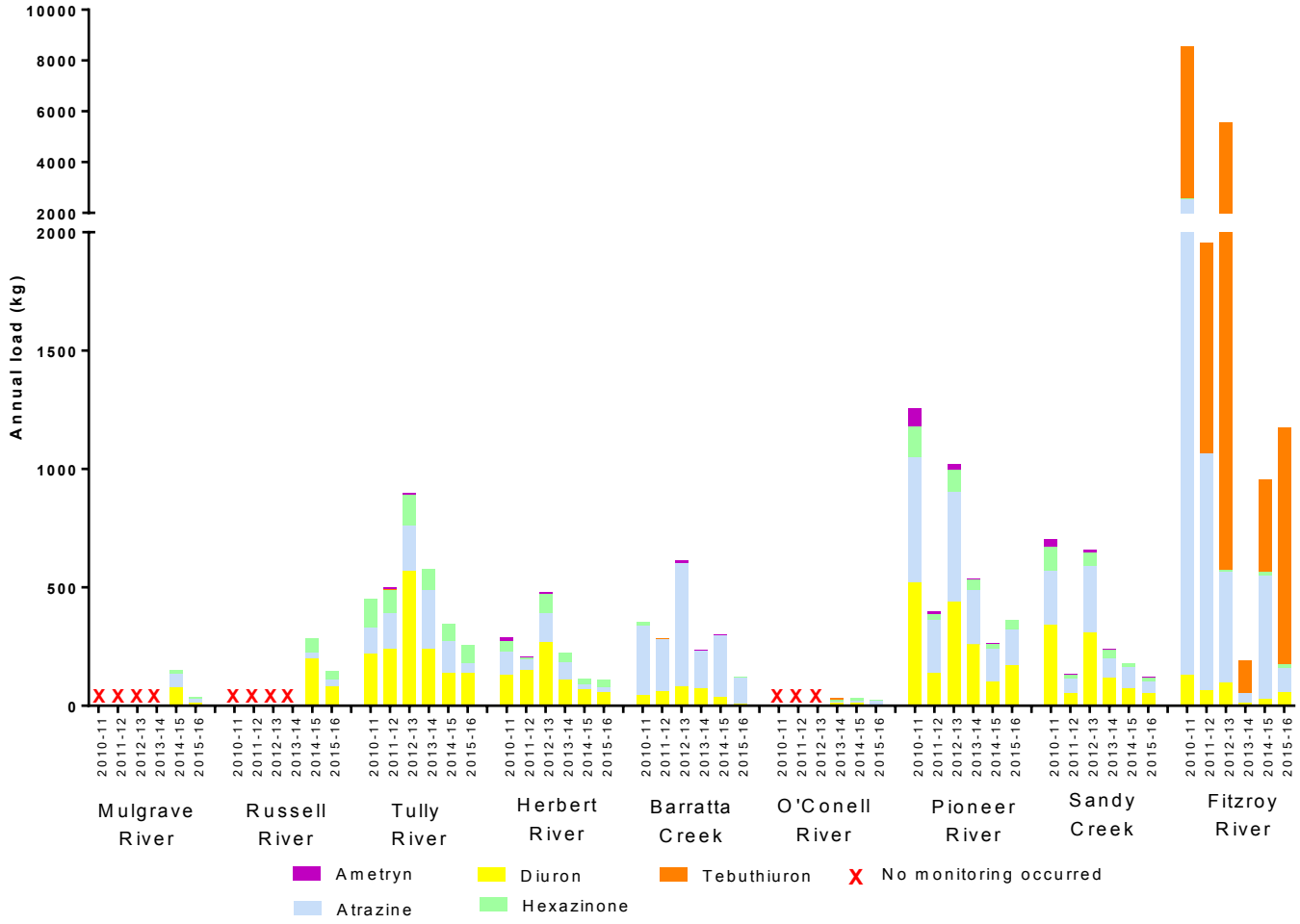


Figure E-4: Historical PSII herbicide loads from monitored Reef catchment rivers (2010–2016). Data collated from GBRCLMP reports (Turner et al. 2013, Wallace et al. 2014, Garzon-Garcia et al. 2015, Wallace et al. 2015, Wallace et al. 2016). 2015-16 data from Huggins et al. (*in prep*)).

Appendix F Fixed monitoring sites – sampler returns and individual site results

Table F-1: Passive sampling return record for the 2015-16 monitoring year. ED sampler numbers are given with PDMS (non-polar) samplers in brackets after.

NRM Region	Site Name	No. of samplers sent	No. of samplers returned and ok to analyse	Comments
Wet Tropics	Low Isles	9	8	Continuous sampling throughout the year, all samplers returned; however, in one sampling period the samplers were deployed with lids on
	High Island	9	9	Last sampled in 2008, recommenced May 2016. Continuous sampling throughout the year, all samplers returned and analysed (PFMs were lost Nov)
	Normanby Island	7	1	No samplers were returned after 1 Jul 2015 - 6 sampler sets were not returned/used, stopped sending samplers Mar-2016
	Dunk Island	9	9	Continuous sampling throughout the year, all samplers returned and analysed (1 PFM lost Nov)
	Lucinda Jetty (CSIRO)	9	9	Mostly continuous sampling, samplers not deployed for two short periods: 19/10-9/11/2015 and 2-10/12/2015. Lids left on PFMs in Feb 2016
Burdekin	Barratta Creek	9	6 (5)	2 sets of samplers lost (May/Jun & Sep/Oct 2015), 1 set "returned unsealed" (Nov 2015). Deployment date for Dec 2015 not known
Mackay Whitsunday	Repulse Bay	8	4 (2)	1 set of samplers damaged (membrane destroyed, Nov 2015), 1 set lost (Jan 2016) and no samplers were deployed Feb-Apr 2016
	Round Top Island	8	5 (3)	1 set of samplers lost (Apr 2016), 2 sets were not deployed (May/Jun & Jul/Aug 2015). Dec 2015 sampler was overdeployed so no Jan 2016 sample
	Sandy Creek	8	5 (3)	1 set of samplers lost, 2 sets unused, overdeployment for Dec/Jan resulted in one less sampling period
	Sarina Inlet	8	3	Samplers consistently overdeployed (e.g. Jun-Sep 2015). Wet season sampler overdeployed (Nov to Feb), biofouled and not useable. Mar/Apr 2016 sets unused
Fitzroy	North Keppel Island	9	9	Continuous sampling throughout the year, all samplers returned; Apr 2016 sampler overdeployed (Apr-Jun 2016). 1 PFM lost (Dec 2015)
TOTAL 2015-16	**11 sites**	**93**	**68 (13)**	**73% return rate**
TOTAL 2014-15	**18 sites**	**114**	**95**	**83% return rate**

Table F-2: Low Isles, Wet Tropics region – Time integrated estimated concentrations in water (ng L^{-1})

Sampling Period	Deployment Dates		Sampler Type	Concentration PSII herbicides (and metabolites) (ng/L) (*included in PSII-HEq Index)														PSII-HEq (ng/L)	Concentration other pesticides (ng/L)										
	START	END		Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	24 D	2,4 DB	Haloxyfop	MCPA	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole
May-15 Jun-15	18-May-15	11-Jul-15	ED	n.d.	0.06	n.d.	n.d.	n.d.	0.05	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Jul-15 Aug-15	11-Jul-15	4-Sep-15	ED	n.d.	0.07	n.d.	n.d.	n.d.	0.10	n.d.	0.03	n.d.	n.d.	n.d.	*0.02*	n.d.	n.d.	0.12	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sep-15 Oct-15	4-Sep-15	3-Nov-15	ED	n.d.	0.04	n.d.	n.d.	n.d.	0.08	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nov-15	3-Nov-15	17-Dec-15	ED	n.d.	0.03	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dec-15	17-Dec-15	11-Jan-16	ED	n.d.	0.17	n.d.	n.d.	n.d.	0.70	n.d.	0.22	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	0.81	n.d.	<0.01	n.d.	n.d.	<0.01	n.d.	n.d.	n.d.	0.03	n.d.	n.d.
Jan-16	11-Jan-16	12-Feb-16	ED	EDs deployed with lids on																									
Feb-16	12-Feb-16	8-Mar-16	ED	n.d.	0.04	n.d.	n.d.	n.d.	0.09	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.11	n.d.	<0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mar-16	8-Mar-16	7-Apr-16	ED**	n.d.	0.14	n.d.	n.d.	n.d.	1.4	n.d.	0.65	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	1.7	0.04	0.05	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	n.d.
Apr-16	7-Apr-16	3-May-16	ED	n.d.	0.22	n.d.	n.d.	n.d.	0.72	n.d.	0.26	n.d.	n.d.	n.d.	*0.02*	0.05	n.d.	0.86	0.03	0.04	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	*0.01*
Summary																													
Samples (n)				8	8	8	8	8	8	8	8	8	8	8	8	8	8		8	8	8	8	8	8	8	8	8	8	8
Detects (n)				0	8	0	0	0	8	0	7	0	0	0	2	3	0		3	2	0	1	1	0	0	0	2	0	1
% Detects				0	100	0	0	0	100	0	88	0	0	0	25	38	0		38	25	0	13	13	0	0	0	25	0	13
Minimum detected concentration				n.d.	0.03	n.d.	n.d.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Maximum concentration				n.d.	0.22	n.d.	n.d.	n.d.	1.4	n.d.	0.6	n.d.	n.d.	n.d.	0.02	0.05	n.d.	1.7	0.04	0.05	n.d.	0.01	0.01	n.d.	n.d.	n.d.	0.03	n.d.	0.01

n.d. - non detect, for these samples the extract concentration was below the instrument LOD. n.d. values are inlcuded as 0 for summary statistics and PSII-HEq calculations

Concentrations that did not exceed 3 x blank levels and are shown preceded by "<" in the tables and are included as for n.d. in summary statistics

Concentrations where the extract concetration was above the instrument LOD but below the instrument LOR (see Table A3, Appendix A) are shown in italics. These values are included in the PSII-HEq calculations but should be treated with caution

Shaded pesticides and herbicides indicate that no calibration data is available and the sampling rate of atrazine was assumed. Water estimatations are approximate

**Concentration is average of duplicate samplers

Table F-3: High Island, Wet Tropics region – Time integrated estimated concentrations in water (ng L^{-1})

Sampling Period	Deployment Dates		Sampler Type	Concentration PSII herbicides (and metabolites) (ng/L) (*included in PSII-HEq Index)														PSII-HEq (ng/L)	Concentration other pesticides (ng/L)										
	START	END		Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	24 D	2,4 DB	Haloxyfop	MCPA	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole
May-15 Jun-15	3-May-15	9-Jul-15	ED**	n.d.	0.02	n.d.	n.d.	n.d.	0.10	n.d.	0.14	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.15	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	0.03
Jul-15 Aug-15	9-Jul-15	20-Sep-15	ED**	n.d.	0.03	n.d.	n.d.	n.d.	0.06	n.d.	0.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.10	0.003	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Sep-15 Oct-15	20-Sep-15	29-Nov-15	ED	n.d.	0.04	n.d.	n.d.	n.d.	0.05	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nov-15	29-Nov-15	23-Dec-15	ED	n.d.	0.09	n.d.	n.d.	n.d.	0.35	n.d.	0.14	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.42	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Only 1 PFM																												
Dec-15	23-Dec-15	25-Jan-16	ED	n.d.	0.38	n.d.	n.d.	n.d.	1.1	n.d.	0.59	n.d.	n.d.	n.d.	*0.02*	n.d.	n.d.	1.4	0.05	<0.03	n.d.	0.01	*0.01*	n.d.	n.d.	n.d.	0.10	n.d.	n.d.
Jan-16	25-Jan-16	26-Feb-16	ED	n.d.	0.46	n.d.	n.d.	n.d.	1.4	n.d.	0.52	0.07	n.d.	n.d.	*0.02*	n.d.	n.d.	1.6	0.01	0.05	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	0.04	n.d.	n.d.
Feb-16	26-Feb-16	16-Mar-16	ED	n.d.	0.34	n.d.	n.d.	n.d.	2.8	n.d.	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.3	0.04	0.27	n.d.	0.02	0.02	n.d.	n.d.	n.d.	0.24	n.d.	n.d.
Mar-16	16-Mar-16	24-Apr-16	ED	n.d.	0.49	n.d.	0.02	n.d.	1.7	n.d.	0.99	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	2.1	0.07	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	0.21	n.d.	n.d.
Apr-16	24-Apr-16	3-Jun-16	ED	n.d.	0.47	0.14	n.d.	n.d.	0.76	n.d.	0.41	n.d.	n.d.	n.d.	0.02	0.04	n.d.	1.0	0.03	0.06	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	0.16	n.d.	0.03
Summary																													
Samples (n)				9	9	9	9	9	9	9	9	9	9	9	9	9	9		9	9	9	9	9	9	9	9	9	9	9
Detects (n)				0	9	1	1	0	9	0	9	1	0	0	4	1	0		6	7	0	3	4	0	0	0	7	0	2
% Detects				0	100	11	11	0	100	0	100	11	0	0	44	11	0		67	78	0	33	44	0	0	0	78	0	22
Minimum detected concentration				n.d.	0.02	n.d.	n.d.	n.d.	0.05	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Maximum concentration				n.d.	0.5	0.14	0.02	n.d.	2.8	n.d.	1.2	0.1	n.d.	n.d.	0.02	0.04	n.d.	3.30	0.07	0.27	n.d.	0.02	0.02	n.d.	n.d.	n.d.	0.24	n.d.	0.0

n.d. - non detect, for these samples the extract concentration was below the instrument LOD. n.d. values are inlcuded as 0 for summary statistics and PSII-HEq calculations

Concentrations that did not exceed 3 x blank levels and are shown preceded by "<" in the tables and are included as for n.d. in summary statistics

Concentrations where the extract concetration was above the instrument LOD but below the instrument LOR (see Table A3, Appendix A) are shown in italics. These values are included in the PSII-HEq calculations but should be treated with caution

Shaded pesticides and herbicides indicate that no calibration data is available and the sampling rate of atrazine was assumed. Water estimatations are approximate

**Concentration is average of duplicate samplers

Table F-4: Dunk Island, Wet Tropics region – Time integrated estimated concentrations in water (ng L^{-1})

Sampling Period	Deployment Dates		Sampler Type	Concentration PSII herbicides (and metabolites) (ng/L) (*included in PSII-HEq Index)														PSII-HEq (ng/L)	Concentration other pesticides (ng/L)										
	START	END		Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	24 D	2,4 DB	Haloxyfop	MCPA	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole
May-15 Jun-15	04-May-15	08-Jul-15	ED	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	0.11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Jul-15 Aug-15	08-Jul-15	19-Sep-15	ED**	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sep-15 Oct-15	19-Sep-15	28-Nov-15	ED	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nov-15	28-Nov-15	22-Dec-15	ED	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	No PFMs																												
Dec-15	22-Dec-15	26-Jan-16	ED	n.d.	0.04	n.d.	n.d.	n.d.	0.15	n.d.	0.18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.22	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Jan-16	26-Jan-16	27-Feb-16	ED	n.d.	0.15	n.d.	n.d.	n.d.	0.09	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Feb-16	27-Feb-16	17-Mar-16	ED**	n.d.	0.39	n.d.	n.d.	n.d.	1.5	n.d.	0.94	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	2.0	0.05	<0.11	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.16	n.d.	n.d.
Mar-16	17-Mar-16	22-Apr-16	ED**	n.d.	0.24	n.d.	n.d.	n.d.	0.64	n.d.	0.61	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	0.92	0.05	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	n.d.
Apr-16	22-Apr-16	5-Jun-16	ED**	n.d.	0.16	n.d.	n.d.	n.d.	0.24	n.d.	0.24	n.d.	n.d.	n.d.	*0.01*	0.02	n.d.	0.36	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Summary																													
Samples (n)				9	9	9	9	9	9	9	9	9	9	9	9	9	9		9	9	9	9	9	9	9	9	9	9	9
Detects (n)				0	7	0	0	0	7	0	8	0	0	0	1	3	0		6	0	0	2	0	0	0	0	2	0	0
% Detects				0	78	0	0	0	78	0	89	0	0	0	11	33	0		67	0	0	22	0	0	0	0	22	0	0
Minimum detected concentration				n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Maximum concentration				n.d.	0.39	n.d.	n.d.	n.d.	1.5	n.d.	0.94	n.d.	n.d.	n.d.	0.01	0.04	n.d.	2.0	0.05	0.00	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.16	n.d.	n.d.

n.d. - non detect, for these samples the extract concentration was below the instrument LOD. n.d. values are inlcuded as 0 for summary statistics and PSII-HEq calculations

Concentrations that did not exceed 3 x blank levels and are shown preceded by "<" in the tables and are included as for n.d. in summary statistics

Concentrations where the extract concetration was above the instrument LOD but below the instrument LOR (see Table A3, Appendix A) are shown in italics. These values are included in the PSII-HEq calculations but should be treated with caution

Shaded pesticides and herbicides indicate that no calibration data is available and the sampling rate of atrazine was assumed. Water estimatations are approximate

**Concentration is average of duplicate samplers

Table F-5: Normanby Island, Wet Tropics region – Time integrated estimated concentrations in water (ng L^{-1})

Sampling Period	Deployment Dates		Sampler Type	Concentration PSII herbicides (and metabolites) (ng/L) (*included in PSII-HEq Index)														PSII-HEq (ng/L)	Concentration other pesticides (ng/L)										
	START	END		Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	24 D	2,4 DB	Haloxyfop	MCPA	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole
May-15 Jun-15	02-May-15	01-Jul-15	ED	n.d.	0.08	n.d.	n.d.	n.d.	0.09	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12	0.01	0.02	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Jul-15 Aug-15	Sampler not returned		ED																									
Sep-15 Oct-15	Sampler not returned		ED																									
Nov-15	Sampler not returned		ED																									
Dec-15	Sampler not used		ED																									
Jan-16	Sampler not used		ED																									
Feb-16	Sampler not used		ED																									
Mar-16	Sampler not sent		ED																									
Apr-16	Sampler not sent		ED																									
Summary																												
Samples (n)				1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1
Detects (n)				0	1	0	0	0	1	0	1	0	0	0	0	0	0		1	1	0	0	1	0	0	0	1	0	0
% Detects				0	100	0	0	0	100	0	100	0	0	0	0	0	0		100	100	0	0	100	0	0	0	100	0	0
Minimum detected concentration				n.d.	0.08	n.d.	n.d.	n.d.	0.09	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12	0.01	0.02	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Maximum concentration				n.d.	0.08	n.d.	n.d.	n.d.	0.09	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12	0.01	0.02	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	0.01	n.d.	n.d.

n.d. - non detect, for these samples the extract concentration was below the instrument LOD. n.d. values are inlcuded as 0 for summary statistics and PSII-HEq calculations

Concentrations that did not exceed 3 x blank levels and are shown preceded by "<" in the tables and are included as for n.d. in summary statistics

Concentrations where the extract concetration was above the instrument LOD but below the instrument LOR (see Table A3, Appendix A) are shown in italics. These values are included in the PSII-HEq calculations but should be treated with caution

Shaded pesticides and herbicides indicate that no calibration data is available and the sampling rate of atrazine was assumed. Water estimatations are approximate

