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Queensland Alliance for **Environmental Health Sciences**

**MARINE MONITORING PROGRAM**

# Annual Report for **inshore pesticide** monitoring

## 2016–2017

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Front cover image: Turbid river plume emerging from the Russell-Mulgrave river mouth following several days of heavy rainfall in February 2015 © 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 |
| DES | Department of Environment and Science (formerly DSITI) |
| 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 |
| 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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The assistance of the numerous volunteers who have deployed passive samplers is gratefully acknowledged:

| | | |
|---|---|---|
| Cahills Couriers | Dan Atherton | Great Barrier Reef Marine Park Authority |
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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 through improved land management practises in the adjacent catchments. In 2016–17, Queensland Alliance for Environmental Health Sciences (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 understand the nearshore pesticide profiles in the context of end-of-catchment pesticide loads discharged from rivers into the Reef lagoon and other pressures impacting the movement of pesticides into the marine environment.

In 2016–17, 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 catchment 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).

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 (NRM) regions–the Wet Tropics, Burdekin, Mackay Whitsunday and Fitzroy). Five of these sites have been continuously monitored for between eight to twelve 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 2014–15 and one new site in the previous 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 in various catchments following tropical cyclone Debbie. Samples were also collected along salinity gradients extending from the Tully River during both the dry and wet season to understand mixing processes of pesticides in flood plumes.

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 run-off (quantified as end-of-catchment pesticide loads), annual rainfall, river discharge and cyclonic activity. The pressures governing the release of pesticides into the Reef lagoon were highly localised in the current monitoring year. In the northern NRMs (Wet Tropics and Burdekin), river discharge was at or below the long-term averages and wet season rainfall was lower than average. Further south, in the Mackay Whitsunday and Fitzroy regions, the impacts of tropical cyclone Debbie in late March 2017 resulted in an overall increase in both wet season rainfall and river discharge compared to long-term averages. Catchment pesticide annual loads determined through the Great Barrier Reef Catchment Load Monitoring Program (GBRCLMP) were generally at least double those of the previous two years. In line with the 2016–17 increased pressures, time integrated (or chronic) pesticide concentrations at fixed monitoring sites were, at most sites, higher than the

previous monitoring year. Overall, however, 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 in January 2017 were the highest since monitoring began (2005). The current ANZECC and ARMCANZ water quality guideline values (levels to protect 99% of marine species) were not exceeded at this or any other site for any pesticide in 2016–17 ; however, concentrations of diuron and imidacloprid were higher than the proposed marine Default Guideline Values (DGVs) developed by the Department of Environment and Science (DES, formerly Department of Science, Information Technology and Innovation) (430 and 33 ng $L^{-1}$, respectively) for one passive sampler deployment period at Round Top Island. These proposed DGVs are under consideration but are not yet approved for reporting within Australia. This is the second year running that the proposed DGVs have been exceeded at this site (incomplete data from 2014–15 does not allow comparison with the first year of sampling), suggesting that if these new DGVs are approved, this may be a higher risk site.

A range of PSII herbicides and other pesticides were detected at all monitoring sites in 2016–17. 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 (580, 320 and 88 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 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 were monitored alongside the PSII herbicides. This increased usage was reflected in an increasing proportion of other pesticides in the total load released to the Reef lagoon in 2016–17 and recent years. Compared to previous years, the end-of-catchment load of 2,4-dichlorophenoxyacetic acid (2,4-D) had notably increased in 2016–17. Mirroring the end-of-catchment loads, 2,4-D, metolachlor, MCPA, imidacloprid and chlorpyrifos were consistently detected in passive samplers in the current monitoring year. Compared to PSII herbicides, detected concentrations of other pesticides were very low (typically <5 ng $L^{-1}$ except for isolated samples from Round Top Island and Sandy Creek).

In both the current year and historically, monitoring sites located in the Mackay Whitsunday region have experienced the highest PSII-HEq concentrations. At the other end of the scale, the Wet Tropics have consistently been at the low end of the PSII-HEq concentration range. 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. Data from a salinity gradient transect collected in the year demonstrated that conservative mixing of pesticides is occurring in wet season flood plumes, and that no loss processes of pesticides (e.g. through flocculation or degradation) are occurring in flood plumes. This suggests that pesticide movement from river mouths into the nearshore environment can be modelled using conservative mixing assumptions.

**Case study.** Non-targeted suspect screening analysis is becoming increasingly useful to gain a broader understanding of the presence of chemicals in complex environmental samples. In the 2016–17 case study, we applied this method to both grab and passive sampler extracts from the 2016–17 monitoring year to identify previously un-targeted chemical pollutants in the Reef waters.

Several chemicals from diverse chemical classes that are not captured by the existing monitoring program were tentatively identified, including pharmaceuticals (eight), personal care products (two), illicit drugs (one), endogenous chemicals (thirteen), fungicides (two) and herbicide metabolites (one). Only qualitative assessments can be made using non-target approaches, so water concentrations could not be determined. There appeared to be differences in the types of chemical classes identified by each sampling technique (passive versus grab), which may reflect the sampler-specific classes of chemicals that the ED passive samplers optimally uptake, but could also be a result of different water concentrations present at the time of

sampling. There may also be seasonal changes in the numbers and types of chemicals present, although a longer-term data set would confirm this.

Despite their likely (but unconfirmed) low concentrations, the cumulative effects of long-term exposure to the mixture of chemicals as identified in this case study on Reef biota are unknown, and there is the potential that this chemical exposure may further reduce resilience of Reef ecosystems considering the multiple local, regional and global stressors already faced. Little monitoring information for any non-agricultural chemical pollutants exists and, whilst not in the current scope of MMP, it would be of value to gain a fuller understanding of the impact of adjacent non-agricultural land uses on coastal marine environments.

**Conclusions and directions for future monitoring.** In conclusion, overall, the DPSIR framework is a logical approach to understand the complexity of pressures that may result in pesticides reaching sensitive Reef ecosystems. In 2016–17, trends in the nearshore pesticide monitoring data could be broadly interpreted in terms of high level pressure data, mainly related to end-of-catchment loads and river discharge patterns. Spatially, consistent with previous years and land-usage in the adjacent catchments, highest time integrated (or chronic) pesticide concentrations in the Reef lagoon were detected at the Mackay Whitsunday region fixed monitoring sites. The longer-term change in nearshore marine pesticide concentrations attributable to changed catchment land management practices, which is the focus of *Reef Plan*, is, however, statistically challenging to elucidate. Whilst it is expected that time-integrated pesticide concentrations measured using passive samplers in the nearshore environment will reflect any changes in pesticide loads leaving the catchments, the predicted 36 per cent reduction in total pesticide load losses to rivers across the Reef catchments due to changed catchment management is only one factor amongst a complex range of highly variable pressures impacting long-term nearshore monitoring data.

Given the high inter- and intra-annual climatic and other pressure variability, meaningful trend comparisons require long-term and comprehensive 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 in 2014–15 means that over half of the current sites have only two or three years of continuous data. With the exception of the localised impact of tropical cyclone Debbie towards the end of the 2016–17 wet season, pressures over the last three 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 end-of-catchment load data (e.g. daily loads) 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. At present these data are not available to the MMP due to inconsistencies in timing of reporting cycles between programs.

The current pesticide metric, the PSII-HEq index, was identified as a suitable interim risk indicator in the 2013–14 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 multi-substance - potentially affected fraction (ms-PAF) model is a step towards this goal. Some inconsistencies in the application of the current concentration addition ms-PAF model (for PSII herbicides) to marine environments were identified through the case study in the previous year's report. Once these considerations have been addressed (if required) and when development of the response addition model (for pesticides with different modes of action) has been completed by the Queensland Government, it will be a highly valuable and recommended risk assessment tool. In the meantime, to avoid retrospective adjustments and consistent risk assessment, the PSII-HEq Index will 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 Great Barrier Reef World Heritage Area covers 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, coastal development, shipping and fishing (GBRMPA 2014, Hairsine 2017). 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, crown-of-thorns starfish 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, Hairsine 2017). 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, Wilkinson et al. 2017).

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* (Reef 2050 Plan (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*". A key component of the *Reef 2050 Plan* is establishing the Reef 2050 Integrated Monitoring and Reporting Program (RIMReP) for the reef and its adjacent catchments.

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 run-off 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 36 per cent reduction in total pesticide loads across the Marine Park catchments should occur by 2018? (Reef Water Quality Protection Plan Secretariat 2017). This includes a 45.2 per cent load reduction (1.2% reduction achieved in the year) in the Mackay region (Reef Water Quality Protection Plan Secretariat 2017) where the highest pesticide exposure has been reported (Brodie et al. 2013, Reef Water Quality Protection Plan Secretariat 2016, 2017).

To monitor the progress towards *Reef Plan's* (2013) and the *Reef 2050 Plan'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. Going forward, data collected under RIMReP, which has been established to track the progress towards targets and objectives of the *Reef 2050 Plan*, will also inform annual and longer-term monitoring initiatives. RIMReP's initial priorities are to integrate existing programs and fill critical information gaps. 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. 2018), the coral cover and composition (Thompson et al. 2018) and seagrass health and extent (McKenzie et al. 2018).

The specific objectives of the 2016–17 pesticide monitoring component of the MMP was to:

- monitor and assess trends in inshore concentrations of pesticides against water quality guideline values relevant to the Marine Park
- understand nearshore pesticide profiles in the context of pesticides' end-of-catchment loads and other pressures.

The program methods and results in 2016–17 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$^{TM}$ 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 2016/2017* (GBRMPA 2017a) and in previous reports (Kennedy et al. 2012, Gallen et al. 2013, Gallen et al. 2014, Gallen et al. 2016, Grant et al. 2017). Supplemental information on methodologies is given in 8

## 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 are outlined in previous reports (Grant et al. 2017). Based on these criteria, 11 inshore Reef sites were selected and have been monitored since 2014-15, which include five continuing long-term monitoring sites (Table 1, 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).

The **Wet Tropics** region encompasses eight catchment areas, covering approximately 2.2 million hectares (ABS 2010). Approximately 49 per cent of land is set aside as conservation and natural environment areas, however beef cattle grazing (31 per cent of total land use) and sugar cane (seven per cent of total land use) are the primary agricultural activities (DSITI 2016). Fixed sampling sites in the Wet Tropics region in 2016–17 were at Low Isles, High Island, Normanby Island, Dunk Island and Lucinda (Figure 1).

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 2012b). The one sampling site in the Burdekin region in 2016–17 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 2012d). Sampling sites in the Mackay Whitsunday region in 2015-16 were Repulse Bay, Round Top Island, Sandy Creek and Sarina Inlet (Figure 1).

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).

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

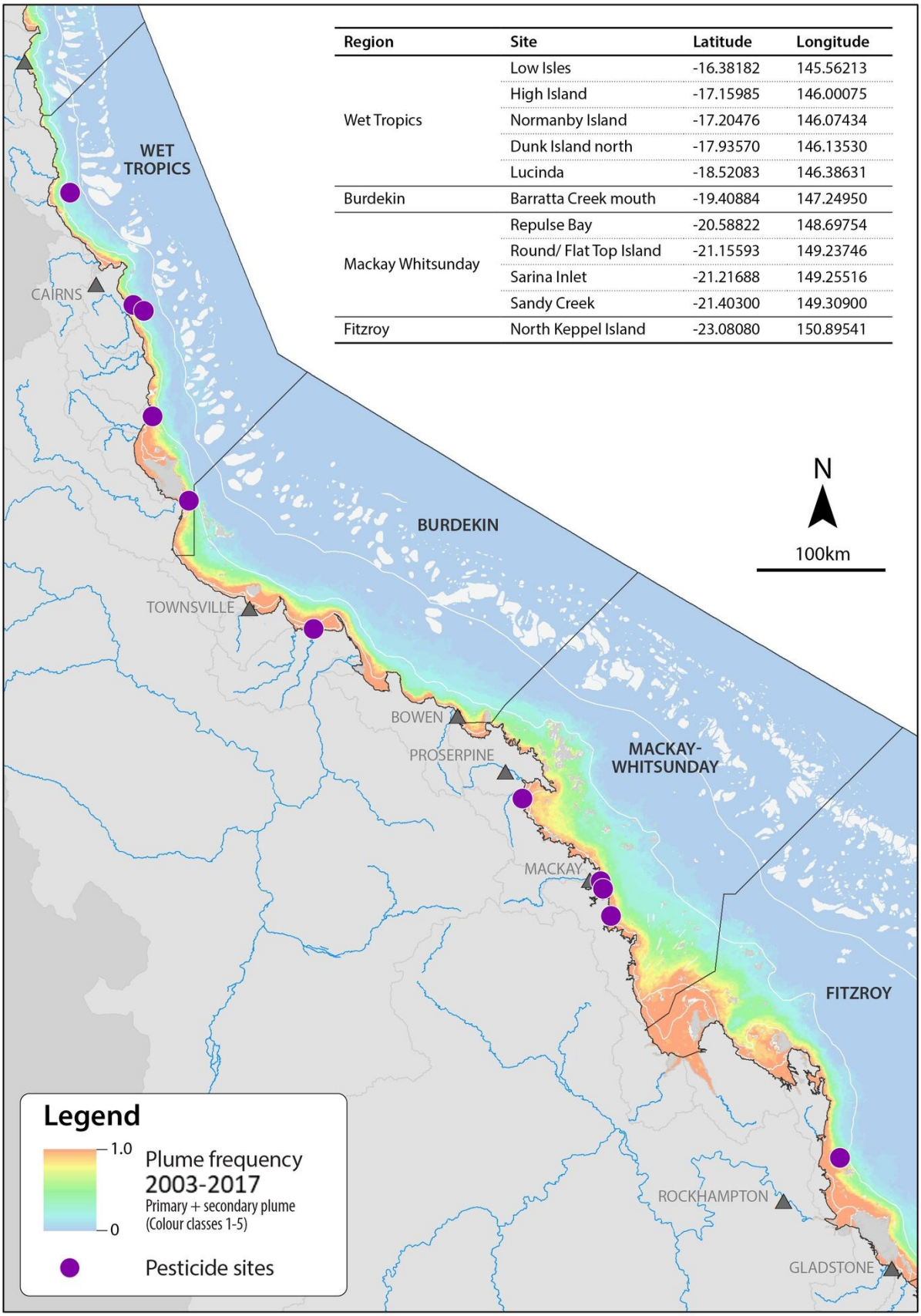
| NRM region | Basin | Major River/ Creek | Fixed site name | Sampled since | Approx. distance from river mouth (km) |
|---|---|---|---|---|---|
| Wet Tropics | Mossman | Mossman River | Low Isles | Aug-2005 | 18 |
| | Mulgrave-Russell | Mulgrave River/ Russell River | High Island | May-2015* | 8.0 |
| | | | Normanby Island | Jul-2005 | 11 |
| | Tully | Tully River | Dunk Island | Sep-2008 | 13 |
| | Herbert | Herbert River | Lucinda | Jul-2014 | 12 |
| Burdekin | Burdekin | Barratta Creek | Barratta Creek mouth | Mar-2014 | 1.5 |
| Mackay Whitsunday | Proserpine/ O'Connell | Proserpine River/ O'Connell River | Repulse Bay | Sep-2014 | 12 / 3.3 |
| | Pioneer/ Plane | Pioneer River/ Sandy Creek | Round Top Island | Sep-2014 | 2.6 / 14 |
| | Plane | Sandy Creek | Sandy Creek | Sep-2014 | 8.6 |
| | | Plane Creek | Sarina Inlet | May-2009 | 2.8 |
| Fitzroy | Fitzroy | Fitzroy River | North Keppel Island | Aug-2005 | 50 |

* High Island was reintroduced to the sampling program in 2015-16 after its discontinuation in 2008.

### *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 2016–17, 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. The Tully transects were extended in 2016–17 to include two sampling events in May 2016 and January 2017 where grab samples were obtained from plume waters with a range of salinities. These samples were used to further understanding of the mixing behaviour of pesticides in flood waters (see Section 4.3.1.2). In addition to the transects, grab samples were collected from Barratta Creek mouth within the Burdekin focus area during three early-season discharge events (Table 2 and Figure 2). This sampling site is a flood-response monitoring site established by the JCU Inshore Marine Water Quality team. Flood sampling was also undertaken following tropical cyclone Debbie in late March/early April 2017 (tropical cyclone Debbie made landfall in the Proserpine region on 28 March 2017). Sampling followed nearshore transects extending from the Proserpine/O'Connell River catchments (Mackay Whitsundays), Pioneer River catchment (Mackay Whitsundays) and Fitzroy River catchment (Fitzroy NRM region), (Table 2 and Figure 2).




| 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 Whitsunday | Repulse Bay | -20.58822 | 148.69754 |
| | Round/ Flat Top Island | -21.15593 | 149.23746 |
| | Sarina Inlet | -21.21688 | 149.25516 |
| | Sandy Creek | -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 2016–17 flood plume frequency map (for more information see Section 3.5.4). Grey triangles indicate towns. (Source – Dieter Tracy, James Cook University)

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 | Longitude | Approximate distance from closest river mouth (km) |
|---|---|---|---|---|---|
| Russell-Mulgrave River (long term flood plume monitoring) | Russell-Mulgrave mouth | Grab | -17.2230 | 145.9689 | 0 |
| | Russel-Mulgrave junction | Grab | -17.2287 | 145.9528 | -2.0 |
| | Normanby Island | Passive sampler | -17.2048 | 146.0743 | 11 |
| | High Island | Grab | -17.1599 | 146.0007 | 8.5 |
| | High Island | Passive sampler | -17.1599 | 146.0008 | 8.5 |
| Tully River (long term flood plume monitoring) | Tully River mouth | Grab | -18.0295 | 146.0609 | 0.7 |
| | Bedarra Island | Grab | -18.0019 | 146.1414 | 10 |
| | Dunk Island north | Grab | -17.9273 | 146.1415 | 15 |
| | Dunk Island north | Passive sampler | -17.9272 | 146.1416 | 15 |
| Burdekin Focus Region | Barratta Creek mouth | Grab | -19.4088 | 147.2495 | 1.5 |
| | Barratta Creek mouth | Passive sampler | -19.4088 | 147.2495 | 1.5 |
| Tully River (salinity gradient* transect I – May-16) | Tully transect - P2-5psu | Grab | -18.0275 | 146.0602 | 0.7 |
| | Tully transect - P3-15psu | Grab | -18.0256 | 146.0654 | 1.3 |
| | Tully transect - P4-11psu | Grab | -18.0256 | 146.0656 | 1.3 |
| | Tully transect - P5-14psu | Grab | -18.0309 | 146.1157 | 6.6 |
| | Tully transect - P6-30psu | Grab | -18.0427 | 146.1536 | 11 |
| | Tully transect - P7-20psu | Grab | -18.0409 | 146.1641 | 12 |
| | Tully transect - P8-25psu | Grab | -18.0409 | 146.1501 | 10 |
| | Tully transect - P9 | Grab | -17.9260 | 146.1460 | 15 |
| Tully River (salinity gradient* transect II – Jan-17) | Tully transect - River-0psu | Grab | -18.0194 | 146.0467 | -1.1 |
| | Tully transect - P2-17psu | Grab | -17.9807 | 146.1135 | 8.2 |
| | Tully transect - P3-5.3psu | Grab | -18.0236 | 146.0712 | 2.0 |
| | Tully transect - P4-35psu | Grab | -17.9977 | 146.1430 | 10 |
| | Tully transect - P5-0.22psu | Grab | -18.0322 | 146.0588 | 0.8 |
| | Tully transect - P8-25psu | Grab | -17.9996 | 146.1390 | 9.6 |
| | Tully transect - P10-0.25psu | Grab | -18.0311 | 146.0607 | 0.9 |
| Post-Tropical Cyclone Debbie flood plume (various catchments) | Burdekin River catchment | Grab | -19.6205 | 147.6364 | 7.3 |
| | Barratta Creek mouth | Grab | -19.4088 | 147.2495 | 1.3 |
| | Proserpine River catchment | Grab | -20.4583 | 148.6973 | -4.3 |
| | Proserpine River catchment | Grab | -20.4931 | 148.7351 | 1.2 |
| | Proserpine/O'Connell catchment | Grab | -20.3750 | 148.8845 | 21 / 31 |
| | O'Connell River catchment | Grab | -20.5754 | 148.6796 | 1.2 |
| | Pioneer River catchment | Grab | -20.8093 | 149.2297 | 38 |
| | Pioneer River catchment | Grab | -21.1432 | 149.2347 | 2.0 |
| | Fitzroy River catchment | Grab | -23.3905 | 150.9392 | 16 |
| | Fitzroy River catchment | Grab | -23.2766 | 150.9701 | 29 |
| | Fitzroy River catchment | Grab | -23.3600 | 150.8433 | 18 |

* Salinity at each grab sampling site is given after the site name (in practical salinity units, psu)

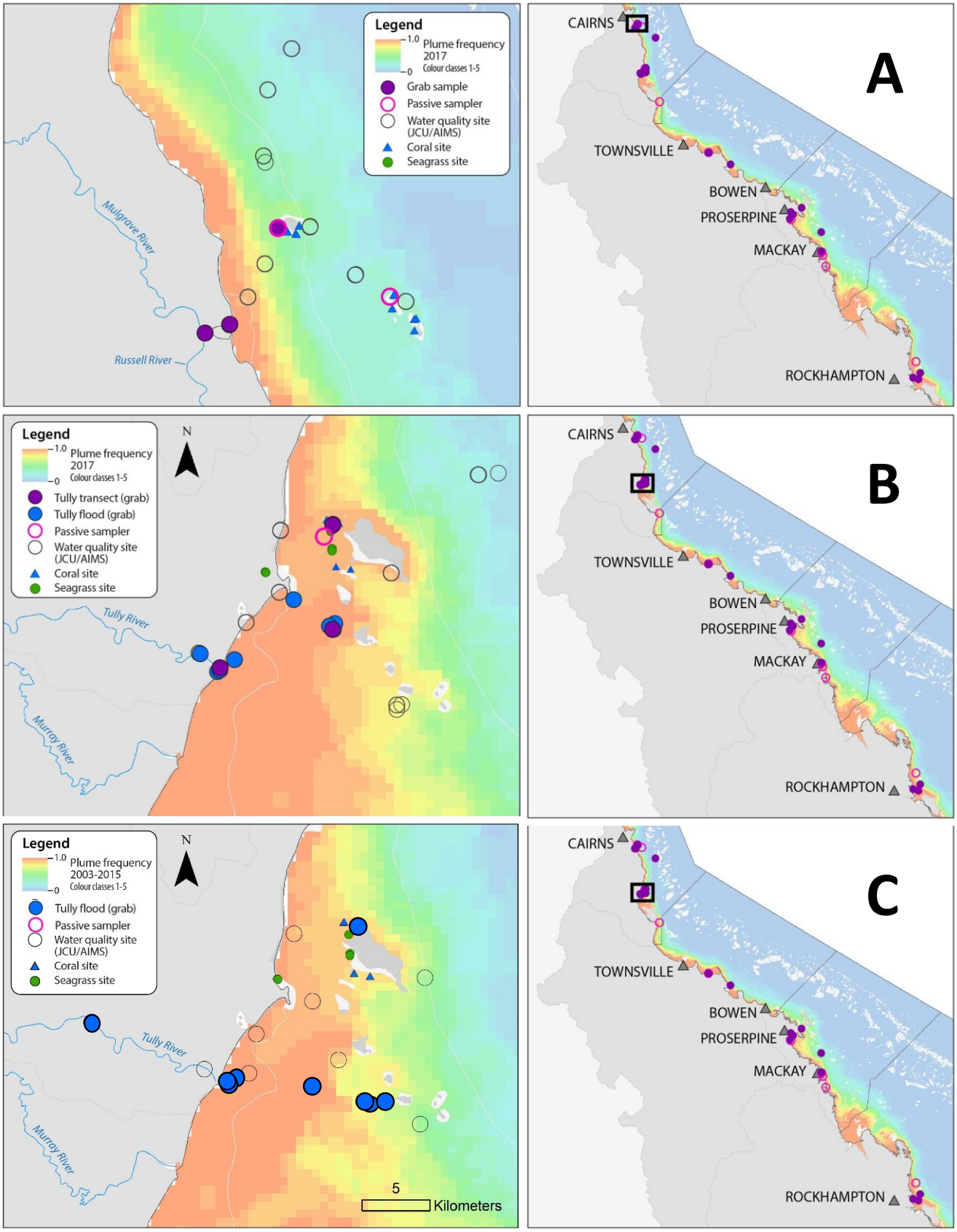



Figure 2: Locations of grab (flood plume monitoring) and passive samplers (fixed monitoring) collected on the (A) Russell-Mulgrave River transect, (B) Tully River transect and salinity gradient (Jan-2017), (C) Tully River salinity gradient (May-2016), (D) Burdekin River focus region, (E) Proserpine/O'Connell River catchment (TC Debbie), (F) Pioneer River catchment (TC Debbie), and (G) Fitzroy River catchment (TC Debbie). Sampling sites are overlaid on a colour-scale representing the frequency of flood plumes for 2003-2017. The water quality/coral/seagrass sites relate to other MMP program monitoring sites (McKenzie et al. 2018, Thompson et al. 2018, Waterhouse et al. 2018). Maps provided by Dieter Tracey, James Cook University (JCU).

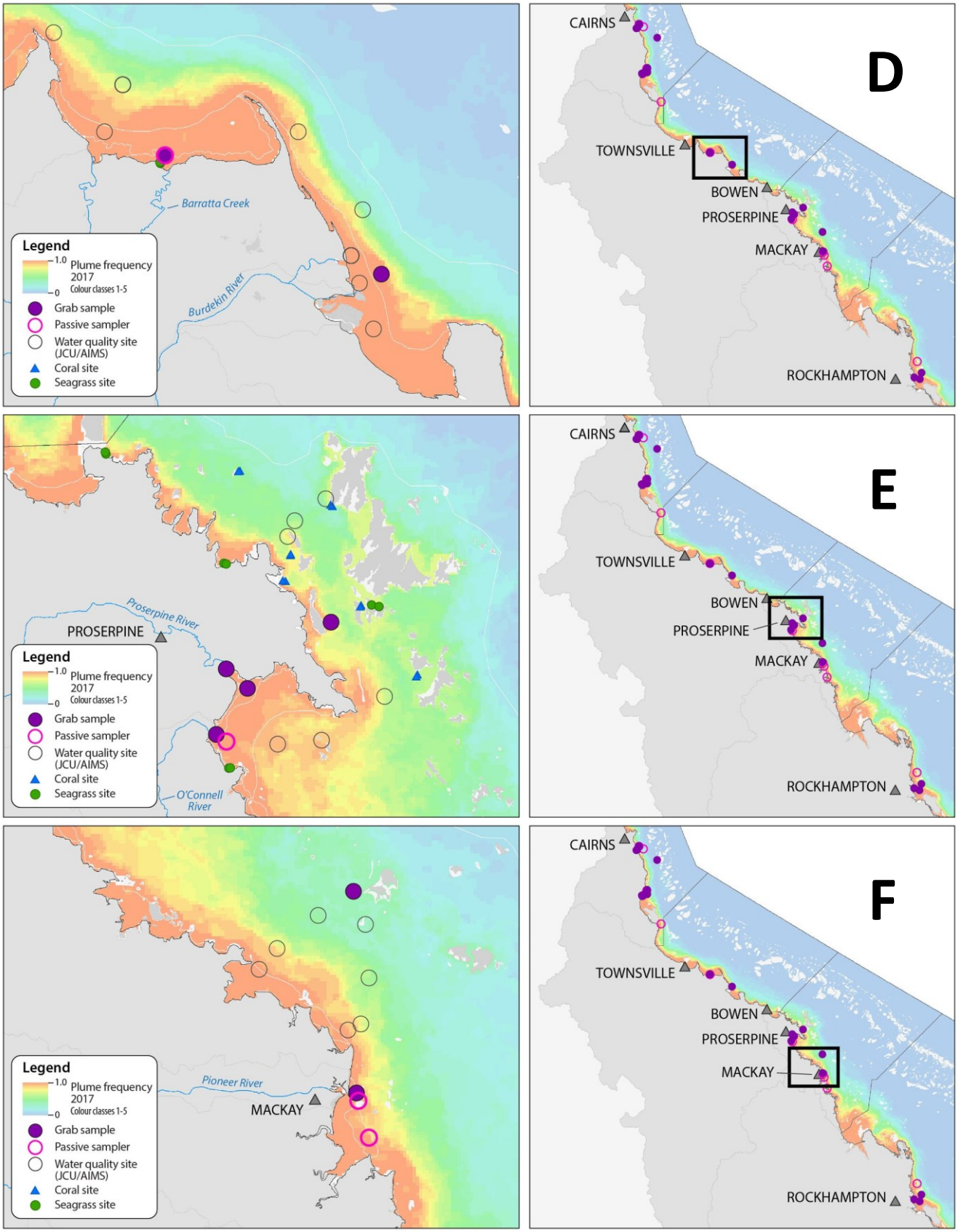



Figure 2 (cont.): Locations of grab (flood plume monitoring) and passive samplers (fixed monitoring) collected on the (A) Russell-Mulgrave River transect, (B) Tully River transect and salinity gradient (Jan-2017), (C) Tully River salinity gradient (May-2016), (D) Burdekin River focus region, (E) Proserpine/O'Connell River catchment (TC Debbie), (F) Pioneer River catchment (TC Debbie), and (G) Fitzroy River catchment (TC Debbie),. Sampling sites are overlaid on a colour-scale representing the frequency of flood plumes for 2003-2017. The water quality/coral/seagrass sites relate to other MMP program monitoring sites (McKenzie et al. 2018, Thompson et al. 2018, Waterhouse et al. 2018). Maps provided by Dieter Tracey, James Cook University (JCU).

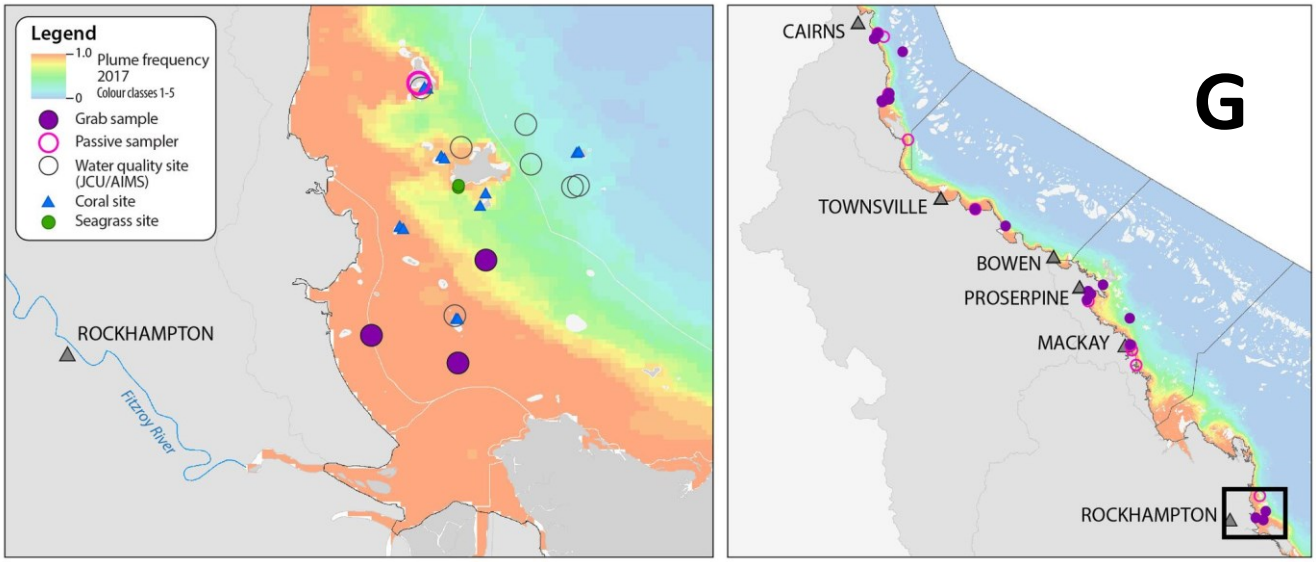



Figure 2 (cont.): Locations of grab (flood plume monitoring) and passive samplers (fixed monitoring) collected on the (A) Russell-Mulgrave River transect, (B) Tully River transect and salinity gradient (Jan-2017), (C) Tully River salinity gradient (May-2016), (D) Burdekin River focus region, (E) Proserpine/O'Connell River catchment (TC Debbie), (F) Pioneer River catchment (TC Debbie), and (G) Fitzroy River catchment (TC Debbie),. Sampling sites are overlaid on a colour-scale representing the frequency of flood plumes for 2003-2017. The water quality/coral/seagrass sites relate to other MMP program monitoring sites (McKenzie et al. 2018, Thompson et al. 2018, Waterhouse et al. 2018). 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 2016/2017 (GBRMPA 2017a)*. An overview of the sampling periods and types of samples collected is given below, with additional details in 8.

### *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 2017. The year is divided into "Dry 2016" (May 2016 to October 2016) and "Wet 2016–17" (November 2016 to April 2017) 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). Time integrated concentrations are reported which reflect the average concentration over the actual period of deployment. A maximum of nine samples are obtained from each location in the monitoring year.

Table 3: The types of passive samplers deployed at each fixed monitoring site in 2016–17 .

| 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 | ✓ | ✓ | ✗ | ✗ |

All eleven fixed sites were monitored in both the Dry 2016 and Wet 2016–17 sampling periods using EDs (Table 3), targeting polar pesticides (see Table A-2) for a list of the polar pesticides in the passive sampler analysis suite). Five sites also had PDMS samplers deployed during the Wet 2016–17 sampling period (Table 3), targeting non-polar pesticides (see 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 (four 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.

### *3.3.2 Grab sampling to assess flood plume profiles*

Sampling activities targeting discharge events from major Reef catchment rivers occurred during the Wet 2016–17 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, assess the correlation of pesticide concentration with salinity (to understand whether ideal mixing is occurring) 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.

Forty-six grab samples were collected in 2016–17. Seventeen were collected to monitor terrestrial run-off from the two river transects (the Tully and Russell-Mulgrave rivers) during four separate flood plume events between January and March 2016. A further four grab samples were collected from the Burdekin focus area during major discharge events in both the dry and wet season. Fifteen grab samples were collected during May 2016 and January 2017 across salinity gradients in flood plumes extending from the Tully River. Finally, ten grab samples were collected in flood plumes following tropical cyclone Debbie in late March/early April 2017. 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*

Details on deployment procedures and approaches for data interpretation when samplers are not/cannot be deployed or are lost are given in 8: Section A-1.

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

### *3.4.1 Target pesticides*

The list of target pesticides included in this report and their rationale for inclusion are given in 8: Section A-2 and Table A-4.

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

Analysis of non-polar pesticides using Gas Chromatography-Mass Spectrometry (GC-MS) and polar pesticides using Liquid Chromatography-tandem Mass Spectrometry (LC-MS/MS) in PDMS and ED samplers and grab samples was conducted at QAEHS. Further analytical details are given in Appendix A.

**QA/QC:** Quality assurance quality control (QA/QC) includes the extraction and analysis of replicate ED samplers (i.e. to test the variability in the overall performance (chemical uptake) of the EDs) together with an interlaboratory comparison of a subset of sample analyses at QHFSS. Duplicate analysis of 25 ED samplers resulted in mean coefficients of variation for replicates ranging from 12% to 42% Table A-1). Fifteen ED samples were included in the interlaboratory comparison. Variability of diuron, atrazine and hexazinone (which are detected most frequently in this monitoring program) were 36, 15 and 11%, respectively (Appendix A, Table A-5). The overall variability (%CVs) in the interlaboratory analysis between QAEHS and QHFSS were comparable with previous reporting periods.

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 Appendix F . Analytical variability was tested by quadruplicate injections of 1 ppb calibration standard, and the median coefficient of variation for these replicates was 5.0% across all pesticides.

The LOD for the LC-MS/MS instrument data are defined as follows: LODs are determined by adding a very low level of analyte to a matrix and injecting 9 times into the 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 LOD but below LOR 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.

## 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. The Australian and New Zealand water quality guidelines (see Appendix B for more details) for freshwater and marine ecosystems are currently being revised to provide new default guideline values (DGVs) (Warne et al. 2015, DoE 2016, Warne et al. 2018). Proposed DGVs for 28 pesticides for freshwater and marine ecosystems have been determined using SSDs by the Department of Environment and Science (DES, formerly DSITI), and are in the process of being submitted for consideration, national endorsement and inclusion into the Australian and New Zealand water quality guidelines (DSITI 2017). If endorsed, they will supersede the Water Quality Guidelines for the Great Barrier Reef Marine Park (GBRMPA 2017b). In advance of endorsed DGVs being released, ecotoxicity threshold (ET) values for diuron, ametryn, hexazinone and simazine in marine waters (PC99, 95, 90, 80) have recently been published (King et al. 2017, Warne et al. 2018). Due to the high ecological value of the Reef, PC99 values are relevant to this ecosystem and are required by the Great Barrier Reef Marine Park Authority water quality guidelines (GBRMPA 2010). The published ETs and the proposed DGVs for 24 other pesticides submitted for endorsement and relevant to the current monitoring period, are detailed in Appendix B (Table B-1).

For the purposes of this report, monitoring data are compared against the ANZECC and ARMCANZ guidelines. For information, pesticide concentrations that exceed the proposed DGVs, which are still undergoing endorsement, are also highlighted.

### *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*

To date, the PSII-HEq Index has been used to assess ecological risk for MMP reporting. This Index defines ranges of PSII-HEq that equate with different levels of PSII inhibition (based on published toxicity data using Reef relevant species). An alternative risk assessment metric, the multisubstance-potentially affected fraction (ms-PAF) method has been proposed as a more robust approach to quantify the overall ecological risk of mixtures of pollutants for ecological communities. A concentration addition model (for 28 PSII herbicides) has been developed by DES and 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 SSDs used in the ms-PAF approach (both additive and non-additive) are also the basis for the proposed DGVs that have been submitted for national endorsement and inclusion into the Australian and New Zealand water quality guidelines (see Section 3.5.1). Further information on both metrics are given in Appendix C

The ultimate aim is to report a single assessment end point (PAF) for all monitored pesticides detected in the MMP program. For the current report, as for previous years, to avoid retrospective adjustment to reported data, the PSII-HEq Index will be used until the SSDs are endorsed and the ms-PAF model outputs for marine species is aligned with the DGVs (see previous year's Case Study (Grant et al. 2017)).

### *3.5.4 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. The Marine Water Quality component of the MMP maps the frequency and extent of (surface) flood plumes (Waterhouse et al. 2017b). Weekly flood plume colour class data was recorded for each of the fixed monitoring sites for the wet season (details provided in Appendix D Table E2). Site maps presented in this report overlay the plume frequency maps to indicate sampling site positions relative to (primary and secondary) flood plume occurrences. Whilst information on colour dissolved organic matter (CDOM) and total suspended solids (TSS) in flood plumes (which are the basis of the flood plume maps) cannot be used to predict expected levels of pesticides reaching a monitoring site, they do 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. Further information on how plumes are characterised is given in Appendix E, Section E.1.

# 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 (GBRMPA 2013) and the focus of *Reef Plan* initiatives. Pesticide run-off may also result from urban and industrial activities (GBRMPA 2013), although the relative contribution of these sources compared to agriculture is not known. 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 2016–17 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 that 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.

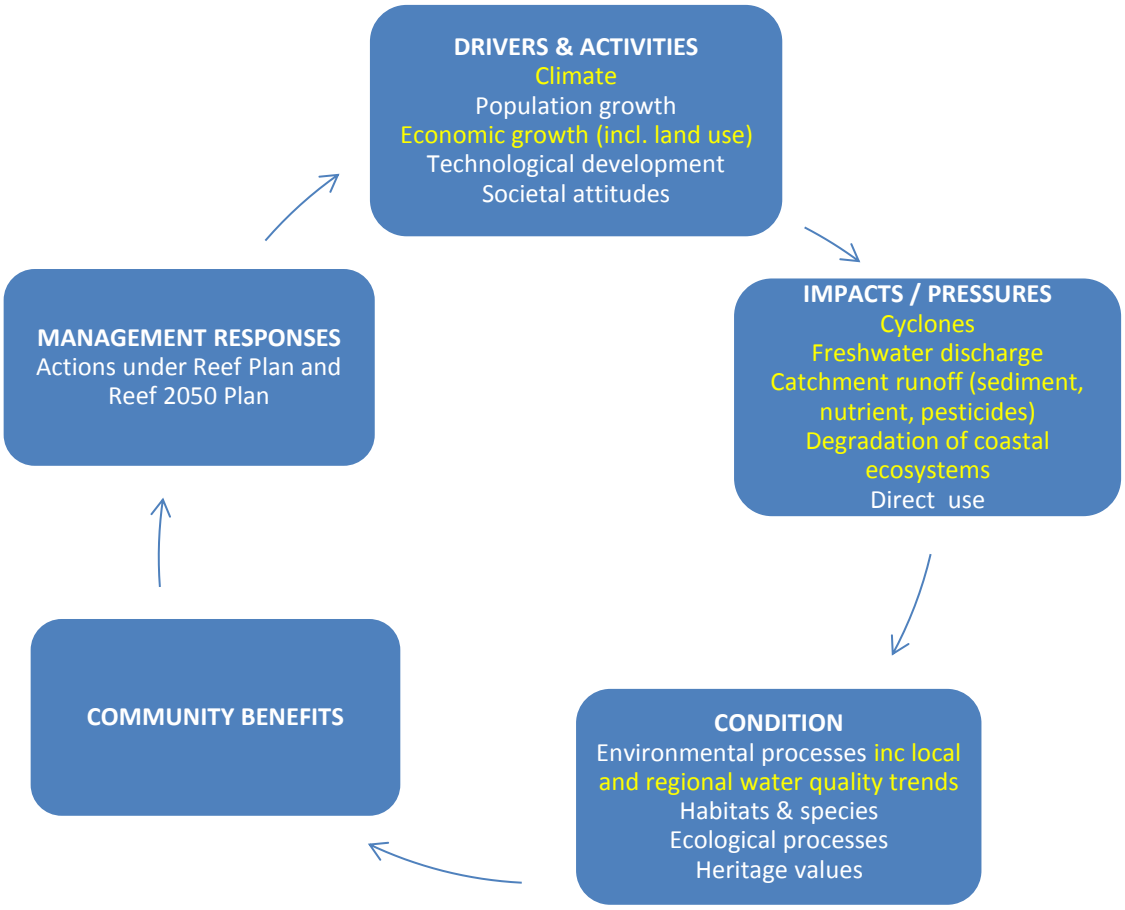



Figure 3: DPSIR framework used to guide the structure of the MMP, derived from the 2015 Great Barrier Reef Strategic Assessment. The aspects highlighted in yellow are included in this report.

## 4.1 Drivers and pressures influencing pesticide concentrations

Consistent with the reporting structure for all MMP projects, this section outlines the 2016–17 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).

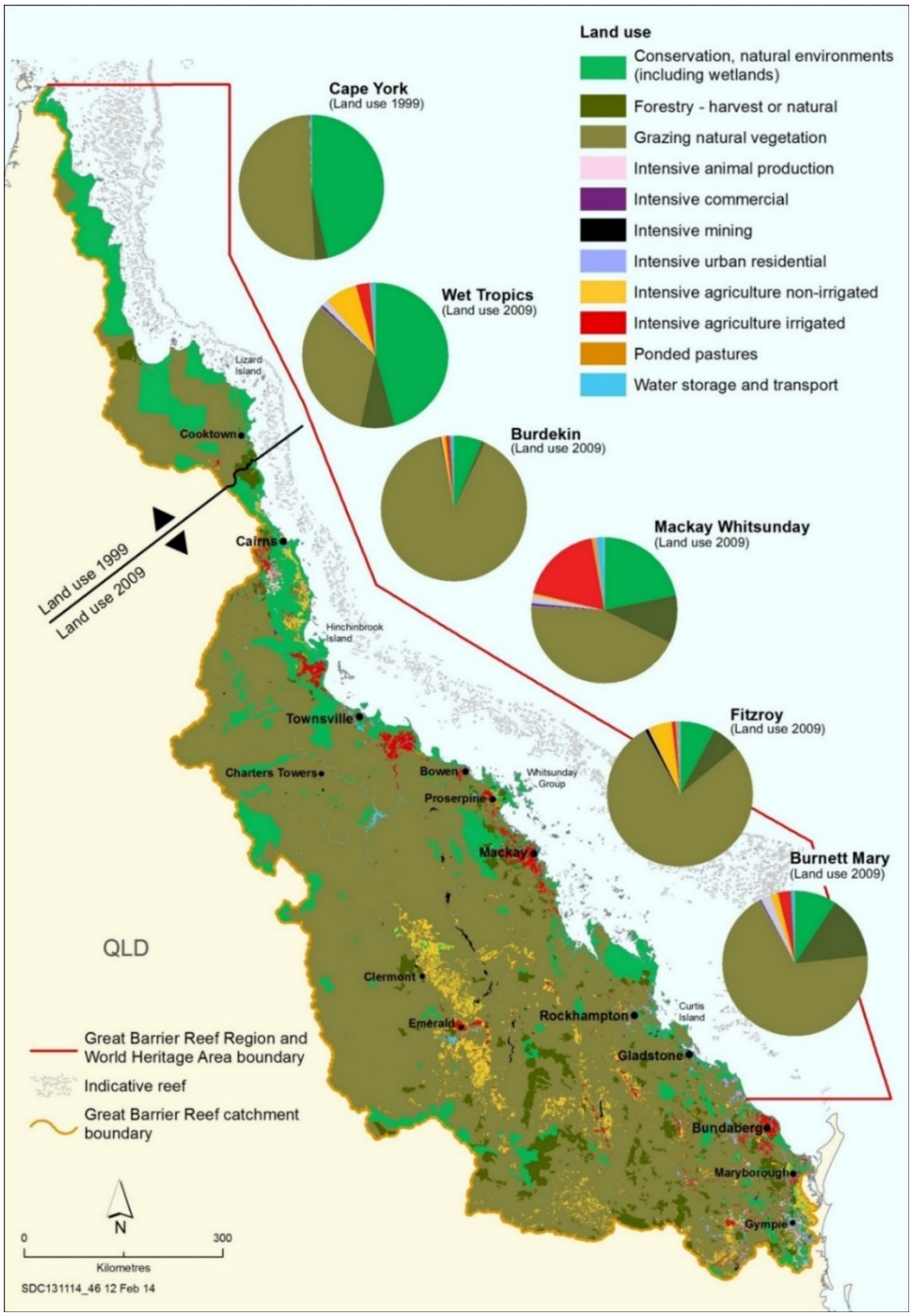



Figure 4: Land use in the Reef catchments. Sourced from GBRMPA (2014)

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 2012b, 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 (49 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 2012d, 2016). 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 2016–17 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*

Annual rainfall across the central and northern Reef catchments continued to be below the wet season averages in 2016–17 with the greatest differences from long-term averages in the catchments in the Cape York, Wet Tropics, Burdekin and Burnett Mary regions (Figure 5). The Mackay Whitsunday catchments and coastal catchments of the Fitzroy region had above average rainfall, largely associated with tropical cyclone Debbie. Wet season rainfall in the Fitzroy catchment was similar to the long-term average for that area. The first significant rainfall event occurred in the coastal areas in early December 2016 with notable events occurring early and late January across the whole Reef region, early February (predominantly Wet Tropics) and late March 2017, the latter following tropical cyclone Debbie and impacting the Mackay Whitsunday region to the greatest extent (Appendix D Figure E-1, Table 4).

