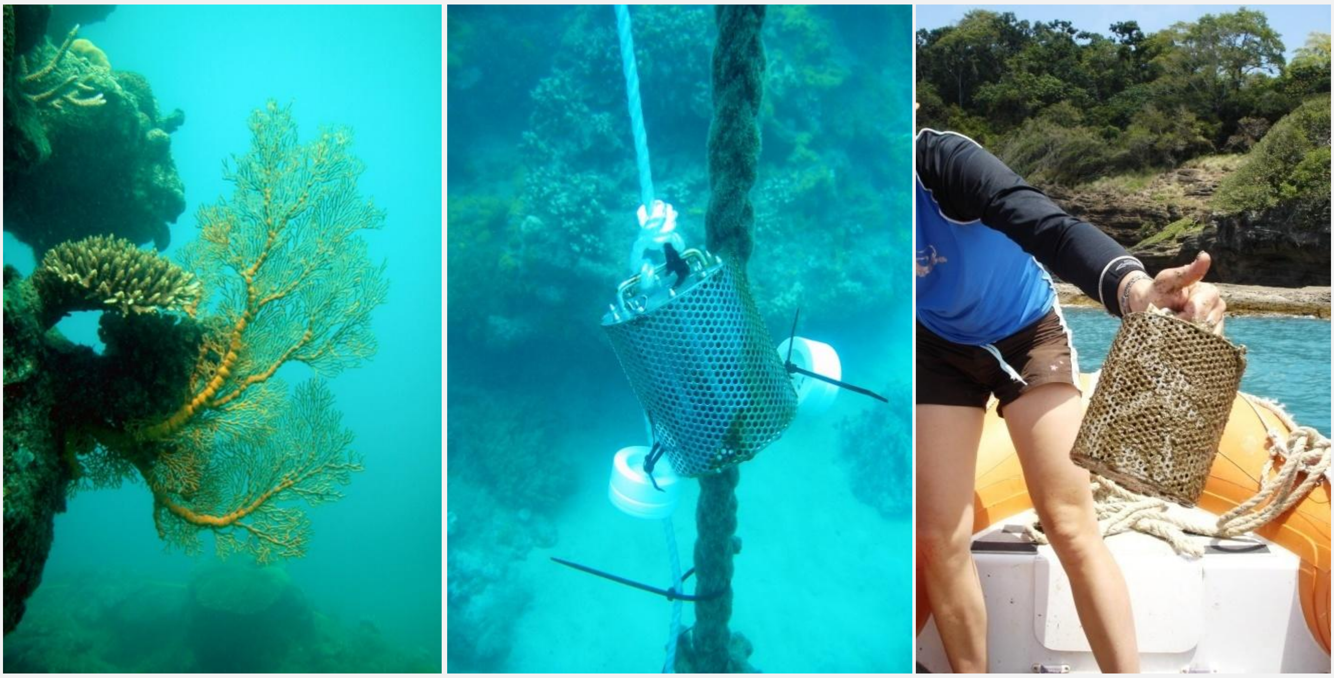
Final Report

Monitoring of organic chemicals in the Great Barrier Reef using time integrated monitoring tools (2009-2010)

Reef Rescue Marine Monitoring Program
Project 3.7.8 - Inshore Marine Water Quality Monitoring