Table F-6: Lucinda, Wet Tropics region – Time integrated estimated concentrations in water (ng L^{-1})

Sampling Period	Deployment Dates		Sampler Type	Concentration PSII herbicides (and metabolites) (ng/L) (*included in PSII-HEq Index)														PSII-HEq (ng/L)	Concentration other pesticides (ng/L)										
	START	END		Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	24 D	2,4 DB	Haloxyfop	MCPA	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole
May-15 Jun-15	12-May-15	14-Jul-15	ED	n.d.	0.17	n.d.	n.d.	n.d.	0.23	n.d.	0.11	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	**0.30**	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Jul-15 Aug-15	14-Jul-15	15-Sep-15	ED	n.d.	0.13	n.d.	n.d.	n.d.	0.10	n.d.	0.05	n.d.	n.d.	n.d.	*0.01*	0.01	n.d.	**0.14**	0.02	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sep-15 Oct-15	15-Sep-15	19-Oct-15	ED	n.d.	0.08	n.d.	n.d.	n.d.	0.11	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.14**	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nov-15	09-Nov-15	02-Dec-15	ED	n.d.	0.05	n.d.	n.d.	n.d.	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.07**	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dec-15	10-Dec-15	19-Jan-16	ED	n.d.	0.26	n.d.	n.d.	n.d.	0.31	n.d.	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.38**	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Jan-16	19-Jan-16	16-Feb-16	ED	n.d.	0.14	n.d.	n.d.	n.d.	0.19	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.23**	0.01	0.02	n.d.	n.d.	*0.01*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Feb-16	16-Feb-16 Lids on PFMs	15-Mar-16	ED	n.d.	0.78	n.d.	0.05	0.03	2.7	n.d.	0.85	n.d.	n.d.	n.d.	*0.03*	0.10	n.d.	**3.2**	0.08	0.25	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	0.47	n.d.	n.d.
Mar-16	15-Mar-16	14-Apr-16	ED	n.d.	0.62	n.d.	n.d.	n.d.	1.2	n.d.	0.43	n.d.	n.d.	n.d.	0.10	0.15	n.d.	**1.4**	0.06	0.05	n.d.	n.d.	*0.01*	n.d.	n.d.	n.d.	0.13	n.d.	n.d.
Apr-16	14-Apr-16	10-May-16	ED	n.d.	0.36	n.d.	n.d.	n.d.	0.82	n.d.	0.27	n.d.	n.d.	n.d.	n.d.	0.15	n.d.	**0.99**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Summary																													
Samples (n)				9	9	9	9	9	9	9	9	9	9	9	9	9	9		9	9	9	9	9	9	9	9	9	9	9
Detects (n)				0	9	0	1	1	9	0	8	0	0	0	3	5	0		7	4	0	0	4	0	0	0	2	0	0
% Detects				0	100	0	11	11	100	0	89	0	0	0	33	56	0		78	44	0	0	44	0	0	0	22	0	0
Minimum detected concentration				n.d.	0.05	n.d.	n.d.	n.d.	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.07**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Maximum concentration				n.d.	0.78	n.d.	0.05	0.03	2.7	n.d.	0.85	n.d.	n.d.	n.d.	0.10	0.15	n.d.	**3.20**	0.08	0.25	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	0.47	n.d.	n.d.

n.d. - non detect, for these samples the extract concentration was below the instrument LOD. n.d. values are inlcuded as 0 for summary statistics and PSII-HEq calculations

Concentrations that did not exceed 3 x blank levels and are shown preceded by "<" in the tables and are included as for n.d. in summary statistics

Concentrations where the extract concetration was above the instrument LOD but below the instrument LOR (see Table A3, Appendix A) are shown in italics. These values are included in the PSII-HEq calculations but should be treated with caution

Shaded pesticides and herbicides indicate that no calibration data is available and the sampling rate of atrazine was assumed. Water estimatations are approximate

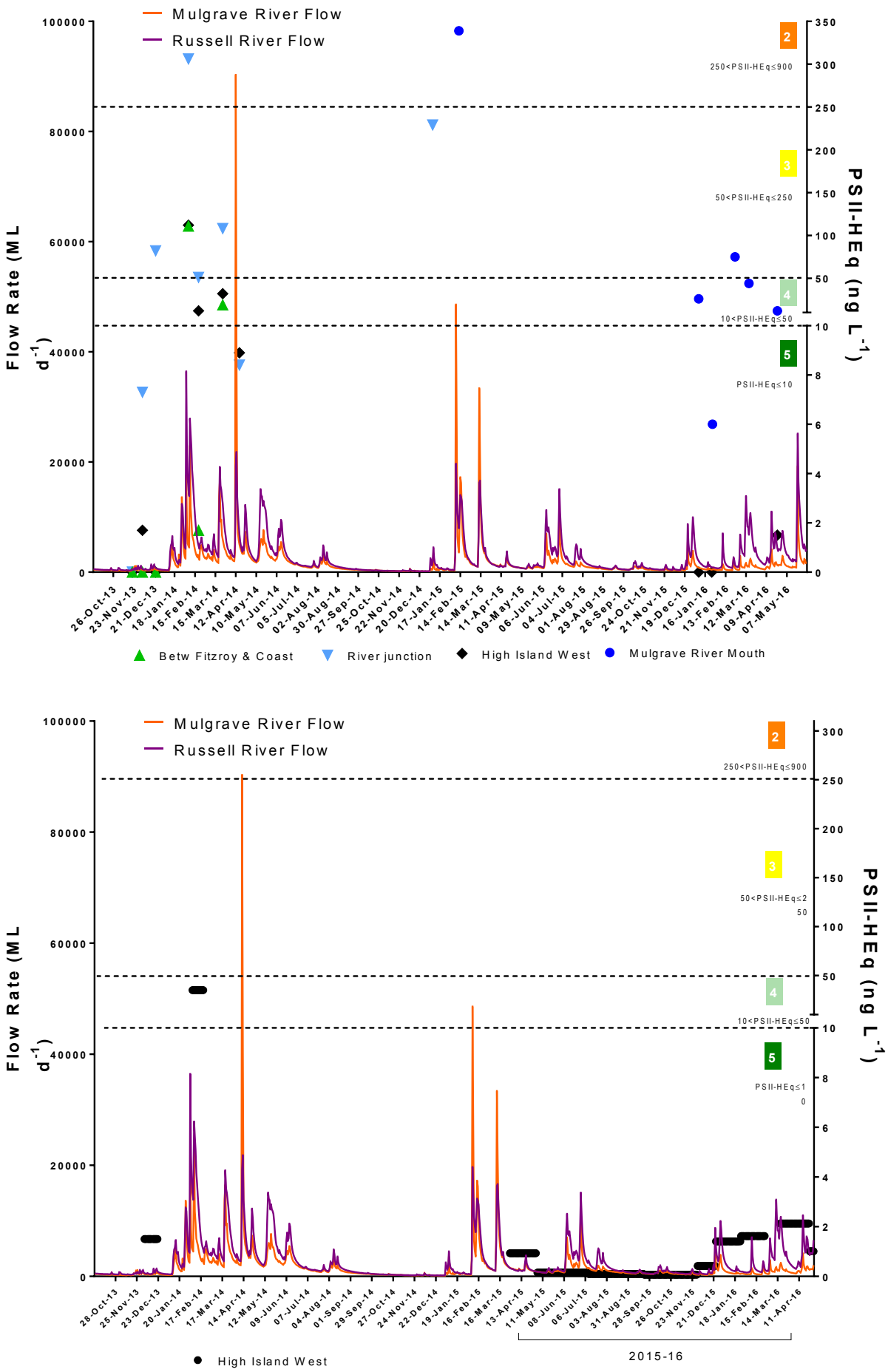
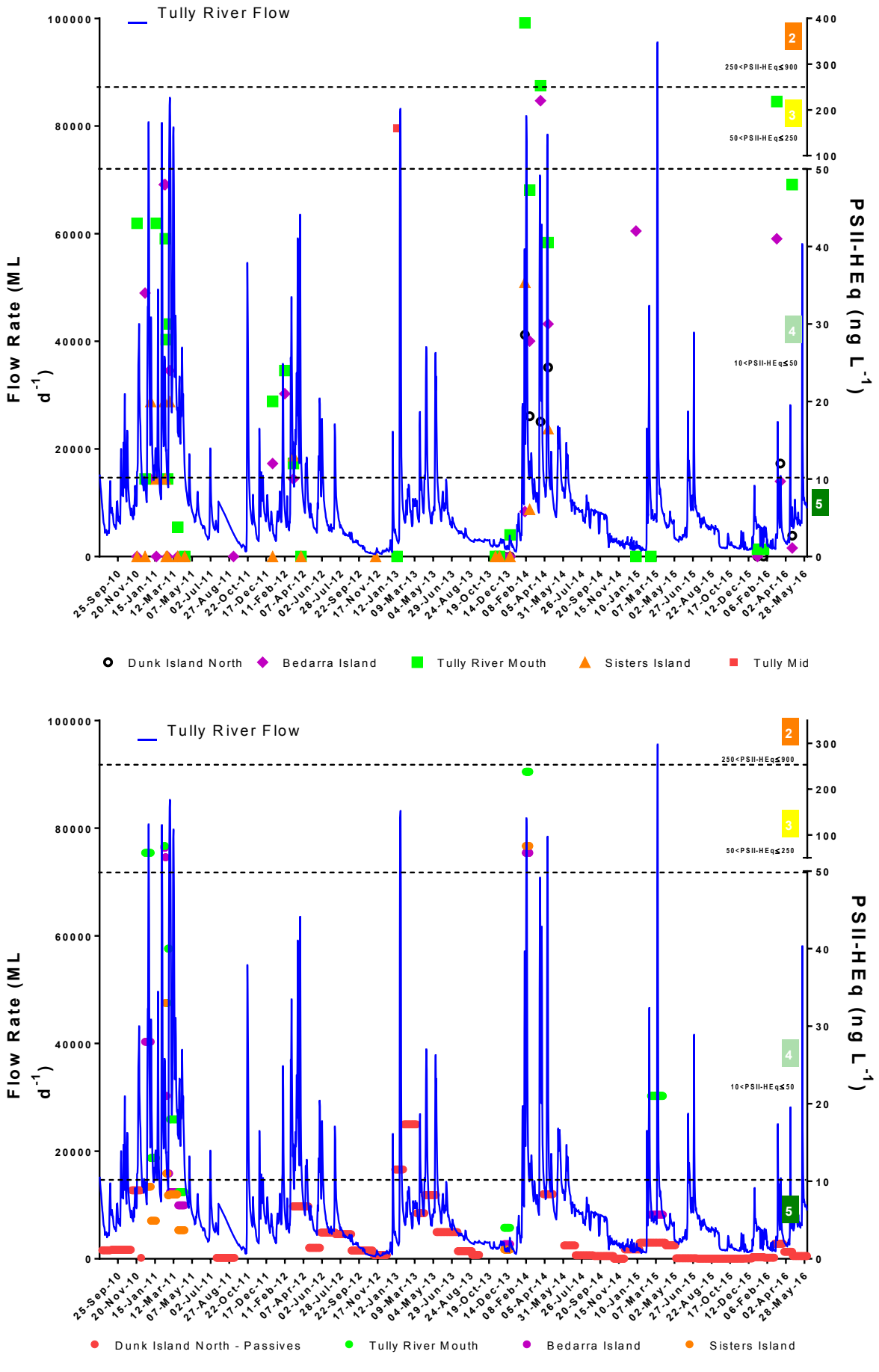


Figure F-1: Timing and location of grab (top) and passive (bottom) samples collected on the Russell-Mulgrave River transect, Wet Tropics, between 2013 and 2016



Note: Tully River Flow data estimated from Gorge station and adjusted to Euramo station from June 2014 - March 2015

Figure F-2: Timing and location of grab (top) and passive (bottom) samples collected on the Tully River transect, Wet Tropics, between 2010 and 2016

Table F-7: Barratta Creek, Burdekin Region – Time integrated estimated concentrations in water (ng L^{-1})

Sampling Period	Deployment Dates		Sampler Type	Concentration PSII herbicides (and metabolites) (ng/L) (*included in PSII-HEq Index)														PSII-HEq (ng/L)	Concentration other pesticides (ng/L)													
	START	END		Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	24 D	2,4 DB	Haloxyfop	MCPA	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole	Chlorpyrifos	Pendimethalin	Propiconazole	Trifluralin
May-15 Jun-15	Samplers/PFMs lost		ED																												
Jul-15 Aug-15	09-Jul-15	04-Aug-15	ED	n.d.	0.39	n.d.	n.d.	n.d.	0.08	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	0.16	0.11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.				
Sep-15 Oct-15	04-Aug-15	Not returned	ED																													
Nov-15	Returned sealed		ED																													
Dec-15	?	05-Jan-16	ED	0.17	14	2.6	0.52	0.02	1.9	n.d.	0.24	0.14	n.d.	0.11	0.04	0.05	n.d.	4.7	0.16	0.36	n.d.	n.d.	0.10	n.d.	0.17	n.d.	n.d.	n.d.	n.d.				
	Deployment date unknown		PDMS**																										n.d.	0.004	n.d.	n.d.
Jan-16	05-Jan-16	06-Feb-16	ED	0.77	52	9.7	1.1	0.39	7.0	n.d.	1.1	1.0	n.d.	0.48	0.26	0.31	n.d.	18	0.76	n.d.	n.d.	0.04	0.01	n.d.	n.d.	n.d.	0.05	0.03	n.d.				
			PDMS																										0.010	0.008	n.d.	n.d.
Feb-16	06-Feb-16	02-Mar-16	ED**	0.40	11	5.4	0.58	0.13	2.0	n.d.	0.53	0.04	n.d.	0.08	0.05	0.28	n.d.	5.2	0.24	0.13	n.d.	0.05	0.07	n.d.	n.d.	n.d.	0.07	n.d.	n.d.				
			PDMS																										0.011	0.026	n.d.	n.d.
Mar-16	02-Mar-16	06-Apr-16	ED	0.26	1.5	1.0	0.17	0.04	0.47	n.d.	0.18	n.d.	n.d.	*0.02*	0.16	0.18	n.d.	1.3	0.09	n.d.	n.d.	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.				
			PDMS																										0.078	0.026	n.d.	n.d.
Apr-16	06-Apr-16	17-May-16	ED**	*0.13*	1.0	0.52	0.17	0.03	0.69	n.d.	0.31	n.d.	n.d.	n.d.	0.18	0.10	n.d.	1.2	0.08	0.05	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.				
			PDMS**																										0.16	0.16	n.d.	n.d.
Summary																																
Samples (n)				6	6	6	6	6	6	6	6	6	6	6	6	6	6		6	6	6	6	6	6	6	6	6	6	6	5	5	5	5
Detects (n)				5	6	5	5	5	6	0	6	3	0	4	5	6	0		6	3	0	2	5	0	1	0	2	1	0	4	5	0	0
% Detects				83	100	83	83	83	100	0	100	50	0	67	83	100	0		100	50	0	33	83	0	17	0	33	17	0	80	100	0	0
Minimum detected concentration				n.d.	0.39	n.d.	n.d.	n.d.	0.08	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	0.16	0.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.004	n.d.	n.d.
Maximum concentration				0.77	52	9.7	1.1	0.39	7.0	n.d.	1.1	1.0	n.d.	0.48	0.26	0.31	n.d.	18	0.76	0.36	n.d.	0.05	0.10	n.d.	0.17	n.d.	0.07	0.03	n.d.	0.16	0.16	n.d.	n.d.

n.d. - non detect, for these samples the extract concentration was below the instrument LOD. n.d. values are inlcuded as 0 for summary statistics and PSII-HEq calculations

Concentrations that did not exceed 3 x blank levels and are shown preceded by "<" in the tables and are included as for n.d. in summary statistics

Concentrations where the extract concetration was above the instrument LOD but below the instrument LOR (see Table A3, Appendix A) are shown in italics. These values are included in the PSII-HEq calculations but should be treated with caution

Shaded pesticides and herbicides indicate that no calibration data is available and the sampling rate of atrazine was assumed. Water estimatations are approximate

**Concentration is average of duplicate samplers

Table F-8: Repulse Bay, Mackay Whitsunday region – Time integrated estimated concentrations in water (ng L^{-1})

Sampling Period	Deployment Dates		Sampler Type	Concentration PSII herbicides (and metabolites) (ng/L) (*included in PSII-HEq Index)														PSII-HEq (ng/L)	Concentration other pesticides (ng/L)													
	START	END		Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	24 D	2,4 DB	Haloxyfop	MCPA	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole	Chlorpyrifos	Pendimethalin	Propiconazole	Trifluralin
May-15 Jun-15	21-May-15	14-Jul-15	ED**	n.d.	0.54	0.10	n.d.	n.d.	0.24	n.d.	0.16	n.d.	n.d.	n.d.	0.04	0.26	n.d.	0.42	0.15	n.d.	n.d.	n.d.	*0.004*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.				
Jul-15 Aug-15	14-Jul-15	16-Sep-15	ED	n.d.	0.30	n.d.	0.02	n.d.	0.17	n.d.	0.15	n.d.	n.d.	n.d.	0.02	0.07	n.d.	0.28	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.				
Sep-15 Oct-15	16-Sep-15	04-Nov-15	ED	n.d.	0.15	n.d.	n.d.	n.d.	0.12	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	0.18	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.				
Nov-15	04-Nov-15	09-Dec-15	ED																													
	ED membrane destroyed		PDMS																											0.004	0.002	n.d.	n.d.
Dec-15	09-Dec-15	20-Jan-16	ED	n.d.	8.8	0.19	n.d.	n.d.	0.95	n.d.	0.65	0.18	n.d.	0.06	0.09	0.04	n.d.	2.6	0.02	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.13	n.d.	n.d.				
			PDMS																											n.d.	0.002	n.d.	n.d.
Jan-16	Samplers lost		ED																													
Feb-16	Samplers unused		ED																													
Mar-16	Samplers not sent		ED																													
Apr-16	Samplers unused		ED																													
Summary																																
Samples (n)				4	4	4	4	4	4	4	4	4	4	4	4	4	4		4	4	4	4	4	4	4	4	4	4	4	2	2	2	2
Detects (n)				0	4	2	1	0	4	0	4	1	0	1	3	4	0		4	1	0	0	1	0	0	0	1	0	0	1	2	0	0
% Detects				0	100	50	25	0	100	0	100	25	0	25	75	100	0		100	25	0	0	25	0	0	0	25	0	0	50	100	0	0
Minimum detected concentration				n.d.	0.15	n.d.	n.d.	n.d.	0.12	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	0.18	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.002	n.d.	n.d.
Maximum concentration				n.d.	8.8	0.19	0.02	n.d.	1.0	n.d.	0.65	0.18	n.d.	0.06	0.09	0.26	n.d.	2.6	0.15	0.07	n.d.	n.d.	0.004	n.d.	n.d.	n.d.	0.13	n.d.	n.d.	0.004	0.002	n.d.	n.d.

n.d. - non detect, for these samples the extract concentration was below the instrument LOD. n.d. values are inlcuded as 0 for summary statistics and PSII-HEq calculations

Concentrations that did not exceed 3 x blank levels and are shown preceded by "<" in the tables and are included as for n.d. in summary statistics