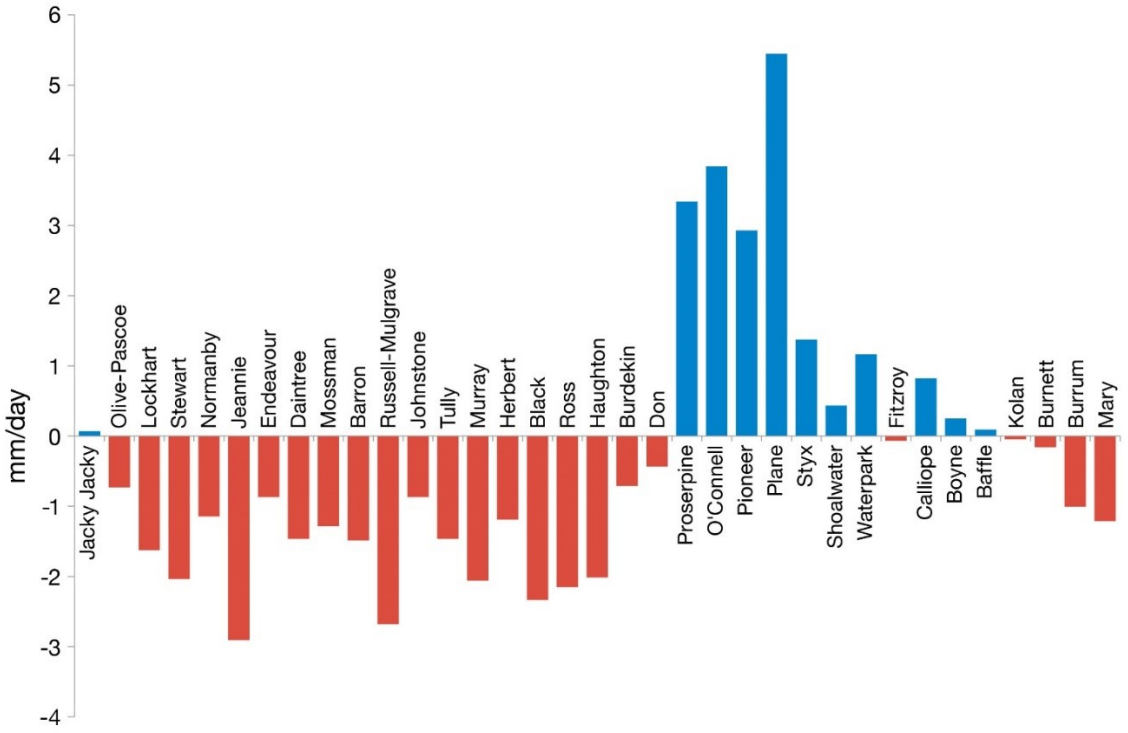
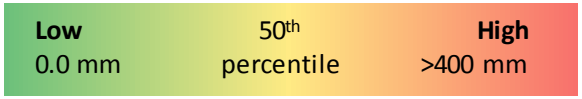



Figure 5: Annual average wet season rainfall (December 2016 - April 2017), as compared to the long-term wet season rainfall average (1961 – 1990). Red and blue bars denote catchments with rainfall below and above the long-term average, respectively. Note that the catchments are ordered from north to south (left to right). Source Waterhouse et al. (2018).

Table 4: Weekly mean catchment rainfall (mm) in catchments adjacent to fixed passive sampler sites during the 2016–17 wet season (beginning 1 December 2016). Data 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-16 | 08-Dec-16 | 15-Dec-16 | 22-Dec-16 | 29-Dec-16 | 05-Jan-17 | 12-Jan-17 | 19-Jan-17 | 26-Jan-17 | 02-Feb-17 | 09-Feb-17 | 16-Feb-17 | 23-Feb-17 | 02-Mar-17 | 09-Mar-17 | 16-Mar-17 | 23-Mar-17 | 30-Mar-17 | 06-Apr-17 | 13-Apr-17 | 20-Apr-17 | 27-Apr-17 |
| Wet Tropics | Mossman | 0.1 | 61 | 20 | 14 | 79 | 170 | 180 | 12 | 54 | 342 | 21 | 79 | 64 | 43 | 31 | 44 | 40 | 102 | 25 | 12 | 11 | 1.1 |
| | Mulgrave-Russell | 1.2 | 111 | 8.6 | 9.3 | 73 | 417 | 116 | 7.6 | 107 | 257 | 41 | 121 | 118 | 76 | 27 | 56 | 28 | 125 | 74 | 28 | 55 | 5.4 |
| | Herbert | 2.4 | 41 | 14 | 10 | 72 | 188 | 66 | 4.1 | 40 | 63 | 13 | 79 | 22 | 47 | 42 | 35 | 22 | 19 | 14 | 12 | 19 | 1.4 |
| | Tully | 0.7 | 67 | 4.1 | 13 | 34 | 487 | 115 | 10 | 130 | 219 | 32 | 87 | 61 | 108 | 62 | 54 | 35 | 66 | 78 | 34 | 79 | 8.5 |
| Burdekin | Burdekin | 1.1 | 25 | 13 | 6.5 | 29 | 43 | 52 | 2.0 | 11 | 3.4 | 7.4 | 29 | 4.1 | 13 | 28 | 43 | 49 | 16 | 1.6 | 0.4 | 1.0 | 0.1 |
| Mackay Whitsunday | Proserpine | 0.0 | 41 | 17 | 13 | 43 | 294 | 100 | 6.0 | 103 | 13 | 4.0 | 24 | 16 | 16 | 15 | 77 | 567 | 285 | 4.8 | 6.0 | 16 | 1.8 |
| | O'Connell | 0.3 | 82 | 28 | 33 | 90 | 288 | 59 | 6.0 | 143 | 8.9 | 30 | 48 | 14 | 27 | 17 | 87 | 584 | 269 | 8.7 | 5.2 | 22 | 4.5 |
| | Pioneer | 3.1 | 91 | 11 | 33 | 110 | 190 | 41 | 11 | 122 | 4.7 | 41 | 37 | 8.9 | 28 | 22 | 91 | 535 | 183 | 10 | 3.9 | 17 | 2.3 |
| | Plane | 0.9 | 164 | 6.3 | 61 | 170 | 147 | 25 | 8.7 | 105 | 3.2 | 42 | 52 | 20 | 38 | 16 | 226 | 605 | 306 | 14 | 3.4 | 13 | 1.5 |
| Fitzroy | Fitzroy | 0.7 | 27 | 8.3 | 17 | 31 | 8.1 | 40 | 1.8 | 14 | 0.3 | 3.8 | 10 | 7.7 | 20 | 25 | 55 | 66 | 83 | 0.3 | 0.0 | 0.6 | 0.4 |




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

### *4.1.2.2 Cyclones*

The only cyclone to influence the Reef region in 2016–17 was severe tropical cyclone Debbie, a Category 4 system that passed through the Whitsunday Islands and crossed the mainland at Airlie Beach in the Mackay Whitsunday region. The cyclone then moved southward over land as a rain depression producing flooding rains across the basins of the Mackay Whitsunday region, the Bowen-Broken-Bogie catchment of the Burdekin, as well as the Fitzroy and Burnett Mary NRM regions. Tropical Cyclone Debbie caused considerable physical damage to the coral reefs and seagrass meadows in the Mackay Whitsunday region.

In the 11 years since the MMP began in 2006–07, ten cyclones have been Category 3 or above and have affected the health of the Reef. All of the Category 5 cyclones that affected the Reef since 1970 have occurred in the last decade (including tropical cyclones Larry, Hamish, Yasi, Ita and Marcia). Many of these cyclones have caused widespread flooding from intensive rainfall events in many parts of the Reef catchment including tropical cyclone Debbie in 2017. For further information on cyclonic activity in the Reef region since 2006, see Waterhouse et al. (2018).

### *4.1.2.3 River discharge*

Total annual discharge of freshwater (based on corrected gauge values for the hydrological year, see Waterhouse et al. (2018)) into the Reef lagoon in 2016–17 was comparable to the long term median (Figure 6) and overall, was higher than the previous two years' of monitoring. All regions where passive or grab sampling sites were located in 2016–17 had annual discharge close to the median and were amongst the highest discharge recorded over the past 4 to 5 years (Figure 7).

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). 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. In 2016–17, a number of the southern rivers had wet season discharges above their long-term median flow, with discharges >1.5 times the long-term median in all of the major rivers adjacent to fixed passive sampler sites in the Mackay Whitsunday and Fitzroy regions (Table 5).

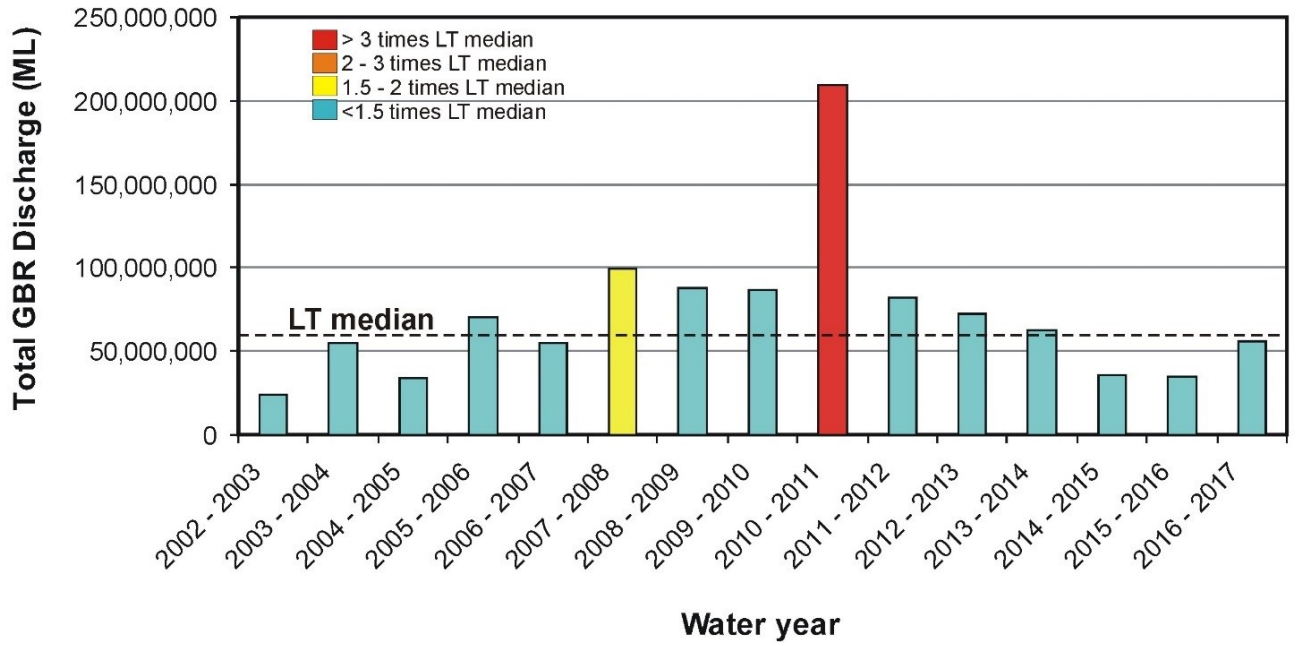



Figure 6: Long-term total annual discharge (ML) (hydrological year: 1 October to 30 September) for the 35 main Reef river catchments. Data derived from DNRM http://watermonitoring.dnrm.qld.gov.au/host.htm. Figure from Waterhouse et al. (2018).

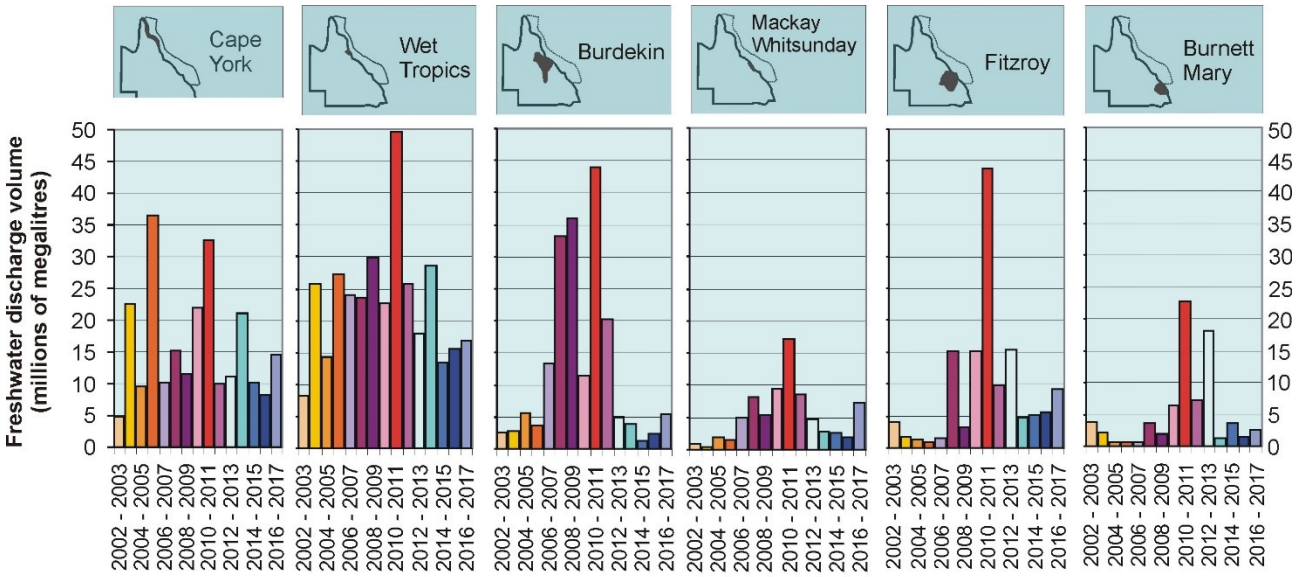



Figure 7: Corrected annual hydrological/water year (1 October to 30 September) discharge from each NRM region (using the correction factors in Table 2-2 (Waterhouse et al. 2018)) for 2002–03 to 2016–17 in millions of megalitres per year. Data derived from DNRM http://watermonitoring.dnrm.qld.gov.au/host.htm and figure reproduced from Waterhouse et al. (2018).

### *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. Forty-three pesticides and metabolites were monitored in 34 catchments (comprising both end-of-catchment and sub-catchment sites) under GBRCLMP in 2016–17 (Huggins et al., *in prep*). Passive samplers were deployed 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 (approach in 2016–17 followed that adopted in 2015–16; see Huggins et al. (2017)). Two rivers adjacent to passive sampling sites were not monitored during 2016–17: Mossman River (Low Isles 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 D Figure E-4). Consistent with previous years, fluometuron and prometryn loads were very low and were only at detectable levels at one/three 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 was also monitored as part of the GBRCLMP program. A total of eight additional pesticides were monitored at both the fixed monitoring sites and as part of the GBRCLMP. All eight other pesticides were detected in discharges from catchments adjacent to fixed monitoring sites in this program (Table 6), and in several instances, annual loads of other pesticides were comparable with those for the PSII herbicides (e.g. the metolachlor load from the Fitzroy river catchment was 270 kg compared to the maximum atrazine load of 350 kg from the Pioneer River).

Table 5: 2016–17 wet season discharge (ML) of the major Reef catchment rivers adjacent to passive sampling sites (c.a., November 2016 to April 2017, inclusive) compared to the long term (LT) median discharge. Relative wet season discharge (fraction of long-term median) for the current wet season and previous 5 years are shown.

| Region | Site | 2016–17 wet season discharge (ML) | LT median wet season discharge (ML) | Relative wet season discharge (fraction of long-term median) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 2011 - 2012 | 2012 - 2013 | 2013 - 2014 | 2014 - 2015 | 2015 - 2016 | 2016 - 2017 |
| Wet Tropics | Mossman | 1,142,698 | 1,195,130 | 1.3 | 1.0 | 1.6 | 0.7 | 1.0 | 1.0 |
| | Mulgrave-Russell | 3,015,734 | 4,415,631 | 1.3 | 0.8 | 1.2 | 0.7 | 0.7 | 0.7 |
| | Tully | 3,098,701 | 3,490,736 | 1.0 | 1.0 | 1.2 | 0.8 | 0.8 | 0.9 |
| | Herbert | 2,248,436 | 3,478,592 | 1.3 | 0.9 | 1.2 | 0.3 | 0.5 | 0.6 |
| Burdekin | Burdekin | 4,165,129 | 4,328,245 | 3.6 | 0.8 | 0.3 | 0.2 | 0.4 | 1.0 |
| Mackay Whitsunday | Proserpine | 1,683,894 | 924,039 | 2.3 | 0.9 | 0.8 | 0.2 | 0.3 | 1.8 |
| | O'Connell | 1,511,187 | 829,266 | 2.3 | 0.9 | 0.8 | 0.2 | 0.3 | 1.8 |
| | Pioneer | 1,388,687 | 804,599 | 1.9 | 1.4 | 0.8 | 2.5 | 0.7 | 1.7 |
| | Plane | 2,613,261 | 1,273,154 | 2.2 | 1.5 | 0.6 | 0.2 | 0.7 | 2.1 |
| Fitzroy | Fitzroy | 6,170,044 | 2,996,149 | 2.7 | 2.8 | 0.5 | 0.9 | 1.2 | 2.1 |

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. (2018) for different placements of gauges within each catchment. The full dataset from which these data were derived is given in Appendix D .

Table 6: Annual end-of-catchment pesticide loads (calculated from extrapolated monitoring data, see Huggins et al. (2017)) from monitored Reef catchments relevant to passive sampling sites (1 July 2016 – 30 June 2017). PSII-HEq loads are derived using PSII relative potency factors (RPFs – see Appendix C) 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) (*incl. in PSII-HEq Index) | | | | | | | | | | | | | | Annual load other (non-PSII) pesticides (kg) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lowest — 50th percentile — Highest | | 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* |
| Catchment (identified by major river) and load monitoring site name | Passive sampling sites | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| *Mossman River* | *Low Isles* | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Mulgrave River at Deeral | High Island & | n.d. | 95 | 16 | 3.20 | 4.8 | 66 | n.d. | 34 | 3.0 | n.d. | n.d. | 2.1 | n.d. | | 96 | 3.8 | 80 | | 2.8 | 59 | | 63 | 4.3 | 18 | 0.7 | | | | | |
| Russell River at East Russell | Normanby Island | 1.7 | 40 | 8.3 | 0.11 | n.d. | 144 | n.d. | 70 | 3.3 | n.d. | n.d. | n.d. | n.d. | | 180 | 3.6 | 49 | | 0.42 | 2.6 | | 8.3 | 19 | 69 | 5.6 | | | | | |
| Tully River at Euramo | Dunk Island | n.d. | 270 | 43 | 6.7 | n.d. | 346 | n.d. | 160 | 72 | n.d. | 0.1 | 0.2 | n.d. | | 455 | 15 | 260 | | 9.7 | 85 | | 18 | 26 | 230 | 12.0 | | | | | |
| Herbert River at Ingham | Lucinda | 1.1 | 100 | 16 | 3.2 | n.d. | 89 | n.d. | 50 | 0.71 | 0.12 | 0.89 | 9.6 | 1.7 | | 128 | 18 | 140 | | 2.3 | 2.9 | | 85 | 4.6 | 54 | 0.83 | | | | | |
| Barratta Creek at Northcote | Barratta Creek | 4.3 | 320 | 25 | 8.8 | 6.1 | 23 | 0.003 | 0.11 | 19 | 0.002 | 0.53 | 1.1 | 0.7 | | 83 | 36 | 130 | | 9 | 27 | | 28 | 1.5 | 1.3 | 0.051 | | | | | |
| Proserpine River at Glen Isla | Repulse Bay | 1.2 | 190 | 25 | 6.2 | n.d. | 250 | n.d. | 270 | 1.3 | n.d. | 0.34 | 0.68 | 1.6 | | 387 | 55 | 160 | | 7.1 | 67 | | 53 | 62 | 230 | 1.2 | | | | | |
| O'Connell River at Caravan Park | | 0.005 | 58 | 6.1 | 1 | n.d. | 21 | n.d. | 19 | 11 | n.d. | 0.01 | 0.046 | 5.7 | | 38 | 6.7 | 55 | | 0.69 | 8.2 | | 13 | 8.5 | 39 | 0.22 | | | | | |
| Pioneer River at Dumbleton PS | Round Top | 7.4 | 350 | 55 | n.d. | 0.065 | 323 | n.d. | 100 | 23 | n.d. | 0.85 | 0.68 | n.d. | | 433 | 21 | 150 | | n.d. | 51 | | 78 | 53 | 170 | 1.5 | | | | | |
| Sandy Creek at Homebush | Sandy Creek | 4.1 | 180 | 23 | 9.1 | n.d. | 133 | n.d. | 63 | 22 | n.d. | 0.06 | 0.37 | n.d. | | 194 | 37 | 93 | | 5.9 | 32 | | 60 | 38 | 85 | 0.58 | | | | | |
| *Plane Creek* | *Sarina Inlet* | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Fitzroy River at Rockhampton | N. Keppel Island | 2.1 | 170 | 13 | 72 | 63 | 18 | n.d. | 50 | n.d. | 0.74 | 2.4 | 580 | 1700 | | 116 | 270 | 60 | | 80 | 40 | | 46 | 3.3 | 7.6 | 5.4 | | | | | |

† 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, 75 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 73 and 83 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 Sarina Inlet) had complete or mostly complete (missing one sampler set) sampling deployments in 2016–17. Following a changeover in the local volunteer organisation, Normanby Island did not have any successful deployments in the current sampling year; this has, however, now been resolved for 2017–18. Repulse Bay experienced some challenging conditions in 2016–17, with the moorings and all samplers being lost in four separate deployment periods. Tropical cyclone Debbie also resulted in samplers being lost in the March 2017 period for four sites (Barratta Creek, Repulse Bay, Round Top Island and Sandy Creek) and three of these sites could not be re-established in time for sampling in April 2017.

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 fourteen compounds, twelve were detected at one or more of the marine monitoring sites (Figure 8). Consistent with previous years, the most commonly detected PSII herbicides were atrazine, diuron and hexazinone. Fluometuron and terbutryn were not detected at any site in 2016–17. Of the fifteen other pesticides in the analysis suite (eleven polar and four non-polar), ten were detected at measurable levels in ED samplers and all four non-polar pesticides were detected in the PDMS samplers (Figure 8). 2,4-DB was not detected at any site. Of the non-polar pesticides, chlorpyrifos and pendimethalin were the most frequently detected at the sites where samplers were deployed.

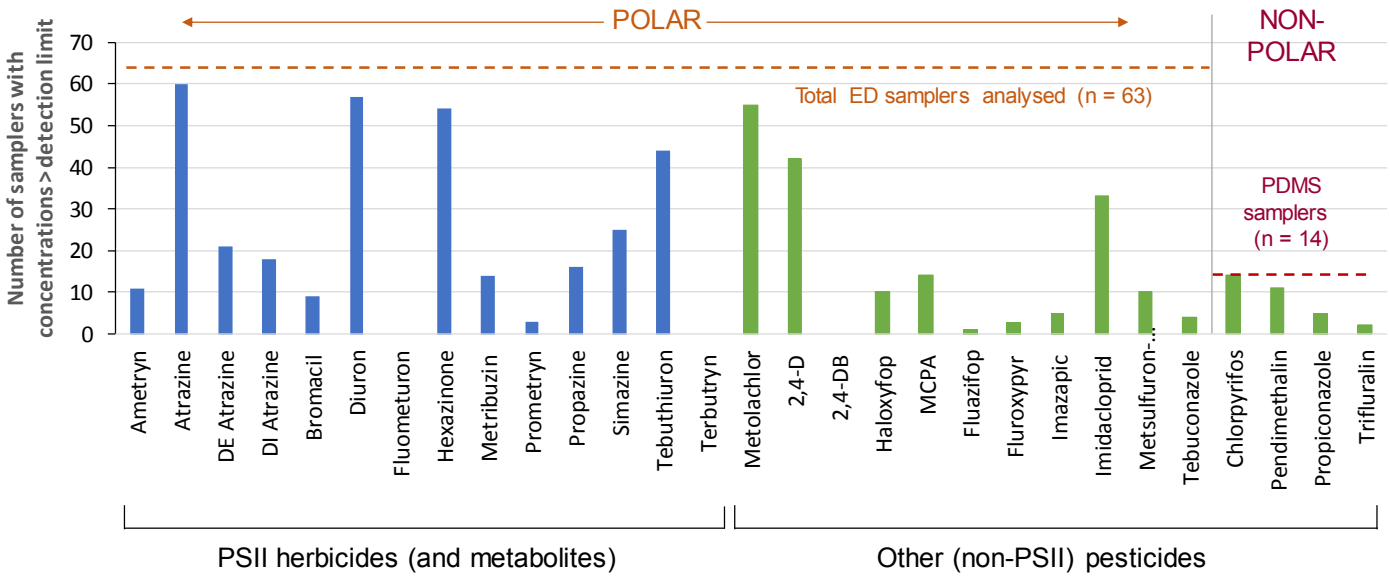



Figure 8: Number of ED and PDMS samplers that had pesticide concentrations above the limit of detection, LOD, for each pesticide included in this study, out of a total of 63 ED samplers and 14 PDMS samplers returned in 2016–17 (Table F-1, Appendix F).

#### *4.2.2.2 Summary of pesticide concentrations in 2016–17*

The PSII herbicides detected at the highest concentrations in 2016–17, which were also the most frequently detected, were diuron (maximum concentration ($C_{max}$) 580 ng $L^{-1}$), atrazine ($C_{max}$ 320 ng $L^{-1}$) and hexazinone

($C_{max}$ 88 ng $L^{-1}$), all detected at Round Top Island, approximately 5-9 km from the Pioneer River and Sandy Creek mouths in the Mackay Whitsunday region (Table 7). Tebuthiuron was also consistently detected along the Reef coastline, although at low concentrations (<2.3 ng $L^{-1}$), with the highest concentration being at North Keppel Island as in previous years. Other pesticides 2,4-D, imidacloprid and metolachlor were also consistently detected across the sampling sites. Concentrations of these three other pesticides were typically lower at most sites compared to the PSII herbicides but were relatively elevated at Round Top Island (Table 7, see regional report below).

In the current monitoring year, the PSII-HEq Max across all sites ranged from 0.77 – 670 ng $L^{-1}$. Five of the sites had maximum PSII-HEq concentrations in the Category 5 risk category (no reported ecosystem effects), which was lower than for 2015-16 (eight sites were classified Category 5 in the previous year). High Island and Barratta Creek reached a Category 4, Sandy Creek and Sarina Inlet 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. It should be noted that the longer-term risk to the viability of Reef species when exposed to pesticide concentrations at Category 2 for a sampling period is not known as reduced photosynthesis capacity may be a reversible endpoint once pesticide levels in water decrease. The effects of reduced photosynthesis in combination with other stressors is, however, not well understood.

Diuron was the dominant contributor to the PSII-HEq Max at all 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 49 per cent (North Keppel Island) to 91 per cent (Lowe Isles and Sandy Creek), and was consistently high in the Wet Tropics (86 to 91 per cent across the sites).

#### *4.2.2.3 Comparison to guideline values*

No exceedances of the ANZECC and ARMCANZ (2000) trigger values occurred in 2016–17. Two exceedances of proposed (but not yet endorsed) default guideline values (DGVs) occurred at the Round Top Island site:

- diuron ($C_{max}$ 580 ng $L^{-1}$, compared to the proposed marine PC99 DGV of 430 ng $L^{-1}$ (Table B-1))
- imidacloprid ($C_{max}$ 53 ng $L^{-1}$, compared to the proposed marine PC99 DGV of 33 ng $L^{-1}$ (Table B-1))

The 2016–17 $C_{max}$ values for diuron and imidacloprid were both higher than in 2015–16 (462 and 36 ng $L^{-1}$, respectively). In 2015–16, chlorpyrifos (0.52 ng $L^{-1}$) exceeded the ANZECC and ARMCANZ (2000) marine PC99 value of 0.50 ng $L^{-1}$ (Table B-1); the current year's $C_{max}$ for chlorpyrifos (0.49 ng $L^{-1}$) was close to but did not exceed the guideline.

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), and under both these guidelines, the 2016–17 Round Top Island maximum diuron value was not an exceedance. Although the proposed DGV for diuron is high reliability (King et al. 2017), until endorsed, comparisons with this proposed value are provided for information only. There are no existing PC99 or trigger values for imidacloprid, nor a proposed DGV for chlorpyrifos.

#### *4.2.2.4 Comparison to previous years: trends in pesticide concentrations*

For all sites, the 2016–17 maximum pesticide concentrations were similar to or higher than in 2015–16 (Figure 9) and, where historical records are available to compare, 2016–17 values were comparable for some sites to the 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 for which monitoring began in 2014–15 (Lucina, Barratta Creek, and three of the four Mackay Whitsunday sites, Repulse Bay, Round Top Island and Sandy Creek). Likewise, for trends at High Island which was re-introduced to the monitoring program in the previous 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 time integrated (or chronic) pesticide concentrations at each fixed passive sampling site. Colour coding reflects lowest (green) to highest (red) values for each pesticide between the monitored NRM regions (yellow is the 50th percentile).

| | | Maximum concentration PSII Herbicides and metabolites (ng/L) (*included in PSII-HEq Index) | | | | | | | | | | | | | | Maximum concentration other pesticides (ng/L) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Region | Passive sampling sites | Ametryn* | Atrazine* | DE Atrazine* | DI Atrazine* | Bromacil | Diuron* | Fluometuron* | Hexazinone* | Metribuzin | Prometryn* | Propazine | Simazine* | Tebuthiuron* | Terbutryn | PSII-Heq Max (ng/L) | Metolachlor | 24 D | 2,4 DB | Haloxyfop | MCPA | Fluazifop | Fluroxypyr | Imazapic | Imidacloprid | Metsulfuron-Methyl | Tebuconazole | Chlorpyrifos | Pendimethalin | Propiconazole | Trifluralin |
| Wet Tropics | Low Isles | 0.02 | 1.1 | 0.03 | n.d. | n.d. | 3.2 | n.d. | 0.66 | n.d. | n.d. | n.d. | 0.04 | 0.05 | n.d. | **3.5** | 0.19 | 0.04 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.08 | n.d. | n.d. | | | | |
| | High Island | n.d. | 1.3 | 0.19 | n.d. | 0.01 | 10 | n.d. | 2.9 | 0.02 | 0.30 | n.d. | 0.05 | 0.04 | n.d. | **11** | 0.18 | 0.51 | n.d. | 0.03 | 0.09 | n.d. | n.d. | n.d. | 1.0 | n.d. | 0.03 | | | | |
| | Normanby Island | No data for 2016-17 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Dunk Island | n.d. | 1.2 | 0.07 | n.d. | n.d. | 6.6 | n.d. | 1.9 | 0.03 | n.d. | n.d. | 0.05 | 0.07 | n.d. | **7.4** | 0.21 | 0.30 | n.d. | 0.01 | n.d. | n.d. | 0.02 | n.d. | 1.4 | n.d. | n.d. | | | | |
| | Lucinda | 0.02 | 1.6 | n.d. | n.d. | 0.00 | 5.8 | n.d. | 1.9 | n.d. | n.d. | 0.01 | n.d. | 0.18 | n.d. | **6.8** | 0.16 | 0.52 | n.d. | 0.01 | 0.04 | n.d. | n.d. | n.d. | 0.32 | n.d. | n.d. | | | | |
| Burdekin | Barratta Creek | 1.9 | 41 | 6.6 | 1.1 | 0.19 | 17 | n.d. | 1.6 | 1.2 | n.d. | 0.27 | 0.48 | 0.20 | n.d. | **25** | 4.4 | 1.4 | n.d. | 0.04 | 0.06 | 0.01 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.15 | 0.11 | 0.21 | n.d. |
| Mackay Whitsundays | Repulse Bay* | n.d. | 1.7 | n.d. | n.d. | n.d. | 3.8 | n.d. | 1.8 | n.d. | n.d. | n.d. | n.d. | 0.03 | n.d. | **4.8** | 0.14 | 0.29 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.23 | n.d. | n.d. | | | | |
| | Round Top Island | 3.2 | 320 | 20 | 4.9 | 0.03 | 580 | n.d. | 88 | 12 | 0.04 | 1.4 | 1.3 | 0.53 | n.d. | **670** | 7.7 | 11 | n.d. | 0.01 | 0.13 | n.d. | 0.49 | 0.82 | 53 | 0.65 | 0.02 | 0.49 | 0.19 | 0.66 | 0.01 |
| | Sandy Creek | n.d. | 18 | 1.7 | 0.39 | 0.04 | 70 | n.d. | 20 | 0.50 | n.d. | 0.07 | 0.15 | 0.41 | n.d. | **77** | 0.38 | 2.2 | n.d. | n.d. | 0.46 | n.d. | n.d. | n.d. | 3.3 | 0.30 | n.d. | 0.01 | 0.03 | 1.2 | n.d. |
| | Sarina Inlet | 0.28 | 75 | 4.5 | 1.1 | n.d. | 120 | n.d. | 40 | 0.88 | n.d. | 0.22 | 0.60 | 1.6 | n.d. | **150** | 7.8 | 7.0 | n.d. | n.d. | 0.78 | n.d. | 0.40 | 0.43 | 4.5 | 0.16 | n.d. | 0.03 | 0.02 | 0.1 | 0.001 |
| Fitroy | N. Keppel Island | n.d. | 0.35 | n.d. | 0.05 | n.d. | 0.38 | n.d. | 0.08 | n.d. | n.d. | n.d. | 1.9 | 2.3 | n.d. | **0.77** | 0.19 | 0.15 | n.d. | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | | | |

n.d. maximum pesticide concentration below limit of detection

* Data from only one wet season sampling period available

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

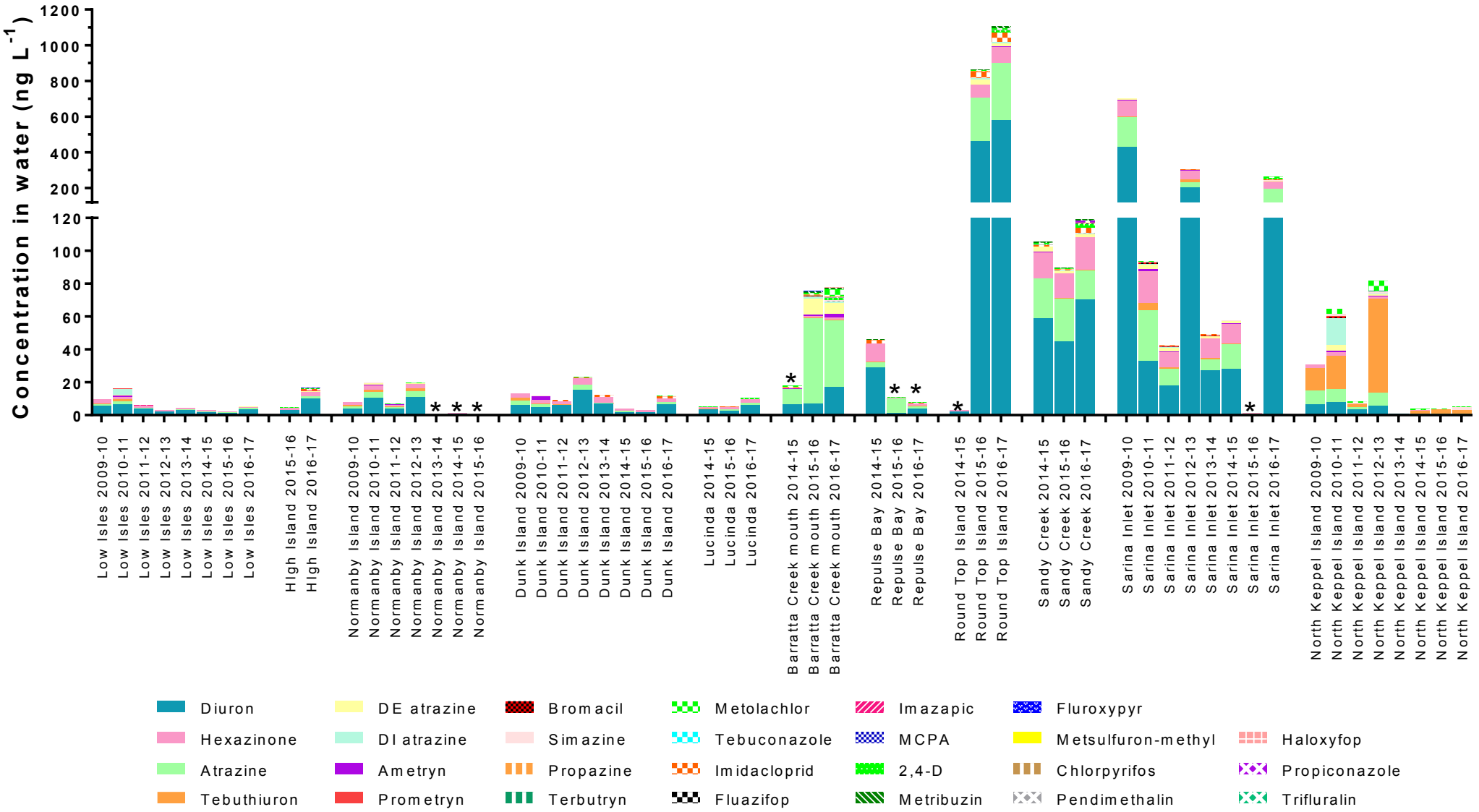



Figure 9: Maximum time integrated (or chronic) concentrations of individual pesticides at all sites monitored in 2016–17 compared to previous years (2009-10 onwards). Diuron dominated the profile at most sites, the exceptions being Barratta Creek mouth (where atrazine was the highest contributor) and 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 onwards). 2,4-DB and fluometuron are not shown as values were <LOD for all sites and all years. * Values with an asterisk are not representative values due to wet season sampling being incomplete and should be interpreted with caution. At Repulse Bay, the 2016–17 maximum may be understated as only one wet season sample was obtained. No data is available for Normanby Island for 2016–17 .

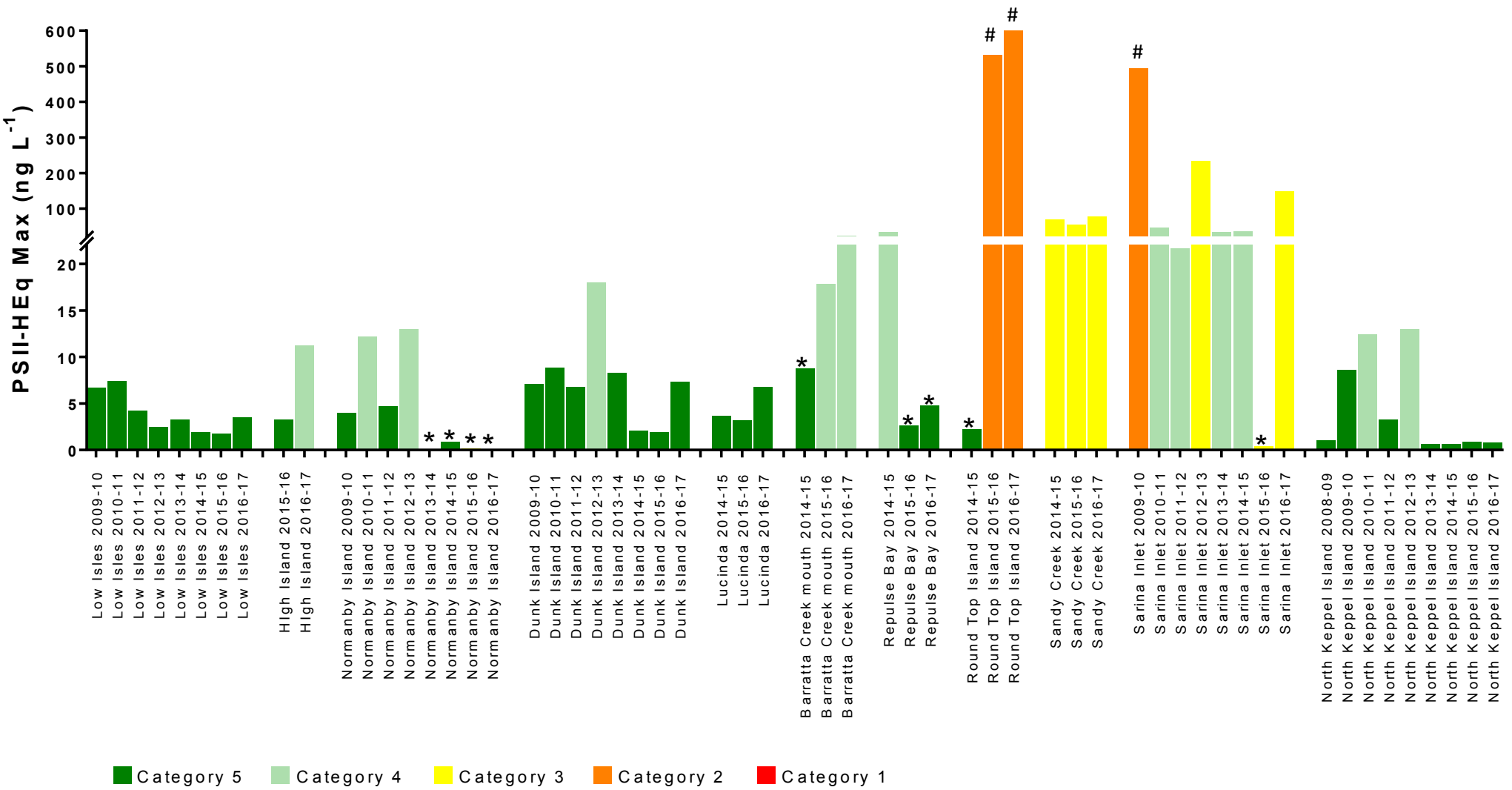



Figure 10: Maximum time integrated (or chronic) PSII herbicide equivalent concentrations at all sites monitored in 2016–17 compared to previous years (2009-10 onwards). The five categories of the PSII index reflect published effects on photosynthesis, where Category 5 is no impact and Category 1 is the 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. Values marked with # exceed the proposed marine Default Guideline Value (PC99, 430 ng/L) for diuron, derived by DES (formerly DSITI) and currently being submitted for national endorsement.

## 4.3 Regional results

### *4.3.1 Wet Tropics Region*

Rainfall in the Wet Tropics in 2016–17 continued to be below the long-term wet season averages and overall river discharge was only marginally higher than the last two monitoring years (Figure 7) and was at or below the long-term average for all the major rivers in the region (Table 5). The overall climatic conditions in this region contributed to low flood plume frequencies at all fixed monitoring sites (frequencies ranged from 0.23 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, on average, the Wet Tropics sites and particularly sites further north were impacted by only tertiary plume waters.