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Whitsunday Moorings

Taylor's Beach Caravan Park

Sarina Bait Supplies

Jace Services

Cassowary Coast Regional Council

Low Isles Caretakers

Quicksilver Connections

Raging Thunder

Fitzroy Island Resort

Queensland Parks and Wildlife Service

Frankland Island Cruise & Dive

Voyages Dunk Island Resort

Orpheus Island Resort

Orpheus Island Research Station

Nautilus Aviation

Mike Ball Dive Expeditions

Mission Beach/Dunk Island Water Taxi

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Daydream Island resort

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Acronyms

ANZECC	Australian and New Zealand Environment and Conservation Council
APVMA	Australian Pesticides and Veterinary Medicines Authority
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
ASE	Accelerated Solvent Extraction
C_W	Estimated concentration in water
DEET	*N*,*N*-Diethyl-*meta*-toluamide
DCM	Dichloromethane
ED	Empore Disk^{TM} passive sampler
Entox	National Research Centre for Environmental Toxicology
GBR	Great Barrier Reef
GBRMP	Great Barrier Reef Marine Park
GBRMPA	Great Barrier Reef Marine Park Authority
GC-MS	Gas Chromatography-Mass Spectroscopy
GPC	Gel Permeation Chromatography
IWL	Interim working level
K_{OW}	Octanol-water partition coefficient
LC-MS	Liquid Chromatography-Mass Spectroscopy
LDPE	Low Density Polyethylene
LOD	Limit of Detection
LOR	Limit Of Reporting
MMP	Reef Rescue Marine Monitoring Program
NATA	National Association of Testing Authorities
PDMS	Polydimethylsiloxane passive sampler
PFM	Plaster Flow Monitor
PSII-HEq	Photosystem II -Herbicide Equivalent Concentration
PTFE	Polytetrafluoroethylene : Common brand name - Teflon
QHFSS	Queensland Health Forensic & Scientific Services
R_S	Sampling Rate
SDB-RPS	Poly(styrenedivinylbenzene) copolymer – reverse phase sulfonated
SOP	Standard Operating Procedure
SPMD	Semi-permeable Membrane Devices
TCPP	Tris(1-chlor-2-propyl)phosphate

1 EXECUTIVE SUMMARY

1.1 Introduction

The Reef Rescue Marine Monitoring Program (MMP) was established in 2005 to assess any improvement in water quality in the Great Barrier Reef (GBR) and the status of key ecosystems. Annual monitoring of inshore GBR sites and several rivers has been conducted by Entox since 2005. The principal objective of the monitoring activities conducted by Entox as part of MMP Project 3.7.8 during 2009 – 2010 was to:

"Determine time integrated baseline concentrations of specific organic chemicals in water with the aim to evaluate long term trends in pesticide concentrations along inshore waters of the GBR"

1.2 Methods

Monitoring has been conducted at sites within five major Natural Resource Management Regions (Cape York, Wet Tropics, Burdekin, Mackay Whitsunday, and Fitzroy) in 2009-2010. Baseline concentrations of specific organic pollutants (pesticides and herbicides) are estimated using passive sampling techniques. The passive sampling techniques which are utilized in the MMP include:

- SDB-RPS Empore™ Disk based passive samplers for relatively hydrophilic organic chemicals with relatively low octanol-water partition coefficients (log K_{OW}) such as diuron.
- Polydimethylsiloxane (PDMS) and Semipermeable Membrane Devices (SPMDs) passive samplers for organic chemicals which are relatively more hydrophobic (higher log K_{OW}) such as chlorpyrifos.

To date the most frequently detected and abundant chemicals at inshore reef sites over the last five years are herbicides: diuron, atrazine, hexazinone, and tebuthiuron. The presence of these herbicides which inhibit photosynthesis through the photosystem II pathway on the GBR is particularly concerning due to potential for impacts on a range of species including seagrass and corals. In the 2008-2009 baseline reporting year a PSII Herbicide Equivalent (PSII-HEq) Index was introduced which aims to provide a mode of action based integrative assessment of concentration. The PSII-HEq Index Categories subsequently refined by the Great Barrier Reef Marine Park Authority (GBRMPA) for 2009-2010 and presented within this report provide a metric for reporting purposes across the GBR. These Index Categories range from "1" (> 900 $ng.L^{-1}$) to "5" (≤ 10 $ng.L^{-1}$) with "1" being the highest concentration category. PSII-HEq within Category "1" are at a higher concentration than the GBRMP Guideline using published scientific effects on the growth and mortality of aquatic plants and animals using diuron as the reference chemical. Conversely, PSII-HEq within Category "5" are below any published scientific results of effects on plants or animals based on toxicity including a reduction in photosynthesis. The reporting parameter for PSII herbicides in the GBR is the maximum PSII-HEq concentration (PSII-HEq Max) within each monitoring year.