Concentrations where the extract concetration was above the instrument LOD but below the instrument LOR (see Table A3, Appendix A) are shown in italics. These values are included in the PSII-HEq calculations but should be treated with caution

Shaded pesticides and herbicides indicate that no calibration data is available and the sampling rate of atrazine was assumed. Water estimatations are approximate

**Concentration is average of duplicate samplers

Table F-9: Round Top Island, Mackay Whitsunday region – Time integrated estimated concentrations in water (ng L^{-1})

Sampling Period	Deployment Dates		Sampler Type	Concentration PSII herbicides (and metabolites) (ng/L) (*included in PSII-HEq Index)														PSII-HEq (ng/L)	Concentration other pesticides (ng/L)													
	START	END		Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	24 D	2,4 DB	Haloxyfop	MCPA	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole	Chlorpyrifos	Pendimethalin	Propiconazole	Trifluralin
May-15 Jun-15	Sampler not used		ED																													
Jul-15 Aug-15	Sampler not used		ED																													
Sep-15 Oct-15	17-Sep-15	05-Nov-15	ED**	n.d.	0.61	0.27	0.05	n.d.	1.5	n.d.	0.26	n.d.	n.d.	n.d.	0.03	0.03	n.d.	1.7	0.04	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.				
Nov-15	05-Nov-15	09-Dec-15	ED**	n.d.	1.2	0.60	0.15	n.d.	1.7	n.d.	0.44	n.d.	n.d.	*0.01*	*0.03*	0.01	n.d.	2.1	<0.06	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	0.59	n.d.				
			PDMS																											0.066	0.005	n.d.	n.d.
Dec-15 Jan-16	09-Dec-15	21-Jan-16	ED**	*0.17*	68	10	3.7	n.d.	130	n.d.	23	0.29	n.d.	0.30	0.53	0.02	n.d.	151	0.75	19	n.d.	n.d.	5.2	n.d.	1.36	1.2	5.9	0.41	n.d.				
Feb-16	21-Jan-16	02-Mar-16	ED**	1.4	245	28	4.8	n.d.	462	n.d.	72	2.0	n.d.	1.0	0.70	0.17	n.d.	533	6.4	0.12	n.d.	0.01	0.04	n.d.	n.d.	0.12	36	0.56	n.d.				
			PDMS																											0.21	0.087	2.1	0.01
Mar-16	02-Mar-16	14-Apr-16	ED**	0.59	29	8.5	1.1	n.d.	94	n.d.	18	0.36	n.d.	0.12	0.08	0.17	n.d.	107	1.2	n.d.	n.d.	0.02	0.03	n.d.	n.d.	0.05	20	0.41	n.d.				
			PDMS																											0.52	0.22	1.4	0.01
Apr-16	Sampler lost		ED																													
Summary																																
Samples (n)				5	5	5	5	5	5	5	5	5	5	5	5	5	5		5	5	5	5	5	5	5	5	5	5	5	3	3	3	3
Detects (n)				3	5	5	5	0	5	0	5	3	0	4	5	5	0		4	4	0	2	3	0	1	3	5	4	0	3	3	2	2
% Detects				60	100	100	100	0	100	0	100	60	0	80	100	100	0		80	80	0	40	60	0	20	60	100	80	0	100	100	67	67
Minimum detected concentration				n.d.	0.61	0.27	0.05	n.d.	1.5	n.d.	0.26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.7	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	0.07	0.005	n.d.	n.d.
Maximum concentration				1.4	245	28	4.8	n.d.	462	n.d.	72	2.0	n.d.	1.0	0.70	0.17	n.d.	533	6.4	19	n.d.	0.02	5.2	n.d.	1.4	1.2	36	0.59	n.d.	0.52	0.22	2.1	0.01

n.d. - non detect, for these samples the extract concentration was below the instrument LOD. n.d. values are inlcuded as 0 for summary statistics and PSII-HEq calculations

Concentrations that did not exceed 3 x blank levels and are shown preceded by "<" in the tables and are included as for n.d. in summary statistics

Concentrations where the extract concetration was above the instrument LOD but below the instrument LOR (see Table A3, Appendix A) are shown in italics. These values are included in the PSII-HEq calculations but should be treated with caution

Shaded pesticides and herbicides indicate that no calibration data is available and the sampling rate of atrazine was assumed. Water estimatations are approximate

**Concentration is average of duplicate samplers

Table F-10: Sarina Inlet, Mackay Whitsunday region – Time integrated estimated concentrations in water (ng L^{-1})

Sampling Period	Deployment Dates		Sampler Type	Concentration PSII herbicides (and metabolites) (ng/L) (*included in PSII-HEq Index)														PSII-HEq (ng/L)	Concentration other pesticides (ng/L)										
	START	END		Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	24 D	2,4 DB	Haloxyfop	MCPA	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole
May-16	25-Mar-15	05-Jun-15	ED	n.d.	0.52	n.d.	n.d.	n.d.	0.90	n.d.	0.56	n.d.	n.d.	n.d.	n.d.	0.18	n.d.	1.2	n.d.	0.04	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.08	n.d.
Jun-15 Jul-15 Aug-15	05-Jun-15	16-Sep-15	ED	n.d.	0.44	n.d.	n.d.	n.d.	0.21	n.d.	0.16	n.d.	n.d.	n.d.	0.04	0.12	n.d.	0.35	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sep-15 Oct-15 Nov-15	16-Sep-15	30-Nov-15	ED	n.d.	0.59	n.d.	0.07	n.d.	0.22	n.d.	0.29	n.d.	n.d.	n.d.	0.02	0.05	n.d.	0.44	n.d.	0.21	n.d.	n.d.	0.03	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Dec-15	30-Nov-15	28-Feb-16	ED																										
Jan-16			ED																										
Feb-16	Sampler fouled (long deployment)		ED																										
Mar-16	Sampler unused		ED																										
Apr-16	Sampler not sent		ED																										
Summary																													
Samples (n)				3	3	3	3	3	3	3	3	3	3	3	3	3	3		3	3	3	3	3	3	3	3	3	3	3
Detects (n)				0	3	0	1	0	3	0	3	0	0	0	2	3	0		1	2	0	0	2	0	0	0	1	1	0
% Detects				0	100	0	33	0	100	0	100	0	0	0	67	100	0		33	67	0	0	67	0	0	0	33	33	0
Minimum detected concentration				n.d.	0.44	n.d.	n.d.	n.d.	0.21	n.d.	0.16	n.d.	n.d.	n.d.	n.d.	0.05	n.d.	0.35	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Maximum concentration				n.d.	0.59	n.d.	0.07	n.d.	0.90	n.d.	0.56	n.d.	n.d.	n.d.	0.04	0.18	n.d.	1.21	0.04	0.21	n.d.	n.d.	0.03	n.d.	n.d.	n.d.	0.01	0.08	n.d.

n.d. - non detect, for these samples the extract concentration was below the instrument LOD. n.d. values are inlcuded as 0 for summary statistics and PSII-HEq calculations

Concentrations that did not exceed 3 x blank levels and are shown preceded by "<" in the tables and are included as for n.d. in summary statistics

Concentrations where the extract concetration was above the instrument LOD but below the instrument LOR (see Table A3, Appendix A) are shown in italics. These values are included in the PSII-HEq calculations but should be treated with caution

Shaded pesticides and herbicides indicate that no calibration data is available and the sampling rate of atrazine was assumed. Water estimatations are approximate

Table F-11: Sandy Creek, Mackay Whitsunday region – Time integrated estimated concentrations in water (ng L^{-1})

Sampling Period	Deployment Dates		Sampler Type	Concentration PSII herbicides (and metabolites) (ng/L) (*included in PSII-HEq Index)														PSII-HEq (ng/L)	Concentration other pesticides (ng/L)													
	START	END		Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	24 D	2,4 DB	Haloxyfop	MCPA	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole	Chlorpyrifos	Pendimethalin	Propiconazole	Trifluralin
May-15	Samplers lost		ED																													
Jun-15																																
Jul-15	Samplers used for Nov		ED																													
Aug-15																																
Sep-15	16-Sep-15	04-Nov-15	ED																													
Oct-15	No samples/PFMs																															
Nov-15	04-Nov-15	09-Dec-15	ED	n.d.	1.0	0.25	0.08	n.d.	0.81	n.d.	0.48	n.d.	n.d.	n.d.	*0.02*	0.02	n.d.	1.2	<0.02	0.01	n.d.	n.d.	*0.01*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.				
	EDs from Jul/Aug		PDMS**																											0.010	0.002	n.d.	n.d.
Dec-15	09-Dec-15	20-Jan-16	ED**	n.d.	7.7	0.79	0.34	n.d.	6.0	n.d.	2.3	n.d.	n.d.	0.03	0.03	0.04	n.d.	8.2	0.18	0.14	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	0.09	0.10	n.d.				
Jan-16			PDMS																											n.d.	0.003	n.d.	n.d.
Feb-16	20-Jan-16	02-Mar-16	ED	0.21	26	1.3	0.26	n.d.	45	n.d.	15	0.44	n.d.	0.13	0.06	0.23	n.d.	55	0.42	0.03	n.d.	n.d.	*0.01*	n.d.	n.d.	n.d.	0.39	0.08	n.d.				
Mar-16	02-Mar-16	12-Apr-16	ED	*0.10*	5.0	0.62	0.06	n.d.	15	n.d.	5.8	0.05	n.d.	0.02	0.02	0.24	n.d.	19	0.24	n.d.	n.d.	n.d.	*0.01*	n.d.	n.d.	n.d.	0.35	0.06	n.d.				
Apr-16	12-Apr-16	19-May-16	ED	n.d.	0.50	n.d.	0.04	n.d.	1.5	n.d.	0.54	n.d.	n.d.	n.d.	n.d.	0.74	n.d.	1.8	0.10	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.				
			PDMS																											0.013	n.d.	n.d.	n.d.
Summary																																
Samples (n)				5	5	5	5	5	5	5	5	5	5	5	5	5	5		5	5	5	5	5	5	5	5	5	5	5	3	3	3	3
Detects (n)				2	5	4	5	0	5	0	5	2	0	3	4	5	0		4	4	0	0	4	0	0	0	3	3	0	2	2	0	0
% Detects				40	100	80	100	0	100	0	100	40	0	60	80	100	0		80	80	0	0	80	0	0	0	60	60	0	67	67	0	0
Minimum detected concentration				n.d.	0.50	n.d.	0.04	n.d.	0.81	n.d.	0.48	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	1.2	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Maximum concentration				0.21	26	1.3	0.34	n.d.	45	n.d.	15	0.44	n.d.	0.13	0.06	0.74	n.d.	55	0.42	0.14	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	0.39	0.10	n.d.	0.01	n.d.	n.d.	n.d.

n.d. - non detect, for these samples the extract concentration was below the instrument LOD. n.d. values are inlcuded as 0 for summary statistics and PSII-HEq calculations

Concentrations that did not exceed 3 x blank levels and are shown preceded by "<" in the tables and are included as for n.d. in summary statistics

Concentrations where the extract concetration was above the instrument LOD but below the instrument LOR (see Table A3, Appendix A) are shown in italics. These values are included in the PSII-HEq calculations but should be treated with caution

Shaded pesticides and herbicides indicate that no calibration data is available and the sampling rate of atrazine was assumed. Water estimatations are approximate

**Concentration is average of duplicate samplers

Table F-12: North Keppel Island, Fitzroy Region – Time integrated estimated concentrations in water (ng L^{-1})

Sampling Period	Deployment Dates		Sampler Type	Concentration PSII herbicides (and metabolites) (ng/L) (*included in PSII-HEq Index)														PSII-HEq (ng/L)	Concentration other pesticides (ng/L)										
	START	END		Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	24 D	2,4 DB	Haloxyfop	MCPA	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole
May-15 Jun 15	02-Apr-15	25-Jun-15	ED	n.d.	0.43	0.04	n.d.	n.d.	0.08	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	0.21	n.d.	**0.20**	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Jul 15 Aug 15	25-Jun-15	15-Sep-15	ED	n.d.	0.05	n.d.	n.d.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	n.d.	**0.06**	0.01	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sep15 Oct 15	15-Sep-15	04-Nov-15	ED	n.d.	0.03	n.d.	n.d.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.06**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nov 15	04-Nov-15	07-Dec-15	ED	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.01**	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dec 15	07-Dec-15 PFM lost	19-Jan-16	ED	n.d.	0.06	n.d.	n.d.	n.d.	0.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.11**	n.d.	<0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Jan 16	19-Jan-16	22-Feb-16	ED	n.d.	0.09	n.d.	n.d.	n.d.	0.26	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	2.0	n.d.	**0.45**	0.18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Feb 16	22-Feb-16	21-Mar-16	ED	n.d.	0.46	n.d.	n.d.	n.d.	0.51	n.d.	0.13	n.d.	n.d.	n.d.	*0.02*	2.6	n.d.	**0.84**	0.34	<0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mar 16	21-Mar-16	14-Apr-16	ED	n.d.	0.32	n.d.	0.02	n.d.	n.d.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	0.09	n.d.	**0.08**	0.05	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Apr 16	14-Apr-16	20-Jun-16	ED	n.d.	n.d.	n.d.	n.d.	n.d.	0.28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	**0.28**	n.d.	0.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Summary																													
Samples (n)				9	9	9	9	9	9	9	9	9	9	9	9	9	9		9	9	9	9	9	9	9	9	9	9	9
Detects (n)				0	8	1	1	0	7	0	4	0	0	0	2	5	0		5	3	0	0	1	0	0	0	0	0	0
% Detects				0	89	11	11	0	78	0	44	0	0	0	22	56	0		56	33	0	0	11	0	0	0	0	0	0
Minimum detected concentration				n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.01**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Maximum concentration				n.d.	0.5	0.04	0.02	n.d.	0.5	n.d.	0.1	n.d.	n.d.	n.d.	0.03	2.6	n.d.	**0.84**	0.34	0.15	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. - non detect, for these samples the extract concentration was below the instrument LOD. n.d. values are inlcuded as 0 for summary statistics and PSII-HEq calculations

Concentrations that did not exceed 3 x blank levels and are shown preceded by "<" in the tables and are included as for n.d. in summary statistics

Concentrations where the extract concentration was above the instrument LOD but below the instrument LOR (see Table A3, Appendix A) are shown in italics. These values are included in the PSII-HEq calculations but should be treated with caution

Shaded pesticides and herbicides indicate that no calibration data is available and the sampling rate of atrazine was assumed. Water estimatations are approximate

Appendix G Terrestrial run-off assessment results

Table G-1: Concentrations in water (ng L^{-1}) measured at various locations offshore and in river mouths (along transects) using 250 mL grab samples during the wet season

Transect	Sample Description	Date collected	Concentration PSII herbicides (and metabolites) (ng/L) (*included in PSII-HEq Index)														PSII-HEq (ng/L)	Concentration other pesticides (ng/L)											
			Ametryn*	Atrazine*	DE Atrazine*	DI Atrazine*	Bromacil	Diuron*	Fluometuron*	Hexazinone*	Metribuzin	Prometryn*	Propazine	Simazine*	Tebuthiuron*	Terbutryn		Metolachlor	24 D	2,4 DB	Haloxyfop	MCPA	Asulam	Fluazifop	Fluroxypyr	Imazapic	Imidacloprid	Metsulfuron-Methyl	Tebuconazole
Burdekin River	Barratta Creek mouth	05-Jan-16	0.81	32	5.6	2.0	n.d.	4.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12	n.d.	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	1.7	0.78	n.d.	n.d.	n.d.
	BUR14	05-Jan-16	n.d.	0.98	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BUR15	05-Jan-16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Barratta Creek mouth	06-Feb-16	n.d.	12	3.0	1.1	n.d.	2.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.2	n.d.	0.61	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Burdekin River mouth	06-Feb-16	n.d.	46	7.0	4.0	n.d.	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.7	n.d.	19	7.8	43	n.d.	n.d.	12	n.d.	n.d.	n.d.	3.5	4.2	n.d.	n.d.
	BUR14	06-Feb-16	n.d.	7.5	1.5	0.71	n.d.	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.5	n.d.	2.9	1.2	7.2	n.d.	n.d.	2.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BUR15	06-Feb-16	n.d.	1.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Barratta Creek mouth	01-Mar-16	n.d.	3.0	1.4	0.31	n.d.	0.48	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.1	n.d.	0.88	n.d.	n.d.	0.52	n.d.	n.d.	0.42	n.d.	n.d.	n.d.	n.d.
	Barratta Creek mouth	06-Apr-16	n.d.	1.8	1.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.28	n.d.	0.44	n.d.	1.1	n.d.	n.d.	1.4	n.d.	n.d.	0.50	n.d.	n.d.	n.d.	n.d.
Russell-Mulgrave River	Russell-Mulgrave mouth	07-Jan-16	n.d.	4.8	4.0	0.31	n.d.	19	n.d.	15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	26	0.31	12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.5	32	2.0	n.d.
	High Island	07-Jan-16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Russell-Mulgrave mouth	26-Jan-16	n.d.	1.3	n.d.	n.d.	n.d.	5.1	n.d.	1.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.0	n.d.	3.5	n.d.	n.d.	1.2	n.d.	n.d.	n.d.	n.d.	2.0	n.d.	n.d.
	High Island	26-Jan-16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Russell-Mulgrave mouth	26-Feb-16	n.d.	23	8.4	2.2	n.d.	64	n.d.	16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	75	n.d.	18	n.d.	0.67	2.8	n.d.	n.d.	3.5	3.7	34	3.5	2.5
	High Island	26-Feb-16	d in transport/storage																										
	Russell-Mulgrave mouth	16-Mar-16	n.d.	4.4	5.7	n.d.	n.d.	36	n.d.	16	1.7	n.d.	n.d.	n.d.	n.d.	n.d.	44	1.1	18	n.d.	n.d.	3.5	n.d.	n.d.	1.9	8.8	34	n.d.	n.d.
	High Island	16-Mar-16	d in transport/storage																										
	Russell-Mulgrave mouth	24-Apr-16	n.d.	2.2	4.4	n.d.	n.d.	7.8	n.d.	8.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12	n.d.	2.3	n.d.	1.2	1.1	n.d.	n.d.	n.d.	1.8	32	n.d.	n.d.
	High Island	24-Apr-16	n.d.	n.d.	n.d.	n.d.	n.d.	1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tully River	Tully River mouth	08-Jan-16	n.d.	n.d.	n.d.	n.d.	n.d.	0.95	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.95	n.d.	0.85	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Bedarra Island	08-Jan-16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Dunk Island north	08-Jan-16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Tully River mouth	26-Jan-16	n.d.	n.d.	n.d.	n.d.	n.d.	0.95	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.95	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Dunk Island north	26-Jan-16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Tully River mouth	06-Mar-16	n.d.	69	11	3.3	n.d.	190	n.d.	42	5.3	n.d.	n.d.	n.d.	n.d.	n.d.	218	1.4	32	n.d.	2.1	n.d.	n.d.	n.d.	2.1	7.1	40	n.d.	n.d.
	Bedarra Island	06-Mar-16	n.d.	9.4	2.0	0.67	n.d.	35	n.d.	9.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	41	0.79	8.4	n.d.	n.d.	n.d.	n.d.	n.d.	0.64	0.77	5.7	n.d.	n.d.
	Dunk Island north	06-Mar-16	d in transport/storage																										
	Tully River mouth	17-Mar-16	d in transport/storage																										
	Bedarra Island	17-Mar-16	n.d.	2.0	0.65	n.d.	n.d.	8.5	n.d.	2.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9.7	0.70	3.6	n.d.	n.d.	n.d.	n.d.	n.d.	3.6	n.d.	3.6	n.d.	n.d.
	Dunk Island north	17-Mar-16	n.d.	2.3	0.73	n.d.	n.d.	11	n.d.	2.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12	0.96	5.0	n.d.	n.d.	n.d.	n.d.	n.d.	3.2	n.d.	3.9	n.d.	n.d.
	Tully River mouth	22-Apr-16	n.d.	13	9.7	2.2	n.d.	40	n.d.	13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	48	1.1	19	n.d.	3.2	n.d.	n.d.	n.d.	2.3	4.5	75	n.d.	5.9
	Bedarra Island	22-Apr-16	n.d.	n.d.	n.d.	n.d.	n.d.	1.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Dunk Island north	22-Apr-16	n.d.	n.d.	n.d.	n.d.	n.d.	2.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.93	n.d.	n.d.