Maximum concentrations of PSII herbicides during the 2016–17 wet season across the Wet Tropics sites were 2-4 times higher than in the previous monitoring year (Table 8; for historical data, see Figure I-1 to Figure I-5). 2016–17 levels were comparable to those in the years prior to the very dry last two years, i.e. comparable to 2013–14 and previous years (for historical data, see Appendix H Figures H-1 to H-5). In 2016–17, the rivers in the Wet Tropics generally flowed year-round with flow events occurring regularly throughout both the wet and dry seasons (Figure 11 A-C, E, G). In the wet season, a relatively small first flush event occurred in most Wet Tropics rivers in early December, followed by high rainfall in early January 2017 that resulted in high flow events in the Russell, Mulgrave, Tully and Herbert Rivers (Figure 11). Maximum PSII HEq concentrations were associated with either this first major flow event (Low Isles, Dunk Island, Figure 11 A,G), or subsequent lower flow but longer duration events in February 2017 (High Island, Lucinda, Figure 11 B,E). Whilst first flush events are expected to contain the highest concentrations of pesticides, the higher concentrations of pesticides observed at the monitoring sites later in the wet season at some sites may be explained by the timing of pesticide applications and/or dilution effects associated with unusually high first flush flows, although the exact cause cannot be confirmed.

Table 8: Summary statistics for passive sampler 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 | | Routiine sampling commenced | Risk category | | | | | | | | | | | | Plume Frequency 2016-17 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 2016-17 | 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 | 2.8 | 0.72 | 0.97 | 1.5 | 1.6 | 2.1 | 4.4 | 1.9 | 2.1 | 3.9 | 2.5 | 5.6 | 0.23 |
| | PSII-HEq Dry Avg | | 1.1 | 0.10 | 0.10 | 1.58 | 0.45 | 0.82 | 0.73 | 0.88 | 1.9 | 0.64 | 0.56 | 1.2 | |
| | PSII-HEq Max | | 3.5 | 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 | 5.8 | 1.6 | | | | | | | | 8.8 | 10 | | 0.55 |
| | PSII-HEq Dry Avg | | 1.3 | 0.11 | | | | | | | | 4.5 | 3.4 | | |
| | PSII-HEq Max | | 11 | 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 | 0.29 |
| | PSII-HEq Dry Avg | | - | - | - | - | 2.1 | 0.6 | 0.7 | 0 | 2.6 | 3.3 | 0.53 | 0.16 | |
| | 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 | 5.2 | 0.61 | 1.3 | 4.4 | 8.9 | 3.4 | 8.8 | 4.4 | 3.0 | | 4.7 | | 0.95 |
| | PSII-HEq Dry Avg | | 0.98 | 0.04 | 0.8 | 2.2 | 2.3 | 0.1 | 2.2 | 1.1 | 0 | | - | | |
| | PSII-HEq Max | | 7.4 | 2.0 | 2.1 | 8.3 | 18 | 6.8 | 8.8 | 7.1 | 4.1 | | 4.7 | | |
| Lucinda | PSII-HEq Wet Avg | 2014-15 | 3.4 | 1.1 | 1.3 | | | | | | | | | | 1.00 |
| | PSII-HEq Dry Avg | | 1.0 | 0.19 | 1.7 | | | | | | | | | | |
| | PSII-HEq Max | | 6.8 | 3.2 | 3.7 | | | | | | | | | | |

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

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

Consistent with 2015–16, PSII herbicides (and metabolites) detected using EDs in the Wet Tropics region in 2016–17 were almost exclusively atrazine, diuron and hexazinone and all three were detected in almost all the 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 and metolachlor, were also detected in the region (in at least four sampling periods at each Wet Tropics site), with the most frequent detections at High Island for all three pesticides.

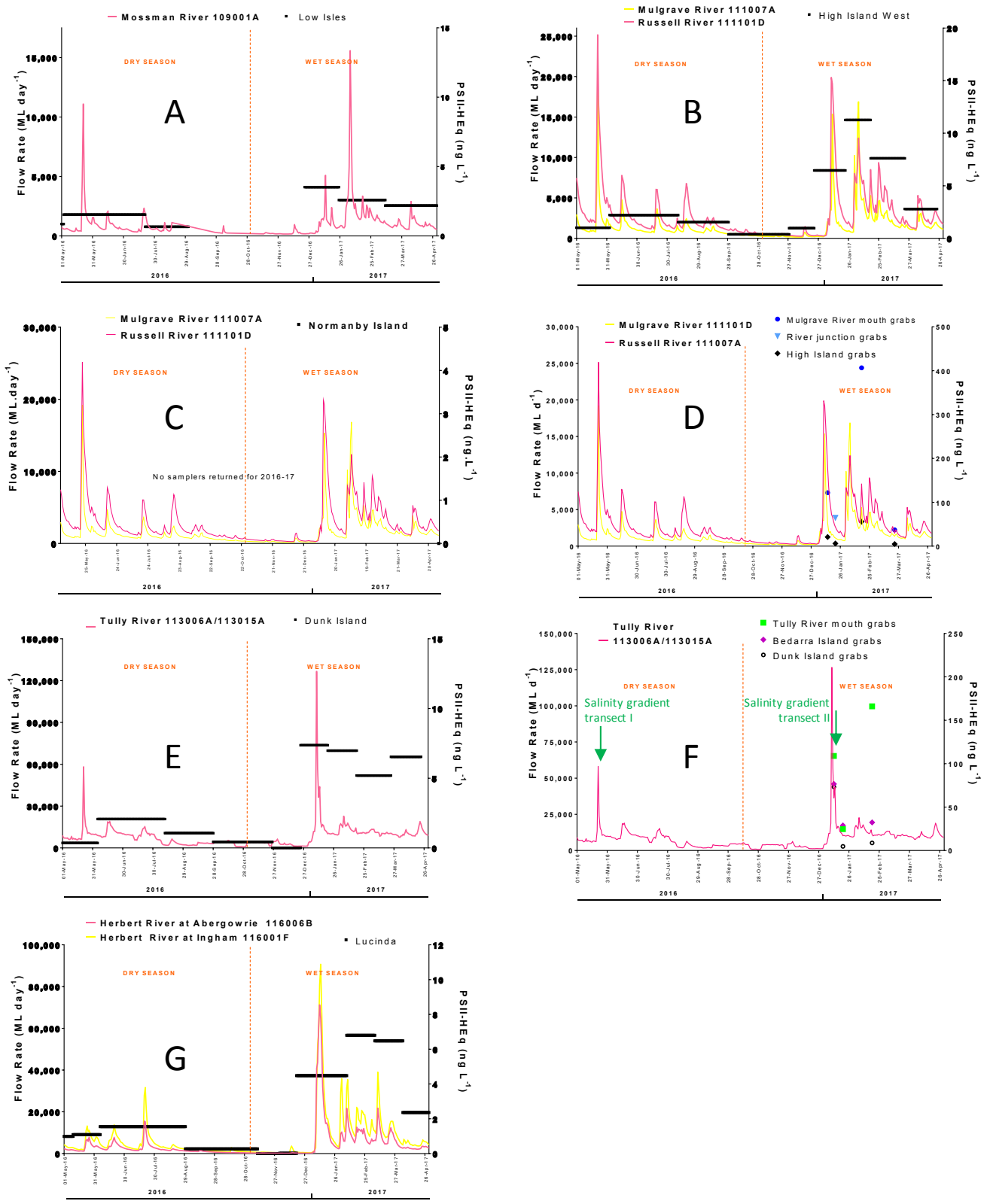



Figure 11: Temporal trends in PSII-HEq at fixed passive sampling sites (A-C, E, G) and in grab samples (D, F) in 2016–17 , relative to the flow rate of rivers influencing the Wet Tropics sampling sites. Flow data provided by DNRM Stream Gauging Network.

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 (0Figure I-1 to Figure I-5) and PSII-HEq Max values (Table 8) did not, however, differ significantly between the Wet Tropics monitoring sites, with all profiles being dominated by the three major PSII herbicides. Diuron generally contributed just over half the total pesticide concentration at all sites and represented 85 per cent of the average PSII-HEq concentration.

Since monitoring commenced, 82 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 2016–17 were Category 5 on the PSII-HEq Index, except for High Island which was Category 4. It should be noted that the concentrations of 2,4-D, imidacloprid and metolachlor were not included in the calculation of the risk category, and therefore the combined risk from all pesticides could be different (e.g. depending on whether synergism or antagonism may be occurring) in this region than what is reported here.

#### *4.3.1.1 Russell-Mulgrave and Tully River long-term transects*

In 2016–17, grab samples were again 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/Mulgrave River mouth (or junction site) and High Island (fixed monitoring site) on four occasions throughout the wet season. Sampling coincided with the first major flow event of the year in January 2018, and two subsequent events in February/March (Figure 11 D). The highest PSII herbicide concentrations were associated with the sample collected in the river mouth during the second flow event in mid-February. The PSII-HEq concentration in this grab sample was over 400 ng $L^{-1}$ (Category 2 on the PSII-HEq Index) and resulted in comparatively elevated concentrations at High Island (37 ng $L^{-1}$, Category 4). These levels were considerably higher than for grab samples collected in the previous year and were consistent with 2014-15 grab sampling from the same river mouth (maximum PSII-HEq concentrations of 339 ng $L^{-1}$). As for the ED passive samples, the grabs associated with this second flood event had higher concentrations than the higher flow event in January 2017, and, as mentioned above, timing of pesticide applications, and also dilution effects with high flows, may have played a role. The profile of the major pesticides in the grab samples was largely consistent with previous years, with dominant contributions of atrazine, diuron, hexazinone, imazapic and imidacloprid (Appendix G Table G-1). In the current year, relatively high levels of 2,4-D and MCPA were also detected (e.g. 306 and 605 ng $L^{-1}$, respectively, in the mid-February sample, Appendix G Table G-1). Whereas in 2015-16 there were no pesticides other than low levels of diuron in the grab samples from High Island, in 2016–17, the relatively higher overall concentrations in the river mouth grab samples were reflected in the High Island grabs, and a similar pesticide profile was observed between the end of catchment and the nearshore monitoring site.

In the Tully region, a similar repeated grab sampling program was undertaken during the wet season, with samples collected on three 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). The samples were collected on the first three sampling events undertaken for the Russell/Musgrave transects, timed to coincide with major flow events in January/February 2017 (Figure 11 F). The Tully River mouth grab samples showed a similar pattern in the PSII-HEq levels and pesticide profiles to the Russell/Mulgrave River mouth grab samples. The highest concentrations were detected in the grab sample collected following the mid-February event (166 ng $L^{-1}$, Category 3) at the Tully river mouth (Table G-1). Offshore, however, the highest PSII-HEq concentration were observed at Bedarra and Dunk Islands following the first high flow event in January 2017 (when the concentration at the river mouth was 109 ng $L^{-1}$). The high volume of water associated with the first event, whilst diluting pesticide concentrations at the river mouth may have provided the energy and water volume to transport higher levels of pesticides out to the islands. Both the Bedarra and Dunk Islands grab samples had a very similar pesticide profile but lower concentrations than at the river mouth (Table G-1). Diuron, atrazine, hexazinone, imidacloprid, metolachlor and 2,4-D were consistently detected pesticides in all the grab samples.

#### *4.3.1.2 Tully River salinity gradient*

In 2016–17, two transects were collected from major flood plumes from the Tully River (see Figure 11 F), comprising grab samples from water of different salinities. For both transects, correlations between individual pesticide concentration and water salinity were assessed to understand mixing behaviour of the pesticide load in the flood plume as freshwater mixes with seawater.

For the transect collected at the start of the dry season (May 2016), concentrations in the grab samples were elevated compared to usual dry season levels (for example, PSII-HEq ranged from 2.9 - 34 ng $L^{-1}$) but were, overall, lower than for the wet season salinity transect collected in January 2017 (PSII-HEq ranged from 4.9 - 248 ng $L^{-1}$) (Table G-1). For the dry season transect, no relationships between pesticide concentrations in the grab samples and water salinity were observed (e.g. correlation $R^2$ <0.25 for the three PSII herbicides dominating the pesticide profile, diuron, atrazine and hexazinone; data not shown). In contrast, for the wet season transect, for the ten pesticides that were detected above LOD in all or most of the grab samples, negative correlations between concentration and salinity were observed with $R^2$ ranging from 0.59 to 0.97 (Figure 12). The highest $R^2$ (0.97) was for metolachlor. For the other pesticides, decreasing $R^2$ values could be linked to inconsistencies in the concentration in the 5.3 psu grab sample (Figure 12); for many, but not all, of the pesticides, the concentration in the 5.3 psu sample was lower than would be expected relative to the other salinity levels. Further samples at this salinity level would be required to understand whether the results are typical of locations close to the river mouth where some but limited mixing has occurred.

Overall, the data for the ten pesticides for the January 2017 transect suggested conservative mixing behaviour along the salinity gradient within the Tully River water plume, with increasing dilution as the river waters progressively mixed with seawater. The reason that conservative mixing could not be observed in the dry season data is not known. Overall, pesticides concentrations in the dry season flow were lower than in the wet season. Furthermore, the May flow volume was approximately half that in the high flow event in January and samples were collected three days after the peak flow when flow was returning to normal flow levels (compared to 2 days after the peak flow in January when flow was still considerably higher than normal). Sampling at different stages of the hydrograph in a river can appreciably affect the observed sample contaminant concentrations (Novic et al. 2017). Whether and how the plume flow rates and timing of sample collection impact the mixing behaviour in the nearshore marine environment are factors to consider for future studies.

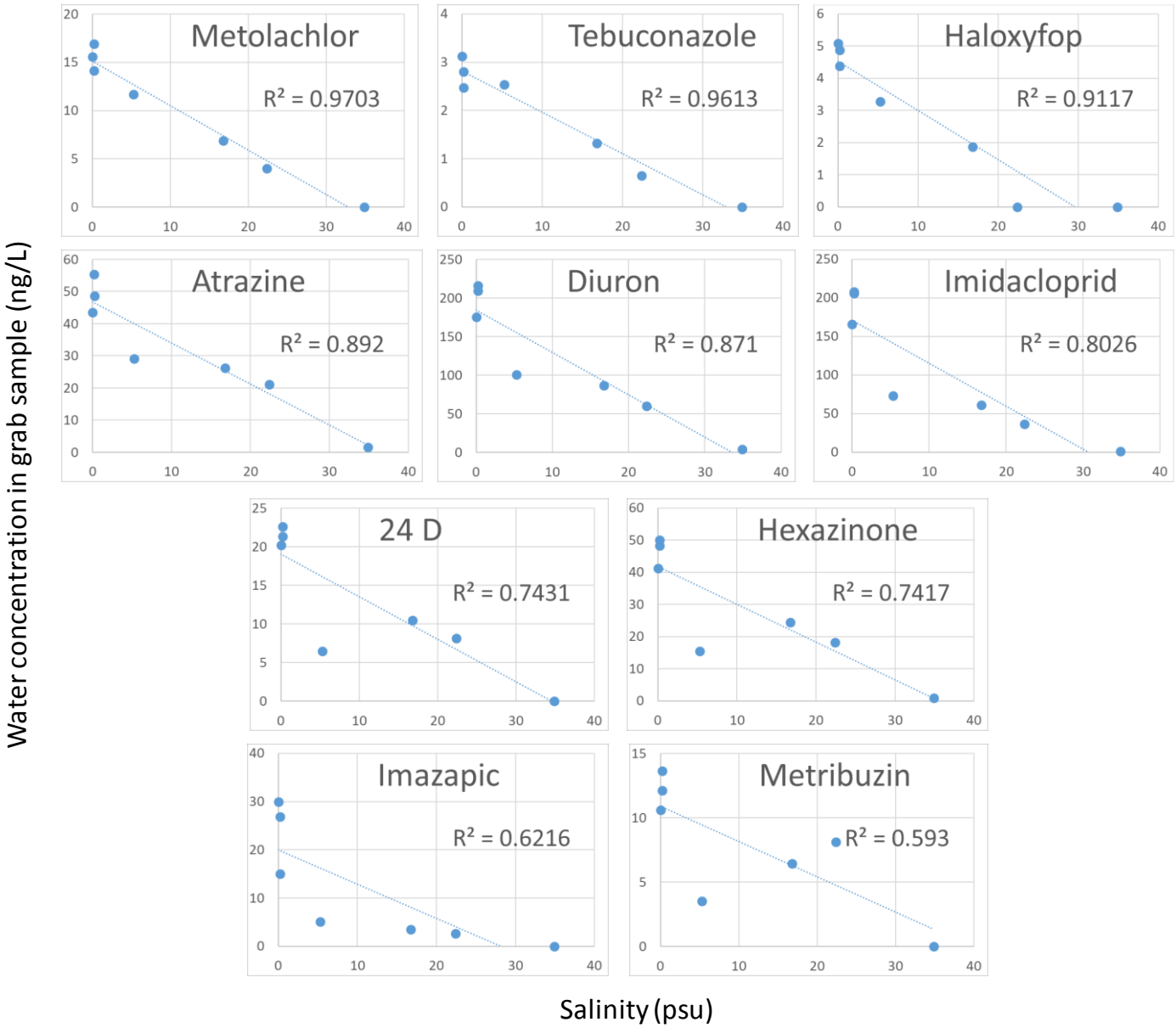



Figure 12: Relationship between pesticide concentrations in grab samples and water salinity (psu) for samples collected on 11 January 2017 along a salinity gradient running from the lower Tully River (0 psu) to marine waters at Bedarra Island (35 psu). The average of concentrations measured in replicate analyses (samples P2 and P10) are plotted.

### *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 2016–17, after two very low discharge years, discharge from the Burdekin catchment to the Reef lagoon had increased back to long-term average levels (Table 5). The first notable rain of the season fell at the end of 2016 with a first flush of Barratta Creek in early January 2017. Two smaller flow events occurred later in January and in March 2017 and river flow was minimal for the remainder of the year (Figure 13). Peak concentrations of PSII herbicides at Barratta Creek monitoring site were associated with the first January high flow event (Figure 13 A). The current year PSII-HEq Max was comparable with the previous monitoring year (Table 9, for historical data see Appendix H Figure H-8).

Table 9: Summary statistics for passive sampler 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 2016-17 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 2016-17 | 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 | 12 | 6.1 | 5.0 | | | | | | | | | | 1.0 |
| | PSII-HEq Dry Avg | | 0.64 | *0.16*† | - | | | | | | | | | | |
| | PSII-HEq Max | | **25** | **18** | **8.8** | | | | | | | | | | |

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

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

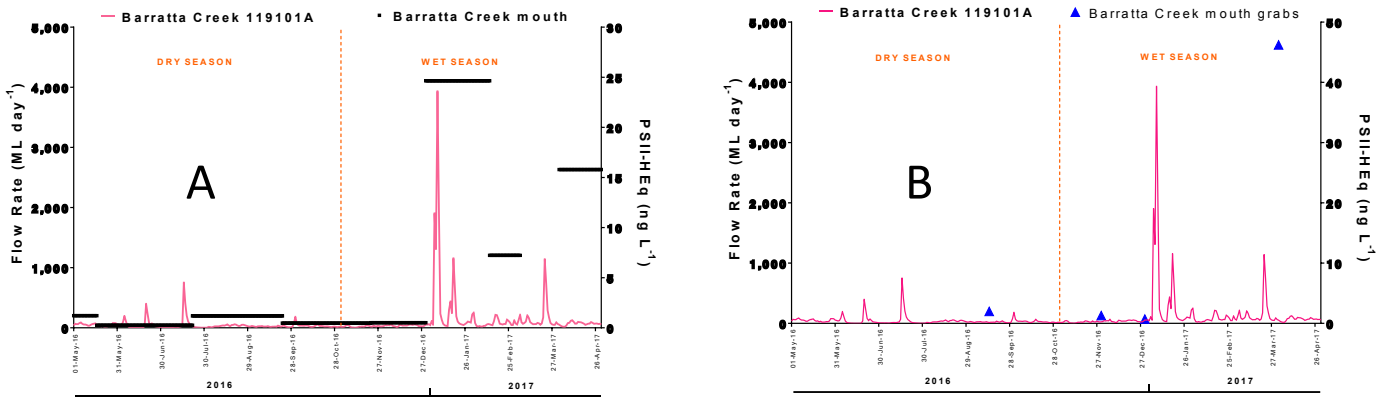



Figure 13: Temporal trends in PSII-HEq at Barratta Creek mouth fixed passive sampling site (A) and PSII-HEq levels in grab samples from (B) Barratta Creek mouth in 2016–17 , relative to the flow rate of the rivers influencing the sampling sites. Flow data provided by Department of Environment and Resource 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 (Appendix F Table F-7), above detection limits in most of the wet season samplers. Only fluometuron, prometryn and terbutryn were not detected in any sampler. Barratta Creek was the only monitoring site in 2016–17 where ametryn was consistently detected, albeit at low levels, throughout the year. Of the other pesticides only metolachlor was frequently detected and unusually elevated levels (for this site) were measured in the dry season, Aug-Sept 2016 sampler (4.4 ng $L^{-1}$). Using PDMS samplers, chlorpyrifos and pendimethalin were detected throughout the wet season but at very low concentrations (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 2016–17 and, in contrast to monitoring sites in the other NRM regions, atrazine levels were higher than diuron in all sampling periods. In early January 2017, when the highest concentrations were measured, atrazine made up 60 per cent of the total PSII herbicide concentration (Figure I-6) and represented 27 per cent of the PSII-HEq concentration.

### *4.3.2.1 Burdekin focus region flood plume sampling*

In addition to deploying passive samplers at the Barratta Creek mouth, grab samples were also collected from this location throughout the year. During the low flow period from September to December 2016, pesticide levels were very low in the grab samples from the creek mouth and mainly atrazine was detected at levels above the LOD (resulting in a PSII-HEq Max of 2.0 ng $L^{-1}$, Table G-1). In contrast, a sample collected on 1 April 2017, following the second major flow event of the wet season (and four days after tropical cyclone Debbie made landfall to the south at Airlie Beach), had a several-fold higher PSII-HEq concentration (46 ng

$L^{-1}$, high Category 4) compared to the previous monitoring year (PSII-HEq Max of 12 ng $L^{-1}$ in the first flush event of the year) (Appendix H, Figure H6-B).

The PSII herbicide profile in the April 2017 Barratta Creek sample was dominated almost exclusively by atrazine. The grab sample also contained relatively elevated levels of 2,4-D and MCPA (18 ng $L^{-1}$ of each). Whilst 2,4-D is typically observed in the passive samplers in this location, MCPA was detected at very low levels in only two sampling periods in 2016–17 . The appearance of MCPA in the grab samples is consistent with an end of catchment annual load of 27 kg (Table 6), however the timing of the load is not known so temporal comparisons between catchment releases and grab/passive sampling activities cannot be made. A grab sample from the Burdekin River mouth collected on the day prior to the Barratta Creek 1 April grab sample, contained only very low levels of pesticides (PSII-HEq of 0.9 ng $L^{-1}$, low Category 5), with tebuthiuron being the highest concentration pesticide in the sample.

### *4.3.3 Mackay Whitsunday region*

The Mackay Whitsunday region had the highest rainfall of all the Reef discharge catchments in 2016–17, largely associated with tropical cyclone Debbie which resulted in over 500 mm of rain falling in all catchments relevant to this monitoring program in the last week of March 2017 (Table 4). Consistent with this, the annual discharge from the major rivers in the region were all above the long-term (LT) median (1.7 – 2.1 times the LT average; Table 5). Three distinct wet season high flow events characterised the river flow across the region (early January, early February and the highest flow in late March), with low or no flow typically through the rest of the year except for one dry season event in July 2016 (Figure 14).

Small first flush events of the wet season, although typically at lower flow rates than the high flows later in the season, were associated with elevated pesticide concentrations at Repulse Bay and Sandy Creek (Figure 14). Incomplete sampling records were available for the rest of the wet season at Repulse Bay, Round Top Island and Sandy Creek, mainly due to sampler losses as a result of tropical cycloneDebbie. For Round Top Island and Sandy Creek, samples were obtained during the first of the wet season's high flow events (January 2017) and these were the highest recorded pesticide concentrations at these sites since 2014-15 when sampling commenced at both sites (PSII-HEq Max of 670 and 148 ng $L^{-1}$, respectively; Table 10, Figure 14 B,C). The PSII herbicide levels recorded at Round Top Island were also the highest reported in ED samplers across all the sites currently being monitored, compared to both current year and all historically reported levels.

At Sarina Inlet, where a complete wet season data set was obtained, the highest pesticide concentrations were observed in late February 2017 following a smaller (fourth) flow event. These high levels may be a result of a small flow event coinciding with pesticide applications in the catchment and therefore dilution effects were minimal. Dilution effects associated with the high post-tropical cyclone Debbie water volumes likely led to relatively lower concentrations during this high flow event (Figure 14). At Sarina Inlet, PSII-HEq Max levels (77 ng $L^{-1}$; Table 10) were higher than the previous two years, but still several fold lower than the concentrations in the 2009-10 and 2012-13 very wet years (Appendix H, Figure H-10).

PSII-HEq Max values at sites located in this region have been consistently higher than sites in other NRM regions and this is the eighth consecutive year that a Mackay Whitsunday's site had 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, 29 per cent of values have been Category 4 and a further 47 per cent as either Category 2 or 3 (Table 10). These comparatively higher concentrations may reflect the land use, pesticide usage and land management practices of the adjacent catchment, but also the ideal positioning of the monitoring sites to intercept flood plumes from nearby rivers.

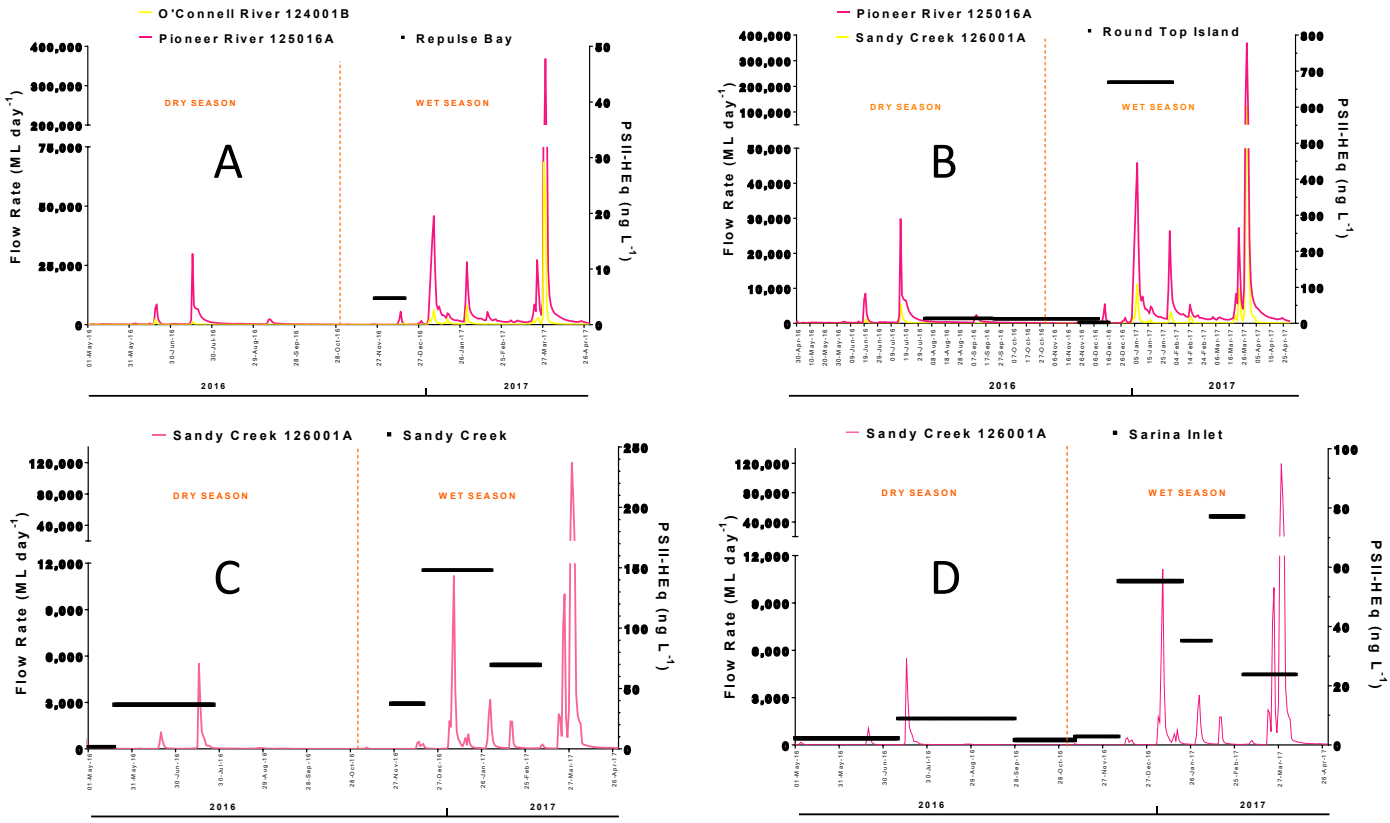



Figure 14: Temporal trends in PSII-HEq in 2016–17 , relative to the flow rate of rivers influencing the four Mackay Whitsunday fixed passive sampler sites. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network.

Table 10: Summary statistics for passive sampler 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 2016-17 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 2016-17 | 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 | *4.8*† | *2.6*† | 11 | | | | | | | | | | 1.0 |
| | PSII-HEq Dry Avg | | - | 0.29 | - | | | | | | | | | | |
| | PSII-HEq Max | | ***4.8***† | ***2.6***† | **34** | | | | | | | | | | |
| Round Top Island | PSII-HEq Wet Avg | 2014-15 | 228 | 198 | 1.6 | | | | | | | | | | 1.0 |
| | PSII-HEq Dry Avg | | *14*† | 1.7† | - | | | | | | | | | | |
| | PSII-HEq Max | | **670** | **533** | **2.2** | | | | | | | | | | |
| Sandy Creek | PSII-HEq Wet Avg | 2014-15 | 85 | 17 | 17 | | | | | | | | | | 1.0 |
| | PSII-HEq Dry Avg | | *37*† | - | - | | | | | | | | | | |
| | PSII-HEq Max | | **148** | **55** | **70** | | | | | | | | | | |
| Sarina Inlet | PSII-HEq Wet Avg | 2009-10 | 39 | - | 18 | 14 | 85 | 12 | 22 | 114 | | | | | 1.0 |
| | PSII-HEq Dry Avg | | 4.3 | 0.39 | 1.7 | 2.3 | 3.6 | 1.4 | 2.4 | 0.88 | | | | | |
| | PSII-HEq Max | | **77** | **0.44*** | **36** | **34** | **234** | **22** | **47** | **495** | | | | | |

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

**Dry season data only*

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

Consistent with 2015-16 profiles, PSII herbicides (and metabolites) detected at sites in this region include ametryn, atrazine (and its metabolites), 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 pesticides, imidacloprid, 2,4-D and metolachlor, were regularly detected, and metsulfuron-methyl was above detection limits in this region only. Using PDMS

samplers, propaconazole and pendimethalin were detected at low concentrations, whilst chlorpyrifos was close to the marine guideline value in one sampling period at Round Top Island. It should be noted that the concentrations of 2,4-D, imidacloprid, metolachlor, metsulfuron-methyl and chlorpyrifos were not included in the calculation of the risk category, and therefore the risk from all pesticides could be different (e.g. depending on whether synergism or antagonism may be occurring) in this region than what is reported here.

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 670 ng $L^{-1}$, which is a Category 2 risk of herbicide exposure on the PSII-HEq Index (Table 10). The current year maximum concentration exceeded the 2015-16 maximum at this site (530 ng $L^{-1}$) and was of a similar magnitude to levels measured at Sarina Creek in the wet 2009-10 year. 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, 47 days (consistent with the sampler deployment period). No samples could be obtained for the rest of the wet season, so it is not known if this was the maximum actual concentration for the year and for how long elevated concentrations were maintained at this site. Round Top Island is not currently a monitoring site for either coral or seagrass under the MMP.

As discussed above, although ANZECC and ARMCANZ (2000) guideline values were not exceeded in 2016–17 , some pesticide concentrations observed at Round Top Island (Figure 14; Appendix F Table F-9) were higher than the proposed DGVs in 2016–17 (diuron and imidacloprid). This is the second year running that wet season levels have exceeded the proposed (but unendorsed) DGVs in a deployment period at this site. 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. In 2015-16, it was concluded that the low dilution effects associated with drier years may explain the high pesticide concentrations observed at Round Top Island. In the current year, this may also hold as the high concentrations were observed in the first flush event of the year and not during the high cyclone-related flows later in the year. Temporal understanding of end-of-catchment releases of pesticides from the Pioneer River, as well as modelling the pesticide movement from the Pioneer River into the nearshore environment, would be options to better understand the observed high levels. The latter 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*

The discharge from the Fitzroy River was higher in 2016–17 than the long term average (2.1 times the LT average; Table 5), however, river flow was low for most of the wet season with one major high flow event occurring in March 2017 following tropical cyclone Debbie (Figure 15). This pattern of flow is similar to the previous two monitoring years, although the major flood event in 2016–17 had higher flow than these previous years (Figure H-13). Despite this, concentrations of PSII herbicides during the wet season at North Keppel Island were low and almost identical to concentrations detected since 2013 at this site (Table 11: for historical data see Figure I-11).

PSII herbicides detected at North Keppel Island in 2016–17 included atrazine, diuron, hexazinone, simazine and tebuthiuron (Table F-12). Atrazine and diuron (maximum concentrations both <1 ng $L^{-1}$) were detected most frequently at this site (in all but one sampler) but at very low concentrations. Tebuthiuron typically

dominates the PSII herbicide profile at North Keppel Island (Figure I-11) and the highest concentration (2.3 ng $L^{-1}$) was observed during the dry season small flow event in July 2016 (Figure 15; Table F-12).

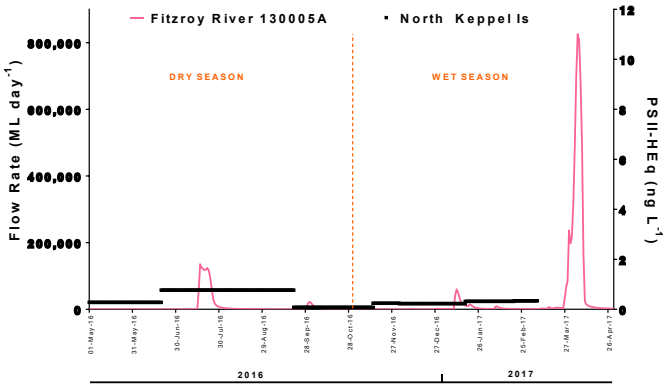



Figure 15: Temporal trends in PSII-HEq in 2016–17 , relative to the flow rate of the Fitzroy River influencing N Keppel Island's fixed passive sampler site. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network.

Table 11**:** Summary statistics for passive sampler 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 2016-17 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 2016-17 | 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 | 0.28 | 0.30 | 0.26 | 0.18 | 4.4 | 1.7 | 4.0 | 4.1 | 0.73‡ | 1.9 | 0.94 | 1.7 | 1.00 |
| | PSII-HEq Dry Avg | | 0.38 | 0.11 | 0.07 | 0.38 | 0.88 | 0.42 | 0.69 | - | 0.86 | - | 0.45 | 0.07 | |
| | PSII-HEq Max | | 0.77 | 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 (ten out of the twelve years) being Category 5 on the PSII-HEq Index. The 2016–17 PSII-HEq Max at this site was the 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 15).

### *4.3.5 Post-tropical cyclone Debbie flood plume sampling (all regions)*

Sampling took place in flood plumes from four Reef catchments (Pioneer, Proserpine, O'Connell and Fitzroy Rivers, all impacted by tropical cyclone Debbie) on 9-11 April 2017, approximately two weeks after the cyclone once conditions were safe to undertake a sampling campaign. The highest PSII-HEq concentrations were observed in a sample from the Pioneer River (65 ng $L^{-1}$; Table G-1; Category 3 on the PSII-HEq Index), and levels were also elevated at its river mouth and in the river mouth of the O'Connell River (both Category 4). The other samples were mostly Category 5, which likely reflects both the timing of the collections and also the very high dilution factors associated with the high volumes of water released from the catchments during this event. The Mackay Whitsunday's grab samples all had very similar pesticide profiles, dominated by atrazine, diuron, hexazinone, 2,4-D and MCPA. The grab sample profiles differed to the passive ED samples in that tebuthiuron was found in all ED samples but not in the grabs, whereas MCPA was in the grabs but not the ED samplers. Differences are may be due to timing of sample collection relative to pesticide application in the catchments.

# 5. Discussion

**Pressures and overall trends in pesticide levels at fixed monitoring sites.** The pressures governing the release of pesticides into the Reef lagoon were highly localised in the current monitoring year. River discharge in the northern NRM catchments (Wet Tropics and Burdekin) was at or below the long-term averages in 2016–17 , and for both regions wet season rainfall was lower than average. Further south, in the Mackay Whitsunday and Fitzroy regions, the impacts of tropical cyclone Debbie in late March 2017 resulted in an overall increase in both wet season rainfall and river discharge compared to long term averages. River discharge was >1.5 times the long-term average, although hydrographs from the region indicated that most of this increase in flow occurred at the end of the wet season and the rest of the wet season, including the first flush events, were comparable to the previous 'dry' years. With a few exceptions, total catchment run-off, quantified as pesticide end-of-catchment annual loads, was at least double that of 2015-16 levels across most catchments, reflecting increases in both PSII herbicide and other pesticide loads. In particular, maximum end-of-catchment loads of bromacil, simazine and MCPA increased between 9- and 132-fold. The profiles of pesticides in the discharged loads were broadly in line with recent years with no major changes except for a shift in profile towards higher tebuthiuron and simazine loads in the Fitzroy catchment, as well as relatively higher atrazine and MCPA in the Tully catchment, compared to the previous two years.

In line with the 2016–17 increased pressures, time integrated (or chronic) pesticide concentrations at fixed monitoring sites were, at most sites, higher than the previous monitoring year. Based on the sampler returns for the year, the observed increase in pesticide concentrations was highest for the northern Reef catchments, consistent with moderately increased river discharge but a doubling of the end-of-catchment loads. The wet season record in the southern regions did not include the period during the maximum river discharge. Highest river flows experienced in the southern regions were associated with tropical cyclone Debbie, and samplers in the most impacted regions were lost during this period. Although the levels of pesticides reaching the southern monitoring sites following the cyclone are not known, dilution effects associated with the large volumes of water during this event are likely to have reduced pesticide concentrations in the flood plume compared to the first flush events, as was observed at Sarina Inlet where the sampler was successfully retrieved.

Overall, despite a year-on-year increase, time integrated (or chronic) pesticide concentrations were generally lower than levels during past 'high' pressure La Niña years when rainfall and cyclonic activity were considerably above long-term averages. As in 2015-16, there was one significant exception to this trend at Round Top Island in the Mackay Whitsunday region. Although incomplete wet season data was obtained, mainly due to sampling equipment losses during the cyclone, the maximum pesticide concentration recorded at this site (January 2017) was the highest since monitoring began for the sites currently monitored. Concomitant with these high pesticide levels, there were proposed guideline value exceedances for two pesticides, diuron and imidacloprid (and chlorpyrifos was close to the existing guideline value). This is the second year running that the proposed DGVs were exceeded at this site (incomplete data from 2014-15 does not allow comparison with the first year of sampling), suggesting that, if the proposed DGVs are endorsed, this may be scored as a higher risk site. To understand the relatively higher concentrations at this site, compared to other sites, it is necessary to consider end-of-catchment loads, location of the monitoring site, flow patterns and other factors effecting the transport of pesticides from the river mouth to the site. In 2016–17 , end-of-catchment loads were almost identical between Tully River (Dunk Island monitoring site) and Pioneer River (Round Top Island monitoring site), yet PSII-HEq Max for the passive sampler deployment period was 100-fold higher at Round Top Island (7.4 and 670 ng $L^{-1}$, respectively). Round Top Island is in close proximity to the Pioneer River mouth (~5 km) making it ideally positioned to intercept flood plumes. In addition, overall flows from the Pioneer River are lower than the Tully (which flows year-round) and more

seasonal (the hydrograph indicates most flow is associated with high flow events) potentially resulting in more concentrated run-off conditions.

As suggested by the current year's data, 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 run-off, 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 run-off 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 run-off 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), should be considered for future reporting.

**PSII herbicide profiles.** Consistent with previous monitoring years, diuron, atrazine and hexazinone were the most consistently 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, Grant et al. 2017). 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 mirrors 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 2012c). 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, d, 2016). 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 2016–17 . 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 (1,700 kg). Following large loads of tebuthiuron discharged from the Fitzroy (total of 11,890 kg) and Burdekin Rivers (total of 1,070

kg) between 2010 – 2013, tebuthiuron levels dropped considerably but as of 2016–17 had increased 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 insecticides, fungicides and other herbicides (i.e. herbicides that are not used as a PSII herbicide alternative weed control e.g. metsulfuron-methyl). The prevalence and loads of other pesticides are now being monitored as part of GBRCLMP alongside the PSII herbicides targeted as a priority for reduction in *Reef Plan* (2009 and 2013). Overall, the contribution of the other pesticides (in sum total) to the annual load of all pesticides was higher in 2016–17 compared to historical load profiles, reflecting increasing usage of other pesticides: for example, in 2016–17 , the load of non-PSII inhibiting pesticides ranged between 19 – 113 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, Herbert and O'Connell Rivers), total loads of other pesticides were higher than the total for PSII herbicides.

A marked shift in the overall load profile of other pesticides released to the Reef lagoon (for catchments adjacent to fixed monitoring sites) was observed in 2016–17 compared to the previous year (Figure 16). For the catchments relevant to this report, run-off, and therefore possibly usage, of 2,4-D dominated in 2016–17 and notable increases in MCPA, haloxyfop and imazapic loads were observed.

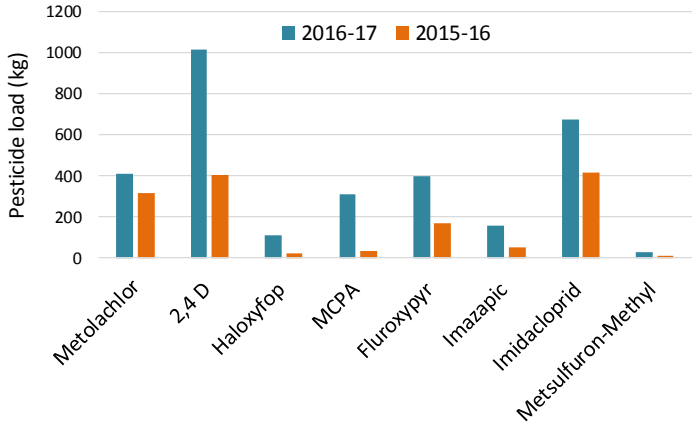



Figure 16: Total end-of-catchment load of other pesticides monitored under the GBRCLMP, summed for all catchments relevant to fixed monitoring sites in this report (excluding Proserpine River which was introduced in 2016–17 ). Data from Huggins et al (*in prep*)

Routine analysis of other pesticides in both passive and grab samples was initiated in 2014-15, and most pesticides have been detected since then in the ED (polar) passive samplers at most sites. Reflecting the end-of-catchment loads in 2016–17 , metolachlor, 2,4-D, MCPA, imidacloprid and chlorpyrifos were consistently detected in passive samplers in the current monitoring year. Fluroxypyr, although increased in load, was only detected in three samples. Compared to PSII herbicides, however, detected concentrations of other pesticides at the monitoring sites were generally very low; except for isolated samples from Round Top Island and Sandy Creek, other pesticide concentrations at all sites were <5 ng $L^{-1}$.

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 herbicides, 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 Sandy Creek and Sarina Inlet, 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, however, 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 other pesticides used in the Reef catchments are less 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 2016–17 ) 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 concentration addition (CA) model (for PSII herbicides with the same mode of action) has been developed by DES (formerly DSITI) and was assessed for use for nearshore pesticides MMP reporting in the previous year's report (Grant et al. 2017). Some inconsistencies in the application of the current CA model to marine environments were identified through

the case study in the previous year's report (Grant et al. 2017). Once these considerations have been addressed (if required) and when development of the response addition model (for pesticides with different modes of action) has been completed (in progress by DES), 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 and salinity gradients.** 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. Pesticide levels over flood plume salinity gradients were also assessed in 2016–17 to understand the mixing processes of pesticides in flood plumes, which in turn informs on the fate and transport mechanisms that are driving pesticide movement into the nearshore environment.

In 2016–17 , matched 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 offshore sites (e.g. up to 14 km in the case of Dunk Island on the Tully River transect) were elevated when compared to pre-event concentrations sites but were generally <20% of those at the river mouth. 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.

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 to pesticides in nearshore marine areas as demonstrated in this MMP may still have negative 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 pesticide 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).

The salinity gradient data for the wet season Tully River flood plume indicated that conservative mixing was occurring for pesticides (i.e. the ten pesticides that were consistently above LOD and could be assessed) in this plume. Consistent with mixing data presented by Lewis et al. (2009) for diuron, atrazine and hexazinone from three Reef catchments, the correlations between water concentration and salinity indicate that pesticides were not being removed from the flood waters during the mixing/dilution with seawater, through physical (e.g. flocculation), chemical (e.g. photolysis) or biological (e.g. biodegradation) processes. The linear relationships further suggest that pesticides remain in the dissolved phase rather than bound to particulates such as sediment (Lewis et al. 2009). The physical removal of sediment-bound pesticides near the mouth of the river via flocculation processes would result in non-linear relationships between concentrations and salinity, as would degradation of pesticide or uptake by biota in the flood plume.

The salinity gradient data from the dry season sampling did not indicate that conservative mixing was occurring in the flood plume. Whether and how the plume flow rates and timing of sample collection impact the mixing behaviour of pesticides are factors to consider for future studies.