1.3 GBR Wide Summary

The PSII-HEq Max ($ng.L^{-1}$) for 2009-2010 and previous monitoring years from 2005-2006 are illustrated in Figure 1. The dominant contributor to PSII-HEq Max at all sites is the phenylurea herbicide diuron due to both its relative abundance (higher concentration) and its relative potency as a PSII inhibitor. Diuron is also more consistently detected during both wet and dry season monitoring across the GBR. Hexazinone and atrazine also contribute a significant proportion and these proportions vary between regions, with atrazine typically contributing a higher relative proportion at sites in the Burdekin and Fitzroy Regions and hexazinone contributing a higher proportion at sites in the Wet Tropics and Mackay Whitsunday Regions. The PSII herbicides contributing the most to the PSII-HEq Max across the GBR (diuron, atrazine and hexazinone) are all associated with sugar cane production and other cropping in GBR catchments. PSII-HEq Index Categories range from "5 - 4", "5 – 3", "4 – 2" and "5" for current sites in the Wet Tropics, Burdekin, Mackay Whitsunday and Fitzroy Regions respectively in 2009-2010 (Table 1).

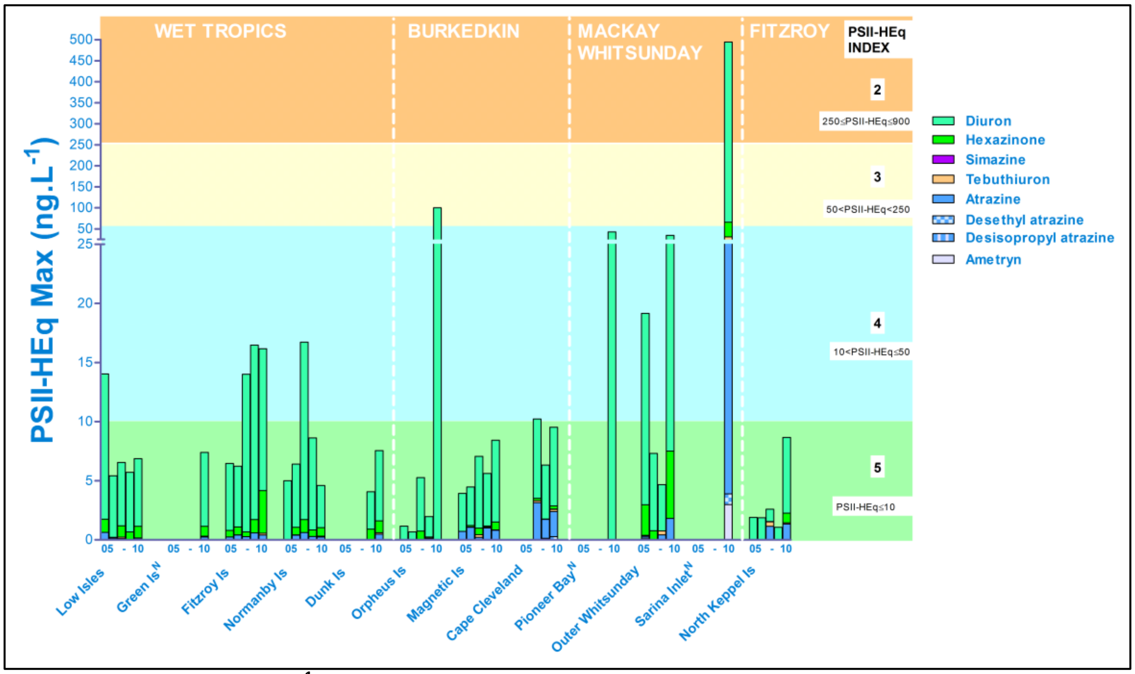

Figure 1 PSII-HEq Max (ng.L^{-1}) for current sites in the Wet Tropics, Burdekin, Mackay Whitsunday and Fitzroy Regions between 2005 and 2010.
("N" indicates a new site in 2009-2010)