Appendix H Mean flow rates, PSII-HEq of passive samplers and plume colour class of major rivers

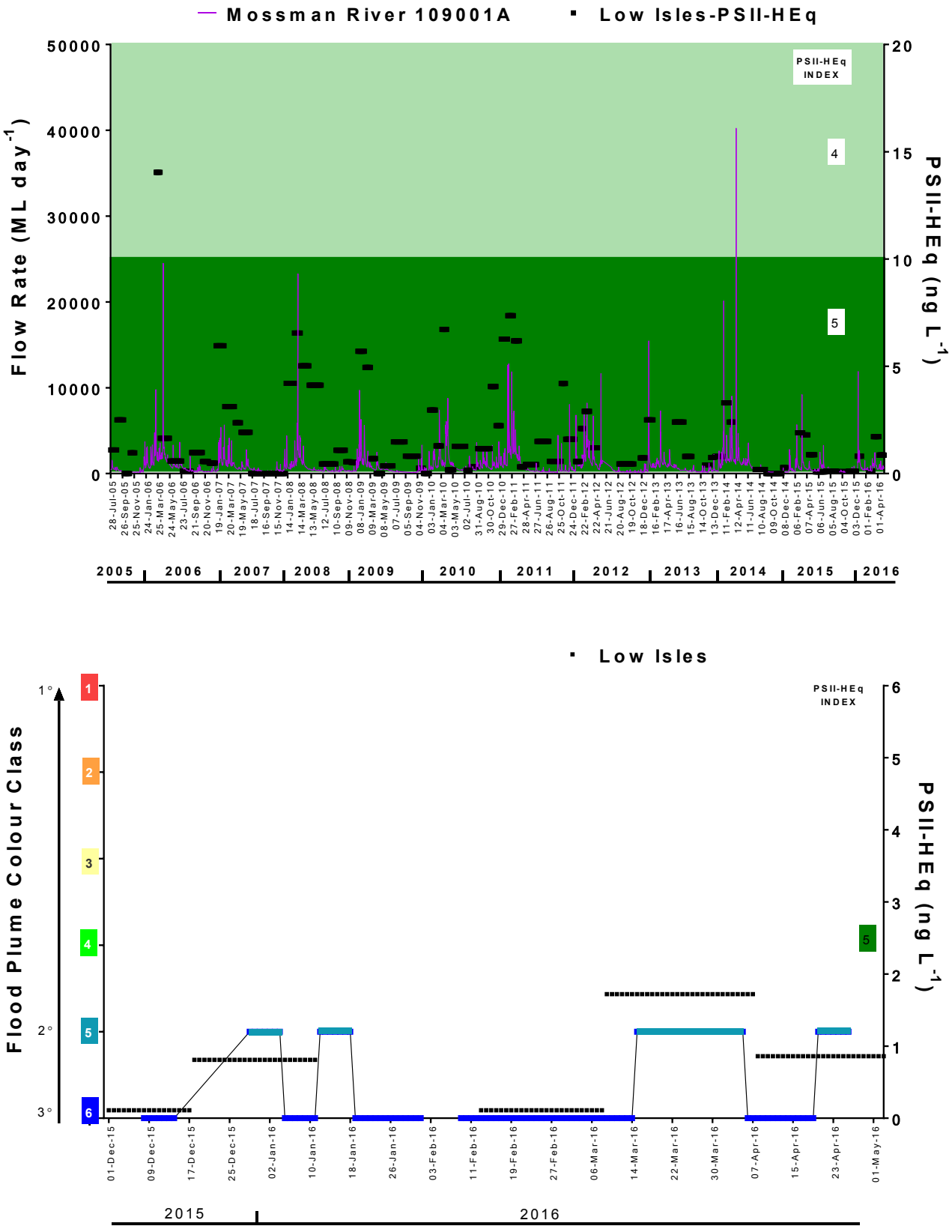


Figure H-1: Temporal trends in PSII-HEq with respect to (top graph) river flow rate influencing passive sampler site at Low Isles in the Wet Tropics region since 2005 and (bottom graph) flood plume colour class for 2015-16. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network. Colour class data provided by Dieter Tracey (JCU)

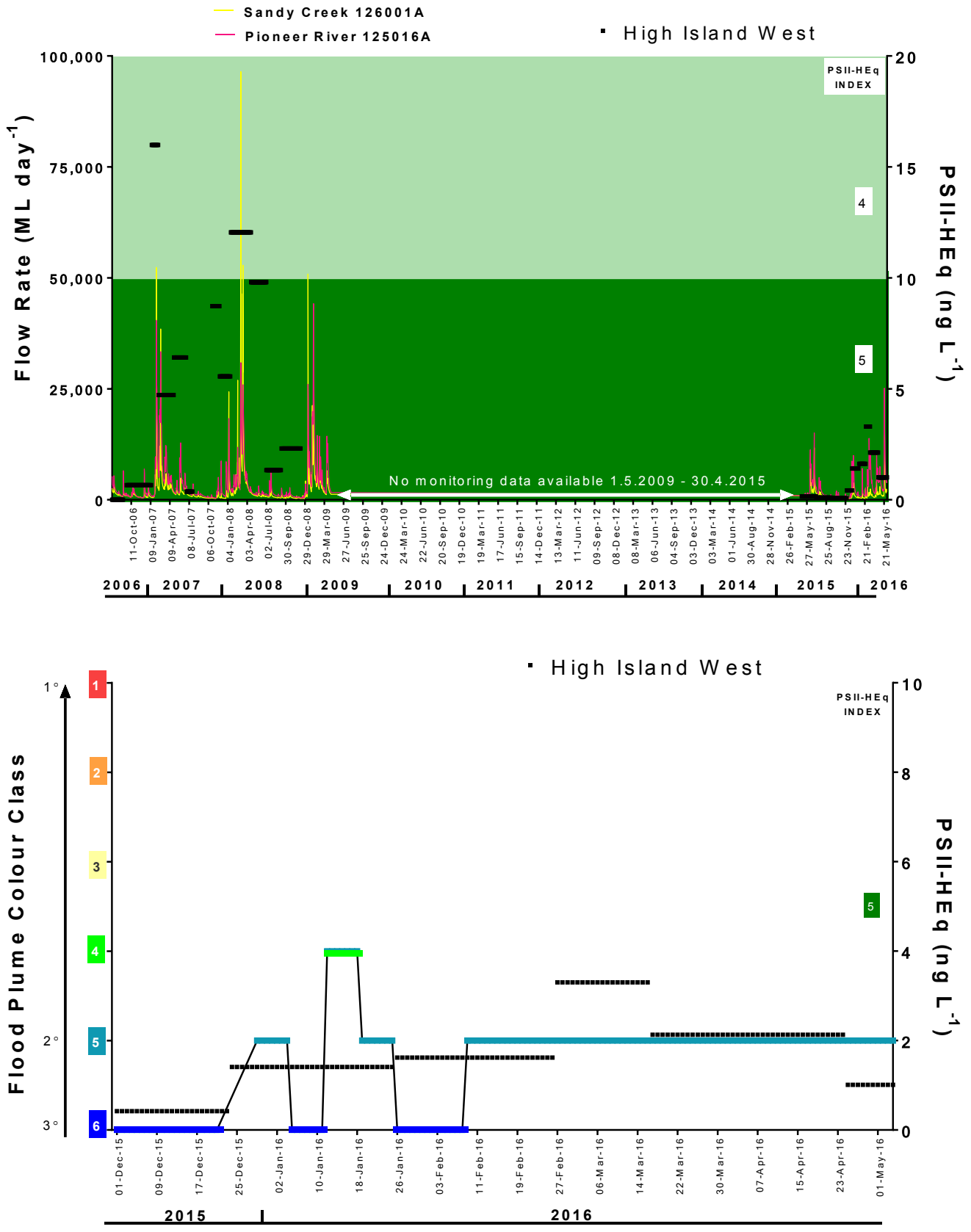


Figure H-2: Temporal trends in PSII-HEq with respect to (top graph) river flow rate influencing passive sampler site at High Island in the Wet Tropics region since 2006 and (bottom graph) flood plume colour class for 2015-16. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network. No monitoring data were available 2009-2015. Colour class data provided by Dieter Tracey (JCU)

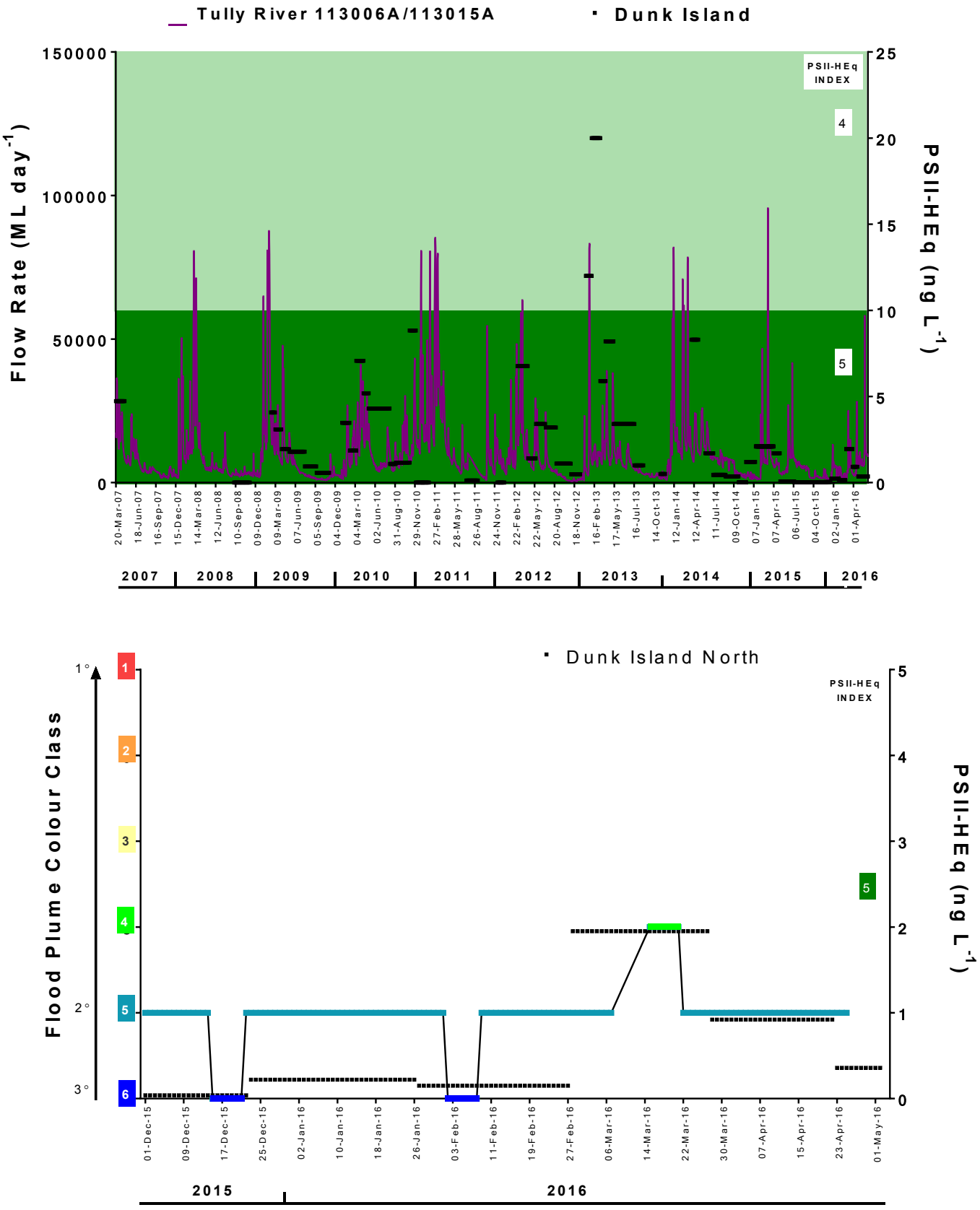


Figure H-3: Temporal trends in PSII-HEq with respect to (top graph) river flow rate influencing passive sampler site at Dunk Island in the Wet Tropics region since 2007 and (bottom graph) flood plume colour class for 2015-16. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network. Colour class data provided by Dieter Tracey (JCU).

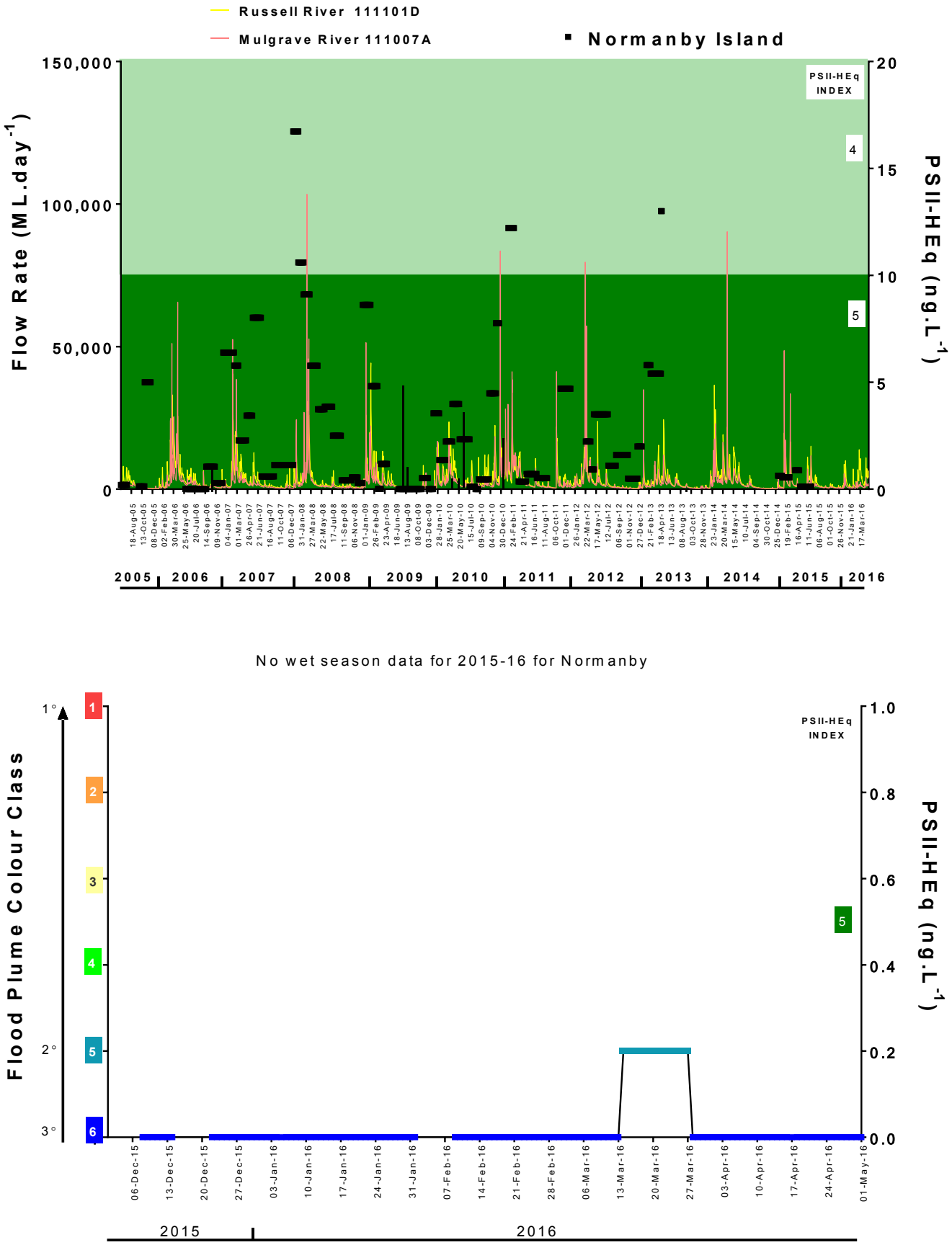


Figure H-4: Temporal trends in PSII-HEq with respect to (top graph) river flow rate influencing passive sampler site at Normanby Island in the Wet Tropics region since 2005 and (bottom graph) flood plume colour class for 2015-16. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network. Colour class data provided by Dieter Tracey (JCU)

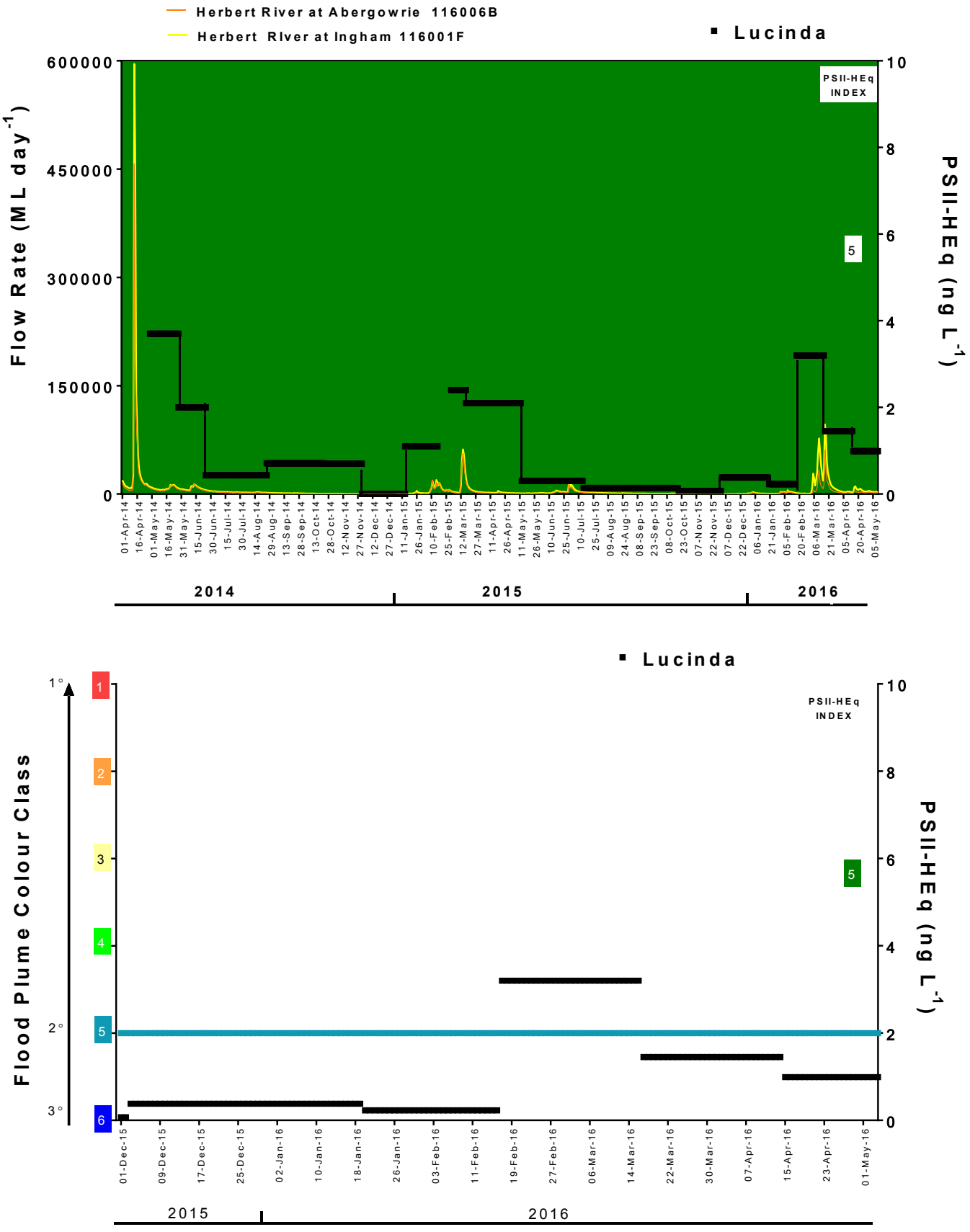


Figure H-5: Temporal trends in PSII-HEq with respect to (top graph) river flow rate influencing passive sampler site at Lucinda in the Wet Tropics region since 2005 and (bottom graph) flood plume colour class for 2015-16. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network. Colour class data provided by Dieter Tracey (JCU).