**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 chemicals 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 run-off (i.e. end-of-catchment loads) and those pesticides monitored in near shore areas. Temporal end-of-catchment data, e.g. daily loads and/or average daily water concentration rather than a single annual load, would allow a more direct comparison between end-of-catchment pesticide data for major flow events and the levels reaching fixed monitoring sites. At present these data are not available to the MMP due to inconsistencies in timing of reporting cycles between monitoring programs.

Relatively low levels of PSII herbicides were detected at most sites in 2016–17 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 2013–14 MMP review, six of the current eleven fixed monitoring sites have at most three years of monitoring data. For these sites, additional years of data are necessary for robust trend analyses. Efforts to ensure that complete sampling records are obtained, wherever possible, in future monitoring years are also essential to allow meaningful trend assessments. In the current monitoring year, no data were obtained for one of the sampling sites (Normanby Island). Whilst this situation has been rectified for the 2017–18 sampling year, appropriate action to minimise avoidable sampler non-deployments are paramount.

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 framework potentially provides 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 a logical approach to attempt to understand the complexity of pressures that may result in pesticides reaching sensitive Reef ecosystems. In 2016–17, 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 pesticide concentrations observed at most fixed monitoring sites were consistent with the end-of-catchment loads and river discharge patterns 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 36 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 two or three years of continuous data. With the exception of the localised impact of tropical cyclone Debbie towards the end of the 2016–17 wet season, pressures over the last three 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 end-of-catchment load data (e.g. daily loads) 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. At present these data are not available to the MMP due to inconsistencies in timing of reporting cycles between programs.

The current pesticide metric, the PSII-HEq index, was identified as a suitable interim risk indicator in the 2013-14 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. Some inconsistencies in the application of the current concentration addition model to marine environments were identified through the case study in the previous year's report (Grant et al. 2017). Once these considerations have been addressed (if required) and when development of the response addition model has been completed by DES, 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.

# 7. CASE STUDY: Non-target suspect screening of selected passive and grab samples

## 7.1 Introduction

The Great Barrier Reef (the Reef) receives run-off from 35 river basins (or catchments). Currently, approximately 80% of the entire Reef catchment area is dedicated to agricultural activities with grazing, forestry and cropping being the primary land uses. Pesticide run-off from diffuse agricultural land uses has been identified as a high risk threat to Reef ecosystems and heritage values (GBRMPA 2014). However, there are many other activities occurring within Reef catchments such as aquaculture, ports, urban run-off, waste water treatment plants (WWTPs) and heavy industry. Effluent discharge from WWTPs is considered one of the most significant sources of pharmaceuticals, personal care products, and other chemicals associated with household consumer products (such as flame retardants and perfluorinated chemicals), with the risk greatest around urban centres and areas of human water activities (Kroon et al. 2015). All of these other activities represent small yet still important sources of land-based chemical pollutants that may also impact the health and resilience of Reef ecosystems. As the human population and development of Reef catchments increases over the coming decades, chemicals associated with urban and industrial uses may become of greater concern to coastal marine ecosystems.

Currently across all Reef water quality monitoring programs, the investigated organic pollutants are measured using targeted liquid or gas chromatography/ tandem mass spectrometry analytical methods. This method is limited to a pre-determined selection of known chemicals and requires a commercially available chemical standard for accurate quantitation and identification. In reality, there is a complex mixture of both ‘known’ and ‘unknown’ chemicals present in the environment. There is a lack of knowledge surrounding exactly what types of pesticides, herbicides and other chemicals associated with human activity are in use in Reef catchments and subsequently entering the marine environment. Environmental monitoring using non-target suspect screening high-resolution mass spectrometry is a comprehensive approach to determine the exposure of marine ecosystems to un-targeted anthropogenic pollutant mixtures. Non-targeted suspect screening analysis is becoming increasingly useful to gain a broader understanding of the presence of chemicals in complex environmental samples. In this case study we applied this method to both grab and passive sampler extracts from the 2016–17 monitoring year to tentatively identify chemical pollutants in the Reef waters. High resolution MS/MS data was screened and matched with comprehensive library spectra. In addition, using a mathematical algorithm approach that uses whole sample peak feature lists, a comparison was made to recognise any chemical profile similarities and differences between sites.

## 7.2 Methods

### 7.2.1 Methodology for suspect screening approach

Samples were analysed by a Shimadzu Nexera X2 UHPLC system coupled to a Sciex 5600 Triple-TOF mass spectrometer. Chromatographic separation was achieved on a Kinetex Biphenyl column (50 × 2.1 mm, 2.6 µm, Penomenex) at 50 °C using 0.1% formic acid in MilliQ water as mobile phase A and 0.1% formic acid in methanol as mobile phase B at a flow rate of 0.4 mL/min. The gradient started at 5% B for 0.1 min, then ramped up to 100% B in 10 min with a non-linear Curve 2 and maintained at 100% B until 14.5 min before changing to 5% B for equilibration for 2.2 min. The mass spectrometer was equipped with a DuoSpray® Ion Source and operated in both positive and negative modes with data-independent SWATH acquisition. The source parameter settings were: curtain gas (CUR) 30, ion source gas 1 and 2 (GS1 and GS2) 60, ionspray voltage floating (ISVF) 5000, and temperature (TEM) 550. Each cycle comprised a MS survey scan with a mass range of m/z 50 to m/z 1200 followed by MS/MS fragmentation scans of 24 SWATH precursor windows covering the same mass range. The total cycle time was 820 msec. For both MS and MS/MS scans,

declustering potential (DP) was set at 80. During MS/MS scans, the collision energy (CE) was set at 35V and the collision energy spread (CES) was set at ± 15V.

### 7.2.2 Data Processing and library search

MS and MS/MS data were acquired in high-sensitivity mode with data independent (Sequential Window Acquisition of all Theoretical fragment-ion spectra, SWATH) mode. The declustering potential and collision energy were (-)80 V and (-)10 eV in the full-scan TOF-MS experiment, with a mass range of 50-1200 m/z. SWATH experiments consisted of a single MS scan (accumulation time, 50 ms) followed by a series of product ion scans (accumulation time, 30 ms each) of 24 isolation windows from m/z 50 to 1200, overlapping by one mass unit. MS/MS spectra were acquired at (±)35 eV with a collision energy spread of 15 eV. Total cycle time for the TOF MS and 24 SWATH MS/MS scans was 800 ms. Data were processed with PeakView®, MS Library and MultiQuant software (SCIEX). Confirmation of target analytes was based on retention time (±0.5 min), accurate mass (mass error <5 ppm; mass error score >80%), isotopic distribution (isotope score >60%) and automatic MS/MS library searching (library score >70%). Extracted ion chromatogram (XIC) parameters were set to >300, corresponding to a signal-to-noise ratio of five, and XIC width was set to 0.01 Da.

Nine samples underwent suspect screening including six passive samplers, and three grab samples (Table 12). Each were processed against a laboratory blank ED extract to eliminate false positives.

Table 12**:** Details of samples that underwent suspect screening

| Sample Location | Sample ID | Deployment Period/ Date | Sample Type |
|---|---|---|---|
| Barratta Creek mouth | BARR_01 | 17/05/16 – 22/07/16 | Passive sampler (ED) |
| Barratta Creek mouth | BARR_02 | 30/12/16 – 12/02/17 | Passive sampler (ED) |
| Barratta Creek mouth | BARR_03 | 12/02/17 – 5/03/17 | Passive sampler (ED) |
| Lucinda | LUC | 10/05/16 – 06/07/16 | Passive sampler (ED) |
| Sandy Creek | SAN | 02/02/17 – 07/03/17 | Passive sampler (ED) |
| Sarina Inlet | SAR | 01/05/16 – 10/07/16 | Passive sampler (ED) |
| Proserpine River mouth | PRO | 09/04/17 | Grab sample |
| Russell Mulgrave River mouth | RM | 17/2/17 | Grab sample |
| Tully River mouth | TUL | 18/2/17 | Grab sample |

### 7.2.3 Methodology for algorithm based non-target ‘unknown’ identification

After peak picking each sample contained around 2,500 features. These features were identified after alignment using an in-house developed algorithm with a retention window of ±0.05 min and a mass window of ±2 mDa. After the alignment, principal component analysis (PCA) was used for the prioritization of features. PCA was performed on the mean centered and standardized data (i.e. division by the standard deviation in each sample). Using the first three principal components, 13 features were identified, which explained most of the variability observed in the dataset. These 13 features underwent a subsequent identification workflow.

For the identification, we manually extracted the top 15 fragments (i.e. those with the highest intensity) for each feature. These fragments combined with the measured accurate mass of the feature were employed in chemical formula prediction. This was performed utilizing CSI:FingerID web version with a mass accuracy of 20 ppm. The candidate chemical formula with highest number of described fragments was selected for further analysis. The selected structure was compared to the PubMed database for further confirmation. Finally, the most likely structure based on the matched fragments and the PubMed database went through *in-silico* fragmentation via CFMID algorithm. This produced an independent confirmation of the finally selected structure.

Six samples from three locations (replicate samples from Barratta Creek mouth, Round Top and Sandy Creek), underwent non-target screening (Table 13). Samples had been diluted 50 times from the original extract due to high concentrations found during target analysis.

Table 13 Details of sampling sites that underwent non-target identification

| Sample Location | Sample ID | Deployment Period/ Date | Sample Type |
|---|---|---|---|
| Barratta Creek mouth | BARR_01 | 17/05/16 – 22/07/16 | Passive sampler (ED) |
| Round Top Island | RFT | 17/02/17 – 02/02/17 | Passive sampler (ED) |
| Sandy Creek | SAN | 17/02/17 – 02/02/17 | Passive sampler (ED) |

## 7.3 Results and Discussion

A range of chemical pollutants were identified at all sampling locations using a combination of passive and grab water sampling techniques. Suspect screening tentatively identified 27 chemicals that have not been previously reported by this MMP. Note that this list is not necessarily exhaustive for these samples but represents the chemicals that could be identified within the time frame and resources available. Identified chemicals included pharmaceuticals (eight), personal care products (two), illicit drugs (one), endogenous chemicals (thirteen), fungicides (two) and herbicide metabolites (one) (Table 14). An example of the LC-QTOF MS/MS output for one identified chemical, tryptamine, is shown in Figure 17. In addition, 14 chemicals (i.e. herbicides and pesticides) that are listed on the MMP priority list for reporting and are already routinely analysed by this MMP (Appendix A, Table A-4) were also identified. As with all suspect and non-target analyses, suspect identifications should be regarded as tentative until mass, retention time and fragmentation pattern can be confirmed with an analytical standard.

Table 14 Chemicals (name, class and uses) identified during suspect screening

| Suspect | Chemical Class | Known Uses |
|---|---|---|
| 17alpha-Hydroxyprogesterone | Endogenous | Progestogen steroid hormone |
| 2-Octenoyl-carnitine | Endogenous | Lipid; fatty ester |
| 3,5-Diiodotyrosine | Endogenous | Precursor in the production of thyroid hormone |
| 5-Aminosalicylic acid, mesalazine | Pharmaceutical | Anti-inflammatory drug used to treat inflammatory bowel diseases |
| 6-APB/5-APB | Illicit | Psychoactive compound, a derivative of the designer drug 6-APB also known as 'benzofury' |
| 6b,17a-hydroxyboldenone | Endogenous | Anabolic steroid metabolite |
| Altretamine | Pharmaceutical | Antineoplastic agent used in cancer treatment |
| Amphetamine | Pharmaceutical | Potent central nervous system (CNS) stimulant that is used in treatment of attention deficit hyperactivity disorder (ADHD), narcolepsy, and obesity |
| Apophedrin | Pharmaceutical | Drug to produce topical vasoconstriction |
| Arterenol | Endogenous | Hormone and neurotransmitter, aka noradrenaline |
| Atrazine-2-hydroxy | Herbicide metabolite | Breakdown product of atrazine |
| Azoxystrobin | Fungicide | Proposed Australian use includes citrus fruit, almonds and legume vegetables |
| DEET | Personal care product | Active ingredient in insect repellent |
| Dehydroepiandrosterone (DHEA) | Endogenous | Steroid hormone |
| Metamfepramone | Pharmaceutical | Stimulant |
| Methyl nicotinate^ | Personal care product | Flavouring ingredient in alcoholic beverages; rubefacient in cosmetics |
| N2-Ethylguanin | Endogenous | DNA adduct |

| Suspect | Chemical Class | Known Uses |
|---|---|---|
| Norepinephrine | Endogenous | Hormone and neurotransmitter |
| O-Desmethylvenlafaxine | Pharmaceutical | Antidepressant |
| Phenethylamin | Endogenous | Neuromodulator/ neurotransmitter |
| Pilocarpine | Pharmaceutical | Medication used to treat increased pressure inside the eye and dry mouth |
| Progesterone | Endogenous | Progestogen steroid hormone |
| Pyridoxine | Endogenous | Also known as Vitamin B6, present in food and dietary supplements |
| Pyroquilon | Fungicide | |
| Serotonin | Endogenous | Neurotransmitter |
| Tranexamic acid | Pharmaceutical | Medication to prevent heavy bleeding |
| Tryptamine | Endogenous | Neuromodulator/ neurotransmitter |

^ Methyl nicotinate found in relatively small intensity in the blank sample

Suspect screening provides a qualitative profile of chemicals but is not quantitative and thus, concentrations could not be estimated. However, an indication of relative concentration between samples was determined by comparing intensities of the spectra peaks (Table 15). A larger intensity value is indicative of relatively higher amounts of a given suspect in a sample assuming similar matrix influences between samples.

Table 15 Relative intensities of chemicals identified during suspect screening

Lowest value 50% percentile Highest value

| Suspects Identified | Passive samplers | | | | | | Grab samples | | |
|---|---|---|---|---|---|---|---|---|---|
| | BARR_01 | BARR_02 | BARR_03 | LUC | SAN | SAR | TUL | PRO | RM |
| 17alpha-Hydroxyprogesterone | | | 247715 | | | | | | |
| 2-Octenoyl-carnitine | 44997 | | | 64156 | | | | | |
| 3,5-Diiodotyrosine | | 88884 | | | | | | | |
| 5-Aminosalicylic acid, mesalazine | | | | | | 1723423 | | | |
| 6-APB/5-APB | | | | | 225758 | 150081 | | | |
| 6β,17α-hydroxyboldenone | | | | 117621 | | | | | |
| Altretamine | | | 38013 | | | | | | |
| Amphetamine | | | | | 17550 | | | | |
| Apophedrin | | 437437 | 283955 | | 211118 | 233032 | | | |
| arterenol | | | | | | 32457 | | | |
| Atrazine-2-hydroxy | | 588473 | 252721 | | 322600 | 43903 | 10243 | 14774 | 27856 |
| Azoxystrobin | | | | | | | | | 207423 |
| DEET | | 1355560 | 3464045 | 113313 | 76693 | 349421 | 27098 | 33378 | 33003 |
| Dehydroepiandrosterone (DHEA) | | | | 35128 | | | | | |
| Metamfepramone | | | | | 161703 | | | | |
| Methyl nicotinate^ | 5305793 | | | | | | | | |
| N2-Ethylguanin | | | 401038 | | | | | | |
| Norepinephrine | | | | | | 32457 | | | |
| O-Desmethylvenlafaxine | | | | | | | | 84287 | |
| Phenethylamin | | 1218521 | 1335966 | 1264505 | 1018066 | 641355 | | | |
| Pilocarpine | | | | | 1169892 | | | | |
| Progesterone | | | 133820 | | | | | | |
| Pyridoxine | | | | | | 32457 | | | |
| Pyroquilon | | | | | | 871888 | | | |
| Serotonin | | | | | 167692 | 142353 | | | |
| Tranexamic acid | | | | | | | | | 10852 |
| Tryptamine | 215732 | 407113 | 501651 | 385716 | 117811 | 213514 | | | |

^Methyl nicotinate found in relatively small intensity in the blank sample

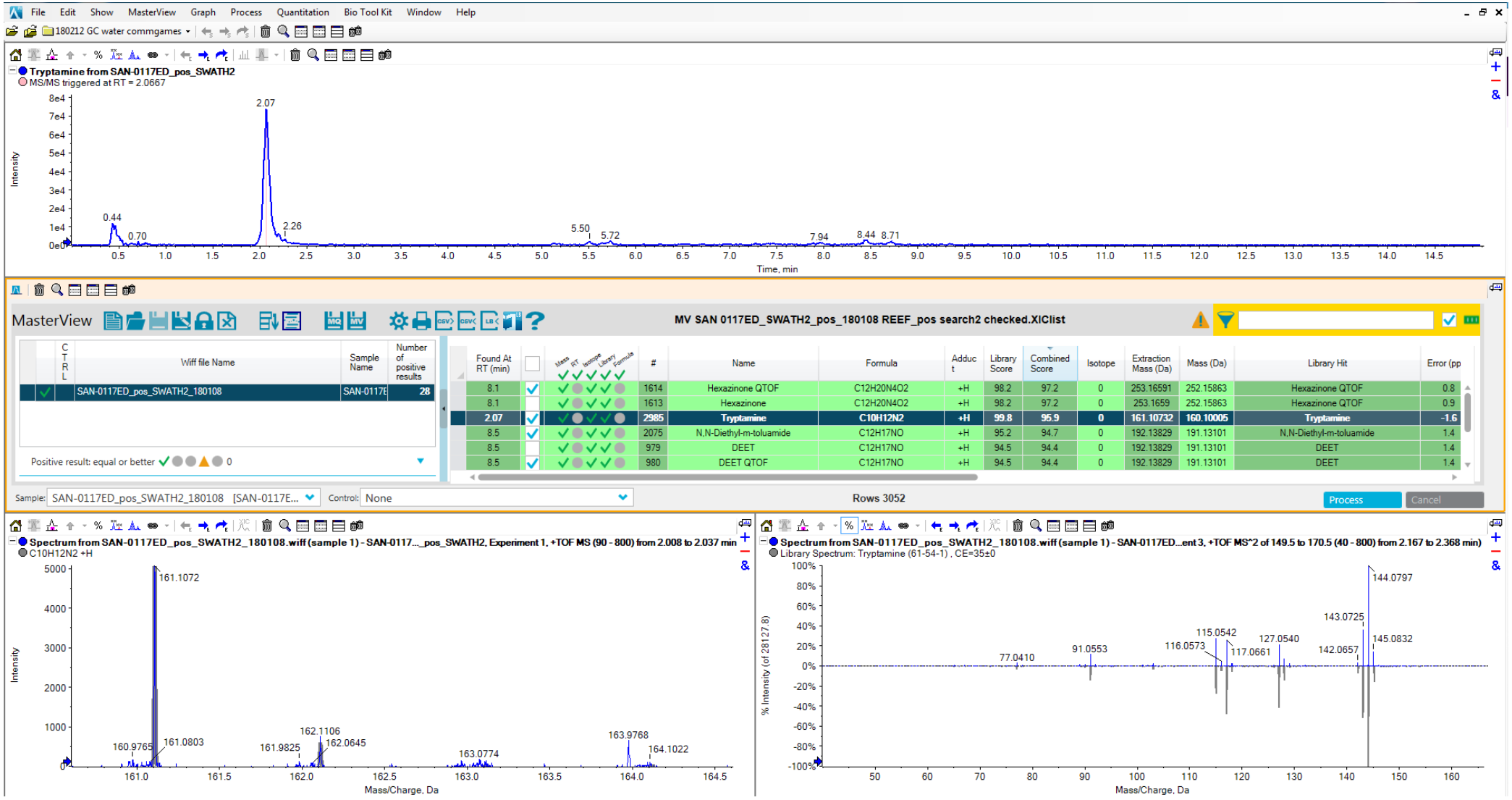



Figure 17. Tryptamide detected in SAN ED passive sampler on LC-QTOF MS/MS, using suspect screening. Top: Total Ion Chromatogram (TIC), Bottom left: MS spectra, Bottom right: MS/MS spectra with library match.

Excluding the MMP priority chemicals, the number of new suspects identified ranged between two and twelve per sample (Figure 18). On average, a greater number of identified suspects were present in the passive sampler extracts (between three and twelve) than the grab sample extracts (between two and four). Excluding the MMP priority chemicals, twenty-two suspects were unique to the passive samples, and three suspects were unique to the grab samples. Pharmaceuticals, personal care products and endogenous chemicals were more frequently detected in the passive samplers than the grab samples, due to longer-term accumulation in the samplers and therefore higher concentrations. This is despite WWTPs discharging treated effluent into Proserpine River and the Mulgrave River where grab samples were collected and screened. These lower frequencies of detection may be due to substantial dilution of the effluent by the time any associated chemicals enter the marine environment. Hence, they may require concentration in the passive samplers to exceed instrument detection limits.

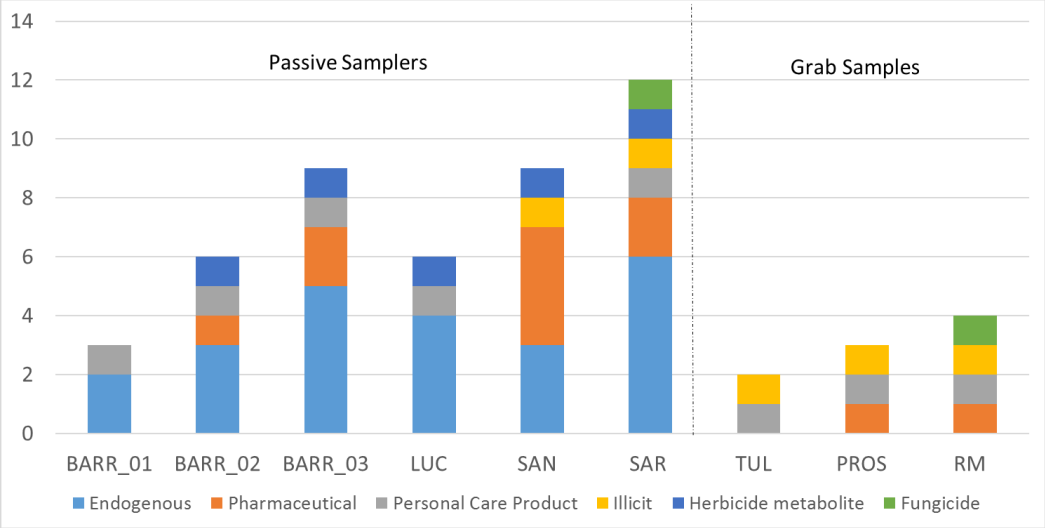



Figure 18. Number and class of suspects identified in each sample

DEET (personal care product present in insect repellents) was the most frequently detected suspect, found in eight out of nine samples (and also present in all blanks as background contamination), followed by the atrazine metabolite atrazine-2-hydroxy (seven samples); and the neuromodulators tryptamine (six samples) and phenethylamine (five samples). Both tryptamine and phenethylamine were detected in the passive samplers only. The flavouring agent methyl nicotinate, was found at the highest relative intensity of all suspects identified, in a single passive sampler located at Barratta Creek mouth.

At Barratta Creek, three passive samplers deployed from May – July 2016 (BARR_01), Jan – Feb 2017 (BARR_02), and Feb - Mar 2017 (BARR_03) were screened. The BARR_01 deployment occurred in the dry season, and the subsequent two deployments occurred during the wet season. The profiles of suspects identified in the two wet season samplers were similar, having five suspects common to both. A higher number of suspects identified in the wet season samples compared to the dry season is consistent with the overall trend observed in the routine pesticide monitoring where concentrations and the frequency of pesticide detections are usually elevated during the wet season.

A comparison of the routine and suspect screening results of the MMP priority chemicals found that the suspect screening was able to identify the most abundant chemicals usually present in both the passive and grab samples (such as diuron, atrazine and hexazinone). However, chemicals present at relatively low amounts (i.e. <10 ng/sample) were not always confirmed by the suspect screening. This is likely due to suppression of the suspect signal due to excessive background noise, as a high number of ions simultaneously flood the MS/MS detector. This is a consideration when interpreting the results of this case study as compounds at low concentrations will not be identifiable using this approach.

The algorithm-based non-target identification of 'unknown chemicals (i.e. looking for other peaks for which no entry in a suspect database exists) yielded 13 features whereby a chemical formula was identified. Eight of these could be tentatively identified with a chemical name (Table 16), although structural isomers are possible for several as indicated.

Table 16 'Unknown' chemicals by non-target identification

| Name | Formula | CAS | Commercial Use |
|---|---|---|---|
| Cycloleucylleucine | C12H22N2O2 | 952-45-4 | Personal Care product |
| 2-propylpentan-1-amine^ | C8H19N | 626-23-3 | - |
| 1-Aminonaphthalene | C10H9N | 134-32-7 | Anti-Infective Agents/ metabolite of Synthetic Cannabinoids MN-18 and Its 5-Fluoro Analog 5F-MN-18 |
| N,N-Dimethylnonamide | C11H23NO | 612-975-5 | Personal Care product |
| Deniose | C20H36O10 | - | - |
| 3-hydroxy-4-(pentan-2-ylamino) butanoic acid^ | C9H19NO3 | - | - |
| Vinylphenol | C8H8O | 695-84-1 | Pharmaceutical |
| Threonic acid^ | C4H8O5 | 3909-12-4 | Personal Care product |

^ Multiple isomers identified for that chemical formula

Three personal care products, one pharmaceutical and one industrial chemical were identified, none of which were identified using the commercial library in the suspect screening. PCA of the samples from the three locations found that the samples from Barratta creek mouth were particularly enriched for these chemicals, having relatively higher intensities than the other two locations (Figure 19).

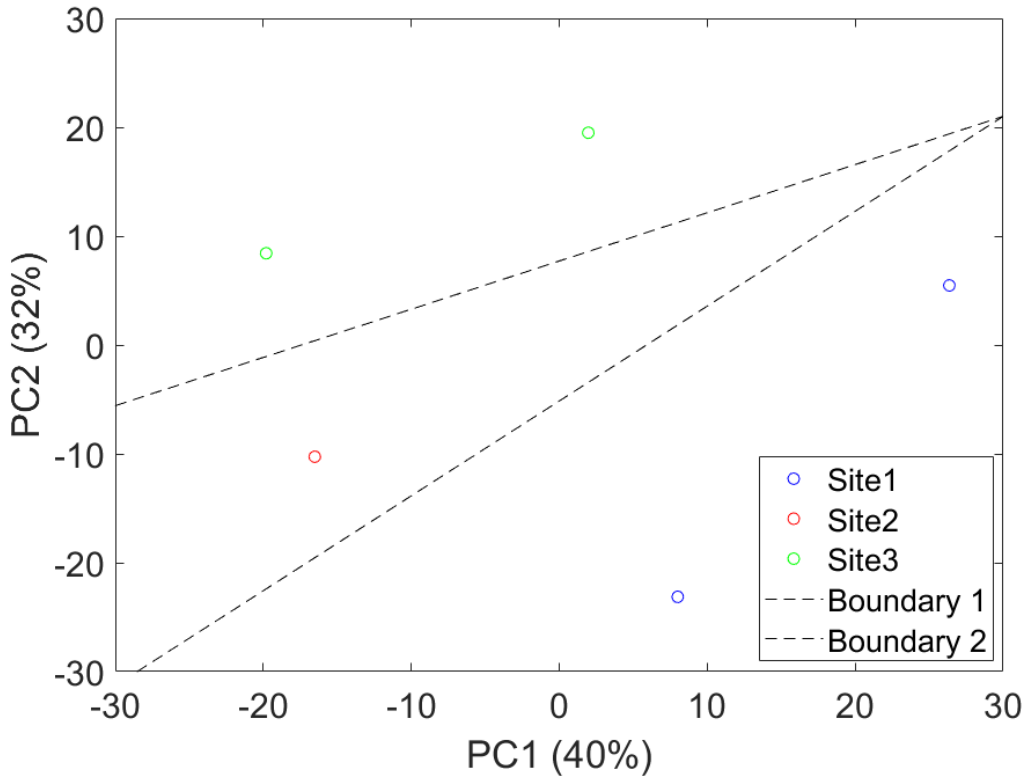



Figure 19. Two-dimensional PCA of the 13 features from non-target identification.

To date, the majority of research and monitoring for chemical pollutants on the Reef has focused largely on the five priority PSII herbicides (ametryn, atrazine, diuron, hexazinone, tebuthiuron) and other pesticides in known use in Reef catchments. More recently, research into the presence and concentrations of other

chemical pollutant groups such as the pharmaceuticals and personal care products (PPCPs) and 'alternative' herbicides is beginning to emerge, and the risk of exposure in marine environments assessed (O'Brien et al. 2014, Scott et al. 2014, Garzon-Garcia et al. 2015, Kroon et al. 2015).

The dominance of pharmaceuticals and endogenous suspects detected in samplers was somewhat surprising, considering agriculture is the primary land use in Reef catchments and the major input of anthropogenic chemical pollutants. However, this appears to agree with a study monitoring 73 Australian rivers that were adjacent to differing land uses (agricultural, industrial, residential, WWTP activities and undeveloped). This study also found widespread detection of pharmaceuticals, regardless of the primary land use in the catchment (Scott et al. 2014). Currently, there are little available data relating to the presence and concentrations of PPCPs in Reef rivers and marine environments. The only known published datasets are limited to the discharged effluent of two WWTPs located in the Wet Tropics region (O'Brien et al. 2014) and a small number of rivers located in northern Queensland (Scott et al. 2014). In total, both studies identified 26 pharmaceuticals and five personal care products, with maximum concentrations reaching low $\mu g\ L^{-1}$ levels. To our knowledge, there is no published data of PPCPs in the marine environment.

A recent unpublished study we conducted (manuscript in preparation) used a 'case-control' approach to identify the external exposure of coastal wildlife compared to a reference site, also using passive and grab sampling techniques. Target analysis combined with a similar suspect screening approach was undertaken to identify 'unknown' chemical pollutants. Target analysis identified catchment-specific profiles of pesticides, industrial chemicals, pharmaceuticals and personal care products, similar to the region-specific pesticide profiles observed in this MMP. The concentrations and frequencies of detections were highest in the coastal sampling locations that were likely influenced by river and urban discharge. Overall, observed concentrations of pharmaceuticals in the coastal marine environment were typically <1 $ng\ L^{-1}$ demonstrating that substantial dilution occurs following effluent release into rivers and the marine environment. It is likely that the concentrations of suspect chemicals identified in this case study are present in similar low levels. Interestingly, suspect screening of grab and passive samples from the coastal wildlife study identified two endogenous chemicals and one personal care product that were also identified in the passive samplers through this case study.

## 7.4 Conclusions

Passive and grab sampling techniques combined with non-target suspect screening approaches, allowed detection of a number of chemicals from diverse chemical classes that are not captured by the existing monitoring program. There appeared to be differences in the types of chemical classes identified by each sampling technique, which may reflect the sampler-specific classes of chemicals that the ED passive samplers optimally uptake, but could also be a result of different water concentrations present at the time of sampling. There may also be seasonal changes in the numbers and types of chemicals present, although a longer-term data set would confirm this.

Despite their likely low concentrations, the cumulative effects of long-term exposure to the mixture of chemicals as identified in this case study on Reef biota are unknown, and there is the potential that this chemical exposure may further reduce resilience of Reef ecosystems considering the multiple local, regional and global stressors already faced. As the population of Townsville and other Reef towns increase over the coming decades, chemicals associated with urban and industrial uses may become of greater concern to coastal marine ecosystems. The incomplete removal of many chemicals (pharmaceuticals and endogenous) from discharged effluent, together with the diffuse release of dermally applied personal care products, are two likely sources of chemicals identified in this case study. Whilst none of the PPCPs are known to be high risk to the Reef ecosystem, little monitoring information for any non-agricultural chemical pollutants exists and it would be of value to gain a fuller understanding of the impact of adjacent non-agricultural land uses on coastal marine environments.

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# Appendix A Supplemental information on methodology

## A-1 Sampler deployment, approaches for missing data and sources of uncertainty

### 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 marine waters. 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.

### 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 32% (mean of 9.8%), showing good agreement (this excludes 26 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, 25 ED sampler sets were analysed in duplicate, with 176 herbicide detections in both duplicates and 24 herbicide detections in only one of the duplicates. Mean coefficients of variation (%CVs) for chemicals (which includes detections in both duplicates only) ranged from 11% (fluroxypyr) to 42% (propazine, imidacloprid). Variability in the estimated water concentrations of diuron, hexazinone and atrazine was 37%, 28% and 40%, respectively (2015-16: 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 (per cent coefficient of variation, % CV) of replicate ED analysis

| Chemical | Detections in both duplicates (n) | Mean % CV | Min % CV | Max % CV |
|---|---|---|---|---|
| 2,4-D | 12 | 16 | 0.34 | 75 |
| Ametryn | 3 | 18 | 0.39 | 51 |
| Atrazine | 23 | 40 | 2.1 | 99 |
| Bromacil | 2 | 12 | 11 | 12 |
| Desethyl atrazine | 4 | 24 | 6.9 | 46 |
| Desisopropyl atrazine | 6 | 18 | 1.4 | 51 |
| Diuron | 20 | 37 | 6.5 | 94 |
| Fluroxypyr | 1 | 11 | 11 | 11 |
| Haloxyfop | 2 | 40 | 32 | 47 |
| Hexazinone | 23 | 28 | 3.5 | 83 |
| Imazapic | 3 | 28 | 14 | 46 |
| Imidacloprid | 12 | 42 | 0.73 | 92 |
| MCPA | 4 | 18 | 7.3 | 30 |
| Metsulfuron methyl | 5 | 25 | 4.7 | 54 |
| Metolachlor | 20 | 38 | 2.0 | 122 |
| Metribuzin | 4 | 34 | 3.2 | 72 |
| Prometryn | 1 | 13 | 13 | 13 |
| Propazine | 6 | 42 | 1.8 | 88 |
| Simazine | 10 | 27 | 0.10 | 74 |
| Tebuthiuron | 16 | 27 | 0.34 | 105 |
| Tebuconazole | 1 | 17 | 17 | 17 |

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

## A-2. Target chemicals

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 (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.

**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 | |
| 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 | |

| Chemical | Description | Priority or of interest | LC-MS/MS | | GC-MS |
|---|---|---|---|---|---|
| | | | LOD | LOR | LOR |
| 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 | |
| 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

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.

## A-4. Interlaboratory comparisons - quality assurance/quality control (QA/QC)

Fifteen ED extracts were selected for comparative interlaboratory analysis between QAEHS and Queensland Health Forensic Scientific Services (QHFSS) to compare the analytical accuracy of QAEHS' methods (Table A-5). Comparison of the results found that mean %CVs of analytes ranged from 4.3 - 91%, (excluding instances where there was only a single detection from one laboratory). Variability of diuron, atrazine and hexazinone (which are detected most frequently in this monitoring program) were 36, 15 and 11%, respectively. The overall variability (%CVs) in the interlaboratory analysis between QAEHS and QHFSS were comparable with previous reporting periods. Duplication of samplers is key to understanding within site variability and the statistical power in detecting true change in pesticide concentrations at a given monitoring site over time.

**Table A-5: Summary of inter-laboratory comparison of ED extracts (% coefficient of variation)**

| Chemical | No. QAEHS detects | No. QHFSS detects | Min % CV | Max % CV | Mean % CV |
|---|---|---|---|---|---|
| Ametryn | 7 | 3 | 4.5 | 44 | 24 |
| Atrazine | 15 | 15 | 2.4 | 34 | 15 |
| Desethyl atrazine | 6 | 4 | 8.1 | 28 | 17 |

| Chemical | No. QAEHS detects | No. QHFSS detects | Min % CV | Max % CV | Mean % CV |
|---|---|---|---|---|---|
| Desisopropyl atrazine | 2 | 2 | 29 | 42 | 36 |
| Bromacil | 4 | 3 | 76 | 111 | 91 |
| Diuron | 15 | 14 | 16 | 75 | 36 |
| Hexazinone | 15 | 13 | 0.36 | 79 | 11 |
| Simazine | 6 | 2 | 0.33 | 8.3 | 4.3 |
| Tebuthiuron | 12 | 10 | 2.1 | 55 | 26 |
| Metolachlor | 15 | 13 | 5.4 | 50 | 32 |
| 2,4-D | 12 | 9 | 9.3 | 108 | 50 |
| Haloxyfop | 7 | 2 | 45 | 121 | 83 |
| MCPA | 4 | 6 | 23 | 90 | 57 |
| Fluroxypyr | 1 | 1 | 8.2 | 8.2 | 8.2 |
| Imazapic | 2 | 2 | 44 | 65 | 54 |
| Imidacloprid | 9 | 10 | 34 | 120 | 87 |
| Metsulfuron methyl | 3 | 2 | 5.4 | 26 | 15 |
| **TOTAL DETECTIONS** | **135** | **111** | | | |

Only instances where a chemical was detected in both replicates has been included

# Appendix B Supplemental information on water quality guidelines

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 in 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.

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

| Chemical | DES proposed default guideline values (DGVs)[a] | | ANZECC and ARMCANZ[c] | | GBRMPA[e] | |
|---|---|---|---|---|---|---|
| | Proposed DGV | Notes | Trigger Value | Notes | PC Value | 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 | | |

| Chemical | DES proposed default guideline values (DGVs)[a] | | ANZECC and ARMCANZ[c] | | GBRMPA[e] | |
|---|---|---|---|---|---|---|
| | Proposed DGV | Notes | Trigger Value | Notes | PC Value | Notes |
| 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 |
| 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 | | | | |

| Chemical | DES proposed default guideline values (DGVs)[a] | | ANZECC and ARMCANZ[c] | | GBRMPA[e] | |
|---|---|---|---|---|---|---|
| | Proposed DGV | Notes | Trigger Value | Notes | PC Value | Notes |
| 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 | | | | |
| 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. (2017) (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 Supplemental information on risk assessment metrics

## C-1. Overview of risk assessment metrics

### 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 (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 below). 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) (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 below 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. 2017) 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. (2017a) 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. 2017b). 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

[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."

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. (2017b) and our previously derived RPF values, and the concomitant PSII herbicide equivalent concentrations using the two different factors, was presented as part of a case study in the previous year's report (Grant et al. 2017).

### Multisubstance-potentially affected fraction (ms-PAF) method

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 2015-16, a case study explored the ms-PAF approach compared to the on-going PSII-HEq Index for that year's data. SSDs for 28 pesticides have been determined by DES (formerly DSITI) and included in an additive ms-PAF model. 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 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 DGVs that have been 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, as for previous years, to avoid retrospective adjustment to reported data, the PSII-HEq Index is used to assess ecological risk.

**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 |
| | | | *Z. capriconi* | 10000 | ↓photosynthesis | LOEC | Macinnis-Ng & Ralph, 2004 |
| | | | *C. serrulata* | 10000 | ↓photosynthesis | LOEC | Haynes *et al* 2000b |

| 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) |
| | | | **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 |
| | | | **Red Algae** | | | | |
| | | | *P. onkodes* | 2900 | ↓ photosynthesis | LOEC | Harrington *et al* 2005 |

| 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) |
| | | | **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 |

**References:**


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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<br>NOEC = 3600 | 1986 | Core |
| **Invertebrates** | | | |
| *M. bahia* (Mysid shrimp) 99% active constituent; static | LC50 = 110, 96h, acute<br>NOEC = 1000 | 1987 | Core |
| *M. bahia* (Mysid shrimp) 96.8% active constituent; early life stage; static | 28d LOEC = 110<br>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<br>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-2. 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

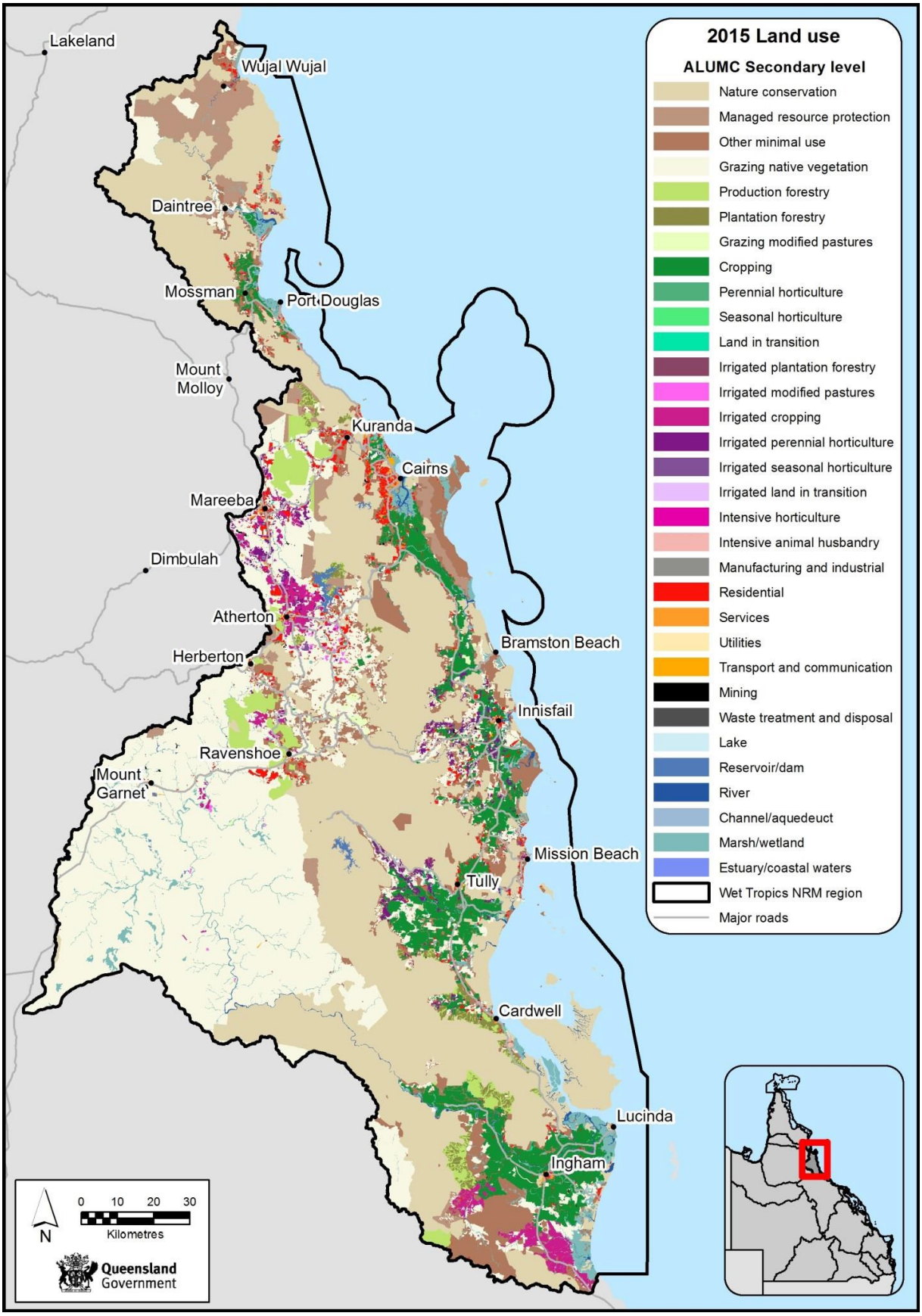



**Figure D-1**: Land Use map of the Reef catchment (2015) (from (DSITI 2016).

# Appendix E Supplemental information on pressures

**Table E-1:** Wet season discharge (ML; million litres) of the main GBR rivers (1 October 2010 to 30 September 2017, inclusive) compared to the previous four wet seasons and long-term (LT) median discharge (1986–87 to 2016–17). Colours indicate levels above the long-term median: yellow for 1.5 to 2 times, orange for 2 to 3 times and red greater than 3 times. Data source: DNRM (http://watermonitoring.dnrm.qld.gov.au/host.htm). Table from Waterhouse et al. (2018) (– = data not available).

| Basin | LT median | 2010 - 2011 | 2011 - 2012 | 2012 - 2013 | 2013 - 2014 | 2014 - 2015 | 2015 - 2016 | 2016 - 2017 |
|---|---|---|---|---|---|---|---|---|
| Jacky Jacky Creek | 2,056,151 | 4,735,197 | 1,820,422 | 1,986,825 | 3,790,832 | 1,498,138 | 630,787 | 2,383,057 |
| Olive Pascoe River | 2,570,189 | 5,918,996 | 2,275,527 | 2,483,531 | 4,738,541 | 1,872,672 | 788,484 | 2,978,821 |
| Lockhart River | 1,627,786 | 3,748,697 | 1,441,167 | 1,572,903 | 3,001,076 | 1,186,026 | 499,373 | 1,886,587 |
| Stewart River | 685,263 | 2,180,850 | 616,070 | 523,353 | 1,311,775 | 298,816 | 311,901 | 685,263 |
| Normanby River | 3,860,395 | 11,333,284 | 2,181,990 | 3,462,238 | 5,059,657 | 2,914,859 | 3,407,359 | 3,780,651 |
| Jeannie River | 1,434,447 | 2,824,817 | 1,048,269 | 695,195 | 1,869,982 | 1,434,447 | 1,581,015 | 1,746,929 |
| Endeavour River | 932,391 | 1,836,131 | 681,375 | 451,877 | 1,215,488 | 932,391 | 1,027,660 | 1,135,504 |
| Daintree River | 1,729,411 | 3,936,470 | 2,396,905 | 1,668,302 | 5,137,023 | 1,905,224 | 1,623,478 | 1,931,878 |
| Mossman River | 1,195,130 | 2,014,902 | 1,526,184 | 1,147,367 | 1,918,522 | 874,068 | 1,245,275 | 1,142,698 |
| Barron River | 516,958 | 2,119,801 | 852,055 | 328,260 | 663,966 | 380,395 | 182,999 | 287,790 |
| Mulgrave-Russell River | 4,415,631 | 7,892,713 | 5,696,594 | 3,529,862 | 5,420,678 | 3,145,787 | 3,253,825 | 3,015,734 |
| Johnstone River | 4,712,497 | 9,276,874 | 5,338,591 | 3,720,020 | 5,403,534 | 3,044,680 | 3,416,331 | 4,017,617 |
| Tully River | 3,490,736 | 7,442,768 | 3,425,096 | 3,341,887 | 4,322,496 | 2,659,775 | 2,942,770 | 3,098,701 |
| Murray River | 1,216,289 | 4,267,125 | 2,062,103 | 1,006,286 | 1,531,172 | 366,212 | 974,244 | 947,985 |
| Herbert River | 3,478,592 | 12,593,674 | 4,545,193 | 3,189,804 | 4,281,607 | 1,095,372 | 1,895,526 | 2,248,436 |
| Black River | 219,909 | 1,424,283 | 747,328 | 188,468 | 419,290 | 17,654 | 129,783 | 64,873 |
| Ross River | 445,106 | 2,092,684 | 1,324,707 | 276,584 | 1,177,255 | - | - | - |
| Haughton River | 535,930 | 2,415,758 | 1,755,712 | 517,069 | 573,976 | 120,674 | 267,986 | 338,245 |
| Burdekin River | 4,328,245 | 34,834,316 | 15,568,159 | 3,424,572 | 1,458,772 | 880,951 | 1,807,104 | 4,165,129 |
| Don River | 360,394 | 3,136,184 | 802,738 | 578,391 | 324,120 | 171,305 | 101,562 | 920,610 |
| Proserpine River | 924,039 | 4,582,697 | 2,171,287 | 851,504 | 720,427 | 157,123 | 316,648 | 1,683,894 |
| O'Connell River | 829,266 | 4,112,676 | 1,948,591 | 764,170 | 646,537 | 141,008 | 284,171 | 1,511,187 |
| Pioneer River | 804,599 | 3,630,422 | 1,567,684 | 1,162,871 | 635,315 | 2,028,936 | 597,117 | 1,388,687 |
| Plane Creek | 1,273,154 | 4,809,239 | 2,854,703 | 1,948,929 | 737,580 | 241,254 | 832,508 | 2,613,261 |
| Styx River | 191,279 | 906,144 | 275,219 | 968,106 | 544,155 | 376,009 | 343,877 | 507,927 |
| Shoalwater Creek | 217,663 | 1,031,129 | 313,180 | 1,101,638 | 619,211 | 427,872 | 391,308 | 577,985 |
| Water Park Creek | 573,838 | 2,718,432 | 825,657 | 2,904,319 | 1,632,466 | 1,128,027 | 1,031,630 | 1,523,780 |
| Fitzroy River | 2,996,149 | 37,942,149 | 7,993,273 | 8,530,491 | 1,578,610 | 2,681,949 | 3,589,342 | 6,170,044 |
| Calliope River | 157,383 | 1,000,032 | 345,703 | 1,558,380 | 283,790 | 479,868 | 148,547 | 406,321 |
| Boyne River | 39,809 | 252,949 | 87,443 | 394,178 | 71,782 | 121,378 | 37,574 | 102,775 |
| Baffle Creek | 409,347 | 3,650,093 | 1,775,749 | 2,030,545 | 275,517 | 710,352 | 257,093 | 829,460 |
| Kolan River | 50,429 | 779,168 | 307,837 | 810,411 | 45,304 | 213,857 | 111,172 | 146,154 |
| Burnett River | 250,839 | 9,421,517 | 643,137 | 7,581,543 | 218,087 | 853,349 | 381,054 | 536,242 |
| Burrum River | 64,940 | 114,492 | 117,762 | 90,921 | 62,188 | 150,113 | 334,681 | 456,549 |
| Mary River | 1,095,811 | 8,719,106 | 4,340,275 | 7,654,320 | 594,612 | 1,651,901 | 480,854 | 582,510 |

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; Endeavour gauge station was ceased 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.