PSII-HEq Max in each monitoring year are more typically observed in wet seasons than dry seasons. A notable exception to this is the Category "3" PSII-HEq Max observed in the dry season at Orpheus Island in the Burdekin Region in 2009-2010. These dry season maximums may be indicative of more localised sources of diuron (local application or leaching from antifoulant paints). Wet season events (peak discharge and flood plumes) in specific monitoring years may contribute to "noise" within these profiles and make an assessment of improvement in water quality between specific years more problematic. When considering all monitoring years there is some indication of increasing PSII-HEq Max for Fitzroy Island in the Wet Tropics, Magnetic Island in the Burdekin Region and North Keppel Island in the Fitzroy Region. Assessment of temporal trends in the Mackay Whitsunday Regions is not possible due to incomplete monitoring records (loss of samplers) for Outer Whitsunday and a range of new sites (Table 1) being incorporated within 2009-2010.

There were no exceedances of GBRMPA Water Quality Guidelines by individual PSII herbicides at inshore GBR sites in 2009-2010 (Table 1). The maximum concentration of the PSII herbicide atrazine (690 ng.L^{-1}) in the Pioneer River is equivalent to the 99 % species protection freshwater ANZECC and ARMCANZ Guideline. The ANZECC & ARMCANZ Interim Working Level for diuron is also exceeded in the Pioneer River. The Pioneer River was the only site with a PSII-HEq Index of

"1" in 2009-2010. The estimated concentrations of the organophosphate insecticide chlorpyrifos at inshore GBR sites in the Wet Tropics Region (Green, Fitzroy, Normanby & Dunk Islands) did exceed the 99 % GBRMPA Guideline (0.5 ng.L^{-1}) where monitoring occurred. Similarly the ANZECC & ARMCANZ Guideline for chlorpyrifos in freshwater was exceeded in the Tully River (99 and 95 %) in the Wet Tropics and in the Pioneer River (99 %) in the Mackay Whitsunday Region. Diazinon concentrations in the Tully River exceed both the 95 and 99 % species protection freshwater ANZECC & ARMCANZ Guidelines. Since the concentrations of chlorpyrifos estimated by passive samplers are time integrative, it is likely that acute (short duration) exposures may be much higher.

Table 1 The PSII-HEq range (ng.L^{-1}) and Index Category of PSII-HEq Max with any exceedance of Guideline values for these locations indicated. Sites which were only monitored for PSII herbicides are indicated by light grey shading.

Region	Site	PSII-HEq		Exceedance of Water Quality Guidelines	
		Range	Index	PSII herbicides	Other Pesticides
Cape York	Pixies Garden[D]	n.d.	5	✗	
Wet Tropics	Low Isles	n.d.-**6.7**	5	✗	
	Green Is[N]	n.d.-**7.4**	5	✗	✓ Chlorpyrifos
	Fitzroy Is	**0.94-16**	4	✗	✓ Chlorpyrifos
	Normanby Is	n.d.-**4.0**	5	✗	✓ Chlorpyrifos
	Dunk Is	**0.57-7.1**	5	✗	✓ Chlorpyrifos
	Tully River[D]	**5.5 - 32**	4	✗	✓ Chlorpyrifos & Diazinon
Burdekin	Orpheus Is	**2.1-100**	3	✗	
	Magnetic Is	**0.88-8.8**	5	✗	✗
	Cape Cleveland	**0.036-9.1**	5	✗	✗
Mackay - Whitsunday	Outer Whitsunday	n.d.-**35**	4	✗	✗
	Daydream Island – Inner Whitsunday[D]	**1.7-57**	3	✗	
	Pioneer Bay-Inner Whitsunday[N]	**3.6-43**	4	✗	
	Sarina Inlet[N]	**0.58-495**	2	✗	
	Pioneer River[D]	**0.77-970**	1	✓ Atrazine & Diuron	✓ Chlorpyrifos
Fitzroy	North Keppel Is	n.d.-**8.7**	5	✗	

"D" and "N" indicate sites which were discontinued or new respectively in 2009-2010

1.4 Regional Results & Discussion

While equivalent concentrations provide a single reporting parameter for PSII-herbicides with a similar mode of action they may obscure differences in the relative abundance of individual PSII herbicides detected in different regions. Furthermore limited monitoring of more hydrophobic chemicals is undertaken at relatively few sites and predominantly in the wet season (Table 1). In order to illustrate more complete exposure scenarios in these regions the maximum concentrations of individual PSII herbicides at all monitoring sites are provided in Figure 2 and the maximum concentrations of other pesticides (herbicides, insecticides and fungicides) are provided in Figure 3.