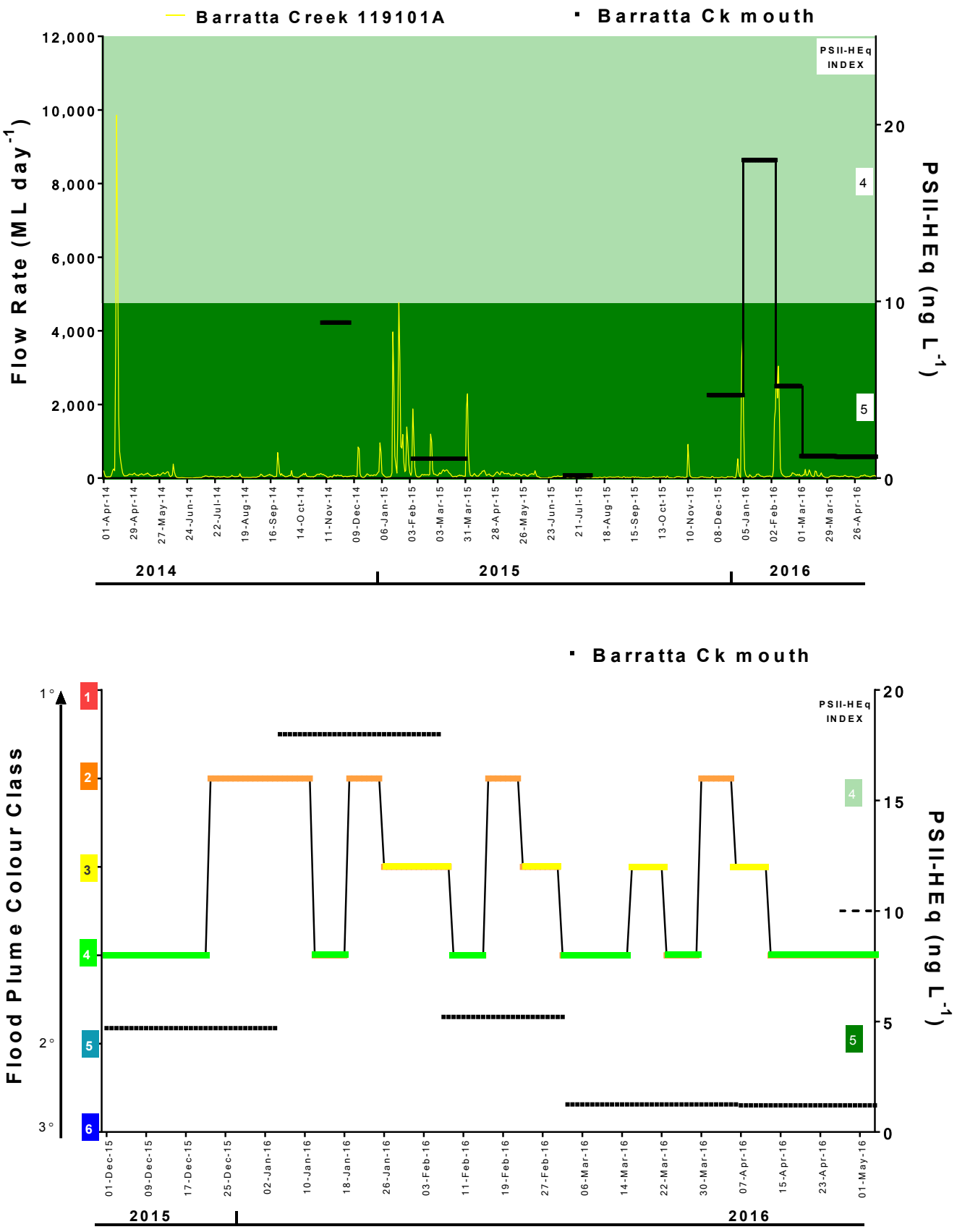


Figure H-6: Temporal trends in PSII-HEq with respect to (top graph) river flow rate influencing passive sampler site at Barratta Creek mouth in the Burdekin region since 2005 and (bottom graph) flood plume colour class for 2015-16. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network. Colour class data provided by Dieter Tracey (JCU).

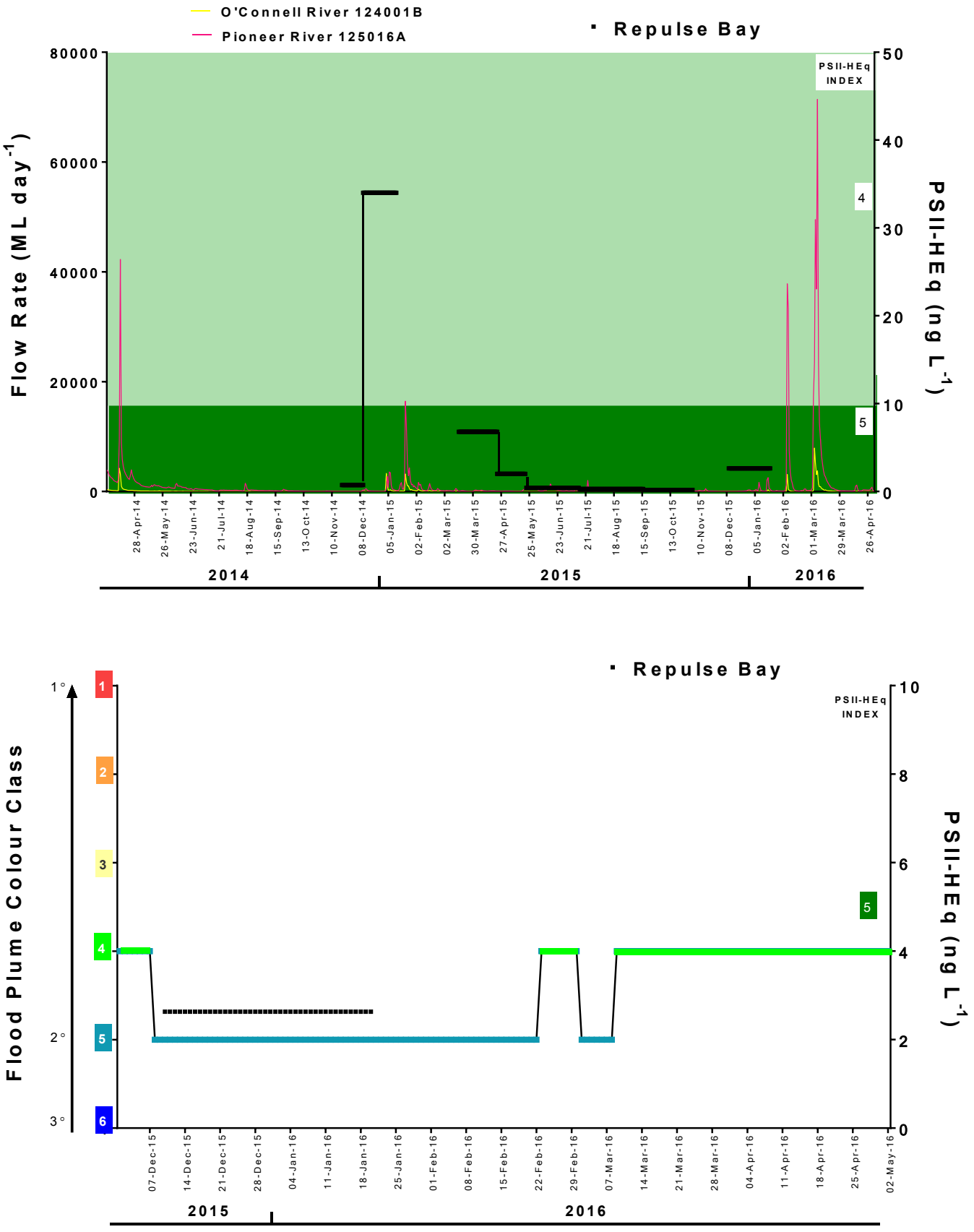


Figure H-7: Temporal trends in PSII-HEq with respect to (top graph) river flow rate influencing passive sampler site at Repulse Bay in the Mackay Whitsunday region since 2005 and (bottom graph) flood plume colour class for 2015-16. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network. Colour class data provided by Dieter Tracey (JCU).

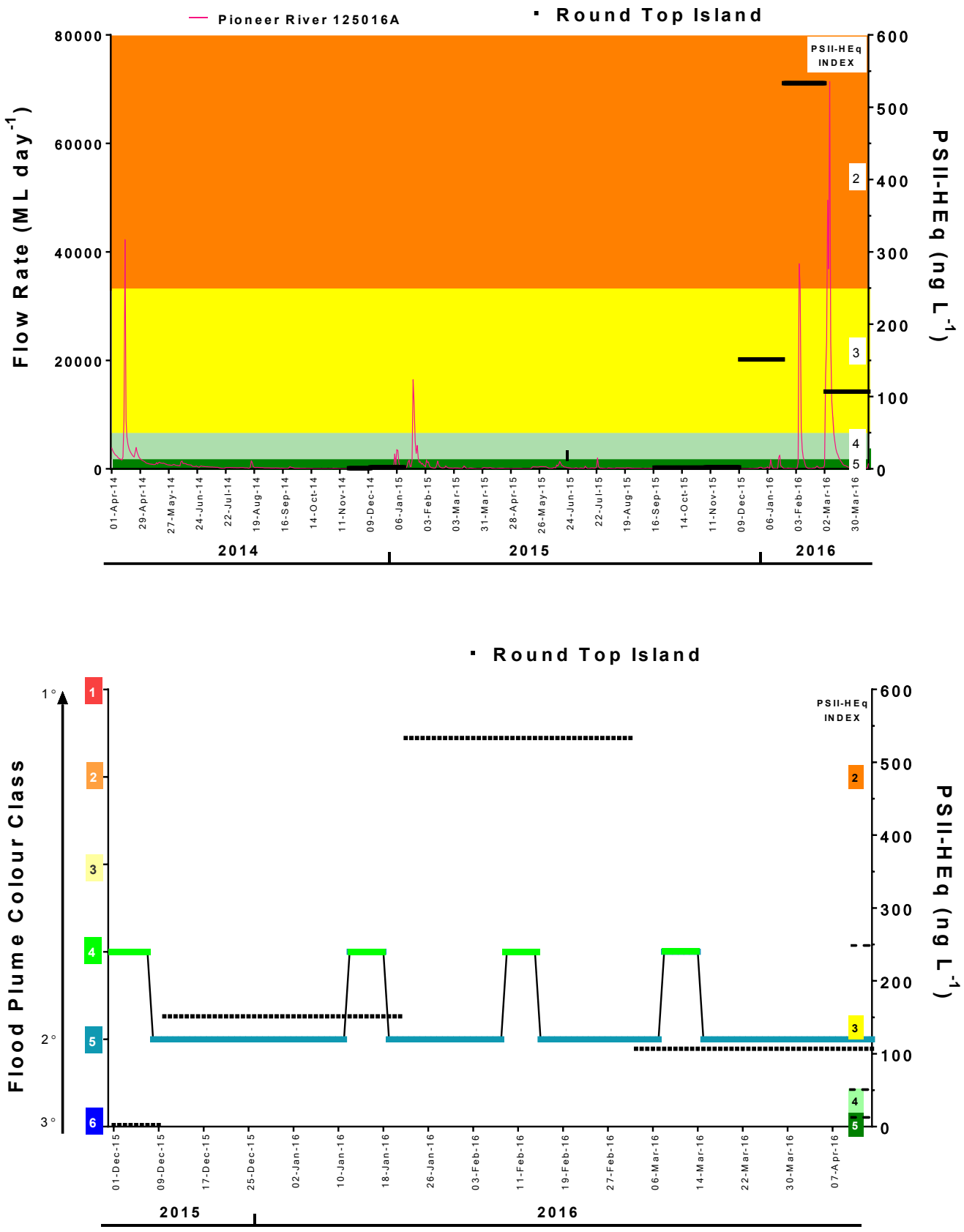


Figure H-8: Temporal trends in PSII-HEq with respect to (top graph) river flow rate influencing passive sampler site at Round Top Island in the Mackay Whitsunday region since 2005 and (bottom graph) flood plume colour class for 2015-16. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network. Colour class data provided by Dieter Tracey (JCU).

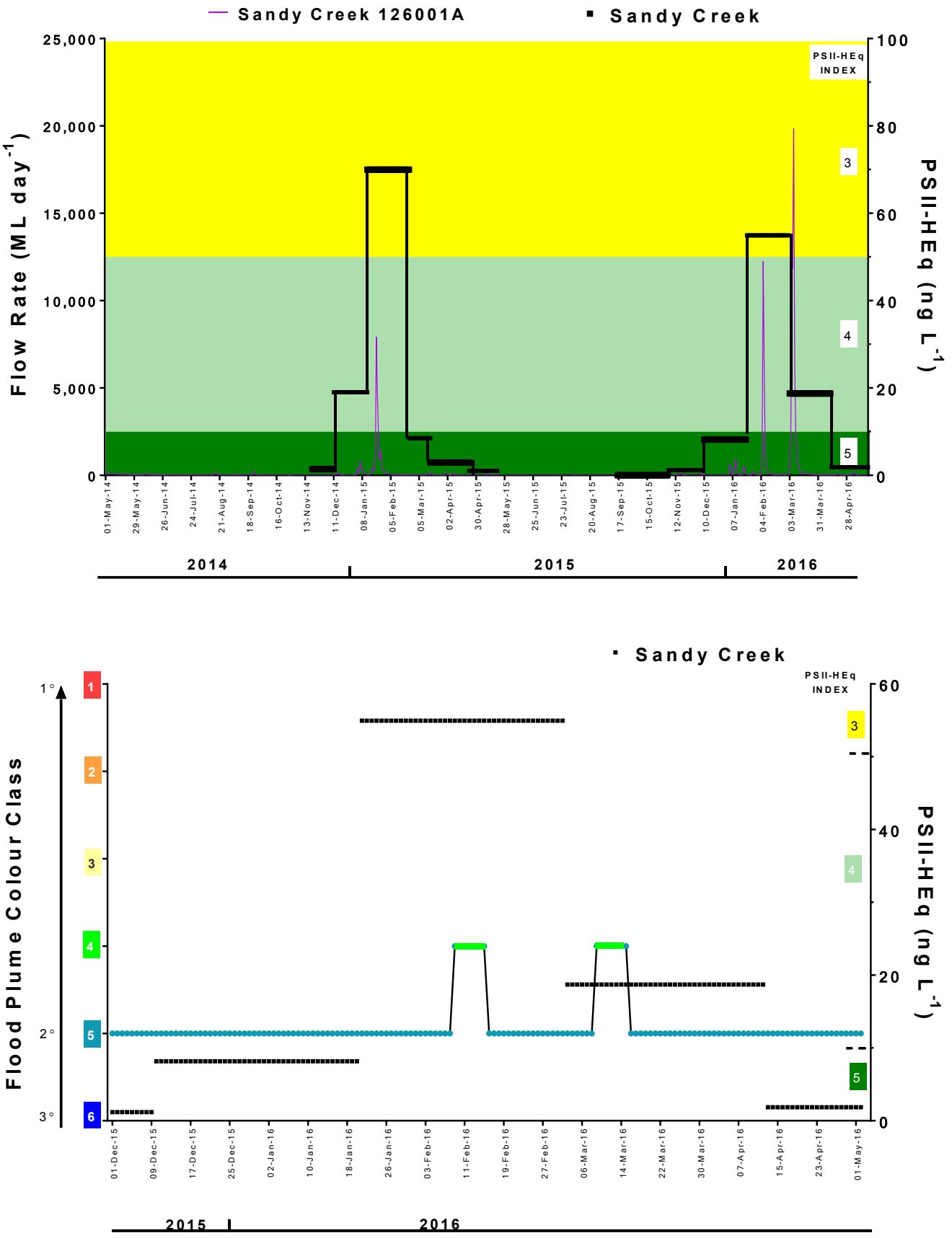


Figure H-9: Temporal trends in PSII-HEq with respect to (top graph) river flow rate influencing passive sampler site at Sandy Creek in the Mackay Whitsunday region since 2005 and (bottom graph) flood plume colour class for 2015-16. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network. Colour class data provided by Dieter Tracey (JCU).