## E.1 Flood plume mapping

Mapping the frequency, spatial extent and duration of 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.

The Marine Water Quality component of the MMP maps the frequency and extent of (surface) flood plumes(Waterhouse et al. 2018). 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.

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 2016) (see Table E-2). 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)).

**Table E-2:** Weekly flood plume colour class (1 – 6) for fixed site passive sampler locations during the 2016–17 wet season (beginning 1 December 2016)

| | | | | Week | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Site** | **Longitude** | **Latitude** | **Region** | **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 | 0.23 | 6 | 6 | 6 | 6 | 6 | 7 | 6 | 6 | 6 | 6 | 5 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 5 | 5 | 5 | 5 |
| High Island West | 146.00075 | -17.15985 | Wet Tropics | 0.55 | 6 | 6 | 5 | 6 | 6 | 4 | 6 | 6 | 5 | 5 | 5 | 6 | 5 | 5 | 5 | 6 | 6 | 6 | 5 | 5 | 5 | 5 |
| Frankland Group West | 146.07434 | -17.20476 | Wet Tropics | 0.29 | 6 | 6 | 6 | 6 | 6 | 7 | 6 | 6 | 6 | 6 | 5 | 6 | 6 | 6 | 5 | 6 | 6 | 6 | 5 | 5 | 5 | 5 |
| Dunk Island North | 146.13530 | -17.93570 | Wet Tropics | 0.95 | 5 | 5 | 5 | 5 | 5 | 6 | 5 | 5 | 5 | 5 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Lucinda | 146.38631 | -18.52083 | Wet Tropics | 1.00 | 5 | 5 | 5 | 5 | 5 | 7 | 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 | 5 | 4 | 4 | 4 | 5 | 3 | 4 | 4 | 4 | 1 | 1 | 4 | 2 | 4 | 2 | 4 | 5 | 2 | 1 | 4 | 2 | 4 |
| Repulse Bay | 148.69754 | -20.58822 | Mackay Whitsunday | 1.00 | 5 | 5 | 5 | 5 | 5 | 2 | 5 | 4 | 5 | 4 | 4 | 5 | 4 | 5 | 5 | 5 | 7 | 4 | 2 | 3 | 4 | 4 |
| Round Top Island | 149.23746 | -21.15593 | Mackay Whitsunday | 1.00 | 5 | 5 | 5 | 5 | 5 | 4 | 5 | 5 | 5 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 1 | 1 | 2 | 4 | 4 | 4 |
| Sarina Inlet | 149.30900 | -21.40300 | Mackay Whitsunday | 1.00 | 5 | 5 | 4 | 5 | 5 | 2 | 5 | 4 | 5 | 2 | 4 | 4 | 4 | 4 | 5 | 3 | 1 | 3 | 2 | 4 | 3 | 4 |
| Sandy Creek | 149.25516 | -21.21688 | Mackay Whitsunday | 1.00 | 5 | 5 | 5 | 5 | 5 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 3 | 1 | 3 | 4 | 4 | 5 |
| North Keppel Island | 150.89541 | -23.08080 | Fitzroy | 1.00 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 4 | 5 | 5 | 5 |

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.

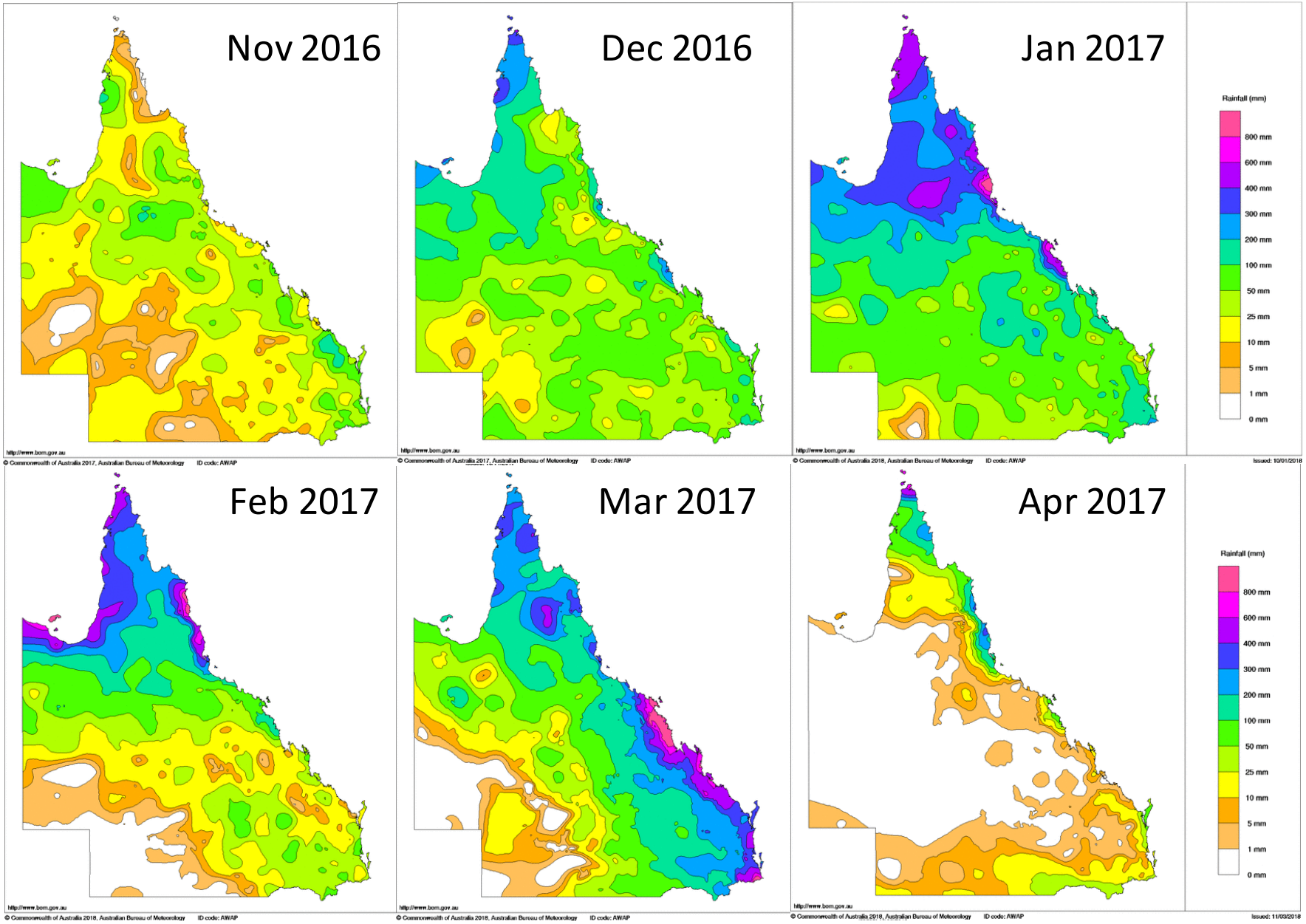



**Figure E-1:** Total monthly rainfall for the wet 2016–17 season across Queensland (Bureau of Meteorology 2018)

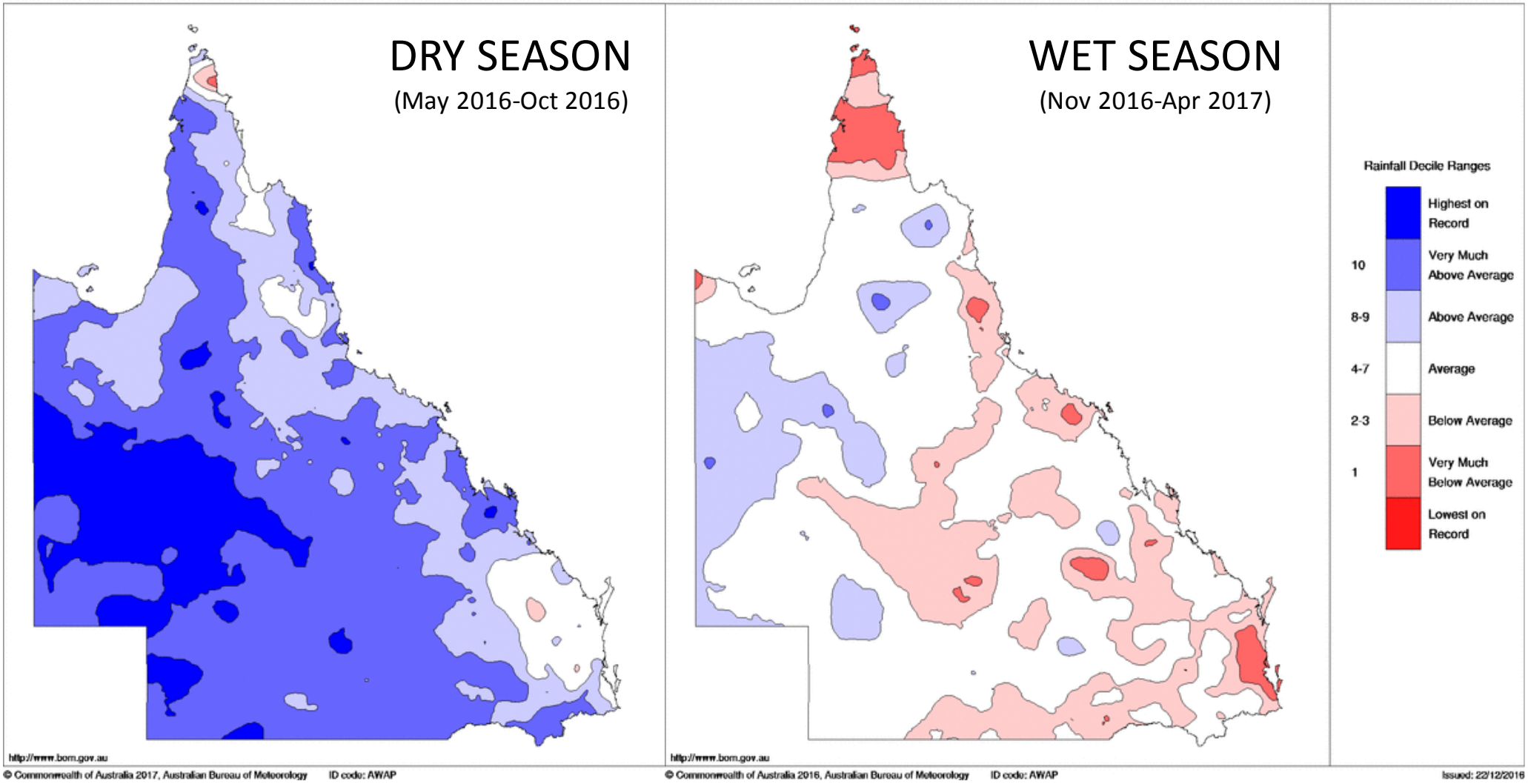



**Figure E-2:** Rainfall decile ranges (comparison of current period with long term average) for the dry season between May 2016- Oct 2016 (left) and wet season between Nov 2016 – 30 April 2017 (right). Figure sourced from (Bureau of Meteorology 2018)

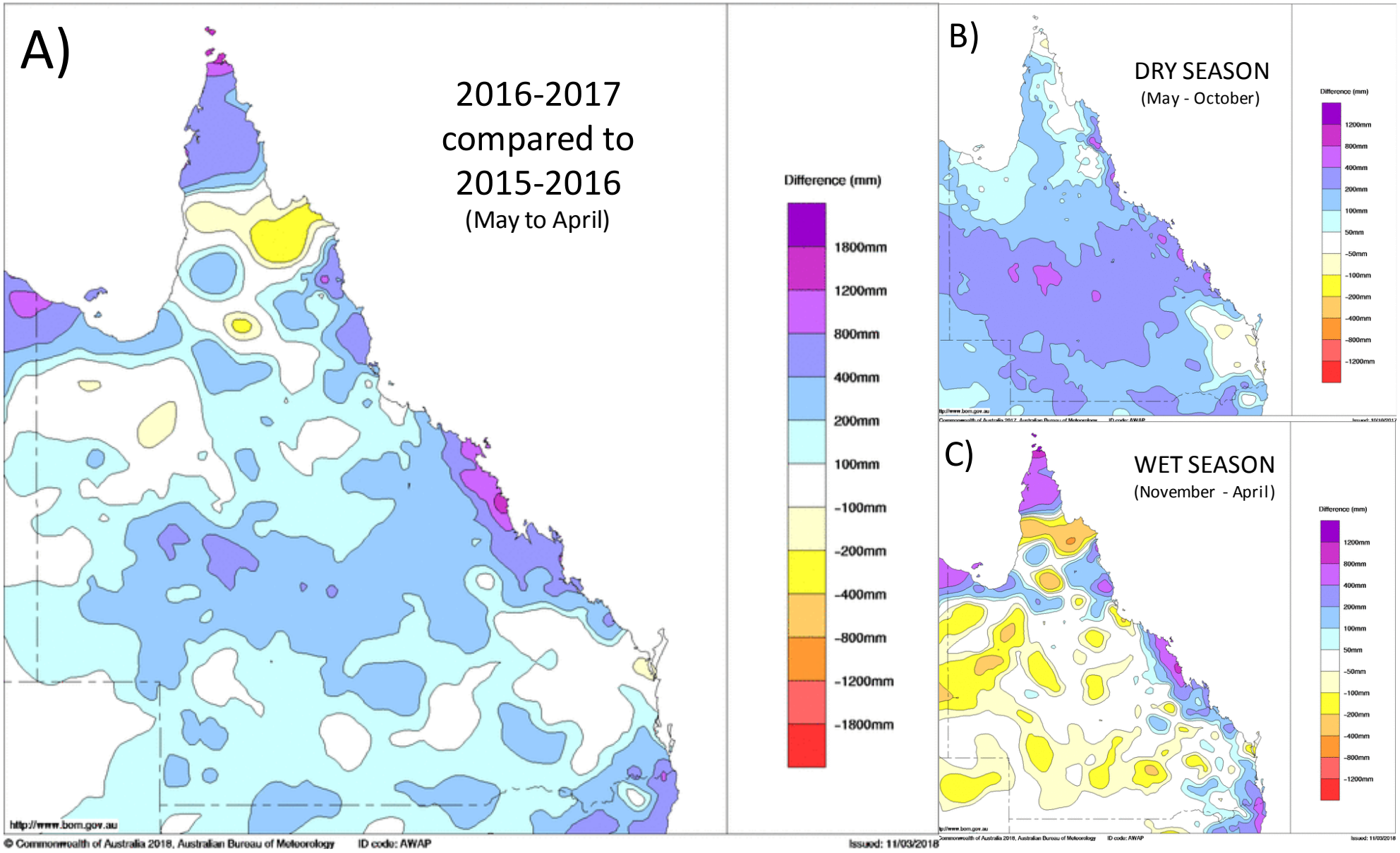

A)
2016-2017
compared to
2015-2016
(May to April)
Difference (mm)
1800mm
1200mm
800mm
400mm
200mm
100mm
-100mm
-200mm
-400mm
-800mm
-1200mm
-1800mm
http://www.bom.gov.au
© Commonwealth of Australia 2018, Australian Bureau of Meteorology ID code: AWAP
Issued: 11/03/2018
B)
DRY SEASON
(May - October)
Difference (mm)
1200mm
800mm
400mm
200mm
100mm
50mm
-50mm
-100mm
-200mm
-400mm
-800mm
-1200mm
C)
WET SEASON
(November - April)
Difference (mm)
1200mm
800mm
400mm
200mm
100mm
50mm
-50mm
-100mm
-200mm
-400mm
-800mm
-1200mm

**Figure E-3:** A) Inter-annual rainfall difference between the previous monitoring year (2015-16) and the current monitoring year (2016–17 ). 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 2018)

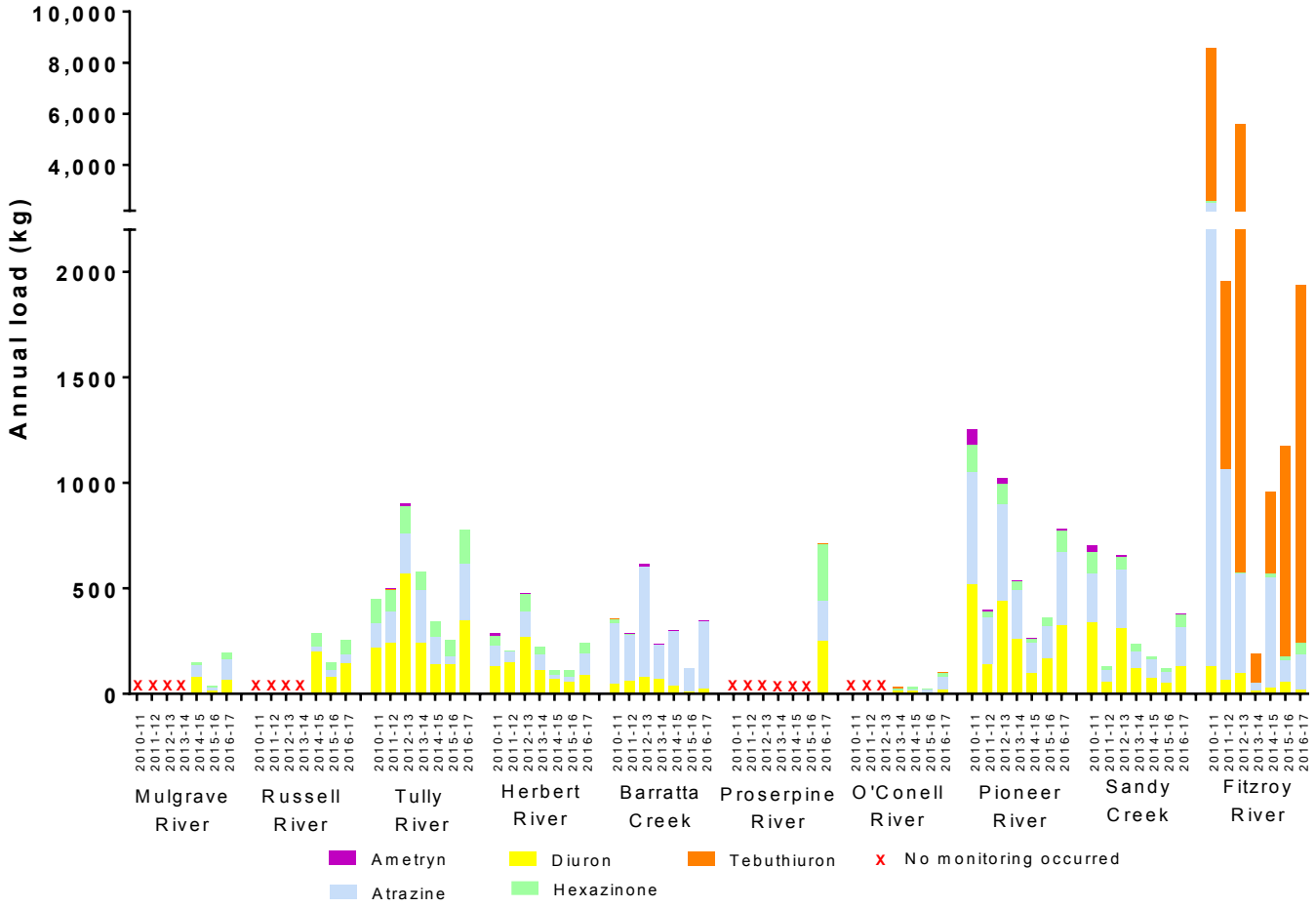



**Figure E-4:** Historical PSII herbicide loads from monitored Reef catchment rivers (2010–2016). Data collated from GBRCLMP reports (Turner et al. 2012, Wallace et al. 2014, Garzon-Garcia et al. 2015, Wallace et al. 2015, Wallace et al. 2016, Huggins et al. 2017). 2016–17 data from Huggins et al. (*in prep*)).

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

**Table F-1**: Passive sampling return record for the 2016–17 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 | 7 | 5 | Lost mooring in Sept/Oct and took until late December to re-establish |
| | Normanby Island | 5 | 0 | Site changed ownership in January 2017after being re-established in October 2016 after volunteer "withdrew" from program previous year. One kit lost to weather or other factors. One lost in transit by courier. One returned unused. Two kits' fate unknown – assumed not deployed |
| | Dunk Island | 9 | 9 | No losses. Some slippage of deployment dates due to weather issues |
| | High Island | 9 | 9 | As above |
| | Lucinda Jetty (CSIRO) | 9 | 9 | One ED sampler (November) lost on retrieval. Replicate was OK. |
| **Burdekin** | Barratta Creek | 8 (5) | 7 (5) | Slippage in deployments caused February sampler to be held back. Partial losses of one ED (December) and two EDs (March). PFMs not deployed in November. |
| **Mackay Whitsunday** | Repulse Bay | 5 (3) | 1 (0) | Lost buoys in July (May/June samplers), Sept/ Oct (Sept/Oct samplers), February (Jan samplers) and March (Feb samplers), the latter due to cyclone. December, March and April kits held back due to deployment date slippage, mooring loss and site inaccessibility due to cyclone |
| | Round Top Island | 8 (5) | 4 (2) | Lost buoy in July (May/June samplers) and February. Two kits returned unused (March and April) due to delays with re-establishing site. December kit held back due to deployment date slippage. |
| | Sandy Creek | 9 (6) | 8 (5) | One ED lost in November, January and February. PDMS lost in March. Both EDs lost in April (cyclone). |
| | Sarina Inlet | 7 (5) | 4 (2) | July/August samplers and buoy lost. Re-established in November. One ED lost (November). December not sent due to deployment date slippage. Partial kit (PDMS cage only) sent in January and combined with undeployed Sept/Oct EDs. Mooring and March samplers lost to cyclone so April sampler returned unused. |
| **Fitzroy** | North Keppel Island | 8 | 7 | July/Aug not sent due to deployment date slippage. Late deployments in Jan and Feb. March sampler over-deployed due to volunteer absence. April samplers deployed in 2017/18. |
| **TOTAL 2016–17** | **11 sites** | **84 (24)** | **63 (14)** | **75% (58%) return rate** |
| **TOTAL 2015-16** | **11 sites** | **93 (21)** | **68 (13)** | **73% (62%) 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-16<br>Jun-16<br>Jul-16 | 3-May-16 | 21-Jul-16 | ED** | 0.02 | 1.1 | 0.03 | n.d. | n.d. | 1.2 | n.d. | 0.36 | n.d. | n.d. | n.d. | 0.03 | 0.02 | n.d. | 1.5 | 0.19 | 0.02 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.02 | n.d. | n.d. |
| Aug-16 | 21-Jul-16 | 1-Sep-16 | ED | n.d. | 0.24 | n.d. | n.d. | n.d. | 0.56 | n.d. | 0.16 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.66 | 0.03 | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.05 | n.d. | n.d. |
| Sep-16<br>Oct-16 | Samplers lost | | ED | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Nov-16 | Samplers not deployed | | ED | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Dec-16 | Samplers not deployed | | ED | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Jan-17 | 23-Dec-16 | 25-Jan-17 | ED | n.d. | 0.84 | n.d. | n.d. | n.d. | 3.2 | n.d. | 0.46 | n.d. | n.d. | n.d. | 0.04 | n.d. | n.d. | 3.5 | 0.07 | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.08 | n.d. | n.d. |
| Feb-17 | 25-Jan-17 | 11-Mar-17 | ED | n.d. | 0.20 | n.d. | n.d. | n.d. | 2.3 | n.d. | 0.66 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2.6 | 0.05 | 0.04 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.04 | n.d. | n.d. |
| Mar-17<br>Apr-17 | 11-Mar-17 | 8-May-17 | ED | n.d. | 0.85 | n.d. | n.d. | n.d. | 1.8 | n.d. | 0.59 | n.d. | n.d. | n.d. | n.d. | 0.05 | n.d. | 2.2 | 0.04 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 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 |
| Detects (n) | | | | 1 | 5 | 1 | 0 | 0 | 5 | 0 | 5 | 0 | 0 | 0 | 2 | 2 | 0 | | 5 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 |
| % Detects | | | | 20 | 100 | 20 | 0 | 0 | 100 | 0 | 100 | 0 | 0 | 0 | 40 | 40 | 0 | | 100 | 80 | 0 | 0 | 0 | 0 | 0 | 0 | 80 | 0 | 0 |
| Minimum detected concentration | | | | n.d. | 0.20 | n.d. | n.d. | n.d. | 0.56 | n.d. | 0.16 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.66 | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Maximum concentration | | | | 0.02 | 1.1 | 0.03 | n.d. | n.d. | 3.2 | n.d. | 0.66 | n.d. | n.d. | n.d. | 0.04 | 0.05 | n.d. | 3.5 | 0.19 | 0.04 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.08 | 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

**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-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 |
| Jun-16 Jul-16 | 03-Jun-16 | 10-Aug-16 | ED** | n.d. | 0.74 | 0.08 | n.d. | n.d. | 1.9 | n.d. | 0.55 | n.d. | n.d. | n.d. | n.d. | 0.005 | n.d. | 2.2 | 0.06 | 0.07 | n.d. | 0.01 | 0.01 | n.d. | n.d. | n.d. | 0.48 | n.d. | n.d. |
| Aug-16 Sep-16 | 10-Aug-16 | 29-Sep-16 | ED | n.d. | 0.54 | 0.19 | n.d. | n.d. | 1.3 | n.d. | 0.43 | n.d. | n.d. | n.d. | 0.05 | n.d. | n.d. | 1.5 | 0.08 | 0.04 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.21 | n.d. | n.d. |
| Oct-16 Nov-16 | 29-Sep-16 | 28-Nov-16 | ED | n.d. | 0.19 | n.d. | n.d. | n.d. | 0.32 | n.d. | 0.08 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.38 | 0.02 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.02 | n.d. | n.d. |
| Dec-16 | 28-Nov-16 | 23-Dec-16 | ED | n.d. | 0.07 | n.d. | n.d. | n.d. | 0.9 | n.d. | 0.24 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1.0 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Jan-17 | 23-Dec-16 | 21-Jan-17 | ED | n.d. | 0.36 | n.d. | n.d. | n.d. | 5.9 | n.d. | 1.2 | n.d. | 0.03 | n.d. | n.d. | n.d. | n.d. | 6.5 | 0.15 | n.d. | n.d. | 0.03 | 0.09 | n.d. | n.d. | n.d. | 0.62 | n.d. | 0.02 |
| Feb-17 | 21-Jan-17 | 17-Feb-17 | ED | n.d. | 0.92 | n.d. | n.d. | n.d. | 10 | n.d. | 2.9 | 0.02 | n.d. | n.d. | n.d. | n.d. | n.d. | 11 | 0.18 | 0.51 | n.d. | 0.03 | n.d. | n.d. | n.d. | n.d. | 1.0 | n.d. | n.d. |
| Mar-17 | 17-Feb-17 | 23-Mar-17 | ED** | n.d. | 1.3 | n.d. | n.d. | 0.01 | 6.1 | n.d. | 2.5 | n.d. | 0.30 | n.d. | n.d. | n.d. | n.d. | 7.6 | 0.03 | 0.15 | n.d. | n.d. | 0.07 | n.d. | n.d. | n.d. | 0.51 | n.d. | n.d. |
| Apr-17 | 23-Mar-17 | 24-Apr-17 | ED | n.d. | 0.25 | n.d. | n.d. | n.d. | 2.4 | n.d. | 0.90 | n.d. | n.d. | n.d. | n.d. | 0.02 | n.d. | 2.8 | 0.04 | 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 | 3 | 0 | 1 | 9 | 0 | 9 | 1 | 2 | 0 | 2 | 3 | 0 | | 8 | 5 | 0 | 3 | 4 | 0 | 0 | 0 | 7 | 0 | 2 |
| % Detects | | | | 0 | 100 | 33 | 0 | 11 | 100 | 0 | 100 | 11 | 22 | 0 | 22 | 33 | 0 | | 89 | 56 | 0 | 33 | 44 | 0 | 0 | 0 | 78 | 0 | 22 |
| Minimum detected concentration | | | | n.d. | 0.07 | n.d. | n.d. | n.d. | 0.32 | n.d. | 0.08 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.38 | 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. | 1.3 | 0.19 | n.d. | 0.01 | 10 | n.d. | 2.9 | 0.02 | 0.30 | n.d. | 0.05 | 0.04 | n.d. | 11 | 0.18 | 0.51 | n.d. | 0.03 | 0.09 | n.d. | n.d. | n.d. | 1.0 | n.d. | 0.03 |

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-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. |
| Jun-16 Jul-16 | 05-Jun-16 | 11-Aug-16 | ED** | n.d. | 0.38 | n.d. | n.d. | n.d. | 1.8 | n.d. | 0.62 | n.d. | n.d. | n.d. | 0.05 | 0.01 | n.d. | 2.1 | 0.07 | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Aug-16 Sep-16 | 11-Aug-16 | 28-Sep-16 | ED | n.d. | 0.57 | n.d. | n.d. | n.d. | 0.87 | n.d. | 0.30 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1.1 | 0.11 | 0.05 | n.d. | n.d. | n.d. | n.d. | 0.02 | n.d. | 0.09 | n.d. | n.d. |
| Oct-16 Nov-16 | 28-Sep-16 | 26-Nov-16 | ED | n.d. | 0.18 | 0.07 | n.d. | n.d. | 0.39 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.43 | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Dec-16 | 26-Nov-16 | 24-Dec-16 | ED | 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. | 0.00 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Jan-17 | 24-Dec-16 | 20-Jan-17 | ED** | n.d. | 0.53 | n.d. | n.d. | n.d. | 6.6 | n.d. | 1.8 | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | 7.4 | 0.21 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1.4 | n.d. | n.d. |
| Feb-17 | 20-Jan-17 | 18-Feb-17 | ED** | n.d. | 0.76 | n.d. | n.d. | n.d. | 6.1 | n.d. | 1.9 | 0.02 | n.d. | n.d. | n.d. | n.d. | n.d. | 7.0 | 0.16 | 0.20 | n.d. | 0.01 | n.d. | n.d. | n.d. | n.d. | 0.24 | n.d. | n.d. |
| Mar-17 | 18-Feb-17 | 24-Mar-17 | ED | n.d. | 0.76 | n.d. | n.d. | n.d. | 4.4 | n.d. | 1.8 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 5.2 | n.d. | 0.30 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Apr-17 | 24-Mar-17 | 23-Apr-17 | ED** | n.d. | 1.2 | n.d. | n.d. | n.d. | 5.6 | n.d. | 1.8 | n.d. | n.d. | n.d. | n.d. | 0.07 | n.d. | 6.5 | 0.06 | 0.28 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.14 | 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 | 0 | 0 | 8 | 0 | 7 | 2 | 0 | 0 | 2 | 3 | 0 | | 7 | 5 | 0 | 1 | 0 | 0 | 1 | 0 | 4 | 0 | 0 |
| % Detects | | | | 0 | 89 | 11 | 0 | 0 | 89 | 0 | 78 | 22 | 0 | 0 | 22 | 33 | 0 | | 78 | 56 | 0 | 11 | 0 | 0 | 11 | 0 | 44 | 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. | 0.00 | 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. | 1.2 | 0.07 | n.d. | n.d. | 6.6 | n.d. | 1.9 | 0.03 | n.d. | n.d. | 0.05 | 0.07 | n.d. | 7.4 | 0.21 | 0.30 | n.d. | 0.01 | n.d. | n.d. | 0.02 | n.d. | 1.4 | 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-16 | | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| Jun-16 | Sampler not sent | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Jul-16 | | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| Aug-16 | Sampler not deployed | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Sep-16 | | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| Oct-16 | Sampler not deployed | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Nov-16 | | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Sampler not deployed | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Dec-16 | | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Sampler not deployed | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Jan-17 | | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Sampler not deployed | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Feb-17 | | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Sampler not deployed | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Mar-17 | | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Sampler lost | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Apr-17 | | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Sampler not deployed | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| **Summary** | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Samples (n) | | | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Detects (n) | | | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| % Detects | | | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | 0 | 0 | 0 | 0 | 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. | n.d. | 0.00 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Maximum 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. | n.d. | 0.00 | n.d. | n.d. | n.d. | n.d. | 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 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-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-16 | 10-May-16 | 6-Jun-16 | ED | n.d. | 0.35 | n.d. | n.d. | n.d. | 0.94 | n.d. | 0.26 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1.1 | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Jun-16<br>Jul-16<br>Aug-16 | 06-Jun-16 | 30-Aug-16 | ED** | n.d. | 0.57 | n.d. | n.d. | n.d. | 1.3 | n.d. | 0.34 | n.d. | n.d. | n.d. | n.d. | 0.02 | n.d. | 1.6 | 0.13 | 0.01 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Sep-16<br>Oct-16 | 30-Aug-16 | 10-Nov-16 | ED** | n.d. | 0.08 | n.d. | n.d. | n.d. | 0.24 | n.d. | 0.02 | n.d. | n.d. | n.d. | n.d. | 0.02 | n.d. | 0.27 | 0.02 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Nov-16 | 10-Nov-16 | 02-Dec-16 | ED | 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. |
| Dec-16 | 02-Dec-16 | 19-Dec-16 | ED | n.d. | 0.10 | 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. | 0.05 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Jan-17 | 19-Dec-16 | 07-Feb-17 | ED** | n.d. | 1.3 | n.d. | n.d. | 0.005 | 3.8 | n.d. | 1.1 | n.d. | n.d. | 0.01 | n.d. | 0.01 | n.d. | 4.5 | 0.12 | 0.10 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.15 | n.d. | n.d. |
| Feb-17 | 07-Feb-17 | 07-Mar-17 | ED** | 0.02 | 1.5 | n.d. | n.d. | n.d. | 5.8 | n.d. | 1.9 | n.d. | n.d. | n.d. | n.d. | 0.05 | n.d. | 6.8 | 0.08 | 0.52 | n.d. | 0.01 | 0.04 | n.d. | n.d. | n.d. | 0.32 | n.d. | n.d. |
| Mar-17 | 07-Mar-17 | 04-Apr-17 | ED** | n.d. | 1.6 | n.d. | n.d. | n.d. | 5.6 | n.d. | 1.6 | n.d. | n.d. | n.d. | n.d. | 0.02 | n.d. | 6.5 | 0.16 | 0.46 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.23 | n.d. | n.d. |
| Apr-17 | 04-Apr-17 | 03-May-17 | ED | n.d. | 0.55 | n.d. | n.d. | n.d. | 2.0 | n.d. | 0.73 | n.d. | n.d. | n.d. | n.d. | 0.18 | n.d. | 2.4 | 0.04 | 0.30 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.07 | 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) | | | | 1 | 8 | 0 | 0 | 1 | 7 | 0 | 7 | 0 | 0 | 1 | 0 | 6 | 0 | | 7 | 6 | 0 | 1 | 1 | 0 | 0 | 0 | 4 | 0 | 0 |
| % Detects | | | | 11 | 89 | 0 | 0 | 11 | 78 | 0 | 78 | 0 | 0 | 11 | 0 | 67 | 0 | | 78 | 67 | 0 | 11 | 11 | 0 | 0 | 0 | 44 | 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. | 0.00 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Maximum concentration | | | | 0.02 | 1.6 | n.d. | n.d. | 0.005 | 5.8 | n.d. | 1.9 | n.d. | n.d. | 0.01 | n.d. | 0.18 | n.d. | 6.8 | 0.16 | 0.52 | n.d. | 0.01 | 0.04 | n.d. | n.d. | n.d. | 0.32 | 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-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-16 Jun-16 Jul-16 | 17-May-16 | 22-Jul-16 | ED | n.d. | 0.29 | n.d. | n.d. | n.d. | 0.19 | n.d. | 0.07 | n.d. | n.d. | n.d. | n.d. | 0.01 | n.d. | 0.26 | 0.06 | 0.06 | n.d. | n.d. | 0.04 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | | | | |
| Aug-16 Sep-16 | 22-Jul-16 | 22-Sep-16 | ED | 0.08 | 5.6 | n.d. | n.d. | 0.04 | n.d. | n.d. | 0.43 | 0.27 | n.d. | n.d. | n.d. | 0.08 | n.d. | 1.2 | 4.4 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | | | | |
| Oct-16 Nov-16 | 22-Sep-16 | 30-Nov-16 | ED** | 0.01 | 2.7 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.08 | n.d. | n.d. | n.d. | n.d. | 0.01 | n.d. | 0.47 | 0.17 | 0.26 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | | | | |
| Dec-16 | 30-Nov-16 | 30-Dec-16 | ED | n.d. | 0 | n.d. | n.d. | n.d. | 0.43 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.51 | 0.06 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.003 | 0.01 | n.d. | n.d. |
| Jan-17 | 30-Dec-16 | 12-Feb-17 | ED | 0.15 | 41 | 6.6 | 1.1 | 0.06 | 17 | n.d. | 0.38 | 1.2 | n.d. | 0.22 | 0.48 | 0.20 | n.d. | 25 | 0.46 | 0.15 | n.d. | 0.01 | 0.06 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.01 | 0.03 | n.d. | n.d. |
| Feb-17 | 12-Feb-17 | 05-Mar-17 | ED | 0.54 | 10 | 1.9 | 0.38 | 0.02 | 4.3 | n.d. | 0.85 | n.d. | n.d. | 0.09 | 0.08 | 0.11 | n.d. | 7.2 | 0.12 | 1.4 | n.d. | 0.01 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | | | | |
| | | | PDMS** | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.02 | 0.02 | n.d. | n.d. |
| Mar-17 | ED samplers lost | | ED | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.02 | 0.03 | 0.21 | n.d. |
| Apr-17 | 01-Apr-17 | 16-May-17 | ED | 1.9 | 35 | 3.3 | 0.41 | 0.19 | 6.8 | n.d. | 1.6 | 0.10 | n.d. | 0.27 | 0.19 | 0.19 | n.d. | 16 | 0.43 | n.d. | n.d. | 0.04 | n.d. | 0.01 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.15 | 0.11 | 0.16 | n.d. |
| **Summary** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Samples (n) | | | | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 5 | 5 | 5 | 5 |
| Detects (n) | | | | 5 | 7 | 3 | 3 | 4 | 5 | 0 | 6 | 3 | 0 | 3 | 3 | 6 | 0 | | 7 | 4 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 5 | 5 | 2 | 0 |
| % Detects | | | | 71 | 100 | 43 | 43 | 57 | 71 | 0 | 86 | 43 | 0 | 43 | 43 | 86 | 0 | | 100 | 57 | 0 | 43 | 29 | 14 | 0 | 0 | 0 | 0 | 0 | 100 | 100 | 40 | 0 |
| Minimum detected concentration | | | | n.d. | 0.29 | n.d. | n.d. | n.d. | 0.19 | n.d. | 0.07 | n.d. | n.d. | n.d. | n.d. | 0.01 | n.d. | 0.26 | 0.06 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.003 | 0.01 | n.d. | n.d. |
| Maximum concentration | | | | 1.87 | 41 | 6.6 | 1.1 | 0.19 | 17.0 | n.d. | 1.6 | 1.2 | n.d. | 0.27 | 0.48 | 0.20 | n.d. | 25 | 4.42 | 1.38 | n.d. | 0.04 | 0.06 | 0.01 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.15 | 0.11 | 0.21 | 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 |
| May-16 Jun-16 | Samplers lost | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| Jul-16 Aug-16 | Samplers not deployed | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| Sep-16 Oct-16 | Samplers lost | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| Nov-16 | Samplers lost | | ED | | | | | | | | | | | | | | | | | | | | | | | | | |
| Dec-16 | 25-Nov-16 | 17-Dec-16 | ED | n.d. | 1.7 | n.d. | n.d. | n.d. | 3.8 | n.d. | 1.8 | n.d. | n.d. | n.d. | n.d. | 0.03 | n.d. | 4.8 | 0.14 | 0.29 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.23 | n.d. | n.d. |
| Jan-17 | Samplers lost | | ED PDMS | | | | | | | | | | | | | | | | | | | | | | | | | |
| Feb-17 | Samplers lost | | ED PDMS | | | | | | | | | | | | | | | | | | | | | | | | | |
| Mar-17 | Samplers lost | | ED PDMS | | | | | | | | | | | | | | | | | | | | | | | | | |
| Apr-17 | Samplers 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 | 1 | 0 | | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| % Detects | | | | 0 | 100 | 0 | 0 | 0 | 100 | 0 | 100 | 0 | 0 | 0 | 0 | 100 | 0 | | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 100 | 0 | 0 |
| Minimum detected concentration | | | | n.d. | 1.7 | n.d. | n.d. | n.d. | 3.8 | n.d. | 1.8 | n.d. | n.d. | n.d. | n.d. | 0.03 | n.d. | 4.8 | 0.14 | 0.29 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Maximum concentration | | | | n.d. | 1.7 | n.d. | n.d. | n.d. | 3.8 | n.d. | 1.8 | n.d. | n.d. | n.d. | n.d. | 0.03 | n.d. | 4.8 | 0.14 | 0.29 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.23 | 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-16 Jun-16 Jul-16 | Samplers lost | | ED | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Aug-16 Sep-16 | 03-Aug-16 | 22-Sep-16 | ED | 0.06 | 12 | 3.2 | 0.64 | 0.03 | 10 | n.d. | 2.7 | 0.08 | n.d. | 0.05 | 0.06 | 0.12 | n.d. | 14 | 1.6 | 1.2 | n.d. | n.d. | 0.13 | n.d. | n.d. | 0.56 | 0.92 | 0.35 | n.d. | | | | |
| Oct-16 Nov-16 | 22-Sep-16 | 09-Dec-16 | ED** | n.d. | 17 | 2.4 | 0.44 | n.d. | 8.4 | n.d. | 3.5 | n.d. | n.d. | 0.05 | 0.05 | 0.07 | n.d. | 13 | 1.0 | 0.05 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.20 | n.d. | 0.01 | | | | |
| Dec-16 | 25-Nov-16 | 17-Dec-16 | ED** | n.d. | 1.5 | n.d. | n.d. | n.d. | 2.0 | n.d. | 1.1 | n.d. | n.d. | n.d. | n.d. | 0.02 | n.d. | 2.7 | 0.06 | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.07 | n.d. | n.d. | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.01 | 0.005 | n.d. | n.d. |
| Jan-17 | 17-Dec-16 | 02-Feb-17 | ED** | 3.2 | 316 | 20 | 4.9 | n.d. | 579 | n.d. | 88 | 12 | 0.04 | 1.4 | 1.3 | 0.53 | n.d. | 670 | 7.7 | 11 | n.d. | 0.01 | n.d. | n.d. | 0.49 | 0.82 | 53 | 0.65 | 0.02 | | | | |
| | | | PDMS** | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.49 | 0.19 | 0.66 | 0.01 |
| Feb-17 | Samplers lost | | ED PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Mar-17 | Samplers not deployed | | ED PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Apr-17 | Samplers not deployed | | ED PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| **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) | | | | 2 | 4 | 3 | 3 | 1 | 4 | 0 | 4 | 2 | 1 | 3 | 3 | 4 | 0 | | 4 | 4 | 0 | 1 | 1 | 0 | 1 | 2 | 4 | 2 | 2 | 2 | 2 | 1 | 1 |
| % Detects | | | | 50 | 100 | 75 | 75 | 25 | 100 | 0 | 100 | 50 | 25 | 75 | 75 | 100 | 0 | | 100 | 100 | 0 | 25 | 25 | 0 | 25 | 50 | 100 | 50 | 50 | 100 | 100 | 50 | 50 |
| Minimum detected concentration | | | | n.d. | 1.5 | 2.4 | 0.44 | n.d. | 2.0 | n.d. | 1.1 | n.d. | n.d. | n.d. | n.d. | 0.02 | n.d. | 2.7 | 0.06 | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.07 | n.d. | n.d. | 0.01 | 0.005 | n.d. | n.d. |
| Maximum concentration | | | | 3.2 | 316 | 20 | 4.9 | 0.03 | 579 | n.d. | 88 | 12 | 0.04 | 1.4 | 1.3 | 0.53 | n.d. | 670 | 7.7 | 11 | n.d. | 0.01 | 0.1 | n.d. | 0.5 | 0.8 | 53 | 0.65 | 0.02 | 0.49 | 0.19 | 0.7 | 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 | Chlorpyrifos | Pendimethalin | Propiconazole | Trifluralin |
| May-16 Jun-16 | 01-May-16 | 10-Jul-16 | ED | n.d. | 0.96 | 0.21 | 0.03 | n.d. | 1.8 | n.d. | 0.61 | n.d. | n.d. | n.d. | 0.08 | 0.41 | n.d. | 2.3 | 0.15 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.05 | n.d. | | | | |
| Jul-16 Aug-16 Sep-16 | 10-Jul-16 | 28-Sep-16 | ED** | n.d. | 4.8 | 0.19 | 0.01 | n.d. | 7.2 | n.d. | 2.3 | n.d. | n.d. | 0.01 | 0.05 | 0.29 | n.d. | 8.9 | 0.38 | 0.26 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.12 | 0.17 | n.d. | | | | |
| Oct-16 | 28-Sep-16 | 08-Nov-16 | ED** | n.d. | 0.80 | n.d. | n.d. | n.d. | 1.3 | n.d. | 0.58 | n.d. | n.d. | n.d. | n.d. | 0.08 | n.d. | 1.7 | 0.09 | 0.02 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | | | | |
| Nov-16 | 08-Nov-16 | 08-Dec-16 | ED | n.d. | 2.0 | 0.31 | 0.08 | n.d. | 2.2 | n.d. | 0.87 | n.d. | n.d. | n.d. | n.d. | 0.05 | n.d. | 2.9 | 0.14 | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.03 | n.d. | n.d. | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.01 | 0.01 | n.d. | n.d. |
| Dec-16 | 08-Dec-16 | 20-Jan-17 | ED | n.d. | 13 | 0.73 | 0.15 | 0.03 | 45 | n.d. | 20 | 0.50 | n.d. | 0.05 | 0.08 | 0.17 | n.d. | 55 | 0.20 | 0.80 | n.d. | n.d. | 0.04 | n.d. | n.d. | n.d. | 3.3 | 0.18 | n.d. | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.03 | 0.02 | n.d. | n.d. |
| Jan-17 | 20-Jan-17 | 09-Feb-17 | ED | n.d. | 9.7 | 0.26 | n.d. | 0.04 | 29 | n.d. | 13 | 0.40 | n.d. | 0.06 | n.d. | 0.22 | n.d. | 35 | 0.15 | 2.2 | n.d. | n.d. | 0.46 | n.d. | n.d. | n.d. | 0.41 | 0.30 | n.d. | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.01 | n.d. | 0.10 | n.d. |
| Feb-17 | 09-Feb-17 | 03-Mar-17 | ED | n.d. | 18 | 1.5 | 0.36 | n.d. | 70 | n.d. | 11 | n.d. | n.d. | 0.06 | n.d. | 0.10 | n.d. | 77 | 0.05 | 1.8 | n.d. | n.d. | 0.24 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.01 | n.d. | n.d. | n.d. |
| Mar-17 | 03-Mar-17 | 08-Apr-17 | ED | n.d. | 9.5 | 1.7 | 0.39 | n.d. | 20 | n.d. | 4.8 | 0.10 | n.d. | 0.07 | 0.15 | 0.12 | n.d. | 24 | 0.07 | 0.57 | n.d. | n.d. | 0.13 | n.d. | n.d. | n.d. | 1.2 | 0.21 | n.d. | | | | |
| | 1 PFM and PDMS cage lost | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Apr-17 | ED samplers lost | | ED | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.01 | n.d. | n.d. | 0.001 |
| **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 | 5 | 5 | 5 | 5 |
| Detects (n) | | | | 0 | 8 | 7 | 6 | 2 | 8 | 0 | 8 | 3 | 0 | 5 | 4 | 8 | 0 | | 8 | 7 | 0 | 0 | 4 | 0 | 0 | 0 | 5 | 5 | 0 | 5 | 2 | 1 | 1 |
| % Detects | | | | 0 | 100 | 88 | 75 | 25 | 100 | 0 | 100 | 38 | 0 | 63 | 50 | 100 | 0 | | 100 | 88 | 0 | 0 | 50 | 0 | 0 | 0 | 63 | 63 | 0 | 100 | 40 | 20 | 20 |
| Minimum detected concentration | | | | n.d. | 0.80 | n.d. | n.d. | n.d. | 1.3 | n.d. | 0.58 | n.d. | n.d. | n.d. | n.d. | 0.05 | n.d. | 1.7 | 0.05 | 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. |
| Maximum concentration | | | | n.d. | 18 | 1.7 | 0.39 | 0.04 | 70 | n.d. | 20 | 0.50 | n.d. | 0.07 | 0.15 | 0.41 | n.d. | 77 | 0.38 | 2.2 | n.d. | n.d. | 0.46 | n.d. | n.d. | n.d. | 3.33 | 0.30 | n.d. | 0.03 | 0.02 | 0.1 | 0.001 |