The least frequently detected PSII herbicides are ametryn and simazine. Ametryn was detected only at Cape Cleveland (0.10 $ng.L^{-1}$), Sarina Inlet (2.3 $ng.L^{-1}$) and in the Tully (1.1 $ng.L^{-1}$) and Pioneer Rivers (3.7 $ng.L^{-1}$) in 2009-2010. Simazine was detected only at Magnetic Island (1.5 $ng.L^{-1}$) and Cape Cleveland (0.36 $ng.L^{-1}$) in the Burdekin region and in the Tully (5.1 $ng.L^{-1}$) and Pioneer Rivers (22 $ng.L^{-1}$). The maximum concentrations of tebuthiuron are observed in the Burdekin region (2.2 – 4.7 $ng.L^{-1}$) and at North Keppel Island (14 $ng.L^{-1}$) in the Fitzroy region which has the highest maximum concentration in 2009-2010. The GBRMPA Guideline for tebuthiuron of 20 $ng.L^{-1}$ is approached at this site.

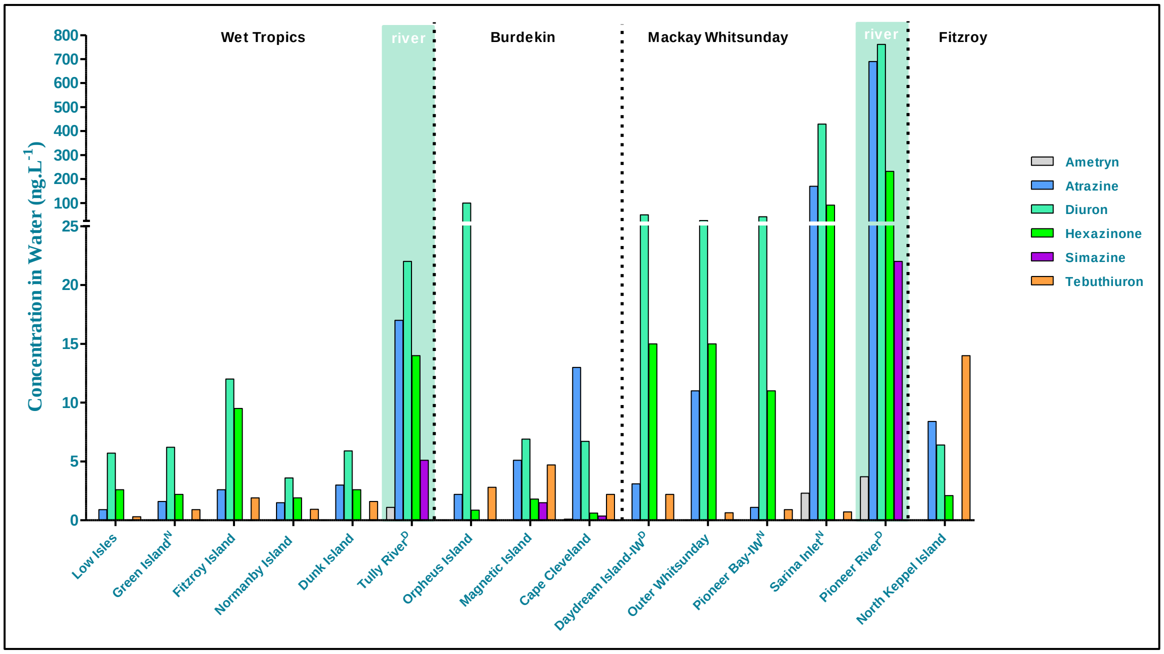

Figure 2 Maximum concentrations of individual PSII herbicides at inshore reefs, nearshore waters and rivers in 2009-2010