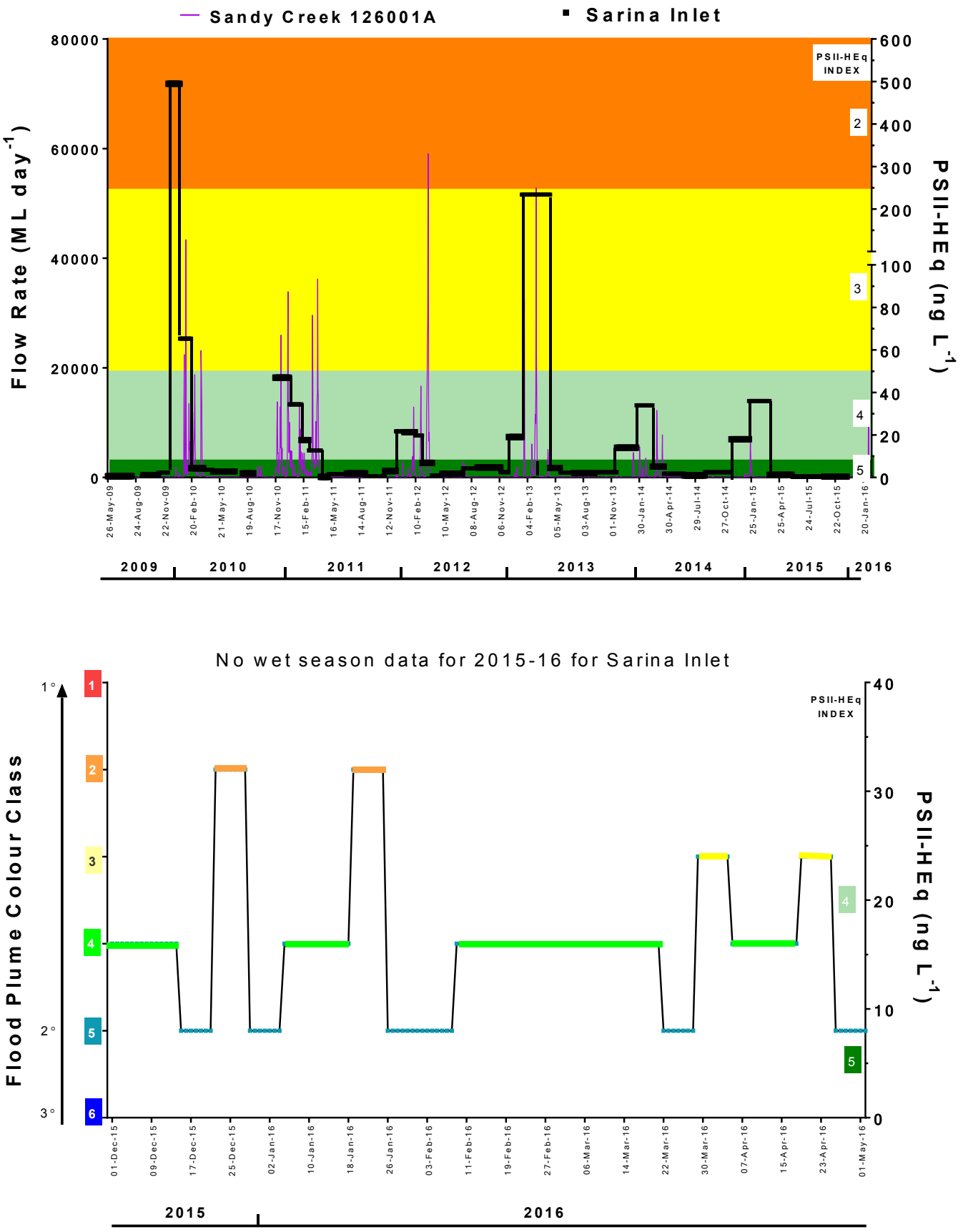


Figure H-10: Temporal trends in PSII-HEq with respect to (top graph) river flow rate influencing passive sampler site at Sarina Inlet in the Mackay Whitsunday region since 2005 and (bottom graph) flood plume colour class for 2015-16. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network. Colour class data provided by Dieter Tracey (JCU).

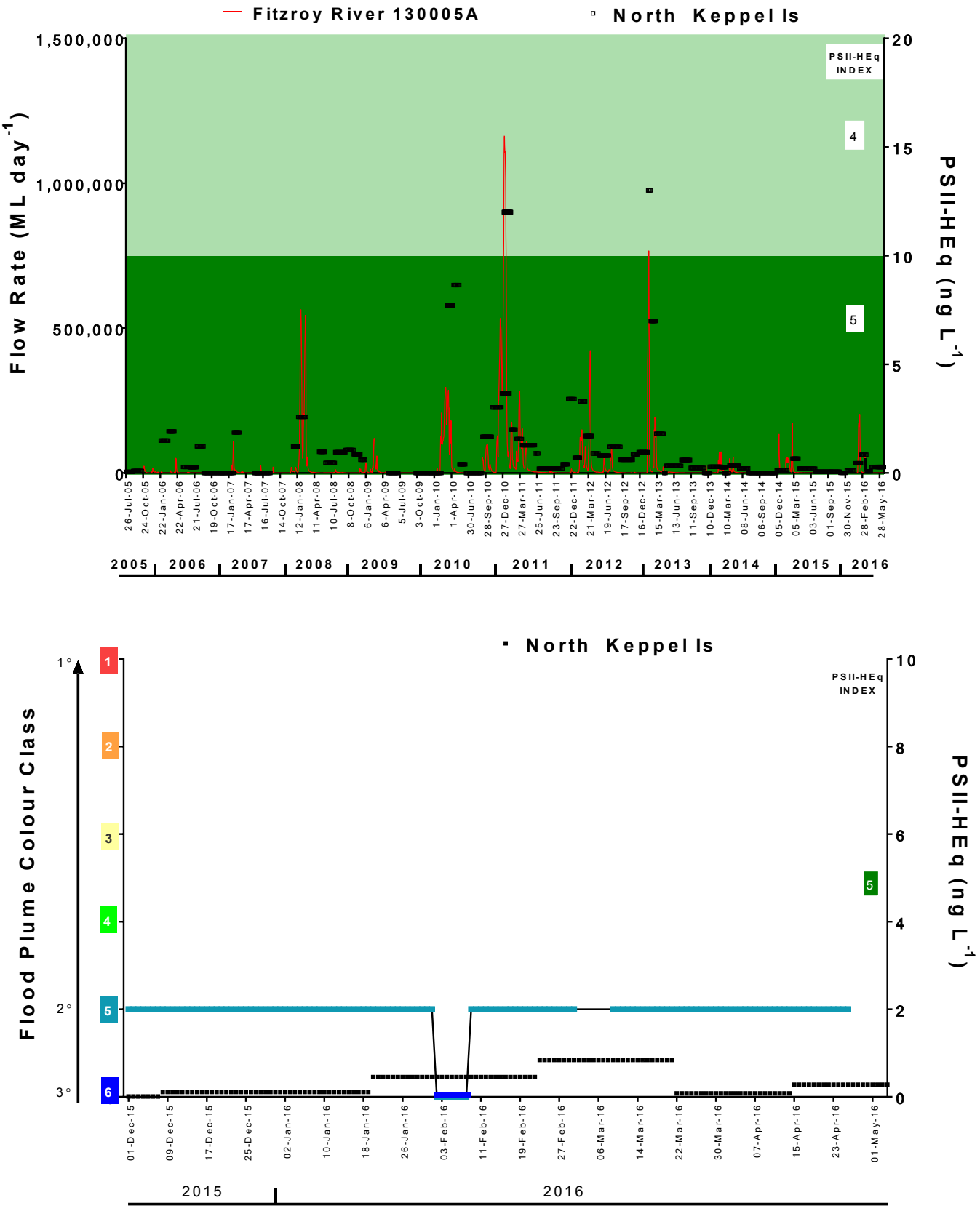


Figure H-11: Temporal trends in PSII-HEq with respect to (top graph) river flow rate influencing passive sampler site at North Keppel Island in the Fitzroy region since 2005 and (bottom graph) flood plume colour class for 2015-16. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network. Colour class data provided by Dieter Tracey (JCU).

Appendix I Historical concentration profiles at fixed monitoring sites

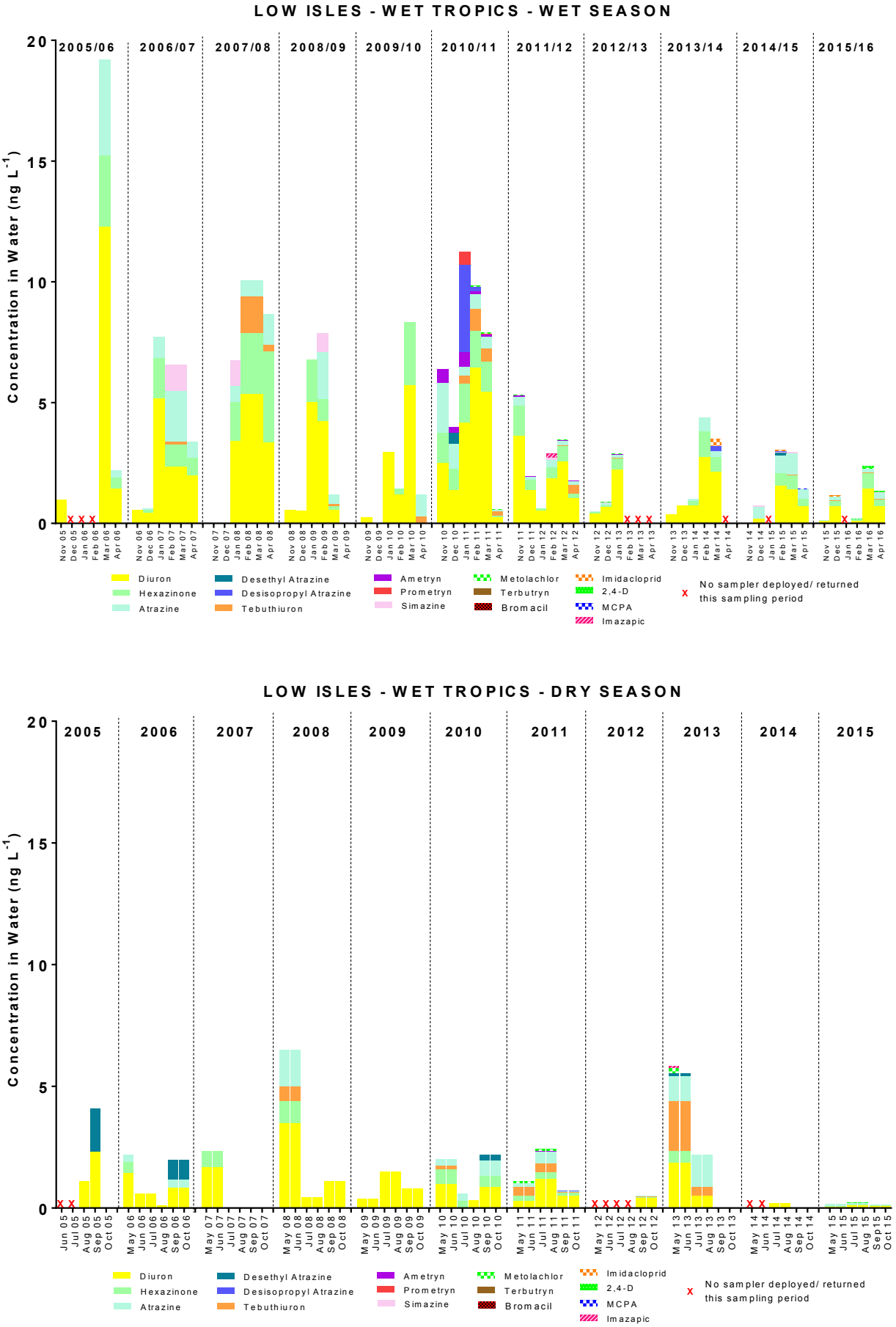


Figure I-1: Temporal concentration profiles of individual herbicides at Low Isles in the Wet Tropics region

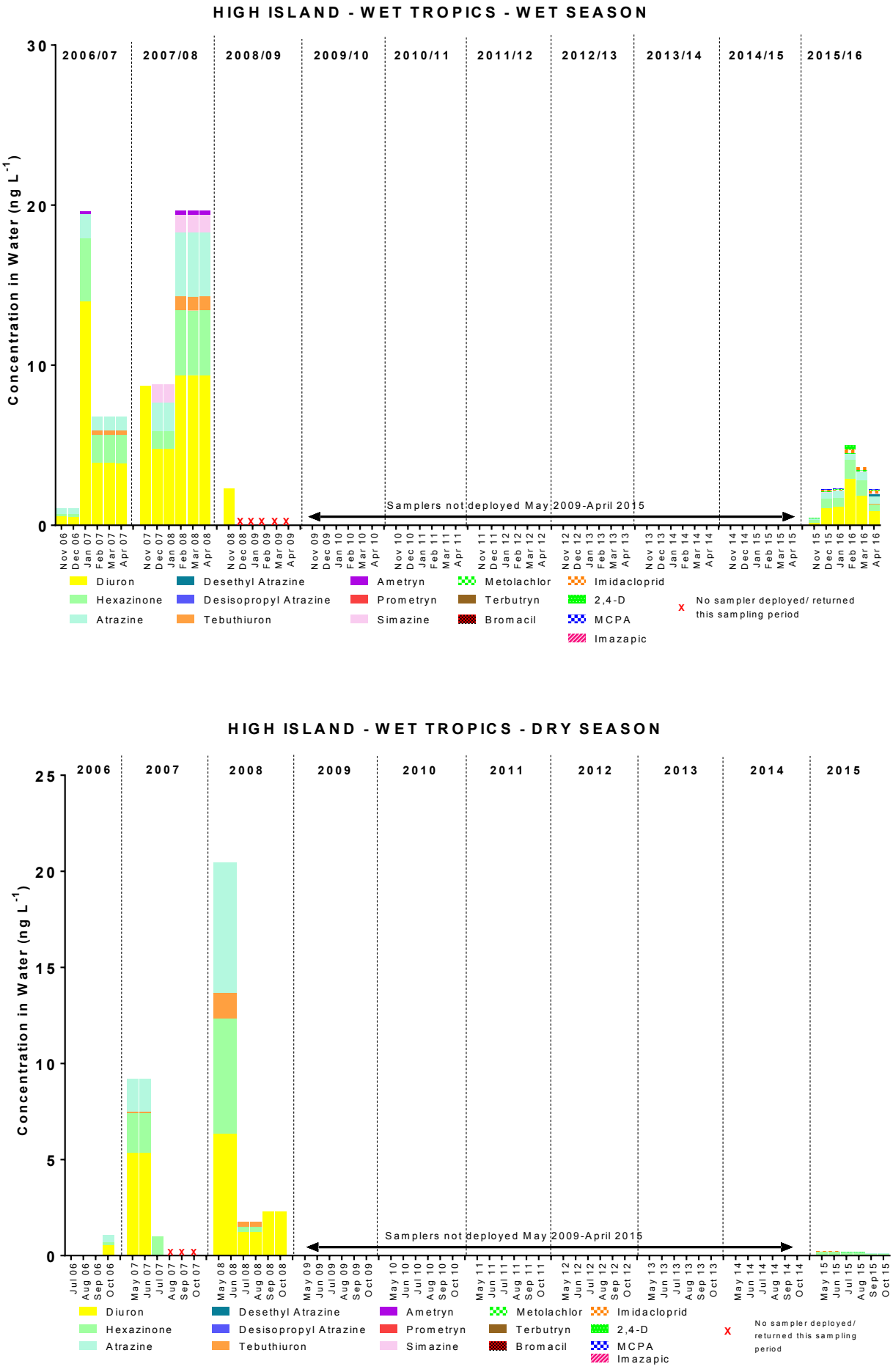


Figure I-2: Temporal concentration profiles of individual herbicides at High Island in the Wet Tropics region

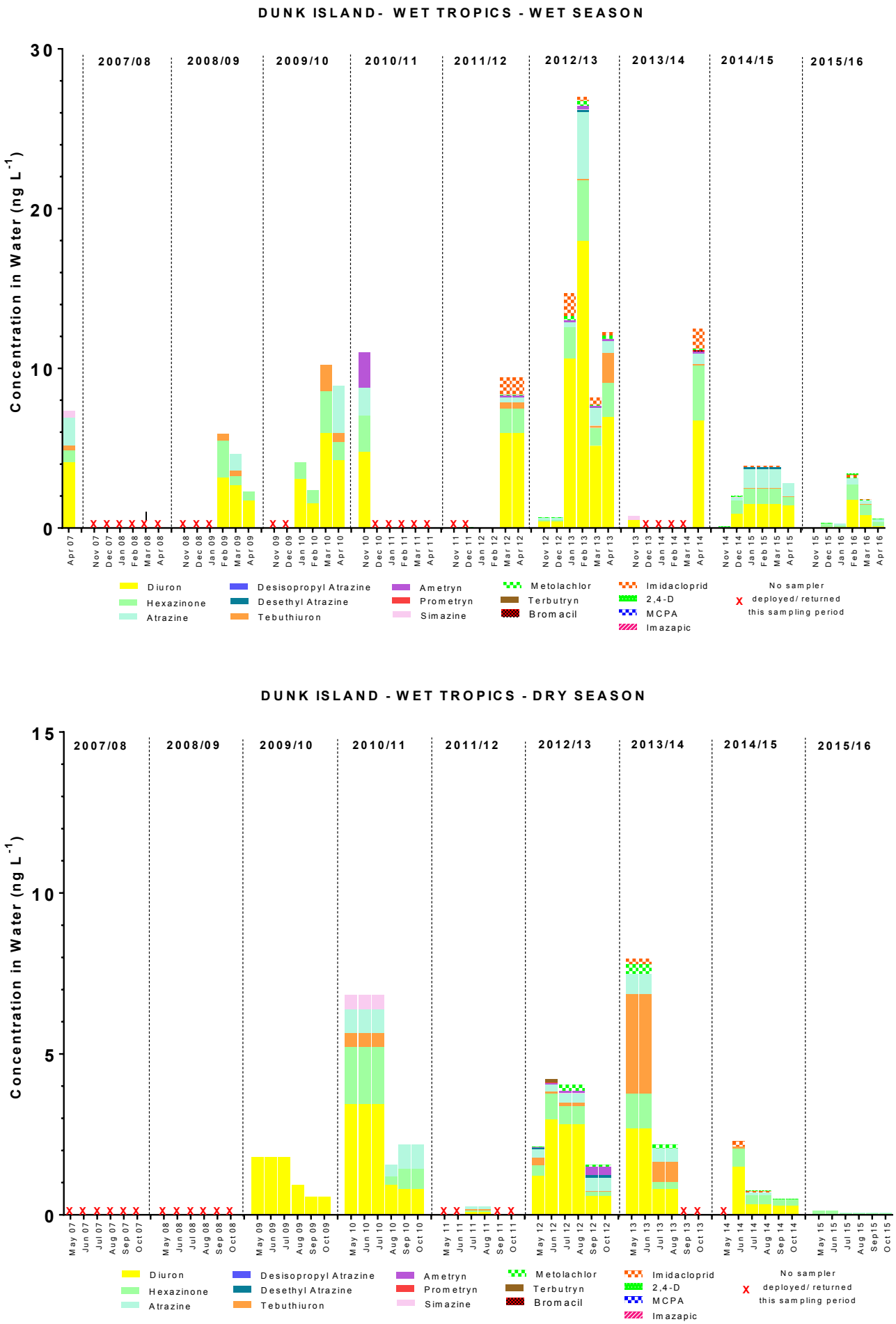
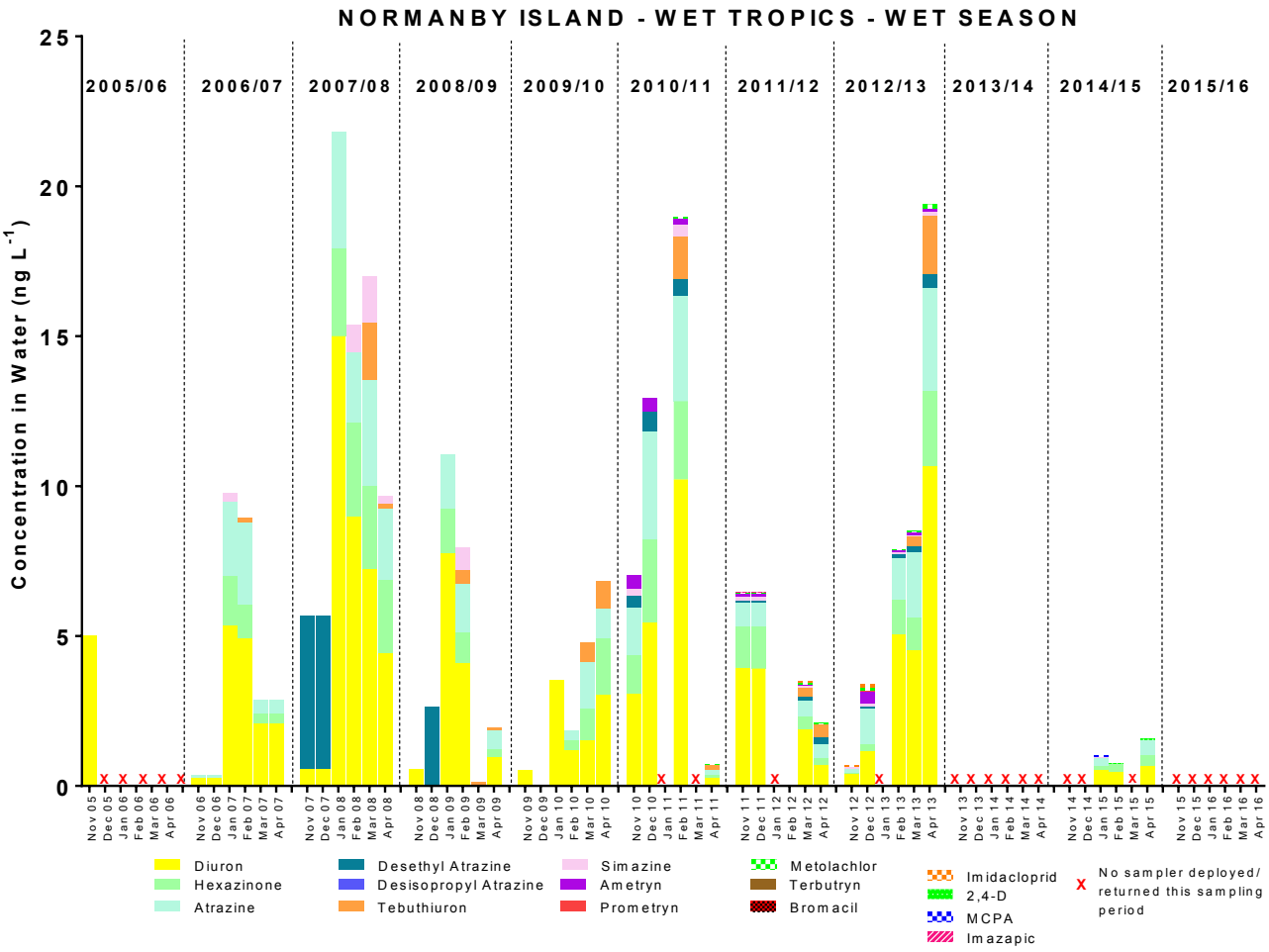