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-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-16<br>Jun-16<br>Jul-16 | 19-May-16 | 26-Jul-16 | ED** | n.d. | 15 | n.d. | 0.03 | n.d. | 30 | n.d. | 10 | 0.11 | n.d. | 0.05 | 0.07 | 1.6 | n.d. | 37 | 7.8 | 3.0 | n.d. | n.d. | 0.78 | n.d. | n.d. | 0.17 | 1.3 | 0.16 | n.d. | | | | |
| Aug-16 | Samplers lost | | ED | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Sep-16<br>Oct-16 | Samplers lost | | ED | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Nov-16 | Samplers lost | | ED | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Dec-16 | 25-Nov-16 | 17-Dec-16 | ED | n.d. | 15 | 0.86 | 0.14 | n.d. | 30 | n.d. | 12 | n.d. | n.d. | 0.02 | n.d. | 0.03 | n.d. | 37 | 0.67 | 0.67 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.07 | 1.7 | n.d. | n.d. | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.01 | 0.03 | n.d. | n.d. |
| Jan-17 | 17-Dec-16 | 02-Feb-17 | ED** | 0.28 | 75 | 4.5 | 1.1 | n.d. | 120 | n.d. | 40 | 0.88 | n.d. | 0.17 | 0.60 | 0.27 | n.d. | 148 | 3.5 | 7.0 | n.d. | n.d. | n.d. | n.d. | 0.40 | 0.43 | 4.5 | 0.09 | n.d. | | | | |
| | Only EDs deployed | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Feb-17 | 02-Feb-17 | 07-Mar-17 | ED** | 0.26 | 42 | 2.6 | 0.49 | n.d. | 56 | n.d. | 15 | 0.46 | n.d. | 0.22 | 0.28 | 0.14 | n.d. | 70 | 0.63 | 1.0 | n.d. | n.d. | 0.45 | n.d. | n.d. | n.d. | 1.1 | 0.15 | n.d. | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.01 | 0.01 | 1.2 | n.d. |
| Mar-17 | Samplers lost | | ED | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Apr-17 | Samplers not deployed | | ED | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | PDMS | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| **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) | | | | 2 | 4 | 3 | 4 | 0 | 4 | 0 | 4 | 3 | 0 | 4 | 3 | 4 | 0 | | 4 | 4 | 0 | 0 | 2 | 0 | 1 | 3 | 4 | 3 | 0 | 2 | 2 | 1 | 0 |
| % Detects | | | | 50 | 100 | 75 | 100 | 0 | 100 | 0 | 100 | 75 | 0 | 100 | 75 | 100 | 0 | | 100 | 100 | 0 | 0 | 50 | 0 | 25 | 75 | 100 | 75 | 0 | 100 | 100 | 50 | 0 |
| Minimum detected concentration | | | | n.d. | 15 | n.d. | 0.03 | n.d. | 30 | n.d. | 10 | n.d. | n.d. | 0.02 | n.d. | 0.03 | n.d. | 37 | 0.63 | 0.67 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1.1 | n.d. | n.d. | 0.01 | 0.01 | n.d. | n.d. |
| Maximum concentration | | | | 0.28 | 75 | 4.5 | 1.1 | n.d. | 120 | n.d. | 40 | 0.88 | n.d. | 0.22 | 0.60 | 1.6 | n.d. | 148 | 7.8 | 7.0 | n.d. | n.d. | 0.78 | n.d. | 0.40 | 0.43 | 4.5 | 0.16 | n.d. | 0.01 | 0.03 | 1.2 | 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-16 Jun-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. |
| Jul-16 Aug-16 Sep-16 | 20-Jun-16 | 20-Sep-16 | ED** | n.d. | 0.27 | n.d. | 0.05 | n.d. | 0.38 | n.d. | 0.08 | n.d. | n.d. | n.d. | 1.9 | 2.3 | n.d. | **0.77** | 0.19 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Oct-16 | 20-Sep-16 | 14-Nov-16 | ED** | n.d. | 0.14 | n.d. | 0.04 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.64 | 0.18 | n.d. | **0.08** | 0.06 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Nov-16 | 14-Nov-16 | 02-Dec-16 | ED | n.d. | 0.14 | n.d. | n.d. | n.d. | 0.19 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.21 | 0.09 | n.d. | **0.24** | 0.02 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Dec-16 Jan-17 | 02-Dec-16 | 17-Jan-17 | ED** | n.d. | 0.32 | n.d. | n.d. | n.d. | 0.12 | n.d. | 0.05 | n.d. | n.d. | n.d. | 0.33 | 0.14 | n.d. | **0.23** | 0.05 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Feb-17 | 17-Jan-17 | 20-Feb-17 | ED** | n.d. | 0.13 | n.d. | n.d. | n.d. | 0.25 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.23 | 0.32 | n.d. | **0.32** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Mar-17 | 20-Feb-17 | 08-Mar-17 | ED | n.d. | 0.35 | n.d. | n.d. | n.d. | 0.20 | n.d. | 0.06 | n.d. | n.d. | n.d. | 0.20 | 0.47 | n.d. | **0.34** | n.d. | 0.05 | n.d. | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Apr-17 | 08-Mar-17 Overdeployed | 19-Jun-17 | ED | | | | | | | | | | | | | | | | | | | | | | | | | | |
| **Summary** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Samples (n) | | | | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
| Detects (n) | | | | 0 | 6 | 0 | 2 | 0 | 6 | 0 | 3 | 0 | 0 | 0 | 6 | 7 | 0 | | 4 | 2 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| % Detects | | | | 0 | 86 | 0 | 29 | 0 | 86 | 0 | 43 | 0 | 0 | 0 | 86 | 100 | 0 | | 57 | 29 | 0 | 14 | 0 | 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. | **0.08** | 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. | 0.35 | n.d. | 0.05 | n.d. | 0.38 | n.d. | 0.08 | n.d. | n.d. | n.d. | 1.9 | 2.3 | n.d. | **0.77** | 0.19 | 0.15 | n.d. | 0.03 | n.d. | 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

**Concentration is average of duplicate samplers

# 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 2016–17 wet season

| 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 FOCUS REGION** | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Barratta Creek mouth | 14-Sep-16 | n.d. | 11 | 2.3 | 0.8 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2.0 | 0.94 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1.2 | n.d. | n.d. |
| Barratta Creek mouth | 30-Nov-16 | n.d. | 0.92 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | <1.1 | n.d. | n.d. | n.d. | n.d. | 1.3 | 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 | 30-Dec-16 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | <0.59 | n.d. | 1.43 | n.d. | <1.5 | 0.7 | 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 RIVERS TRANSECT** | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Russell/Mulgrave mouth | 13-Jan-17 | n.d. | 27 | 5.9 | 1.7 | n.d. | 105 | n.d. | 32 | 1.3 | n.d. | n.d. | 0.76 | n.d. | <1.7 | 122 | 4.2 | 9.0 | n.d. | n.d. | 2.3 | n.d. | n.d. | 3.9 | 2.4 | 33 | 1.7 | 0.57 |
| High Island | 13-Jan-17 | n.d. | 5.4 | 0.92 | n.d. | n.d. | 18 | n.d. | 4.6 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 21 | 1.0 | 1.7 | n.d. | 0.53 | n.d. | n.d. | n.d. | n.d. | n.d. | 3.3 | n.d. | n.d. |
| Russell/Mulgrave Junction | 21-Jan-17 | n.d. | 18 | 13 | 2.2 | n.d. | 49 | n.d. | 30 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 65 | 2.7 | 17 | n.d. | 4.7 | n.d. | n.d. | n.d. | 4.0 | 1.6 | 99 | 2.2 | 0.52 |
| High Island | 21-Jan-17 | n.d. | 3.0 | n.d. | n.d. | n.d. | 5.0 | n.d. | 1.5 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 6.0 | n.d. | 1.2 | n.d. | 1.1 | 3.9 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Russell/Mulgrave mouth | 17-Feb-17 | n.d. | 417 | 29 | 11 | 7.4 | 299 | n.d. | 99 | 1.5 | n.d. | 3.9 | 3.1 | n.d. | <0.53 | 407 | 23 | 306 | n.d. | 9.1 | 605 | n.d. | n.d. | 70 | 48 | 25 | 10 | 3.0 |
| High Island | 17-Feb-17 | n.d. | 44 | 2.9 | 1.0 | n.d. | 39 | n.d. | 23 | n.d. | <0.60 | n.d. | n.d. | n.d. | <0.56 | 56 | n.d. | 37 | n.d. | n.d. | 52 | n.d. | n.d. | 11 | 3.4 | 3.0 | 1.9 | n.d. |
| Russell/Mulgrave mouth | 23-Mar-17 | n.d. | 15 | 5.6 | 0.93 | n.d. | 27 | n.d. | 18 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 37 | n.d. | 17 | n.d. | 0.93 | 12 | n.d. | n.d. | n.d. | 3.8 | 24 | 5.1 | 0.60 |
| High Island | 23-Mar-17 | n.d. | 3.0 | 0.67 | n.d. | n.d. | 3.6 | n.d. | 1.7 | n.d. | n.d. | n.d. | n.d. | n.d. | <0.55 | 4.8 | n.d. | 1.1 | n.d. | n.d. | 1.1 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| **TULLY RIVER TRANSECT** | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Tully River Mouth | 11-Jan-17 | n.d. | 23 | 2.9 | 1.2 | n.d. | 97 | n.d. | 20 | 6.0 | n.d. | n.d. | n.d. | n.d. | <1.3 | 109 | 6.5 | 8.4 | n.d. | 2.1 | n.d. | n.d. | n.d. | n.d. | n.d. | 80 | n.d. | 1.3 |
| Dunk Island north | 12-Jan-17 | <1.6 | 19 | 2.8 | 1.3 | n.d. | 59 | n.d. | 20 | 5.6 | <1.0 | n.d. | 0.51 | n.d. | <1.6 | 73 | 3.7 | 8.7 | n.d. | 1.0 | n.d. | n.d. | n.d. | n.d. | 4.3 | 42 | n.d. | 0.61 |
| Bedarra Island | 12-Jan-17 | n.d. | 19 | 3.1 | 1.3 | n.d. | 65 | n.d. | 22 | 6.8 | n.d. | n.d. | n.d. | n.d. | <1.7 | 77 | 4.8 | 9.6 | n.d. | 1.5 | n.d. | n.d. | n.d. | n.d. | 4.3 | 54 | n.d. | 0.72 |
| Tully River Mouth | 20-Jan-17 | n.d. | 10 | 1.5 | 0.77 | n.d. | 20 | n.d. | 8.4 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 25 | 1.8 | 3.4 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1.1 | 11 | n.d. | n.d. |
| Dunk Island north | 20-Jan-17 | n.d. | 1.8 | n.d. | n.d. | n.d. | 3.6 | n.d. | 1.4 | n.d. | <2.0 | <0.26 | n.d. | n.d. | 2.1 | 4.7 | 0.26 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.57 | n.d. | <0.26 |
| Bedarra Island | 20-Jan-17 | n.d. | 11 | 1.6 | 0.82 | n.d. | 23 | n.d. | 9.2 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 29 | 3.0 | 5.1 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 4.4 | n.d. | n.d. |
| Tully River Mouth | 18-Feb-17 | n.d. | 150 | 12 | 3.8 | n.d. | 115 | n.d. | 67 | 25 | n.d. | 0.82 | n.d. | n.d. | <0.71 | 166 | 0.97 | 79 | n.d. | 4.0 | n.d. | n.d. | 1.0 | 3.8 | 3.8 | 58 | n.d. | 4.7 |
| Dunk Island north | 18-Feb-17 | n.d. | 5.9 | 0.75 | n.d. | n.d. | 6.4 | n.d. | 3.5 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 8.8 | n.d. | 3.6 | n.d. | n.d. | n.d. | n.d. | n.d. | 2.0 | n.d. | 0.88 | n.d. | n.d. |
| Bedarra Island | 18-Feb-17 | n.d. | 24 | 1.9 | 0.75 | n.d. | 24 | n.d. | 13 | 0.75 | n.d. | n.d. | n.d. | n.d. | n.d. | 32 | n.d. | 15 | n.d. | 0.59 | n.d. | n.d. | n.d. | 3.3 | n.d. | 5.40 | n.d. | n.d. |
| **TULLY RIVER SALINITY TRANSECT I (MAY 2016)** | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Tully River upstream | 25-May-16 | n.d. | 1.9 | 3.0 | n.d. | n.d. | 12 | n.d. | 5.3 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 15 | 0.76 | 5.9 | n.d. | 0.54 | n.d. | n.d. | n.d. | n.d. | 2.1 | 41 | n.d. | n.d. |
| Tully River mouth | 25-May-16 | n.d. | 2.1 | 1.1 | n.d. | n.d. | 8.0 | n.d. | 2.2 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 9.3 | n.d. | 4.4 | n.d. | n.d. | n.d. | n.d. | n.d. | 1.7 | n.d. | 10 | n.d. | n.d. |
| Tully offshore transect (P2) | 25-May-16 | n.d. | 3.6 | 3.7 | 0.71 | n.d. | 26 | n.d. | 6.6 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 29 | 0.80 | 14 | n.d. | 0.86 | n.d. | n.d. | n.d. | 2.5 | 3.0 | 54 | n.d. | n.d. |
| Tully offshore transect (P3) | 25-May-16 | n.d. | 3.4 | 3.2 | n.d. | n.d. | 22 | n.d. | 5.7 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 25 | 0.83 | 13 | n.d. | 0.60 | n.d. | n.d. | n.d. | 1.8 | 1.6 | 44 | n.d. | n.d. |
| Tully offshore transect (P4) | 25-May-16 | n.d. | 3.3 | 3.2 | 0.35 | n.d. | 22 | n.d. | 5.7 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 25 | 0.71 | 13 | n.d. | 0.62 | n.d. | n.d. | n.d. | 1.3 | 2.7 | 45 | n.d. | n.d. |
| Tully offshore transect (P5) | 25-May-16 | n.d. | 3.2 | 3.2 | 0.77 | n.d. | 22 | n.d. | 6.7 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 25 | 1.7 | 16 | n.d. | 1.3 | n.d. | n.d. | n.d. | n.d. | 2.7 | 41 | n.d. | n.d. |
| Tully offshore transect (P6) | 25-May-16 | n.d. | 1.8 | 0.82 | n.d. | n.d. | 10 | n.d. | 3.7 | n.d. | n.d. | n.d. | 1.7 | n.d. | n.d. | 12 | 1.3 | 7.9 | n.d. | n.d. | n.d. | n.d. | n.d. | 1.8 | 0.97 | 7.6 | n.d. | n.d. |
| Tully offshore transect (P7) | 25-May-16 | n.d. | 2.9 | 2.5 | n.d. | n.d. | 30 | n.d. | 7.9 | n.d. | n.d. | n.d. | 1.1 | n.d. | n.d. | 34 | 0.83 | 24 | n.d. | 0.91 | n.d. | n.d. | n.d. | 3.0 | 3.1 | 29 | n.d. | n.d. |
| Tully offshore transect (P8) | 25-May-16 | n.d. | 2.1 | 1.4 | n.d. | n.d. | 22 | n.d. | 7.5 | 4.3 | n.d. | n.d. | 2.2 | n.d. | n.d. | 26 | 0.79 | 18 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2.1 | 17 | n.d. | n.d. |
| Dunk Island north (P9) | 25-May-16 | n.d. | 2.1 | 0.58 | n.d. | n.d. | 2.3 | n.d. | 0.69 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2.9 | n.d. | 0.61 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |

**Table G-1 (cont.)**: Concentrations in water (ng $L^{-1}$) measured at various locations offshore and in river mouths (along transects) using 250 mL grab samples during the 2016–17 wet season

| 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 |
| **TULLY RIVER SALINITY TRANSECT II (JANUARY 2017)** | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Tully River upstream | 11-Jan-17 | n.d. | 43 | 5.9 | 2.9 | n.d. | 175 | n.d. | 41 | 11 | n.d. | n.d. | 0.93 | n.d. | n.d. | 198 | 16 | 20 | n.d. | 5.1 | n.d. | n.d. | n.d. | n.d. | 30 | 166 | 2.3 | 3.1 |
| Tully offshore transect (P2) | 11-Jan-17 | <1.3 | 26 | 3.3 | 0.92 | n.d. | 86 | n.d. | 25 | 6.4 | <0.75 | n.d. | 0.45 | n.d. | <0.53 | 103 | 6.9 | 10 | n.d. | 1.9 | n.d. | n.d. | n.d. | n.d. | 3.5 | 61 | n.d. | 1.3 |
| Tully offshore transect (P3) | 11-Jan-17 | n.d. | 29 | 1.9 | 0.87 | n.d. | 101 | n.d. | 15 | 3.5 | n.d. | n.d. | n.d. | n.d. | <1.3 | 112 | 12 | 6.5 | n.d. | 3.3 | n.d. | n.d. | n.d. | n.d. | 5.1 | 73 | n.d. | 2.5 |
| Tully offshore transect (P4) | 11-Jan-17 | n.d. | 1.6 | n.d. | n.d. | n.d. | 4.3 | n.d. | 0.93 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 4.9 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1.4 | n.d. | n.d. |
| Tully offshore transect (P5) | 11-Jan-17 | <2.4 | 55 | 7.2 | 3.4 | n.d. | 216 | n.d. | 50 | 14 | n.d. | n.d. | 0.89 | n.d. | n.d. | 248 | 17 | 23 | n.d. | 4.9 | n.d. | n.d. | n.d. | n.d. | 15 | 208 | n.d. | 2.8 |
| Tully offshore transect (P8) | 11-Jan-17 | n.d. | 21 | 2.9 | 1.1 | n.d. | 60 | n.d. | 18 | 8.1 | <0.52 | n.d. | n.d. | n.d. | <1.9 | 71 | 4.0 | 8.1 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2.7 | 37 | n.d. | 0.64 |
| Tully offshore transect (P10) | 11-Jan-17 | <2.1 | 49 | 6.7 | 3.0 | n.d. | 210 | n.d. | 48 | 12 | n.d. | n.d. | 0.34 | n.d. | <1.2 | 239 | 14 | 21 | n.d. | 4.4 | n.d. | n.d. | n.d. | n.d. | 27 | 206 | 1.1 | 2.5 |
| **TC DEBBIE FLOOD PLUME (VARIOUS CATCHMENTS)** | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Burdekin River mouth | 31-Mar-17 | n.d. | 1.5 | 0.58 | 0.31 | n.d. | n.d. | n.d. | 0.45 | n.d. | n.d. | n.d. | n.d. | 6.0 | n.d. | 0.95 | n.d. | 2.8 | n.d. | n.d. | 1.1 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Barratta Creek mouth | 01-Apr-17 | 14 | 128 | 15 | 5.3 | 5.8 | 5.8 | n.d. | 0.88 | n.d. | n.d. | 1.8 | n.d. | n.d. | <0.56 | 46 | 1.3 | 18 | n.d. | 1.7 | 18 | n.d. | n.d. | 9.0 | 2.4 | n.d. | 1.1 | n.d. |
| Fitzroy River mouth | 11-Apr-17 | n.d. | 1.9 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.67 | n.d. | n.d. | n.d. | 0.54 | 15 | <1.3 | 1.8 | 2.8 | 1.7 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Fitzroy River: 1/2 way to Egg Is | 11-Apr-17 | n.d. | 3.3 | 0.52 | 0.77 | n.d. | 1.3 | n.d. | 1.2 | n.d. | n.d. | n.d. | 0.72 | 26 | n.d. | 4.5 | 4.6 | 1.8 | n.d. | n.d. | 0.77 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Fitzroy River: east of Girt Is | 11-Apr-17 | n.d. | 12 | 1.3 | 2.4 | n.d. | 2.8 | n.d. | 3.6 | n.d. | <0.62 | n.d. | 2.2 | 85 | <1.3 | 14 | 18 | 5.5 | n.d. | 0.91 | n.d. | n.d. | n.d. | 1.4 | n.d. | 1.2 | n.d. | 1.4 |
| Pioneer River: Brampton Island | 10-Apr-17 | n.d. | 2.1 | n.d. | n.d. | n.d. | 1.7 | n.d. | 0.81 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2.3 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Pioneer River mouth | 10-Apr-17 | n.d. | 2.8 | 0.74 | n.d. | n.d. | 2.3 | n.d. | 1.4 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 3.4 | n.d. | 0.52 | n.d. | n.d. | 0.48 | n.d. | n.d. | n.d. | n.d. | 1.1 | n.d. | n.d. |
| Proserpine/O'Connell: Pine Is | 09-Apr-17 | n.d. | 6.4 | 1.1 | n.d. | n.d. | 6.9 | n.d. | 2.4 | n.d. | n.d. | n.d. | n.d. | n.d. | 2.2 | 8.9 | n.d. | 3.7 | n.d. | n.d. | 1.8 | n.d. | n.d. | n.d. | 0.53 | 1.8 | n.d. | n.d. |
| Proserpine River | 09-Apr-17 | n.d. | 28 | 5.1 | 2.1 | n.d. | 52 | n.d. | 18 | n.d. | n.d. | n.d. | n.d. | 3.2 | <1.4 | 65 | 9.1 | 25 | n.d. | 1.6 | 10 | n.d. | n.d. | n.d. | 0.80 | 27 | n.d. | n.d. |
| Proserpine River mouth | 09-Apr-17 | n.d. | 22 | 3.7 | 1.8 | n.d. | 33 | n.d. | 12 | n.d. | n.d. | n.d. | n.d. | 1.6 | <0.89 | 42 | 4.5 | 19 | n.d. | 1.1 | 7.0 | n.d. | n.d. | 3.0 | n.d. | 15 | n.d. | n.d. |
| W O'Connell River mouth | 09-Apr-17 | n.d. | 18 | 3.0 | 1.6 | n.d. | 28 | n.d. | 13 | n.d. | n.d. | n.d. | n.d. | 1.3 | <1.4 | 36 | 3.3 | 15 | n.d. | 0.68 | 5.8 | n.d. | n.d. | 3.2 | 2.6 | 11 | n.d. | n.d. |

# Appendix H Long term river flow rates and PSII-HEq of passive and grab samples

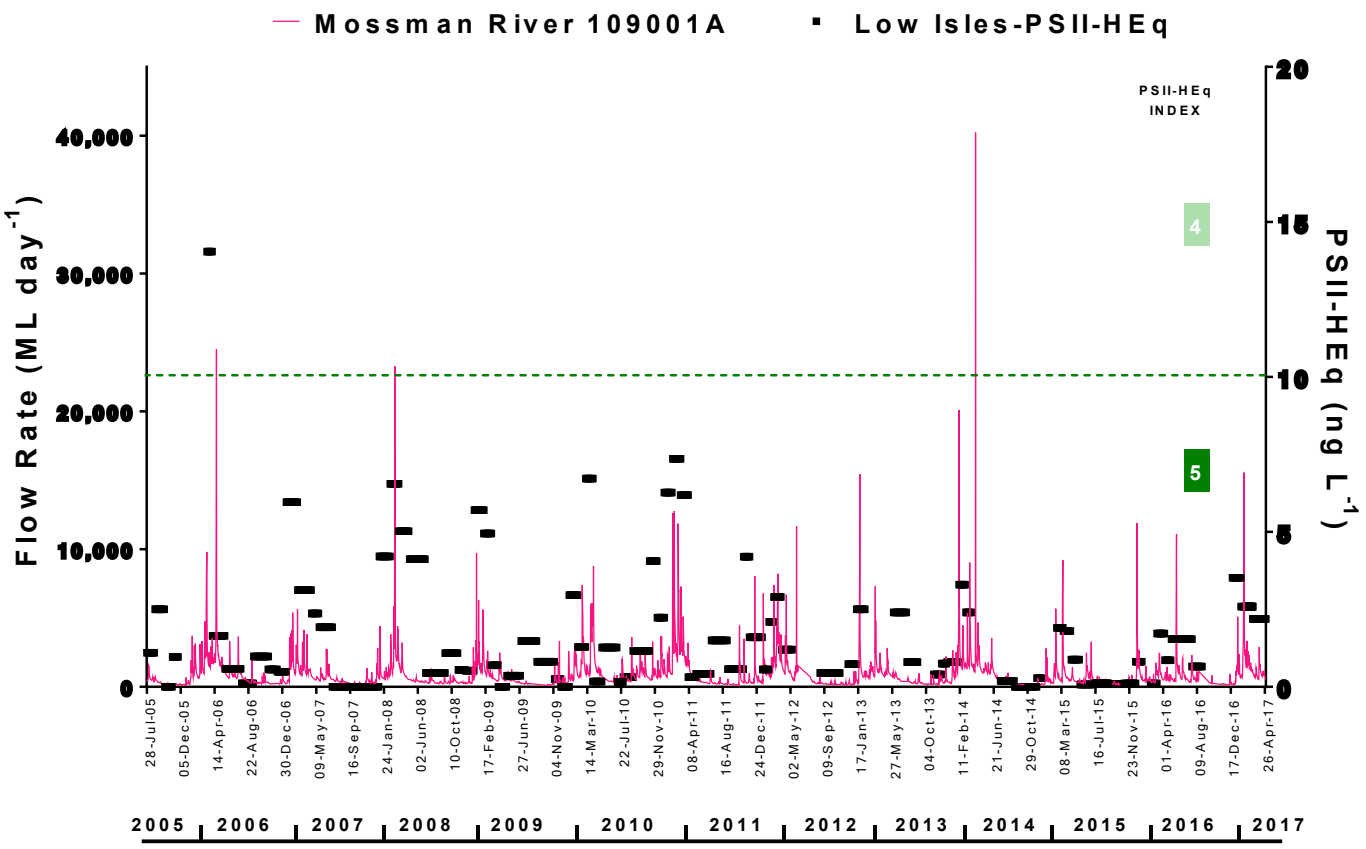



Figure H-1: Temporal trends in PSII-HEq with respect to river flow rate influencing passive sampler site at Low Isles in the Wet Tropics region since 2005. Flow data provided by DNRM, Stream Gauging Network.

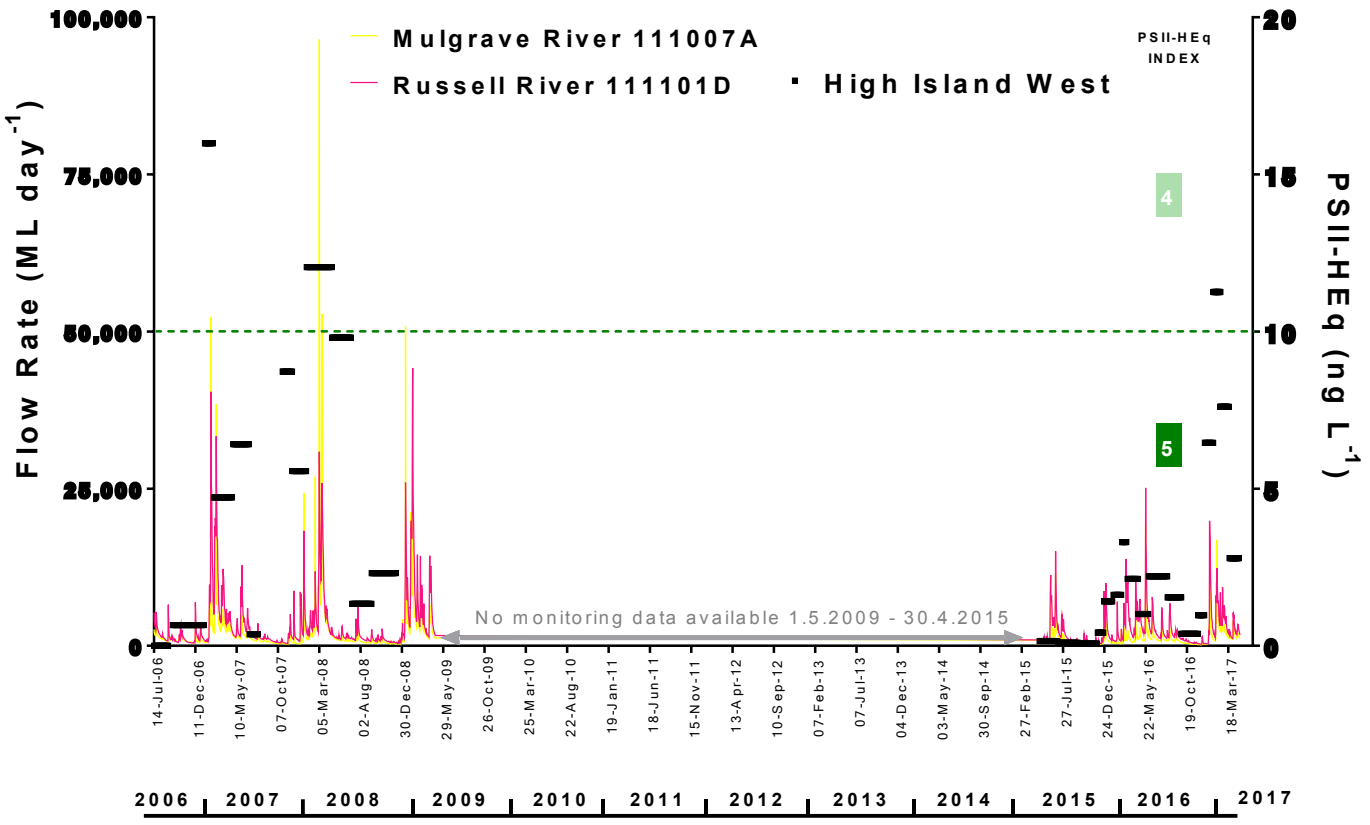



Figure H-2A: Temporal trends in PSII-HEq with respect to river flow rate influencing passive sampler site at High Island in the Wet Tropics region since 2006. Flow data provided by DNRM, Stream Gauging Network. No monitoring data were available 2009-2015.

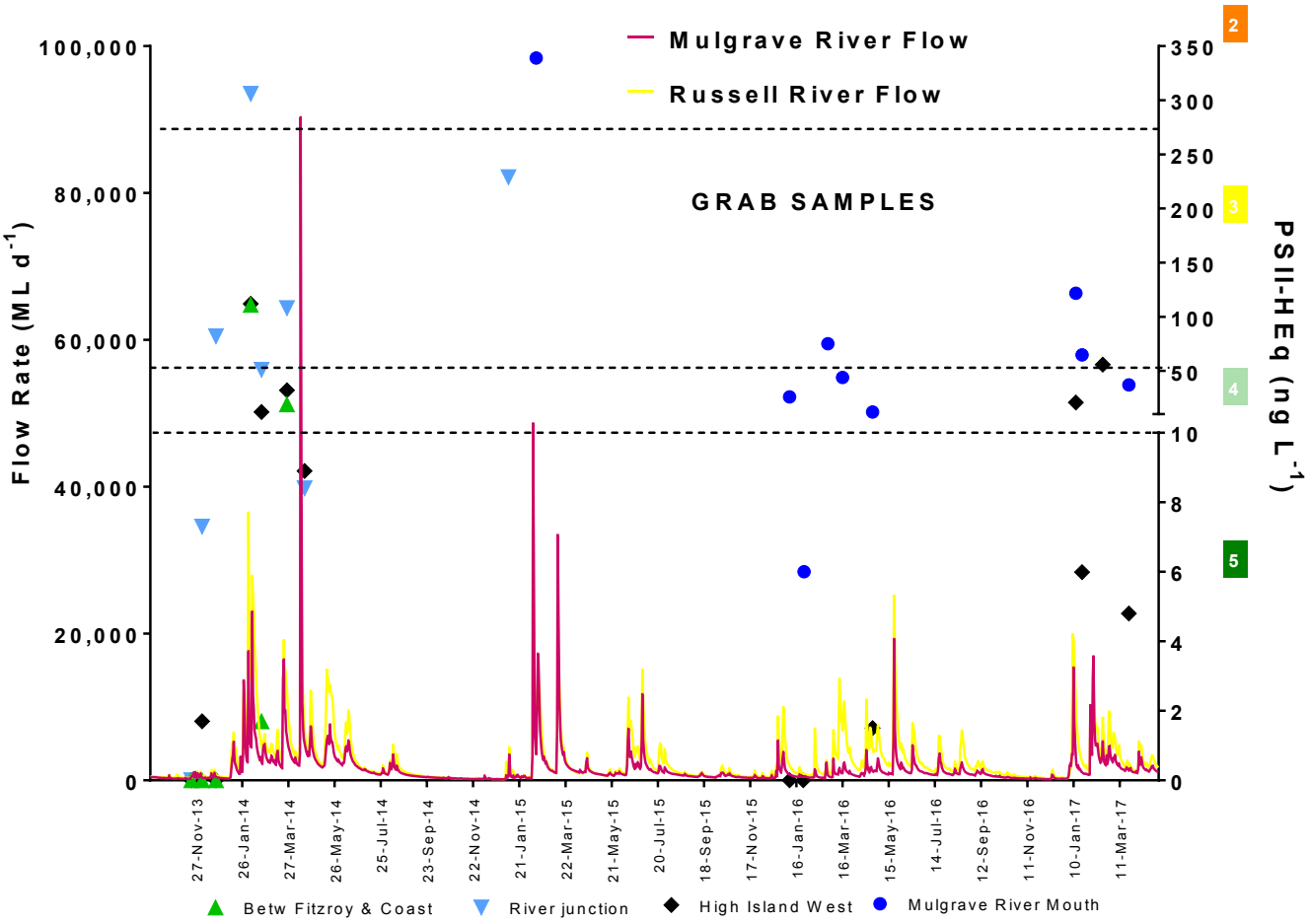



Figure H-3B: Temporal trends in PSII-HEq for grab sample with respect to Russel and Mulgrave Rivers' flow rate influencing flood plumes in the Wet Tropics region since 2007. Flow data provided by DNRM, Stream Gauging Network.

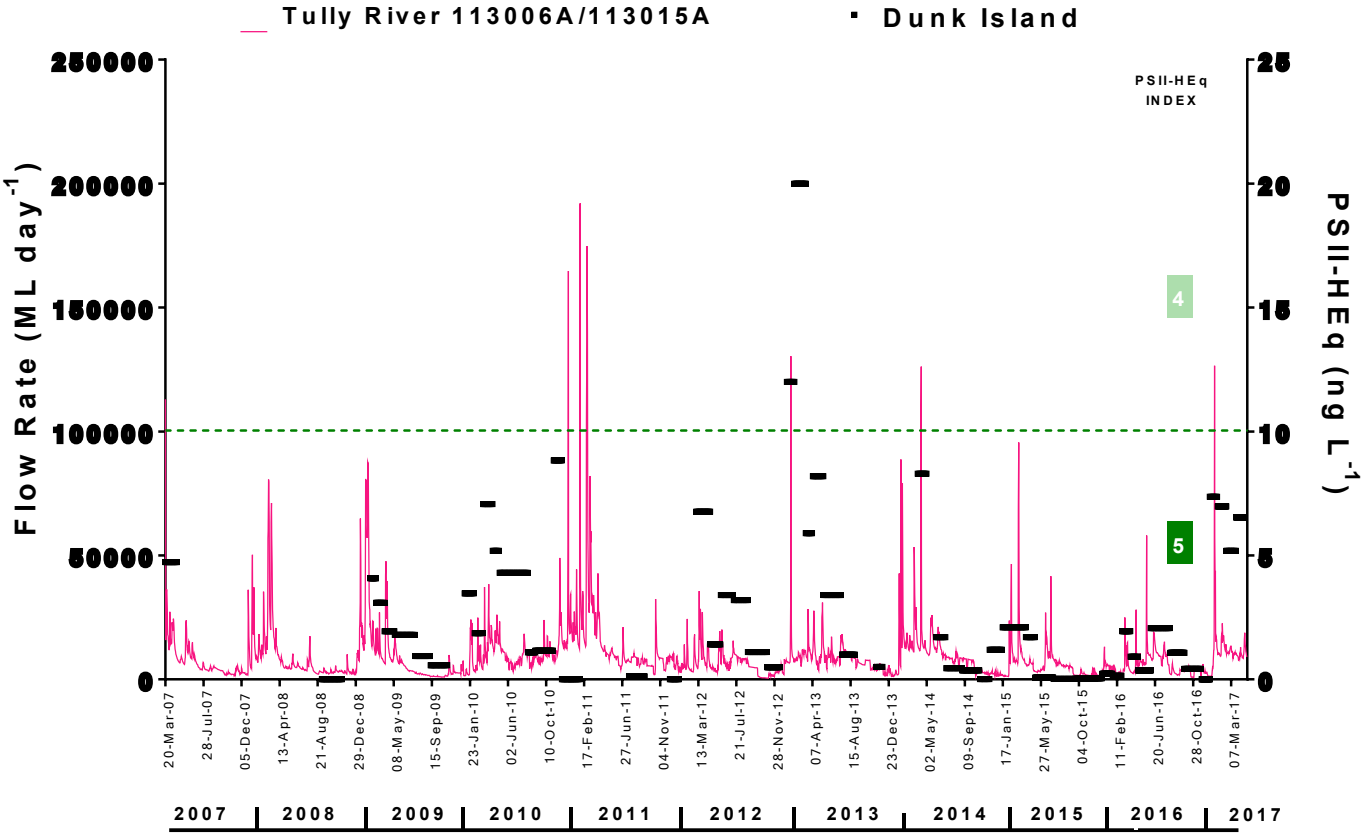



Figure H-4A: Temporal trends in PSII-HEq with respect to river flow rate influencing passive sampler site at Dunk Island in the Wet Tropics region since 2007. Flow data provided by DNRM, Stream Gauging Network.