"D" and "N" indicate sites which were discontinued or new in 2009-2010

The PSII herbicide profiles in both the Tully River in the Wet Tropics and the Pioneer River in the Mackay Whitsundays are remarkably similar with diuron > atrazine > hexazinone > simazine > ametryn. However the maximum concentrations of each individual PSII herbicide are higher in the Pioneer River by factors of between 3 and 41. Since diuron is the dominant contributor to PSII HEq it is important to illustrate the ranges in the maximum concentration of this herbicide within these regions. Maximum diuron concentrations at inshore GBR sites ranged from 3.6 – 12 $ng.L^{-1}$, 6.7 – 100 $ng.L^{-1}$, 27 – 429 $ng.L^{-1}$ and 6.4 $ng.L^{-1}$ in the Wet Tropics, Burdekin, Mackay Whitsunday and Fitzroy (one site) Regions respectively. The regional profiles indicate that diuron has typically occurred at the highest concentration at most sites in 2009-2010. The exceptions are Cape Cleveland in the Burdekin Region where the maximum atrazine concentration (13 $ng.L^{-1}$) is higher than that of diuron (6.7 $ng.L^{-1}$) and North Keppel Island in the Fitzroy Region where both the maximum concentration of atrazine (8.4 $ng.L^{-1}$) and tebuthiuron (14 $ng.L^{-1}$) are higher than that of diuron (6.4 $ng.L^{-1}$). While the diuron concentration at North Keppel Island is lower than for either atrazine or tebuthiuron, this is the highest diuron concentration which has been monitored at this location and has contributed significantly to the observed increase in PSII-HEq Max at this location. Atrazine was frequently the dominant PSII-herbicide at both Cape Cleveland and Magnetic Island in the Burdekin Region which is indicative of the dominance of atrazine in loads from rivers in this region. Maximum hexazinone concentrations in the Wet

Tropics and in the Mackay Whitsunday Regions are typically less than that of diuron but higher than atrazine. In comparison, in the Burdekin and Fitzroy Regions hexazinone maximum concentrations are typically less than those of atrazine or tebuthiuron. The Sarina Inlet site in the Mackay Whitsunday Region has the highest concentrations for inshore GBR sites for most PSII herbicides including ametryn (2.3 $ng.L^{-1}$), atrazine (170 $ng.L^{-1}$), diuron (429 $ng.L^{-1}$) and hexazinone (91 $ng.L^{-1}$) reflecting both its proximity to the coast and inputs from significant areas of sugar cane production in this region.