Figure I-3: Temporal concentration profiles of individual herbicides at Dunk Island in the Wet Tropics region



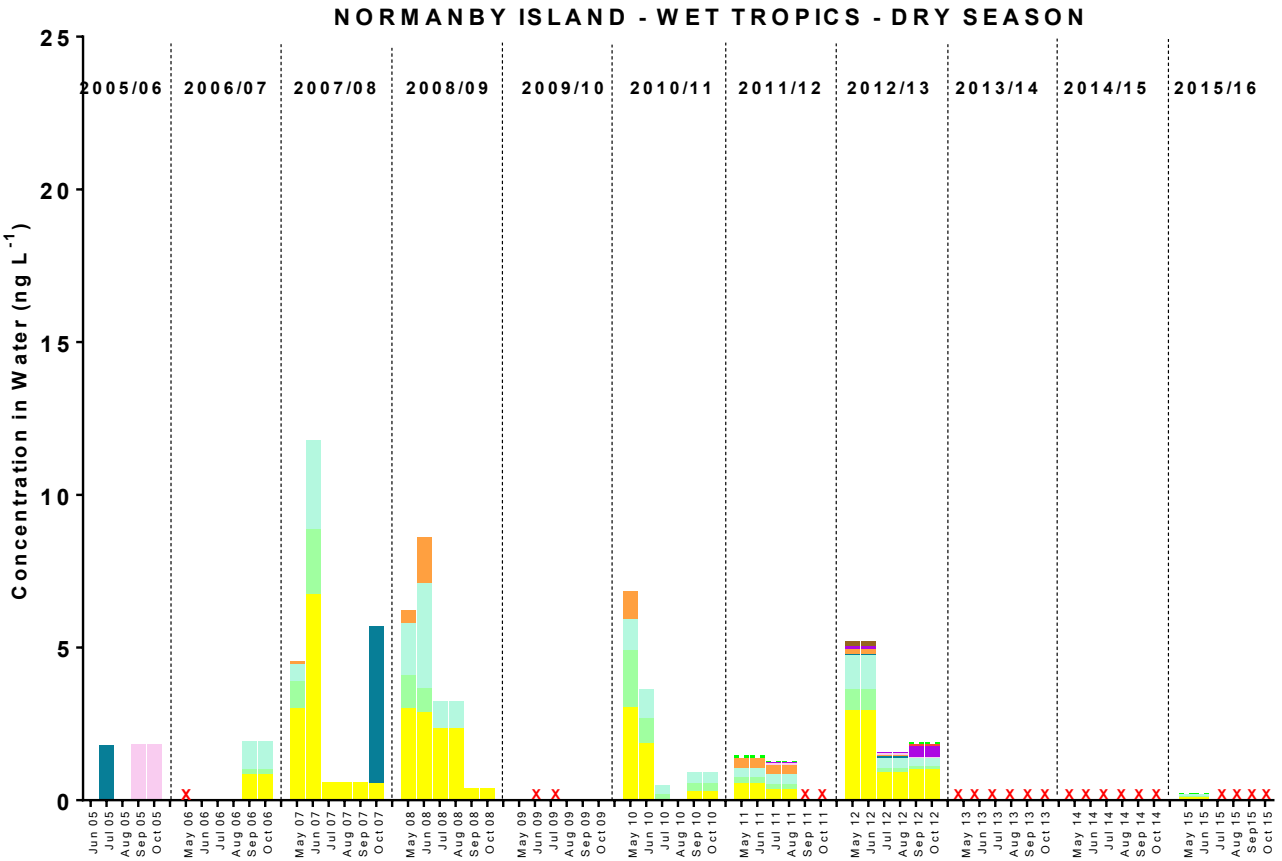
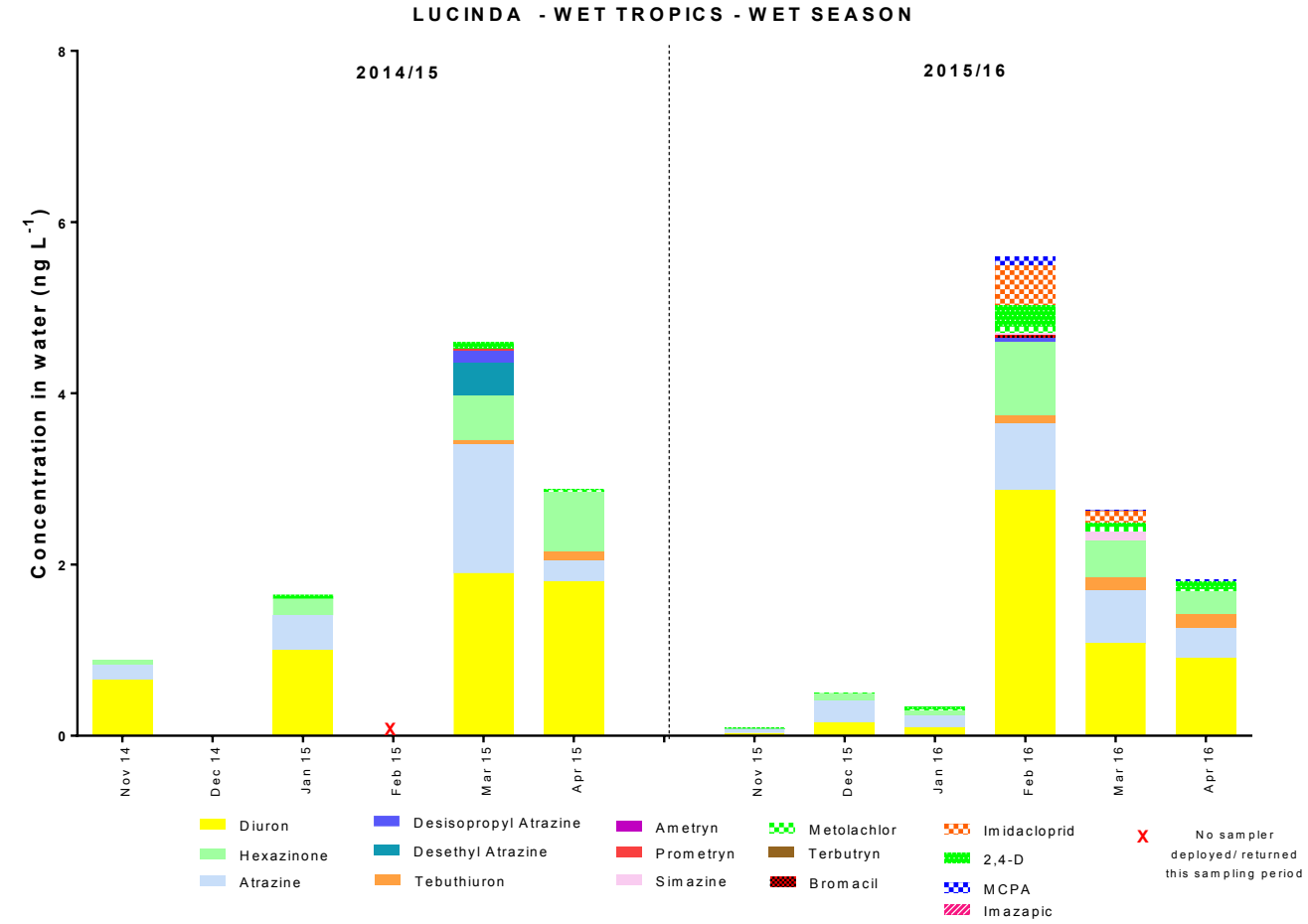


Figure I-4: Temporal concentration profiles of individual herbicides at Normanby Island in the Wet Tropics region



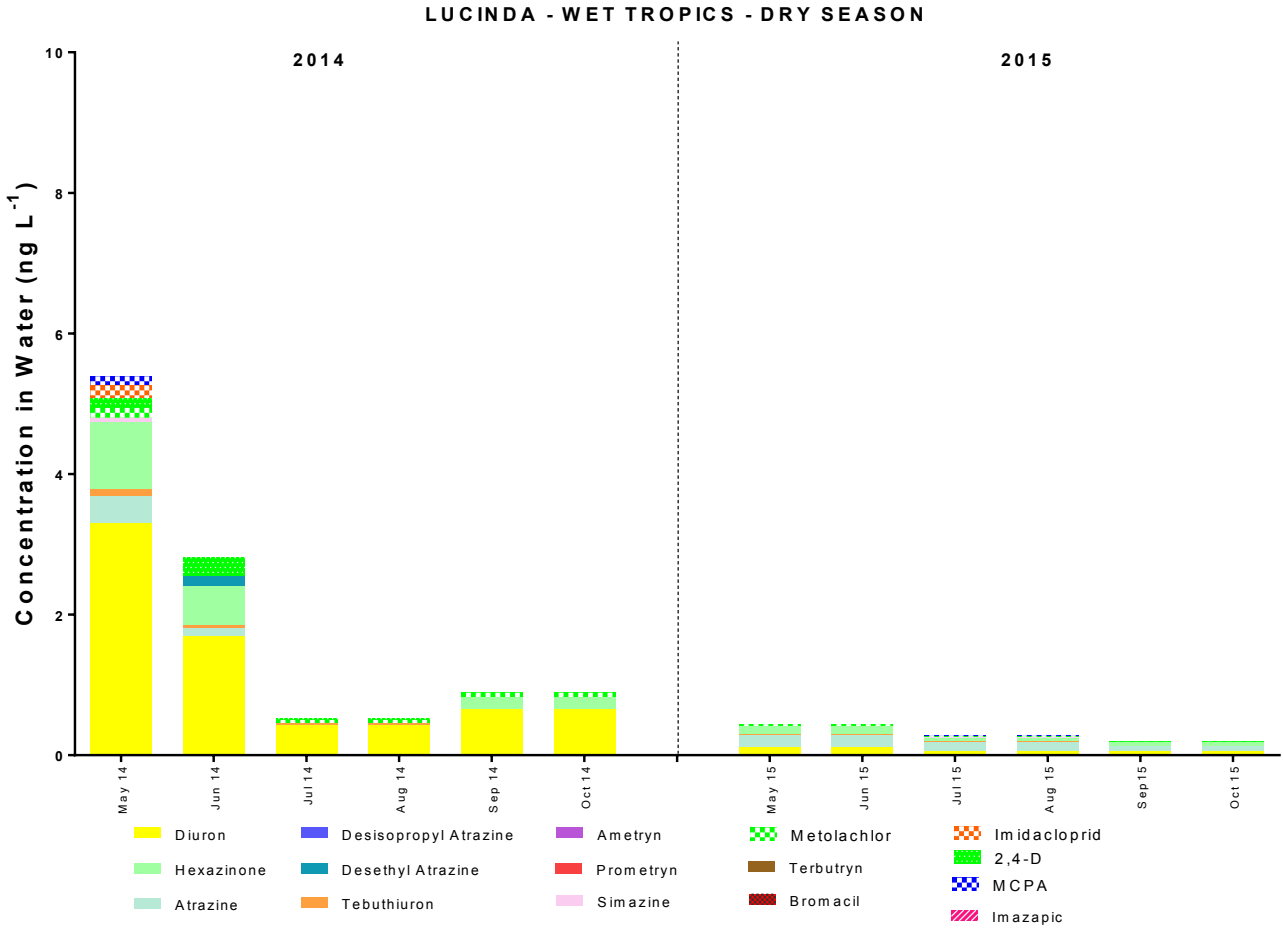


Figure I-5: Temporal concentration profiles of individual herbicides at Lucinda in the Wet Tropics region

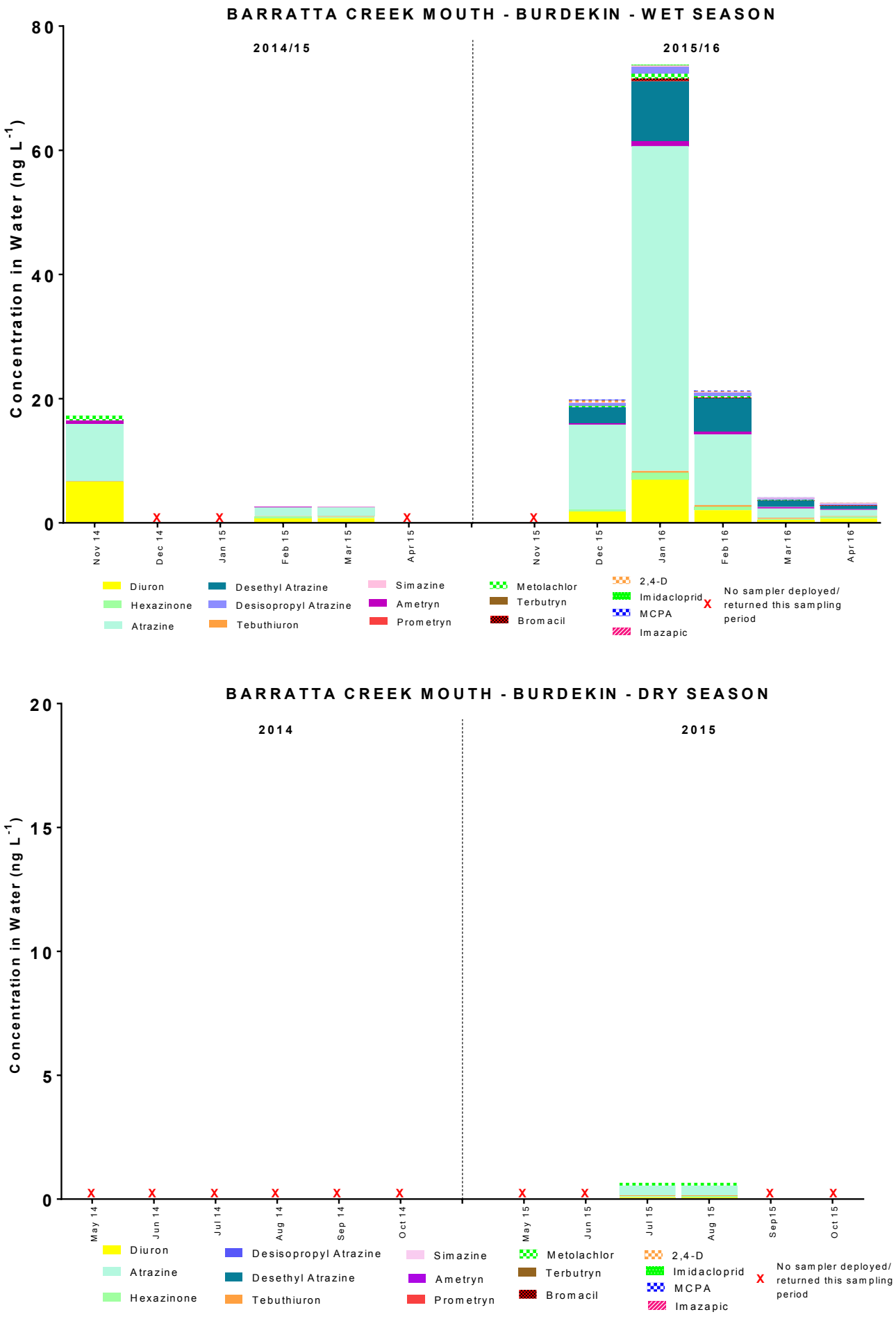


Figure I-6: Temporal concentration profiles of individual herbicides at Barratta Creek mouth in the Burdekin region