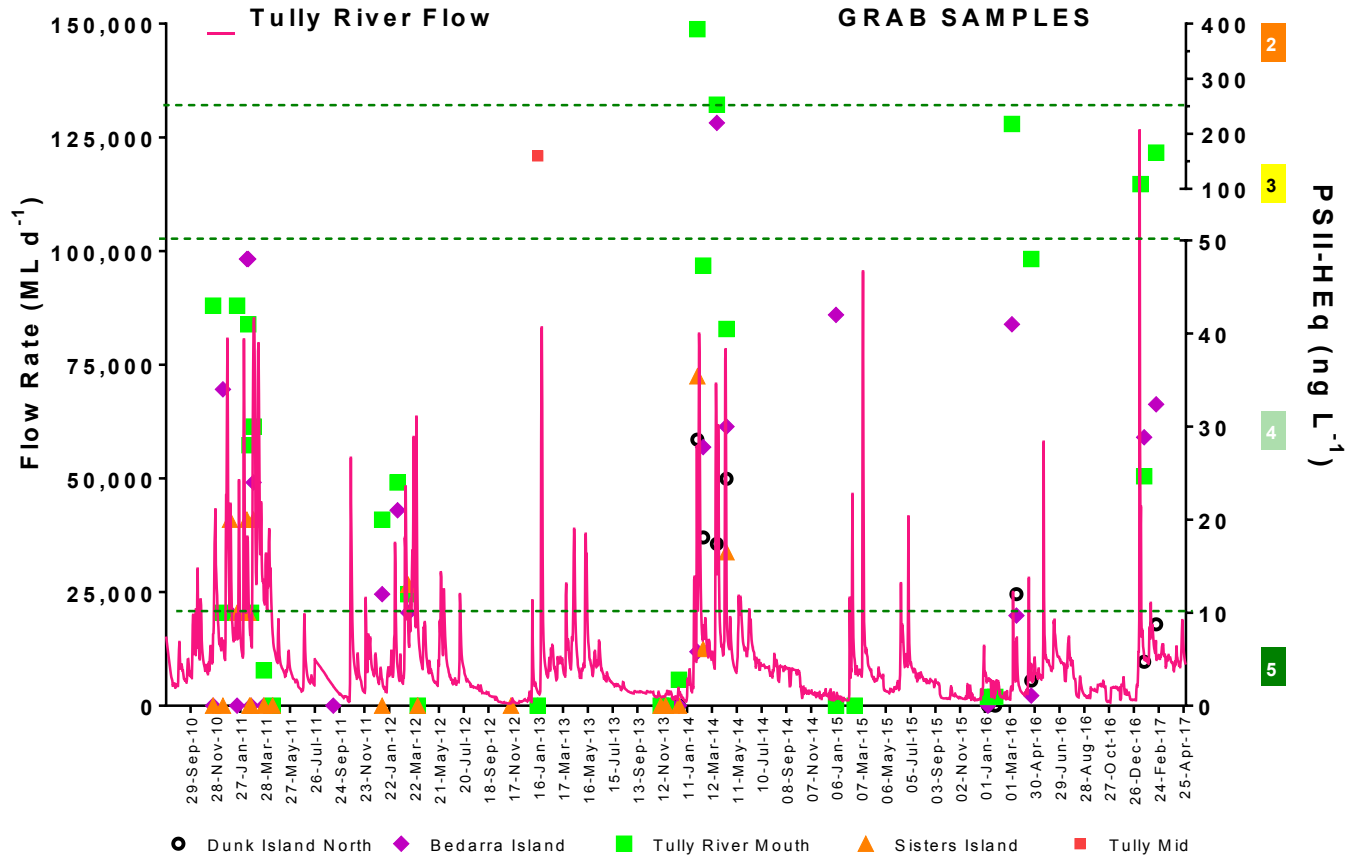


Figure H-5B: Temporal trends in PSII-HEq for grab samples with respect to Tully River flow rate influencing flood plumes in the Wet Tropics region since 2007. Flow data provided by DNRM, Stream Gauging Network.

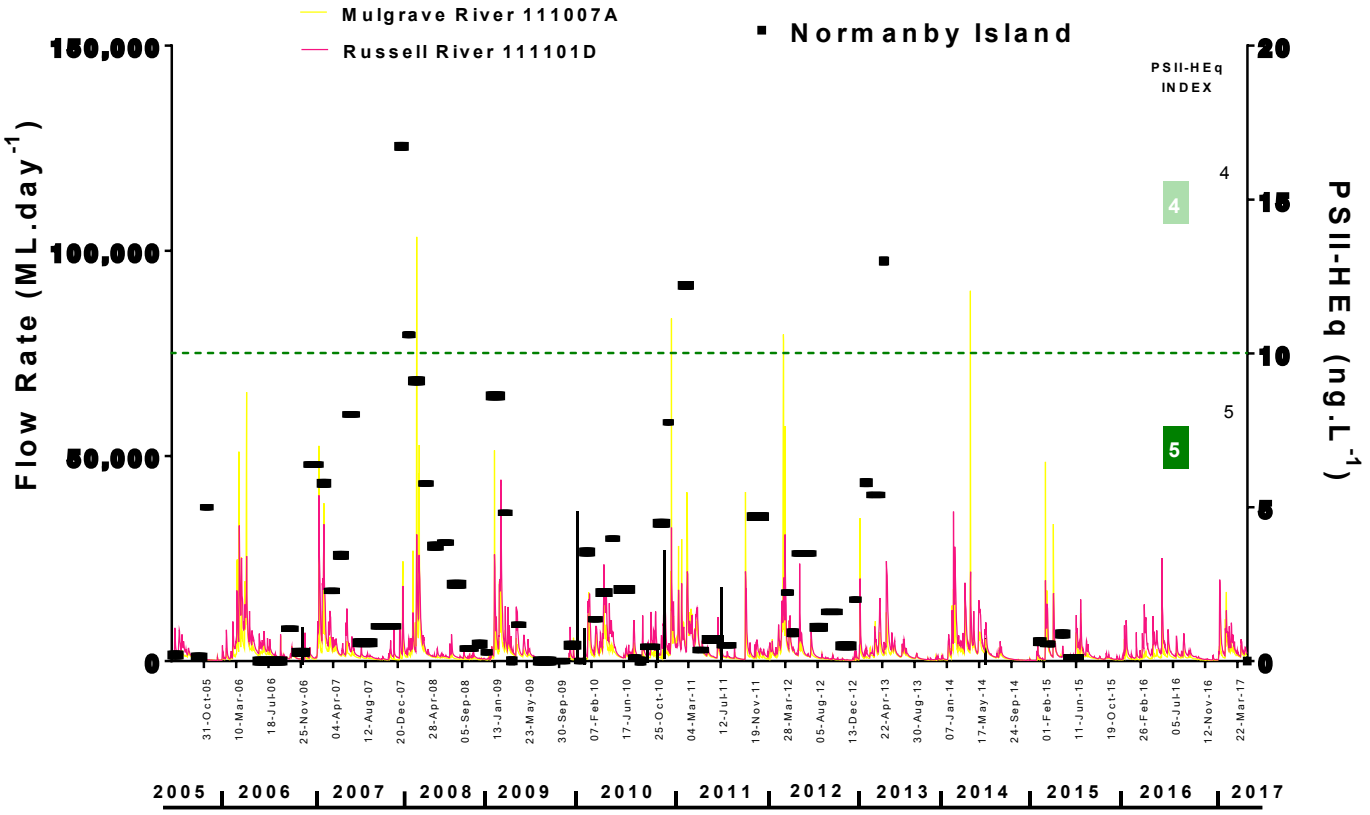



Figure H-6: Temporal trends in PSII-HEq with respect to river flow rate influencing passive sampler site at Normanby Island in the Wet Tropics region since 2005. Flow data provided by DNRM, Stream Gauging Network.

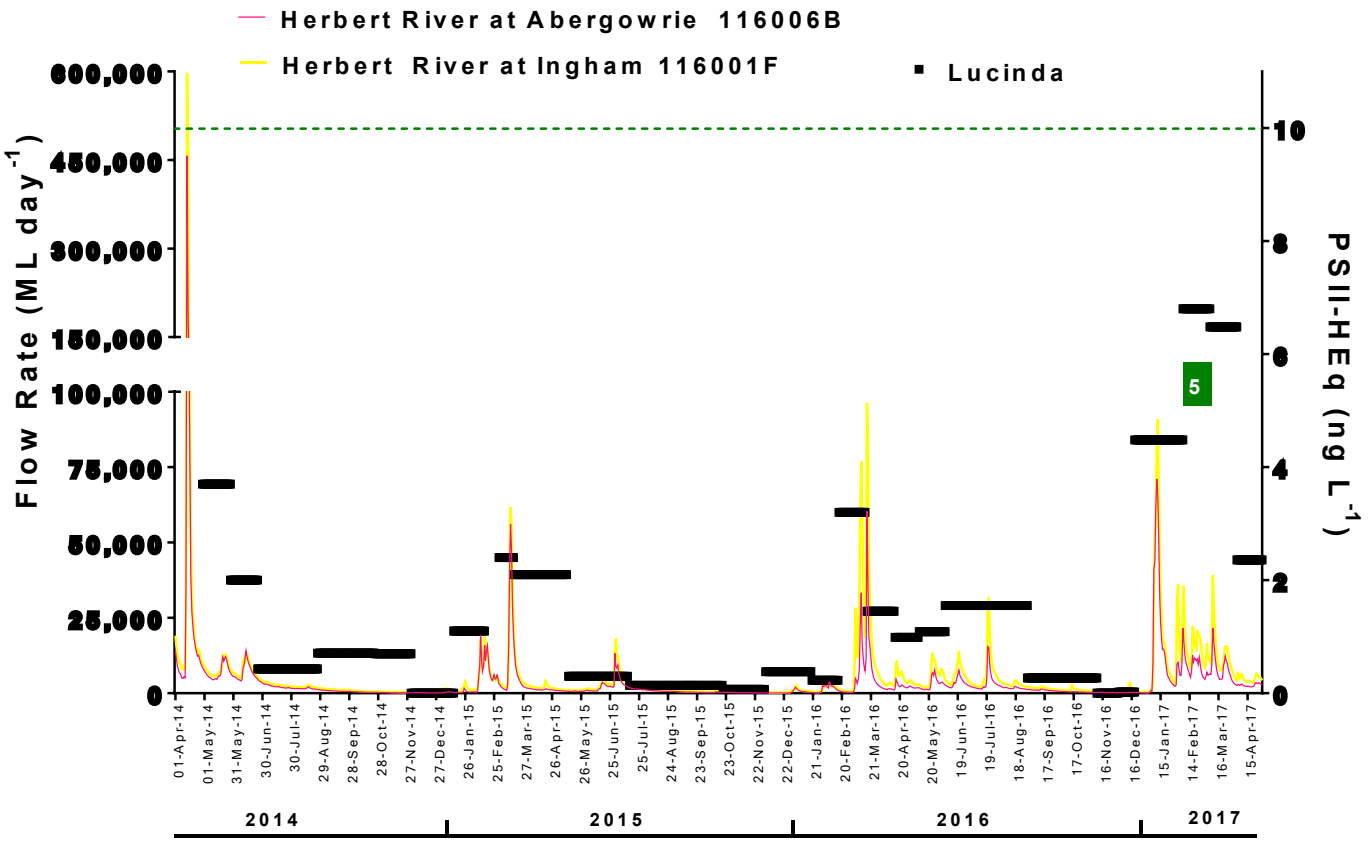



Figure H-7: Temporal trends in PSII-HEq with respect to river flow rate influencing passive sampler site at Lucinda in the Wet Tropics region since 2014. Flow data provided by Department of Environment and Resource Management, Stream Gauging Network.

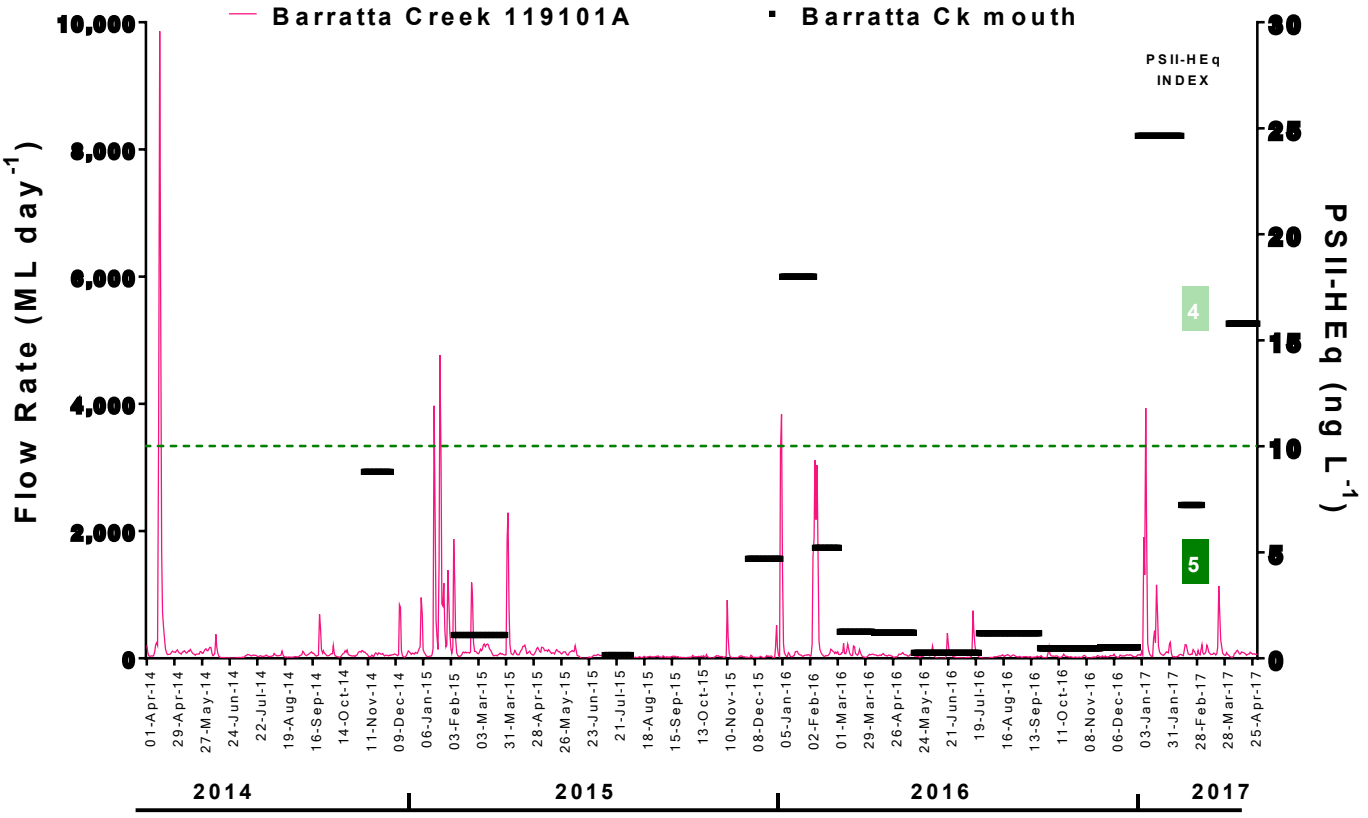



Figure H-8A: Temporal trends in PSII-HEq with respect to river flow rate influencing passive sampler site at Barratta Creek mouth in the Burdekin region since 2014. Flow data provided by DNRM, Stream Gauging Network.

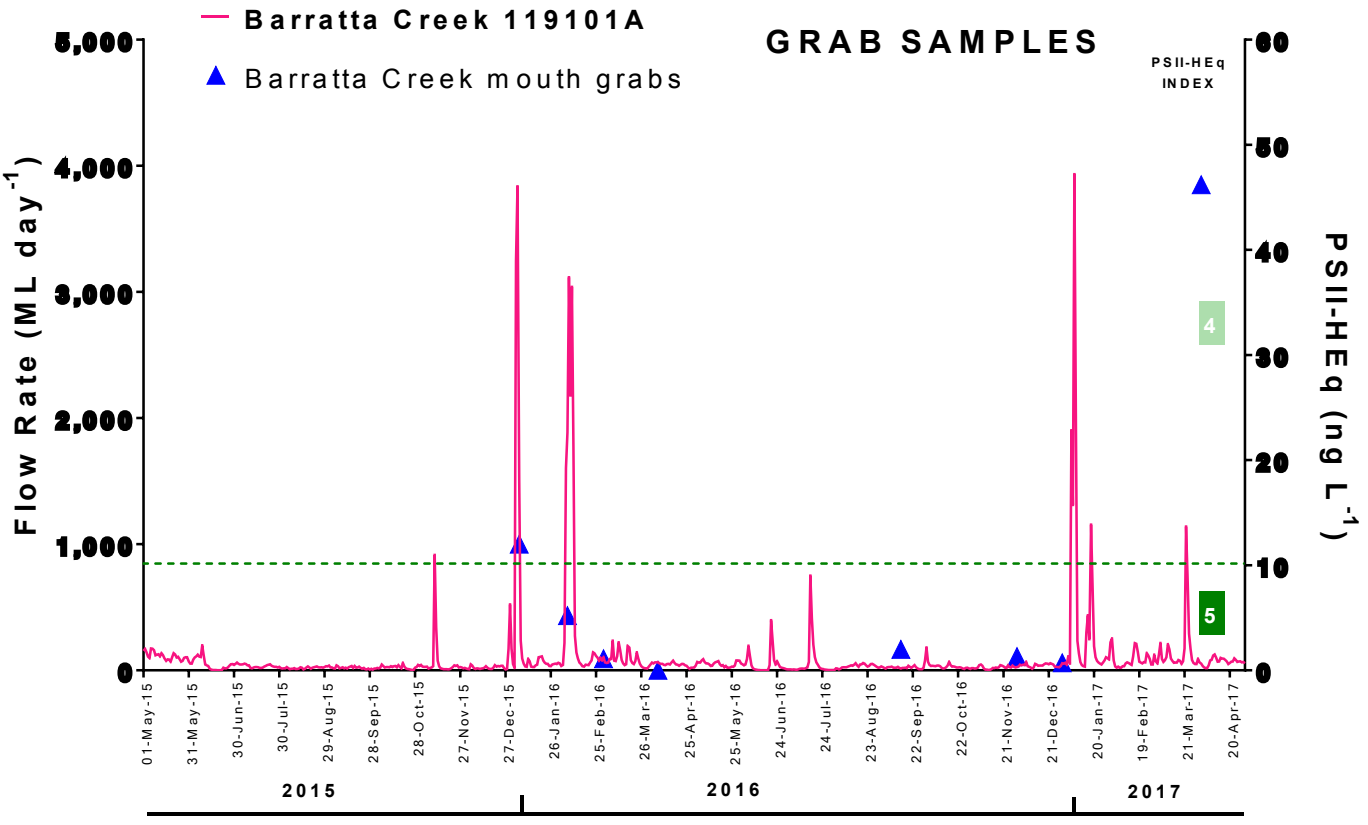



Figure H-6B: Temporal trends in PSII-HEq for grab samples with respect to river flow rate at Barratta Creek mouth in the Burdekin region since 2015 (in 2014-15, grab samples were collected upstream in Barratta Creek, data not shown). Flow data provided by DNRM, Stream Gauging Network

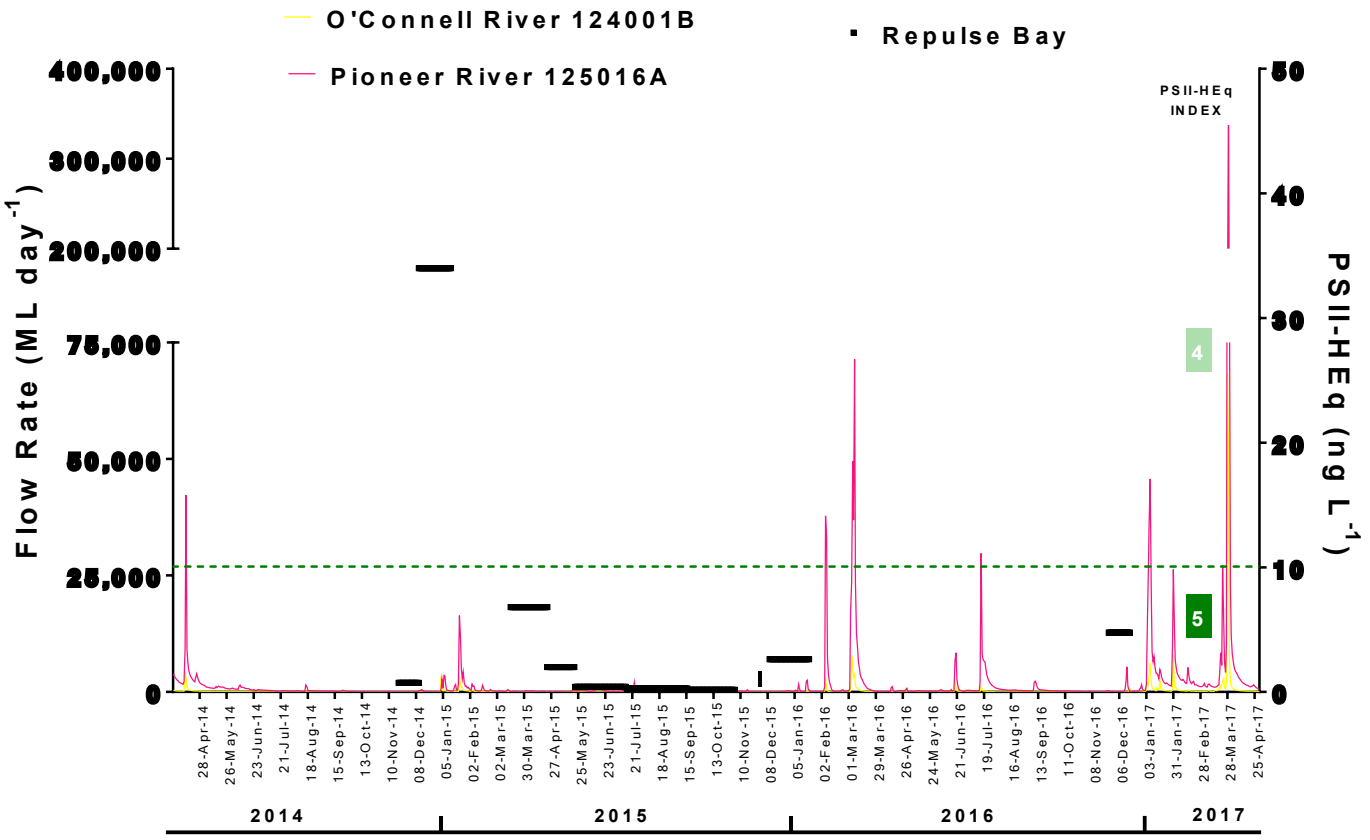



Figure H-9: Temporal trends in PSII-HEq with respect to river flow rate influencing passive sampler site at Repulse Bay in the Mackay Whitsunday region since 2014. Flow data provided by DNRM, Stream Gauging Network.

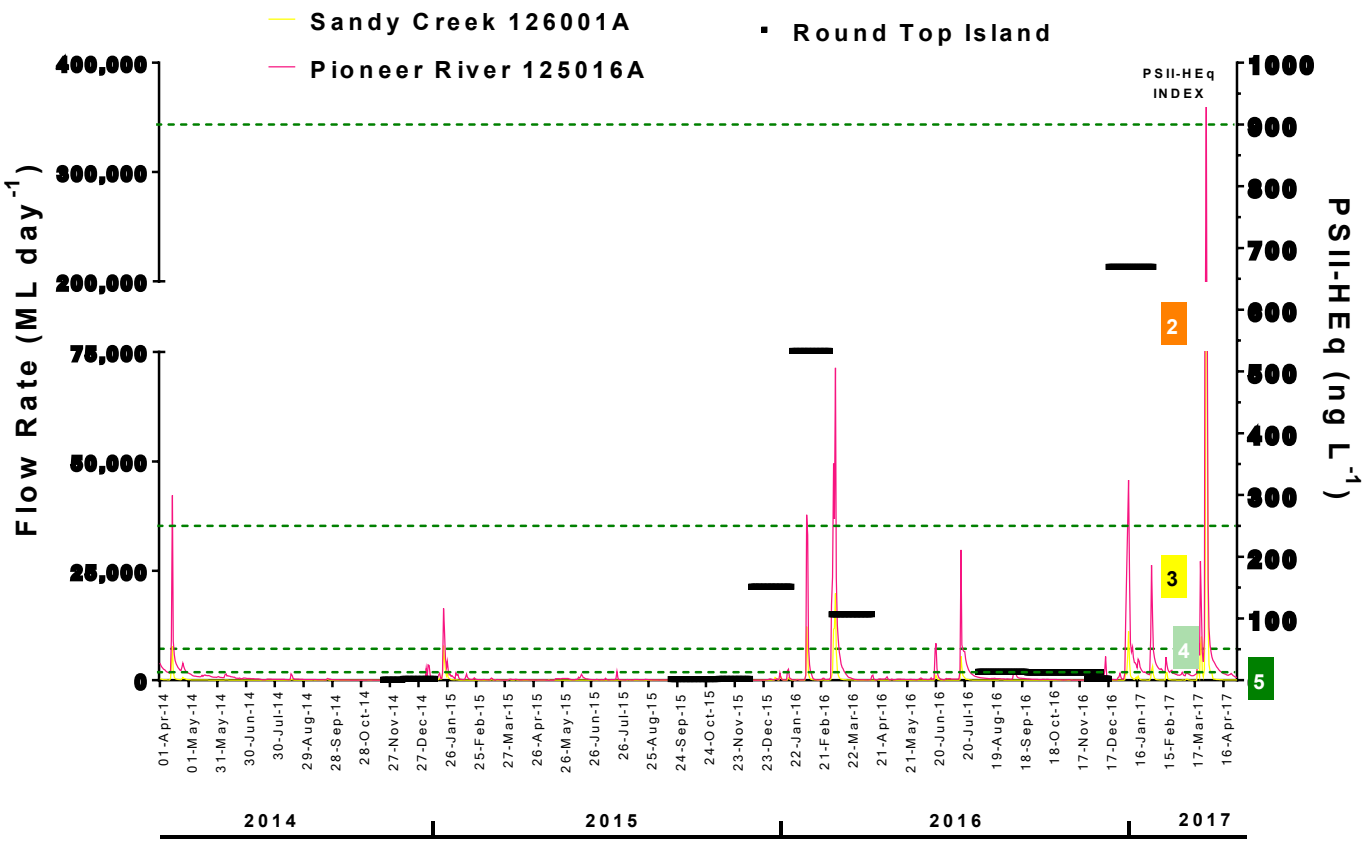



Figure H-10: Temporal trends in PSII-HEq with respect to river flow rate influencing passive sampler site at Round Top Island in the Mackay Whitsunday region since 2014. Flow data provided by DNRM, Stream Gauging Network.

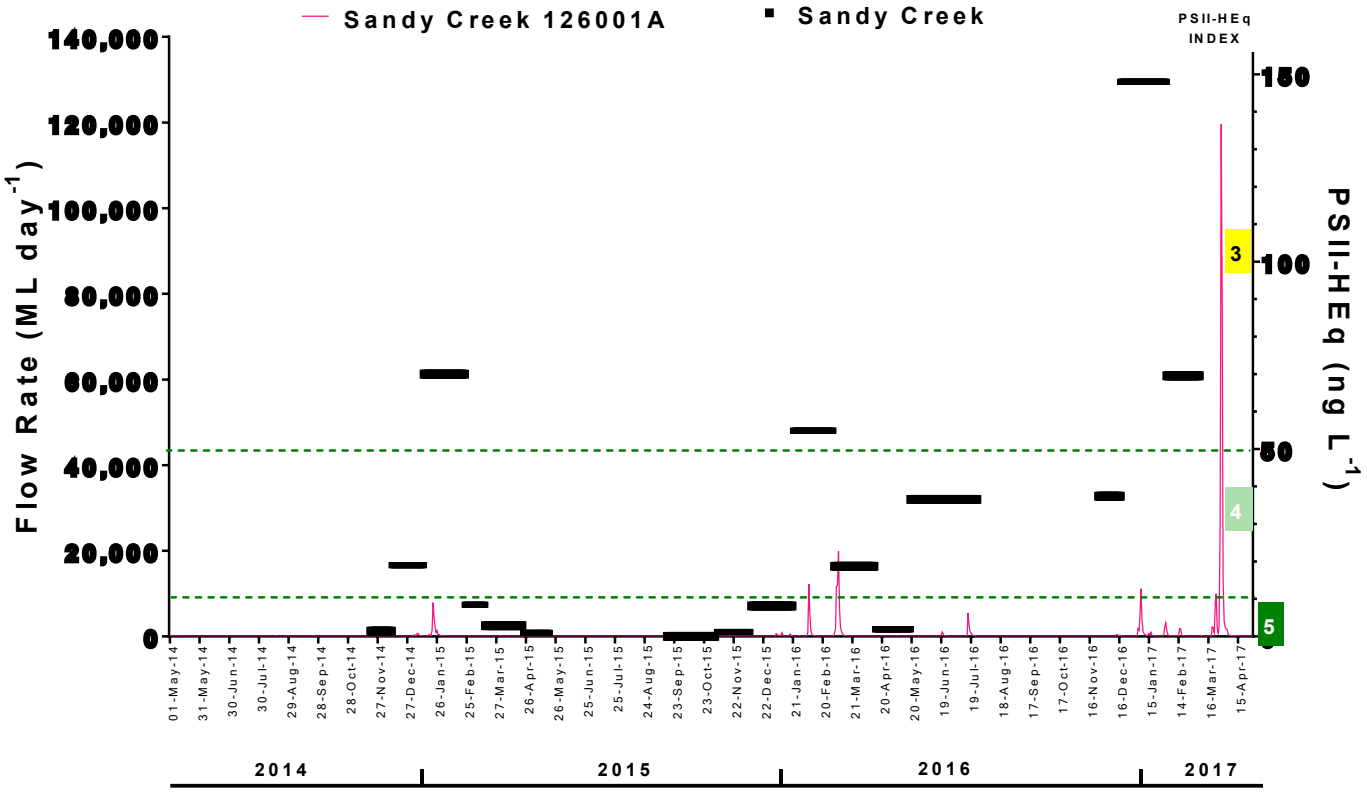



Figure H-11: Temporal trends in PSII-HEq with respect to river flow rate influencing passive sampler site at Sandy Creek in the Mackay Whitsunday region since 2014. Flow data provided by DNRM, Stream Gauging Network.

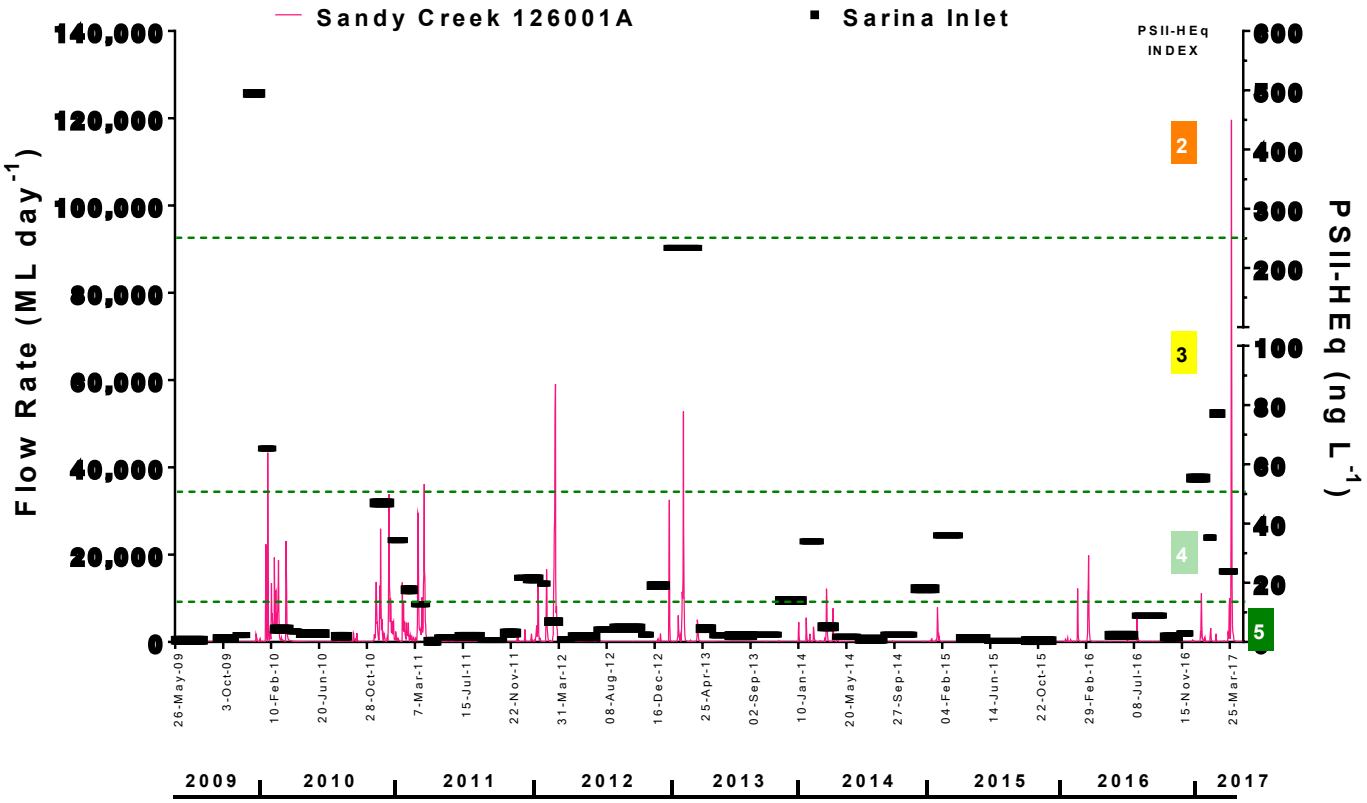



Figure H-12: Temporal trends in PSII-HEq with respect to river flow rate influencing passive sampler site at Sarina Inlet in the Mackay Whitsunday region since 2009. Flow data provided by DNRM, Stream Gauging Network.

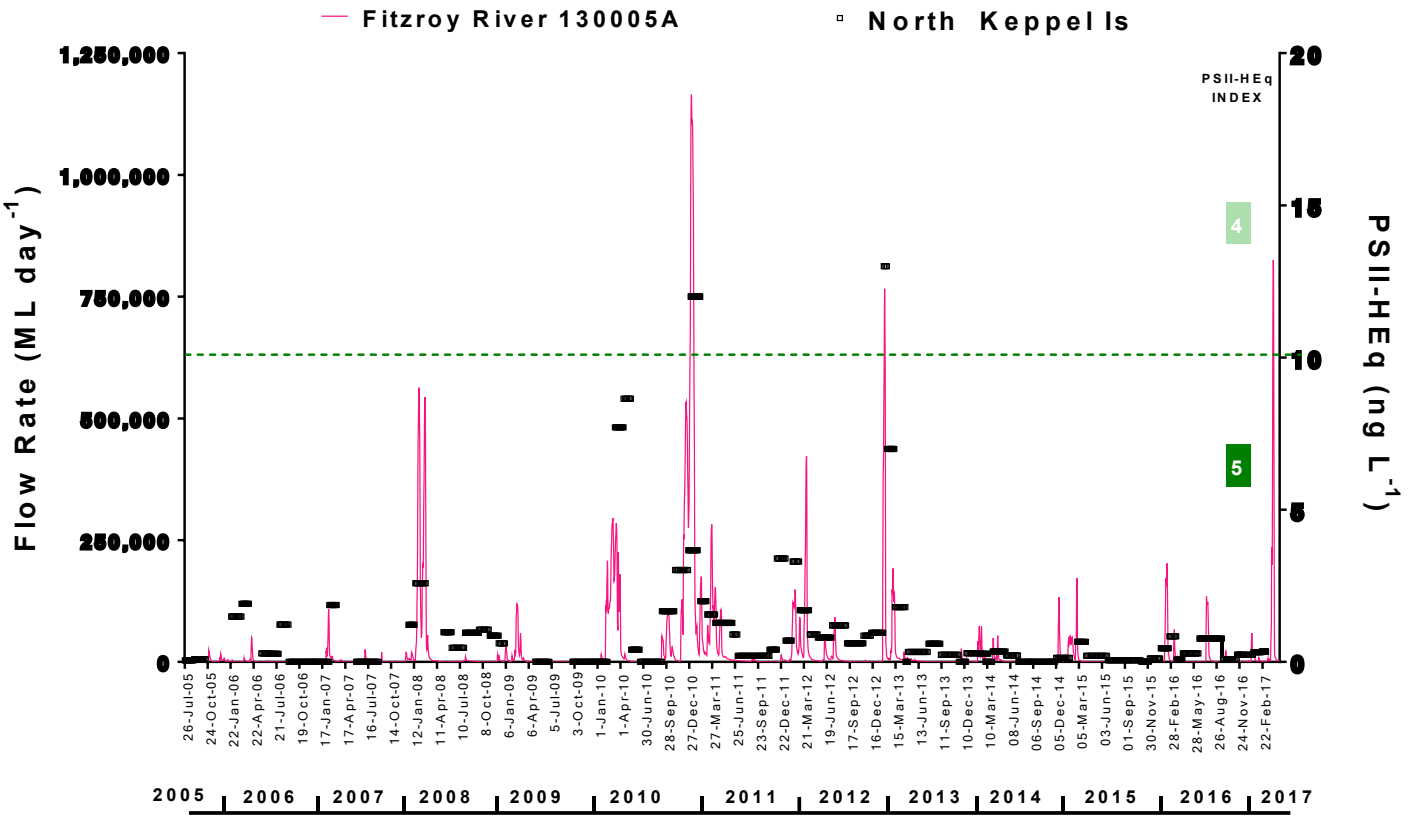



Figure H-13: Temporal trends in PSII-HEq with respect to river flow rate influencing passive sampler site at North Keppel Island in the Fitzroy region since 2005. Flow data provided by DNRM, Stream Gauging Network.

# Appendix I **Historical concentration profiles at fixed monitoring sites**

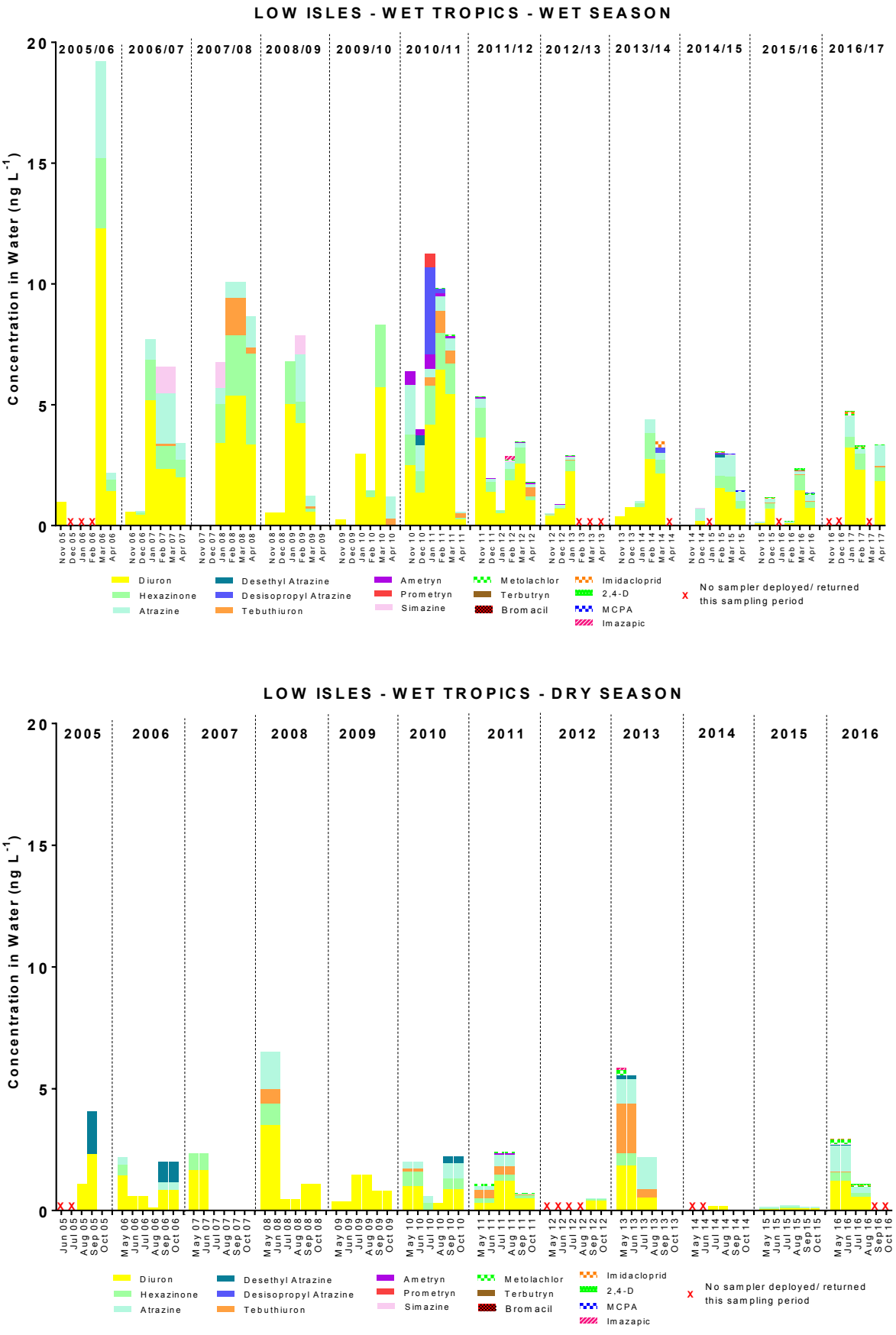
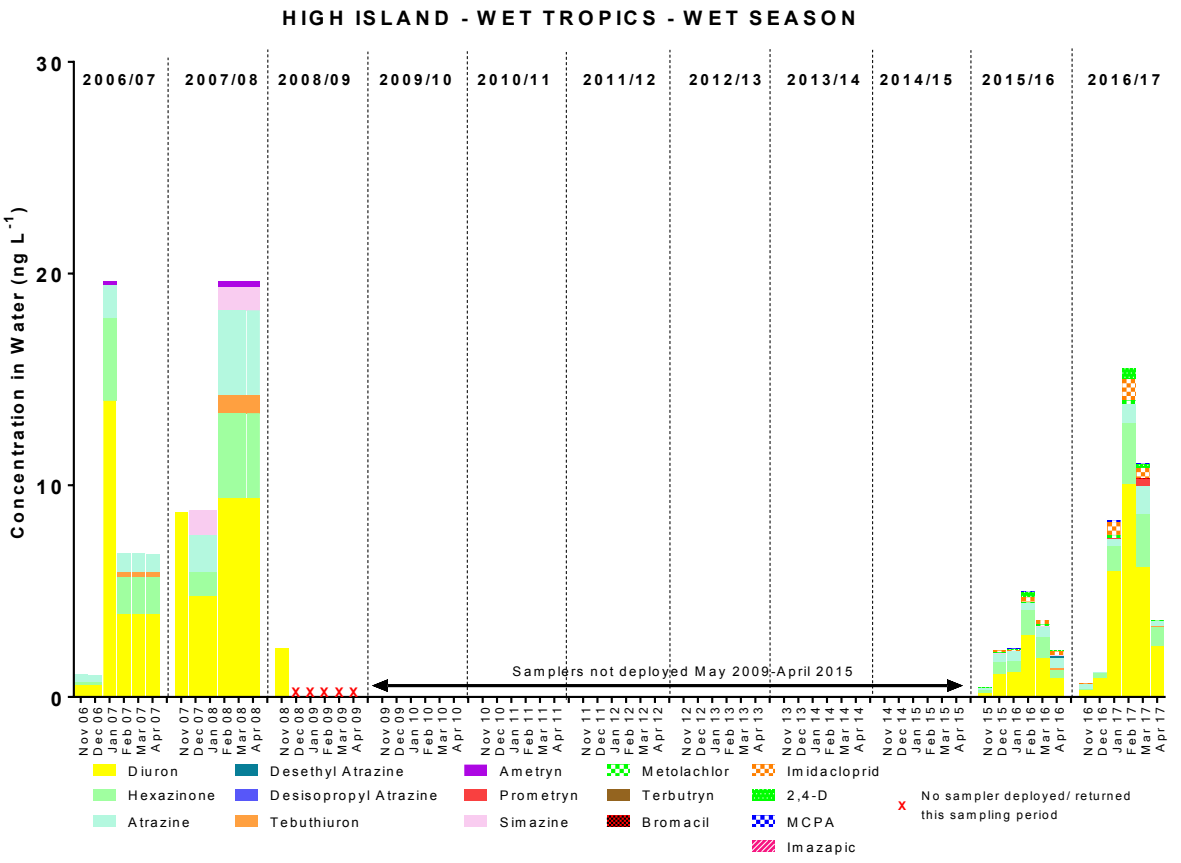



**Figure I-1**: Temporal concentration profiles of individual herbicides at Low Isles in the Wet Tropics region


HIGH ISLAND - WET TROPICS - WET SEASON
Concentration in Water (ng L-1)
2006/07
2007/08
2008/09
2009/10
2010/11
2011/12
2012/13
2013/14
2014/15
2015/16
2016/17
Samplers not deployed May 2009-April 2015
Diuron
Hexazinone
Atrazine
Desethyl Atrazine
Desisopropyl Atrazine
Tebuthiuron
Ametryn
Prometryn
Simazine
Metolachlor
Terbutryn
Bromacil
Imidacloprid
2,4-D
MCPA
Imazapic
No sampler deployed/ returned this sampling period

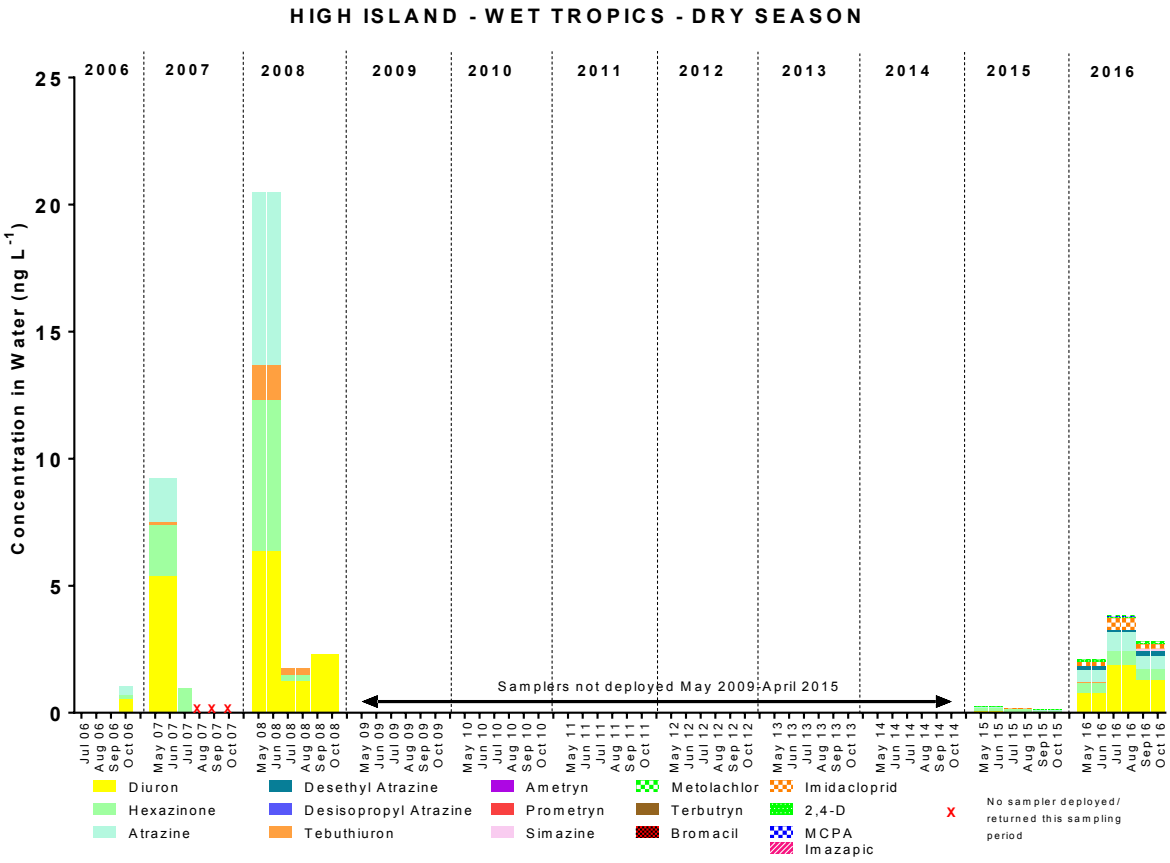

HIGH ISLAND - WET TROPICS - DRY SEASON
Concentration in Water (ng L-1)
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
Samplers not deployed May 2009-April 2015
Diuron
Hexazinone
Atrazine
Desethyl Atrazine
Desisopropyl Atrazine
Tebuthiuron
Ametryn
Prometryn
Simazine
Metolachlor
Terbutryn
Bromacil
Imidacloprid
2,4-D
MCPA
Imazapic
No sampler deployed/ returned this sampling period

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

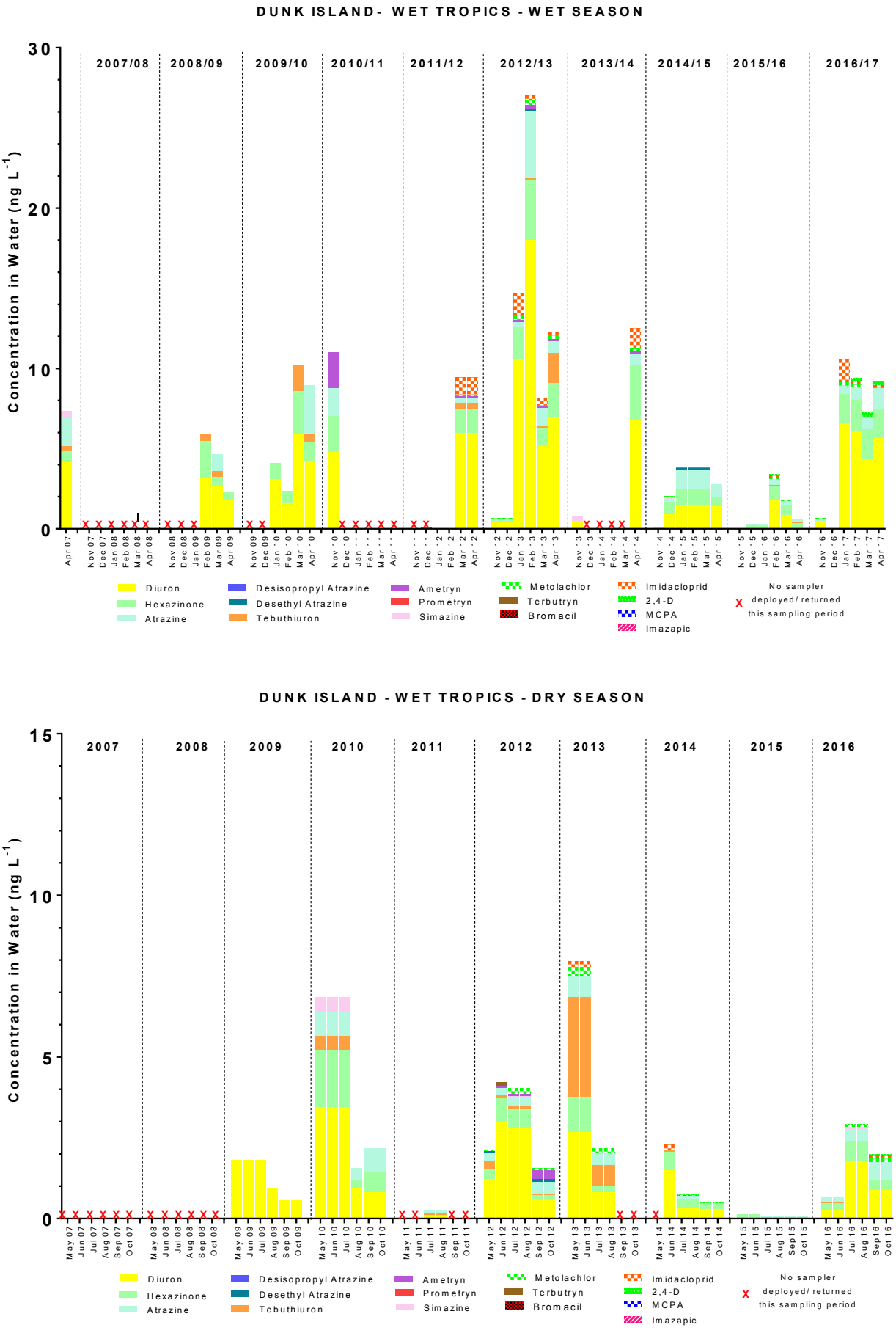



**Figure I-3**: Temporal concentration profiles of individual herbicides at Dunk Island in the Wet Tropics region

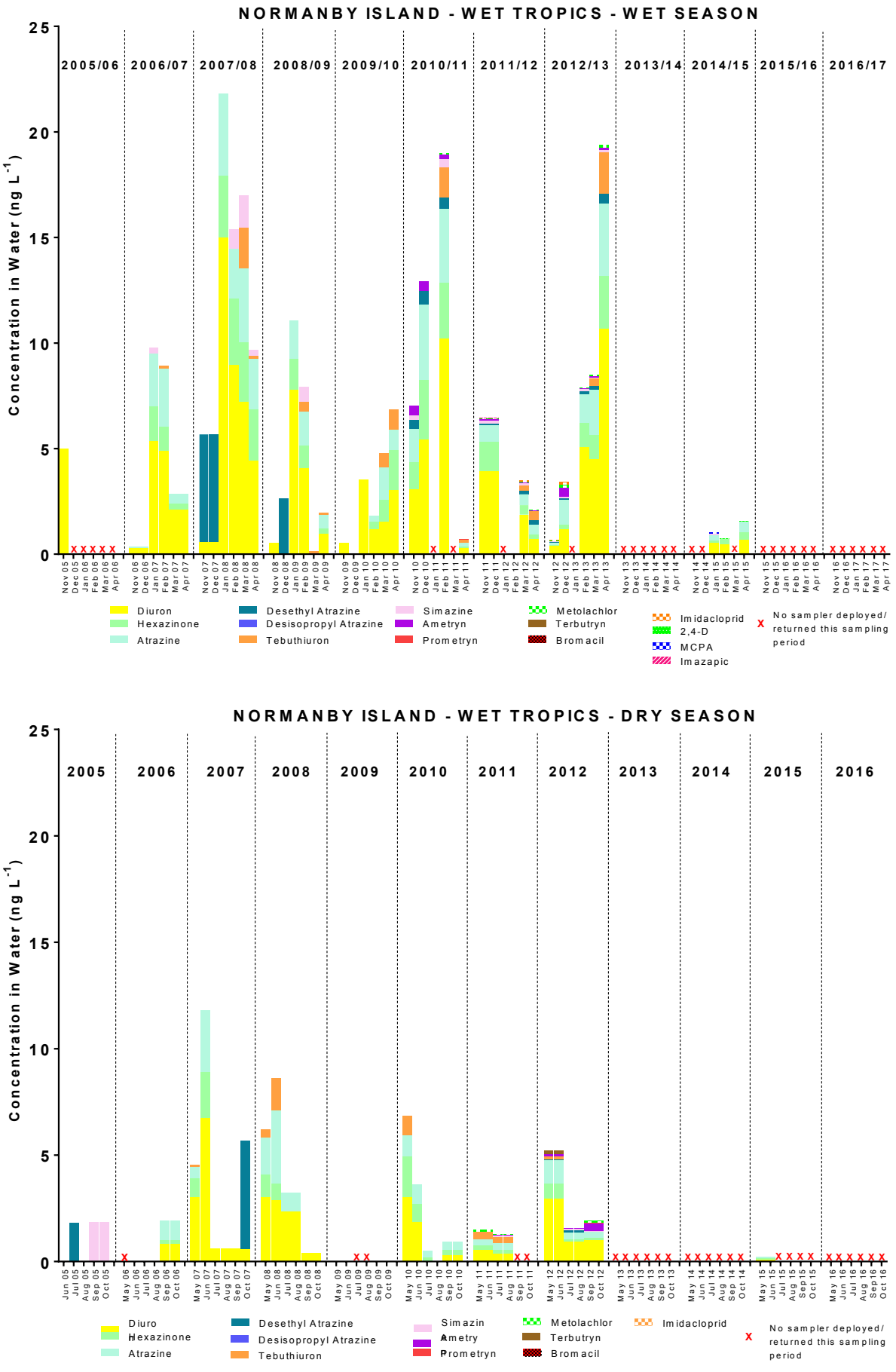
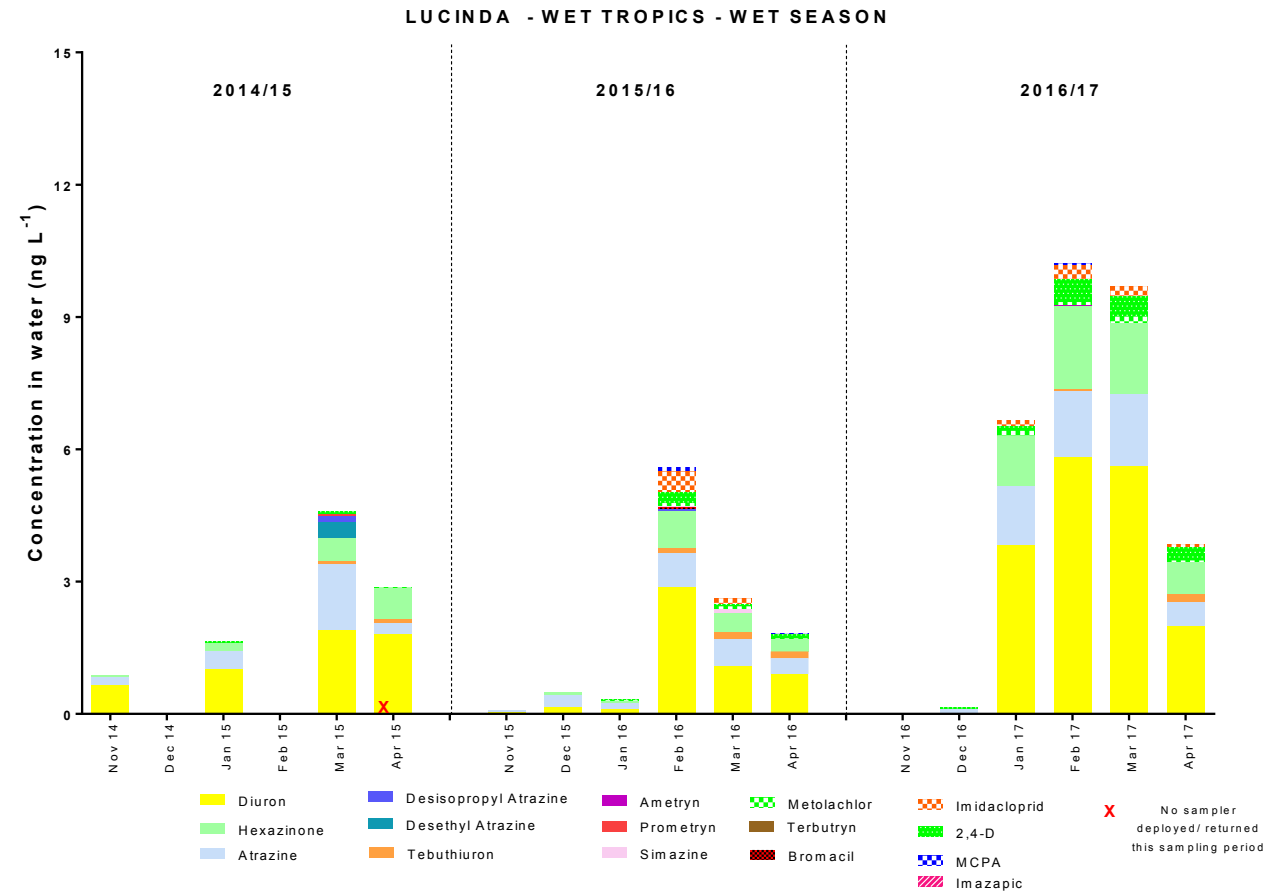



**Figure I-4**: Temporal concentration profiles of individual herbicides at Normanby Island in the Wet Tropics region


LUCINDA - WET TROPICS - WET SEASON
2014/15
2015/16
2016/17
Concentration in water (ng L-1)
0
3
6
9
12
15
Nov 14
Dec 14
Jan 15
Feb 15
Mar 15
Apr 15
Nov 15
Dec 15
Jan 16
Feb 16
Mar 16
Apr 16
Nov 16
Dec 16
Jan 17
Feb 17
Mar 17
Apr 17
Diuron
Hexazinone
Atrazine
Desisopropyl Atrazine
Desethyl Atrazine
Tebuthiuron
Ametryn
Prometryn
Simazine
Metolachlor
Terbutryn
Bromacil
Imidacloprid
2,4-D
MCPA
Imazapic
X
No sampler deployed/ returned this sampling period

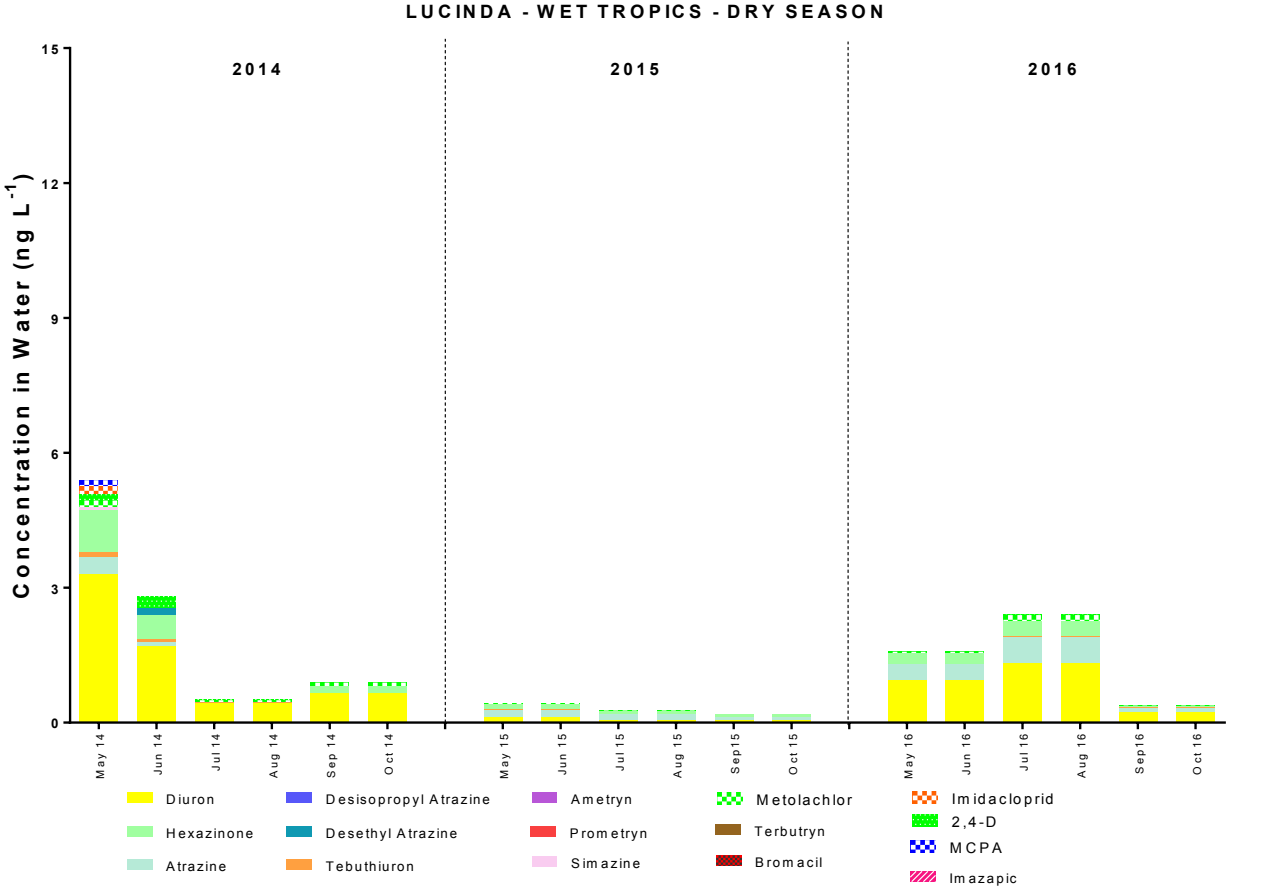

LUCINDA - WET TROPICS - DRY SEASON
2014
2015
2016
Concentration in Water (ng L-1)
0
3
6
9
12
15
May 14
Jun 14
Jul 14
Aug 14
Sep 14
Oct 14
May 15
Jun 15
Jul 15
Aug 15
Sep15
Oct 15
May 16
Jun 16
Jul 16
Aug 16
Sep16
Oct 16
Diuron
Hexazinone
Atrazine
Desisopropyl Atrazine
Desethyl Atrazine
Tebuthiuron
Ametryn
Prometryn
Simazine
Metolachlor
Terbutryn
Bromacil
Imidacloprid
2,4-D
MCPA
Imazapic

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

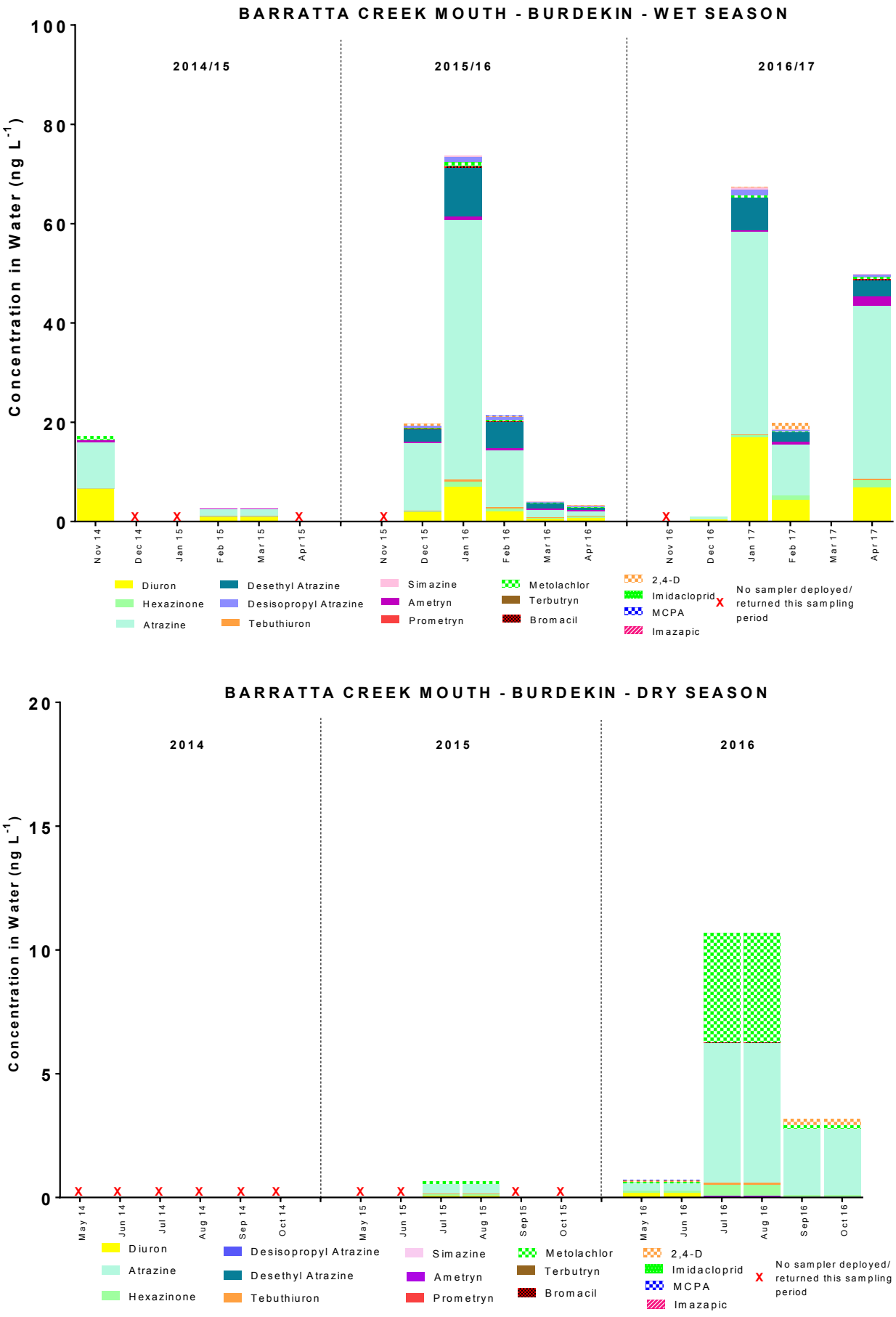



**Figure I-6**: Temporal concentration profiles of individual herbicides at Barratta Creek mouth in the Burdekin region

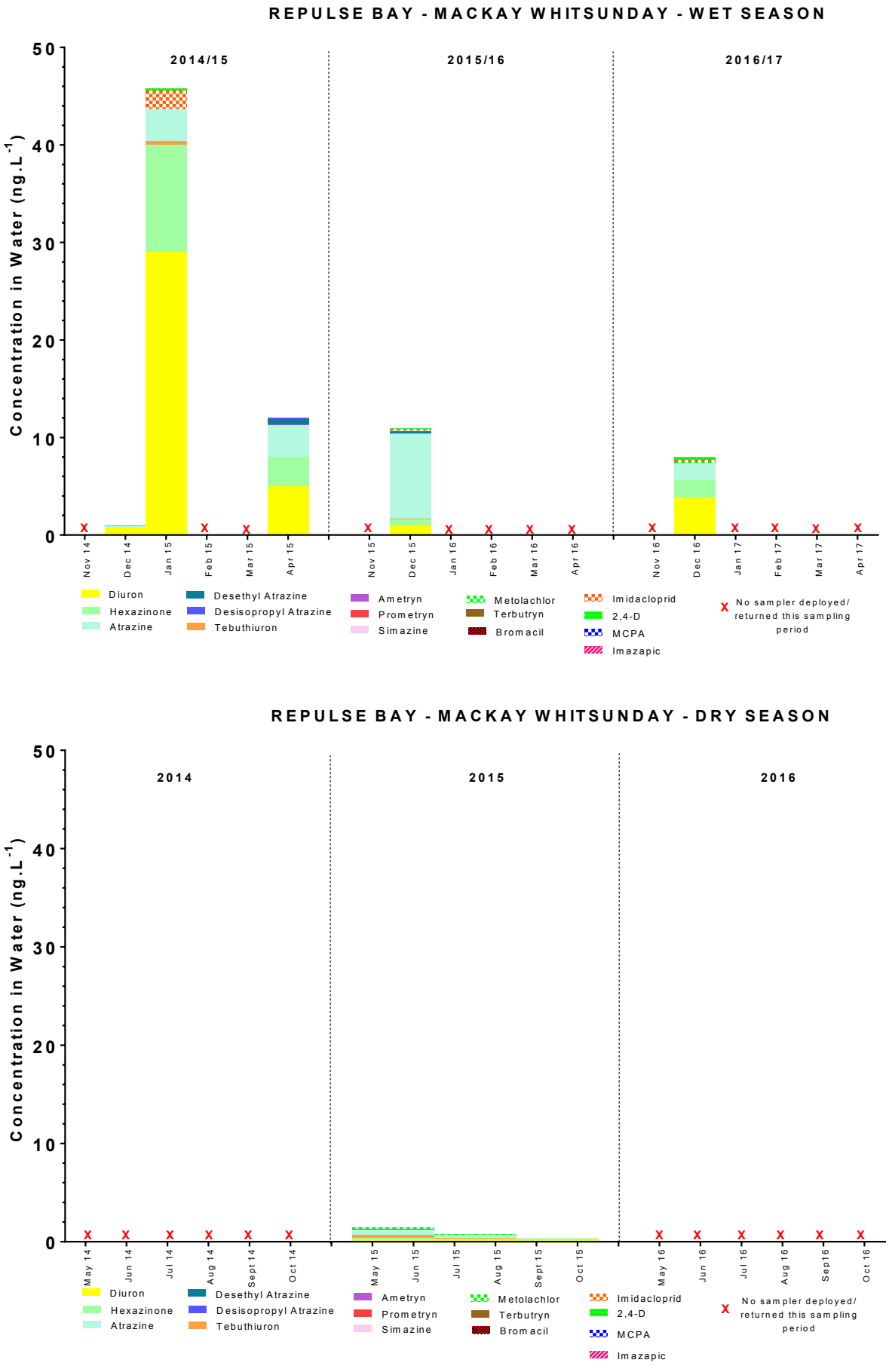



**Figure I-7**: Temporal concentration profiles of individual herbicides at Repulse Bay in the Mackay Whitsunday region

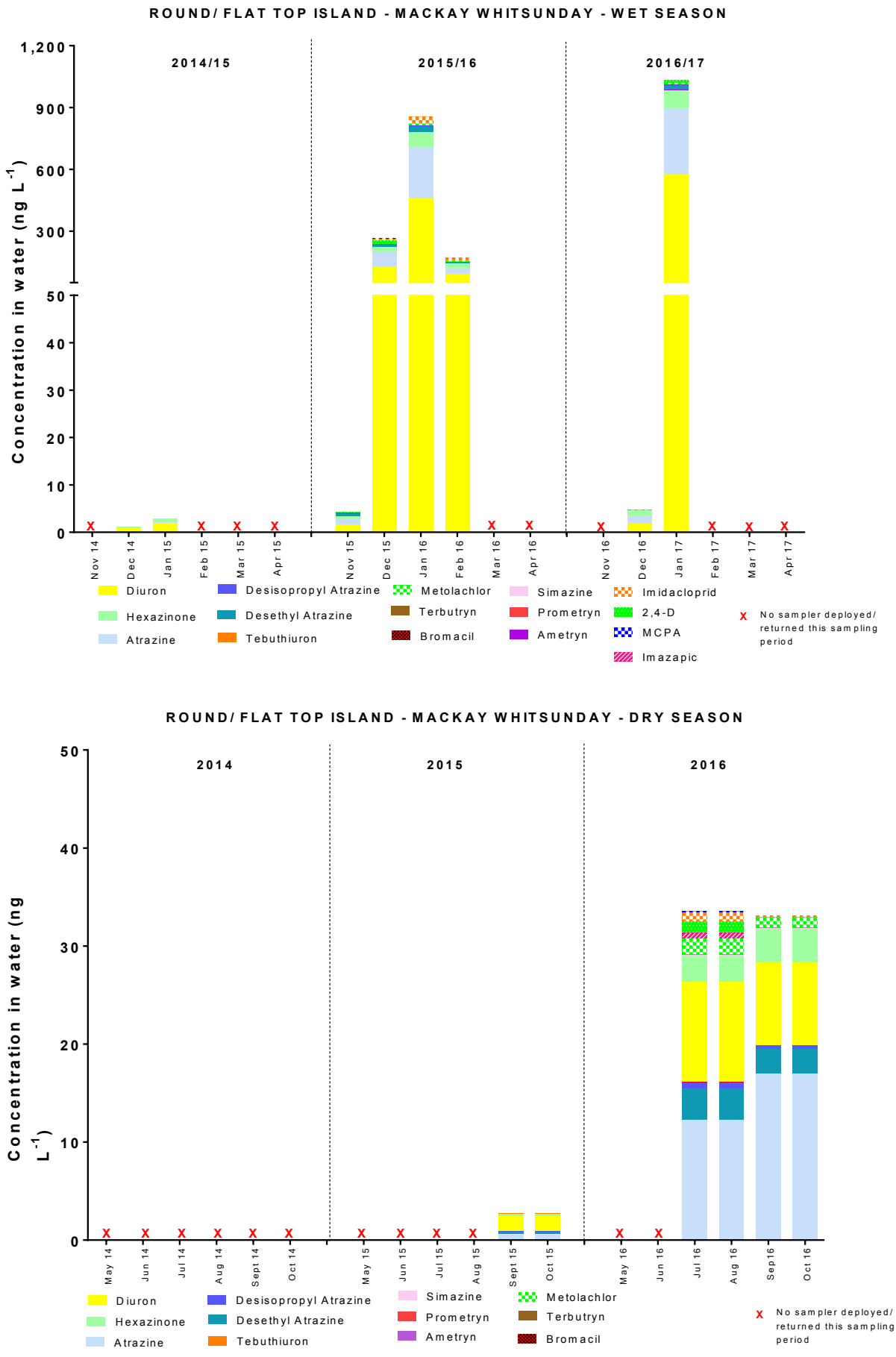



**Figure I-8**: Temporal concentration profiles of individual herbicides at Round Top Island in the Mackay Whitsunday region

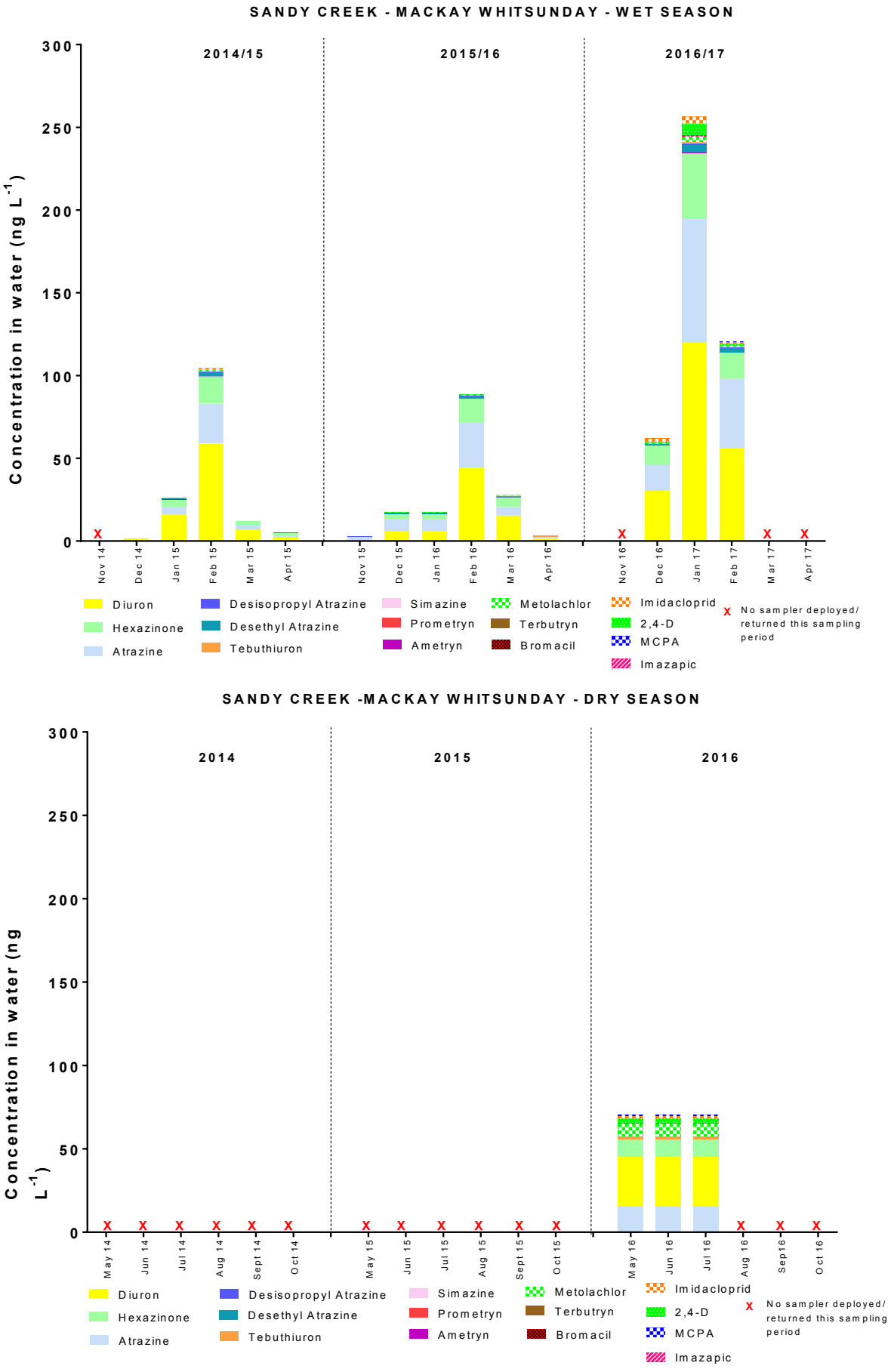
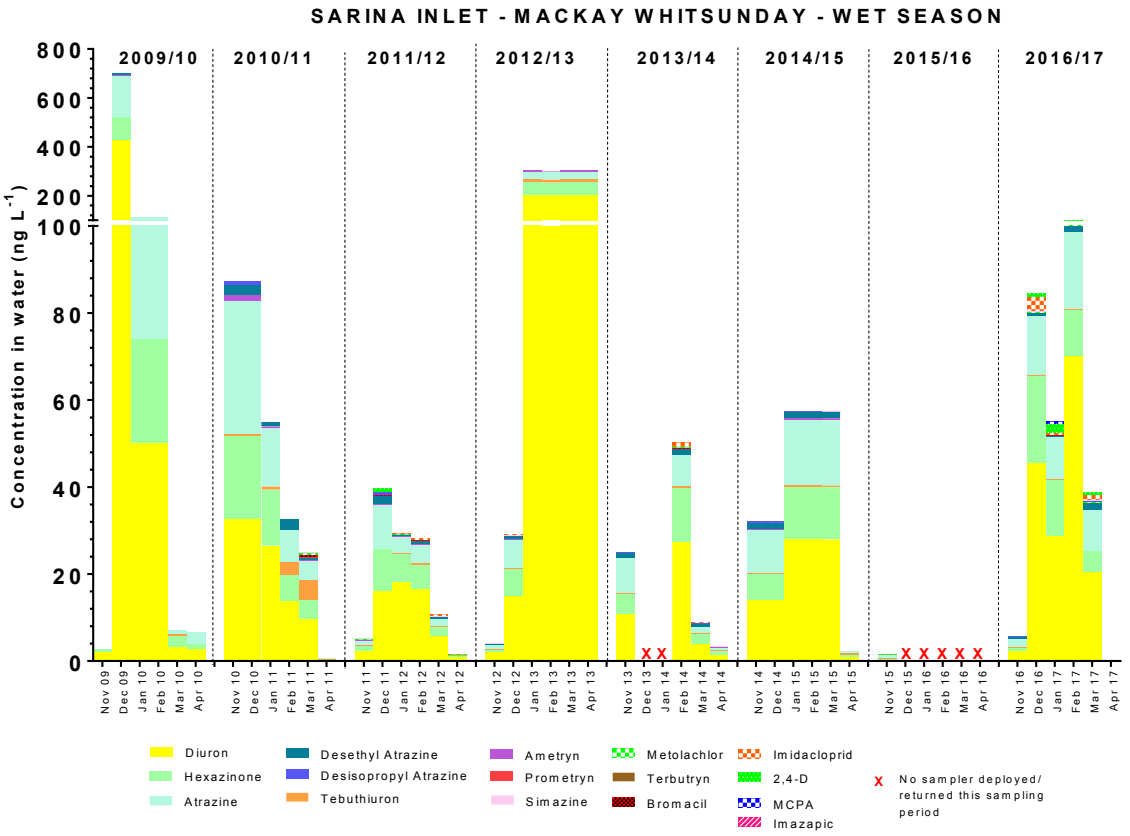



**Figure I-9**: Temporal concentration profiles of individual herbicides at Sandy Creek in the Mackay Whitsunday region



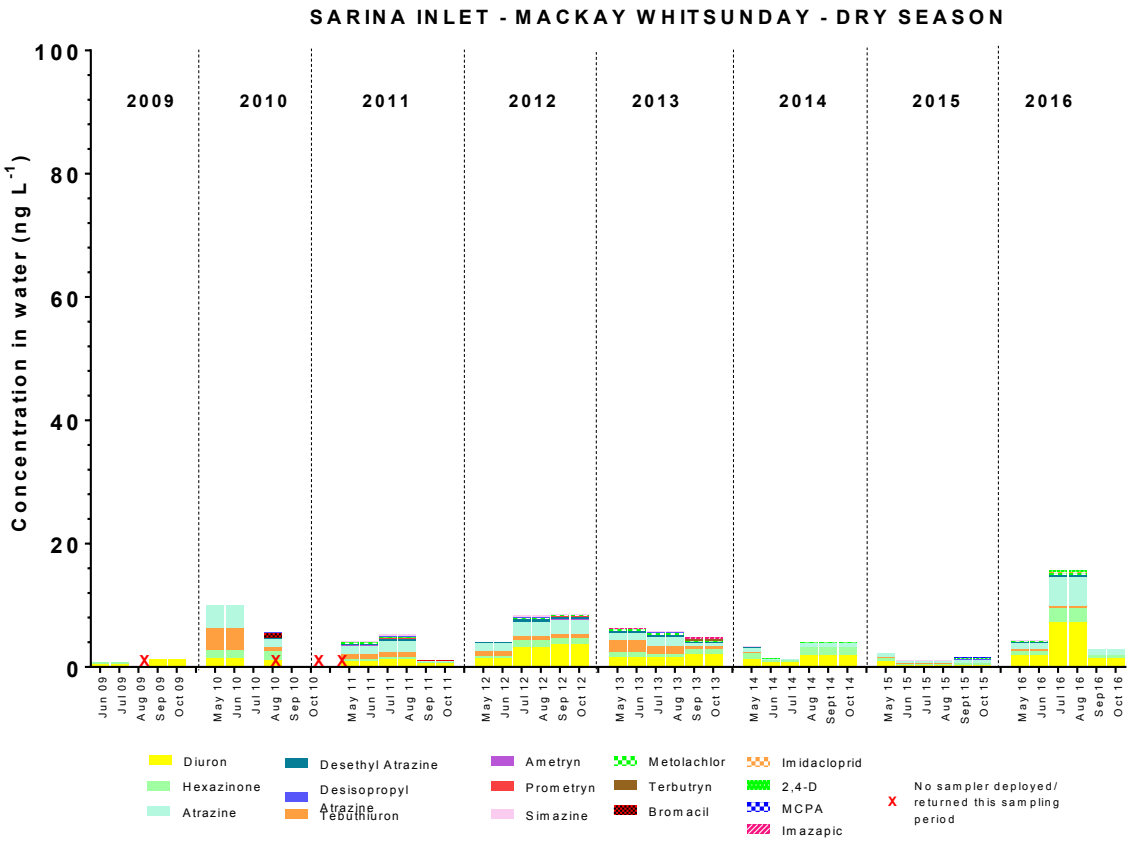




**Figure I-10**: Temporal concentration profiles of individual herbicides at Sarina Inlet in the Mackay Whitsunday region

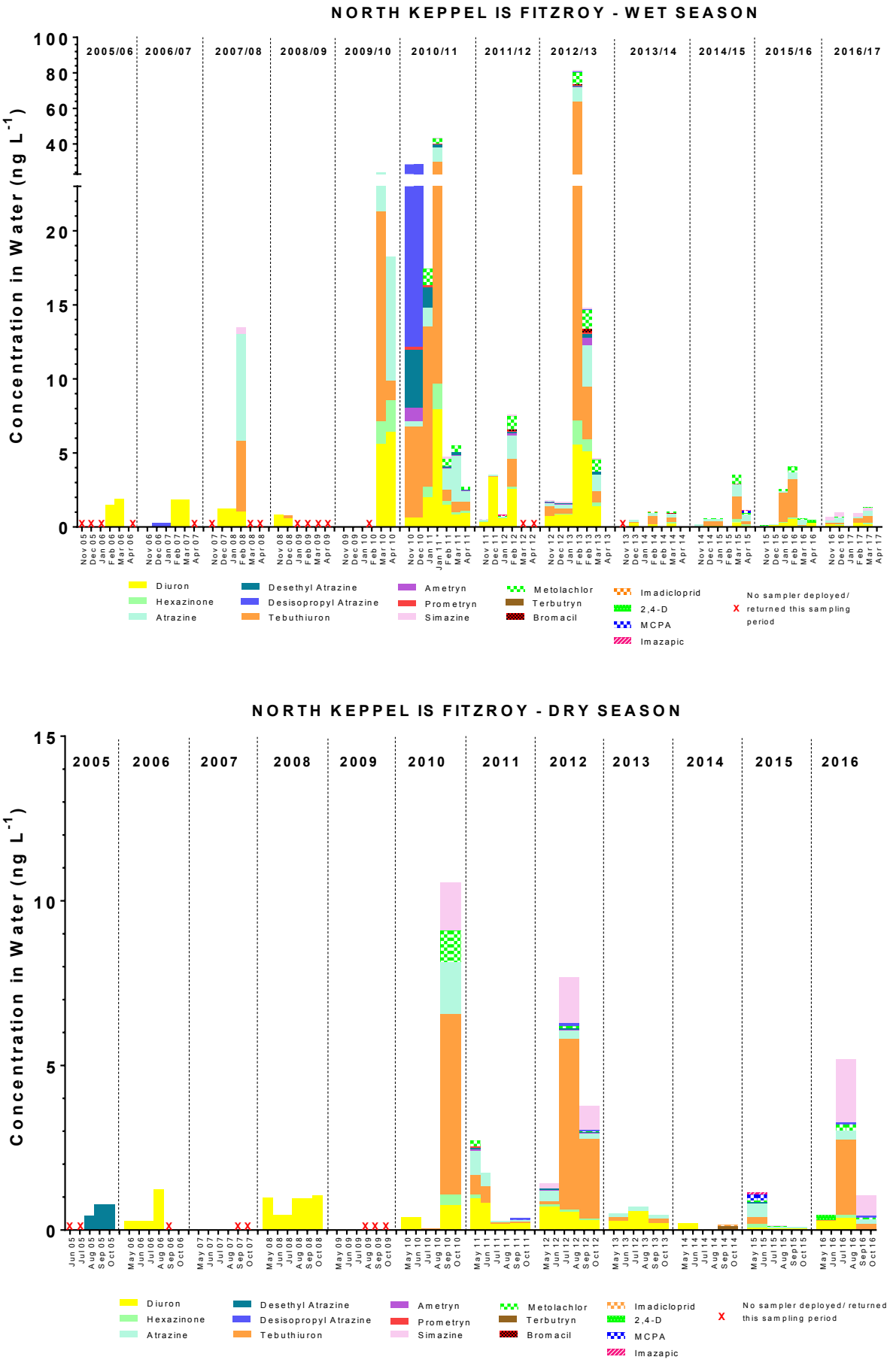



**Figure I-11**: Temporal concentration profiles of individual herbicides at North Keppel Island in the Fitzroy region