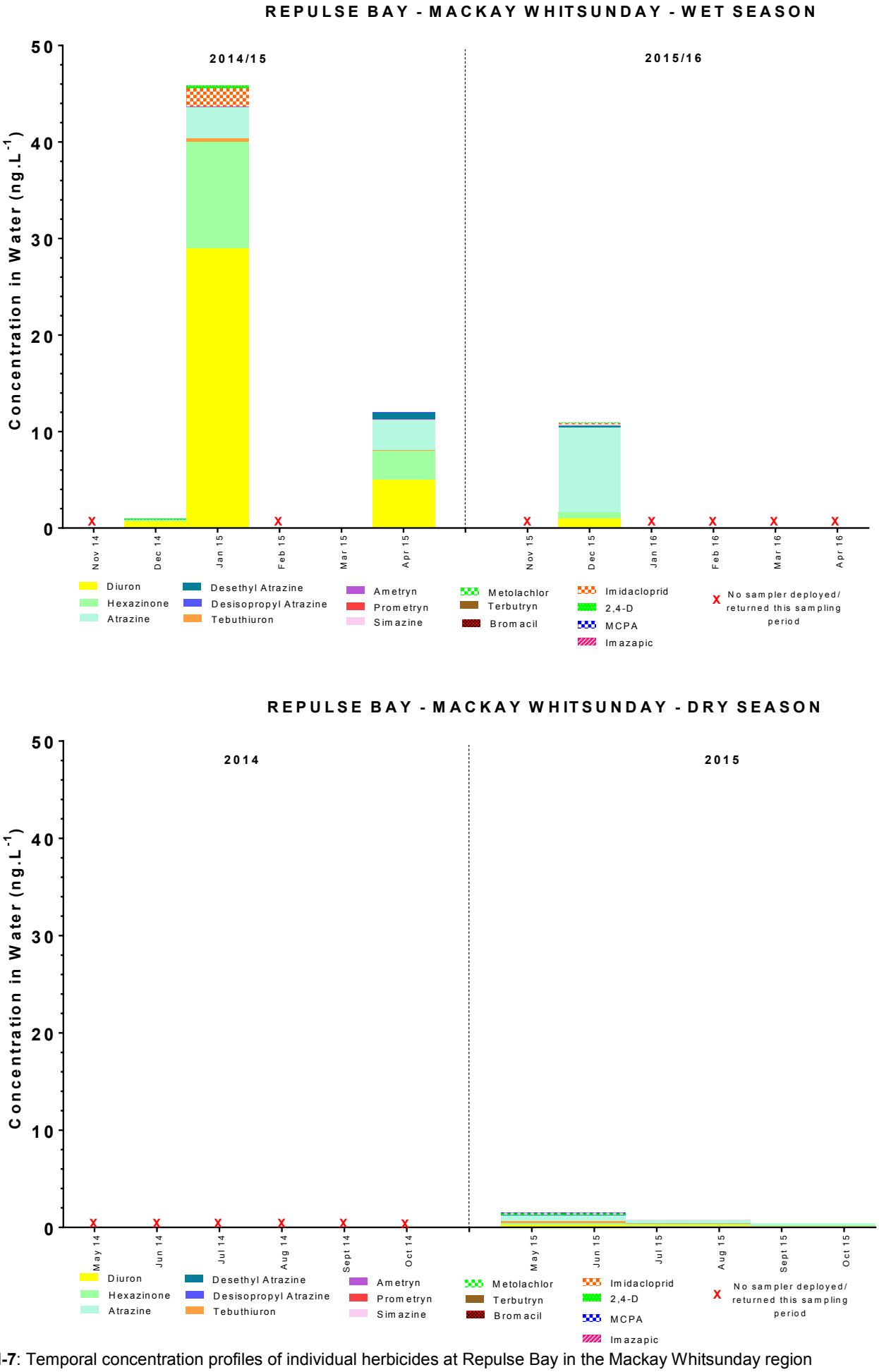


Figure I-7: Temporal concentration profiles of individual herbicides at Repulse Bay in the Mackay Whitsunday region

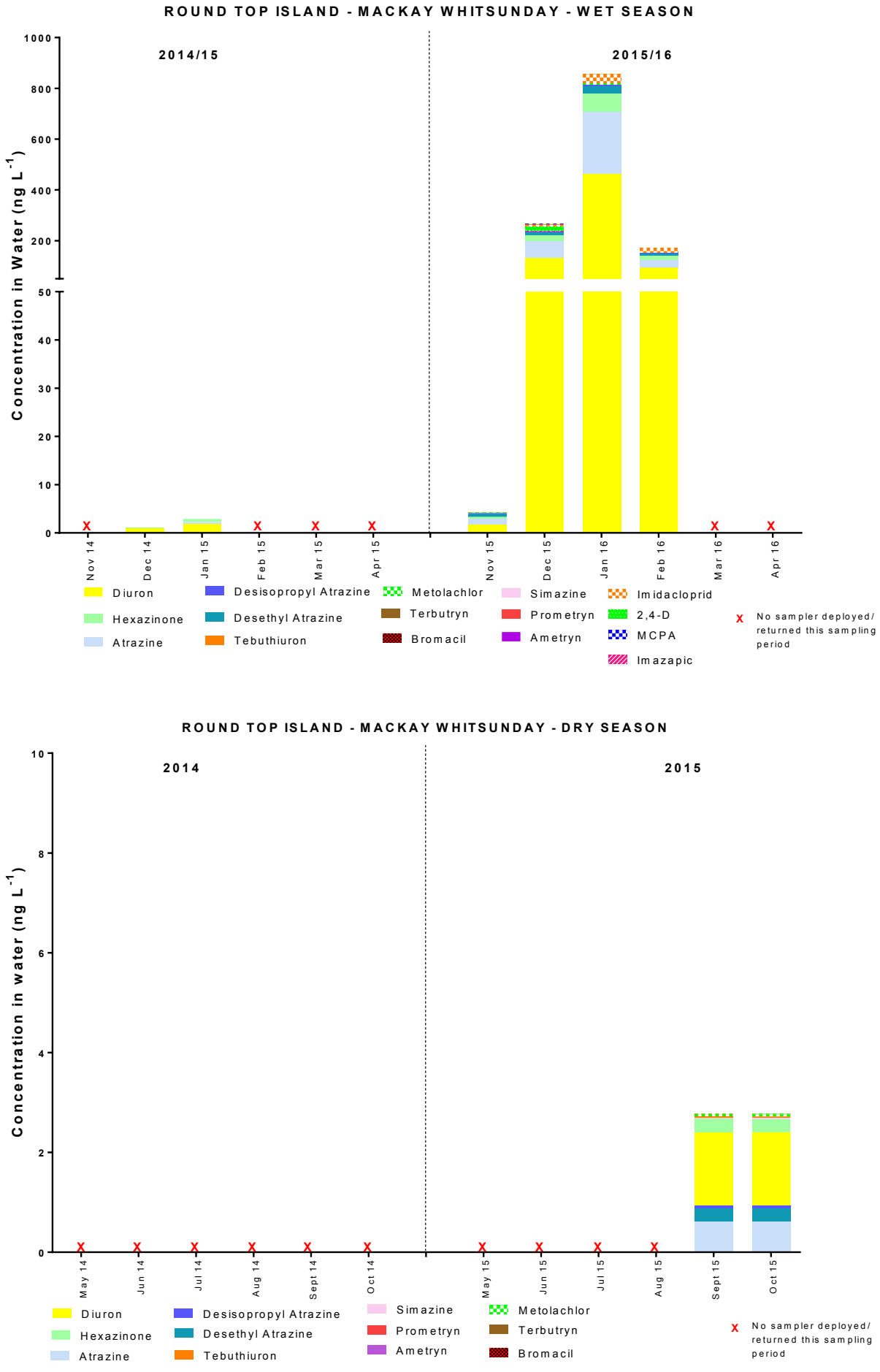


Figure I-8: Temporal concentration profiles of individual herbicides at Round Top Island in the Mackay Whitsunday region

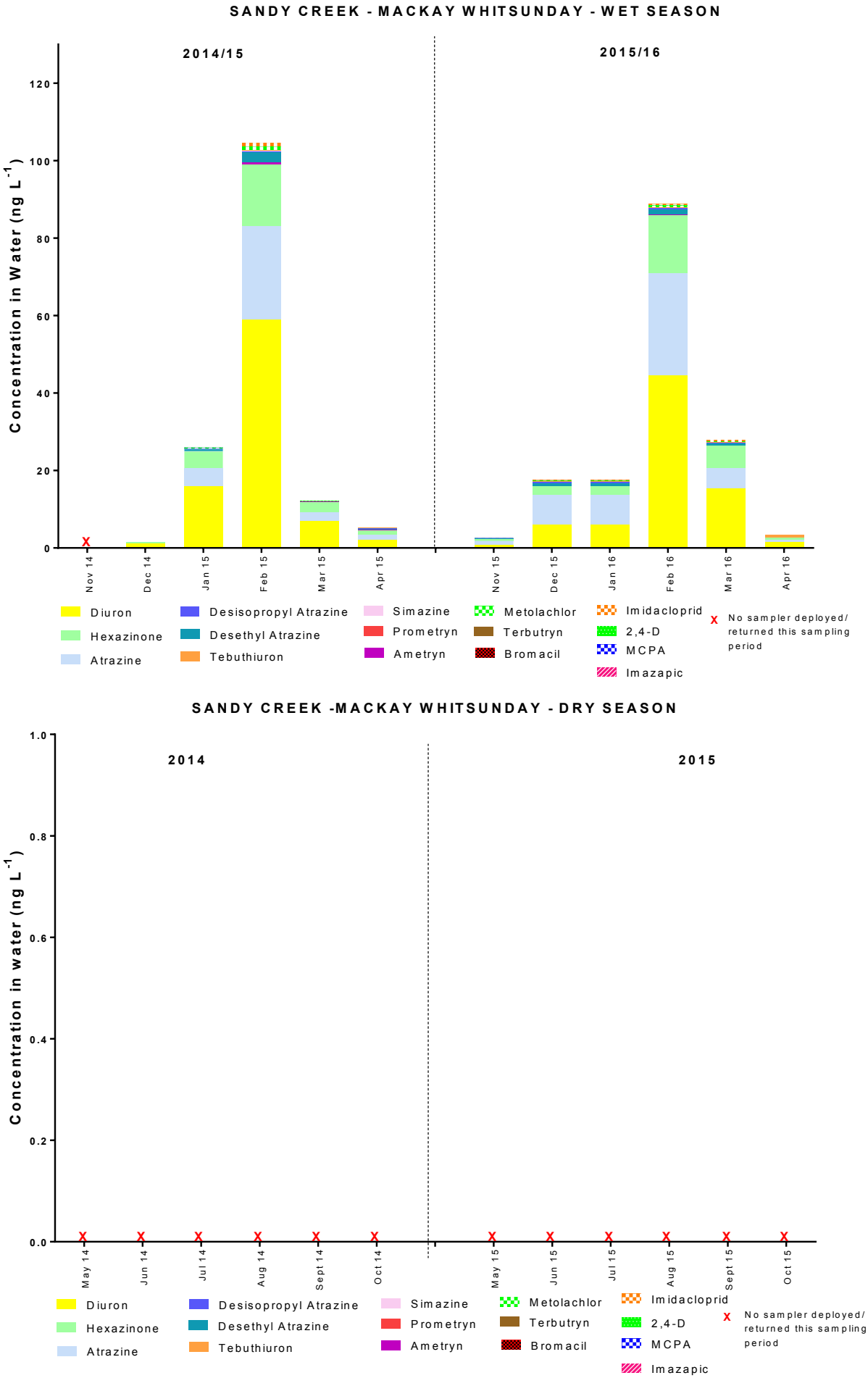


Figure I-9: Temporal concentration profiles of individual herbicides at Sandy Creek in the Mackay Whitsunday region

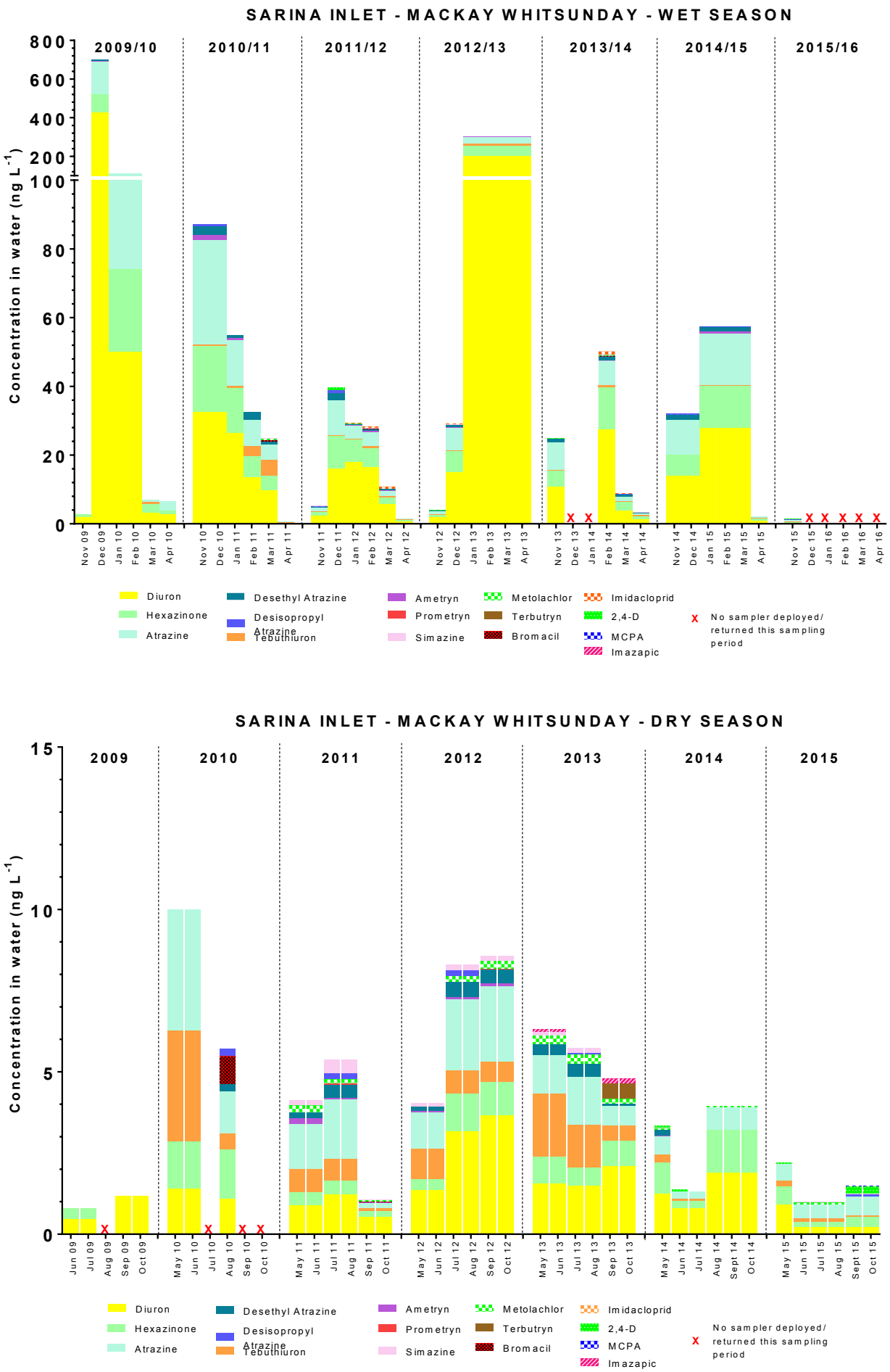


Figure I-10: Temporal concentration profiles of individual herbicides at Sarina Inlet in the Mackay Whitsunday region

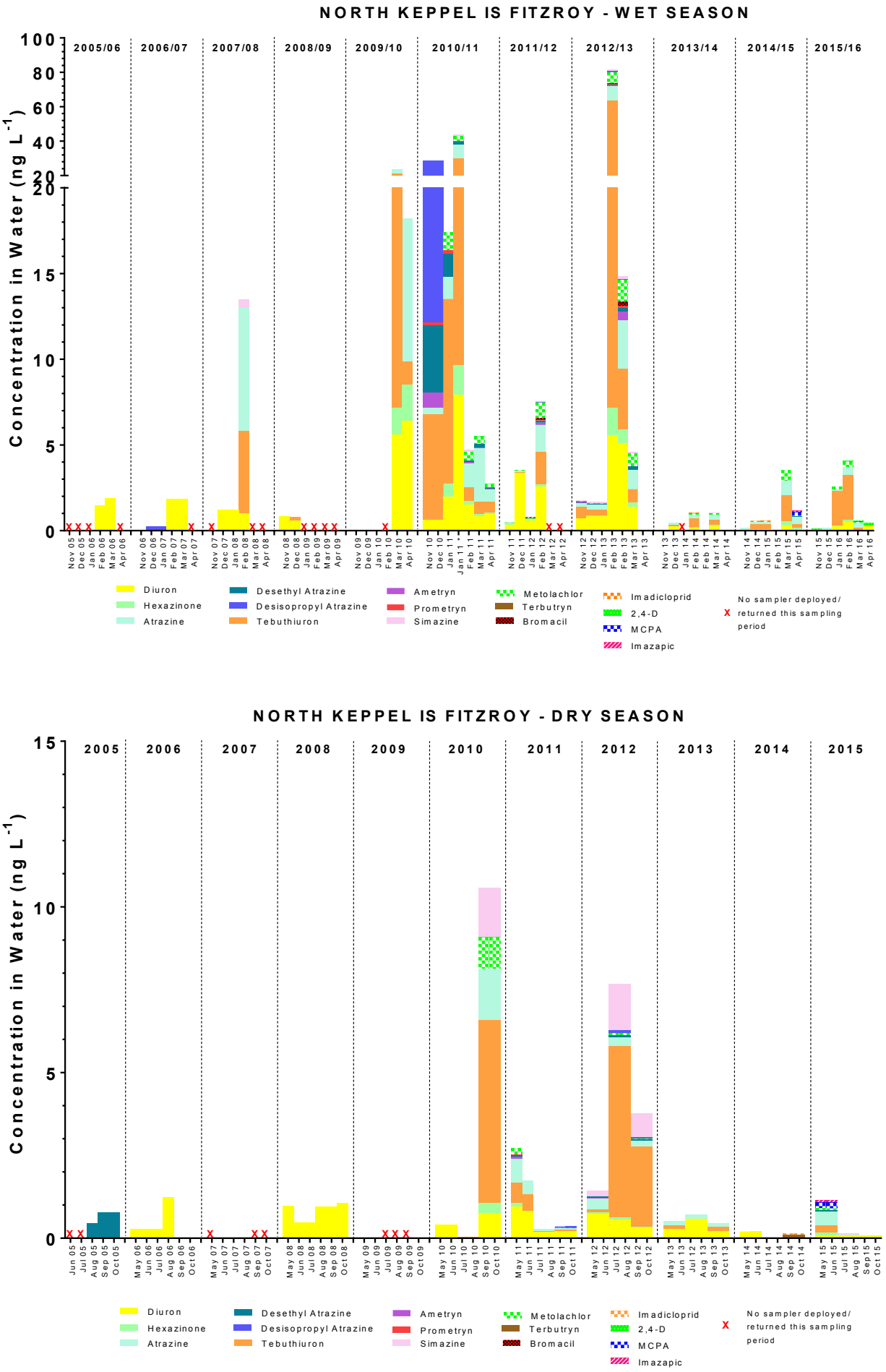


Figure I-11: Temporal concentration profiles of individual herbicides at North Keppel Island in the Fitzroy region