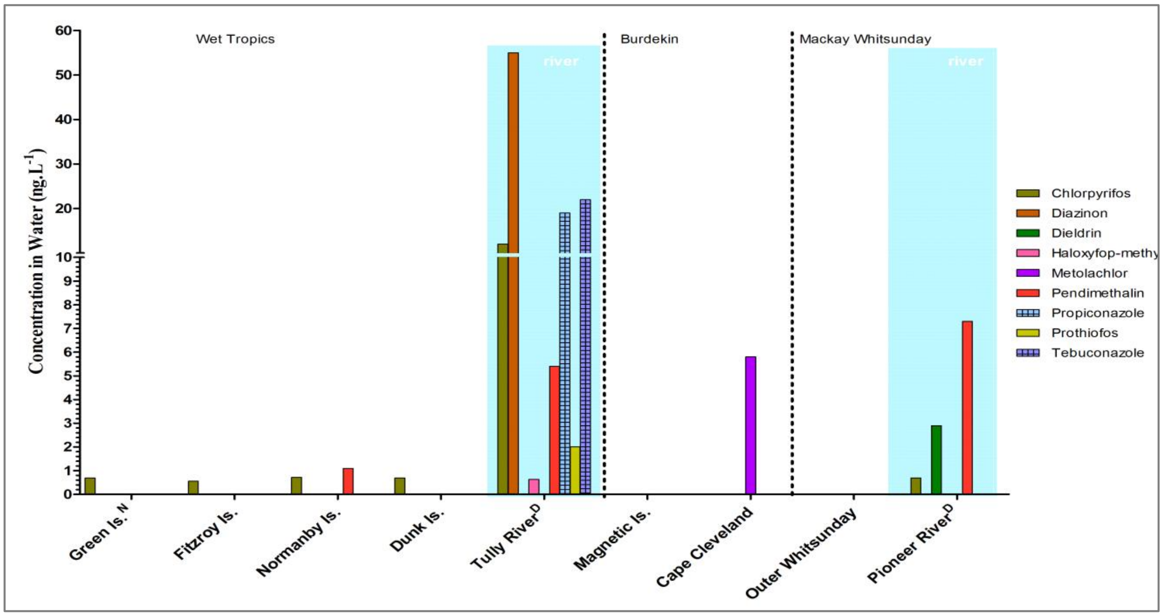

Figure 3 Maximum concentrations of other herbicides, insecticides and fungicides at sites where PDMS sampling occurred in 2009-2010

"D" and "N" indicate sites which were discontinued or new in 2009-2010

A broader range of pesticides (Figure 2) were detected using PDMS sampling in the Tully River than in the Pioneer River in 2009-2010. The organophosphate insecticides diazinon (46-55 $ng.L^{-1}$) and prothiofos (0.19-2.0 $ng.L^{-1}$), the phenoxy herbicide haloxyfop methyl (0.63 $ng.L^{-1}$) and the conazole fungicides propiconazole (11-19 $ng.L^{-1}$) and tebuconazole (13 – 22 $ng.L^{-1}$) were detected only in the Tully River. Chlorpyrifos was detected in both the Pioneer (0.25 – 0.69 $ng.L^{-1}$) and Tully (2.4 – 12 $ng.L^{-1}$) Rivers but at a higher maximum concentration in the Tully River. However, pendimethalin was detected at higher concentrations in the Pioneer River (0.36 – 7.3 $ng.L^{-1}$) than in the Tully River (0.85 – 5.4 $ng.L^{-1}$) and the organochlorine insecticide dieldrin (0.87 – 2.9 $ng.L^{-1}$) was detected only in the Pioneer River. Chlorpyrifos (0.56 – 0.72 $ng.L^{-1}$) was also detected at all inshore GBR sites in the Wet Tropics Region where monitoring occurred. Apart from the Rivers, the dinitroaniline herbicide pendimethalin (1.1 $ng.L^{-1}$) was detected only at Normanby Island in the Wet Tropics Region of the GBR. Metolachlor, a chloracetanilide herbicide, was not detected in either river in 2009-2010 but was detected at Cape Cleveland (5.8 $ng.L^{-1}$) in the Burdekin Region.

1.5 Discussion & Conclusions

PSII Herbicides were present at all inshore GBR sites except for Pixies Garden in the Cape York Region. The concentrations of PSII herbicides are particularly elevated at inshore GBR sites in the Mackay Whitsunday Region. The time integrated concentrations estimated for individual PSII herbicides using passive sampling techniques have not exceeded GBRMPA Guidelines for individual chemicals at inshore GBR sites. However, the risks to reef ecosystems as a whole posed by exposure to mixtures of PSII herbicides and the potential for synergistic effects with concomitant changes in other water quality parameters remain largely uncharacterized.

PSII-HEq concentrations did occasionally reach known sub-lethal effect levels (such as reduced photosynthesis) for a number of marine species at inshore GBR sites in the Wet Tropics, Burdekin and Mackay Whitsunday Regions in 2009-2010. The ecological significance of sub-lethal effects is uncertain. Scientific evidence to date indicates full recovery from the effects of a reduction in photosynthesis when the organism is no longer exposed. Some uncertainty remains regarding how much exposure and for how long, and what, if any, long term effects might occur as a consequence. However, as the effect reduces natural function the potential exists that it will be detrimental to photosynthesising organisms and present an additional stressor on ecosystems already facing a number of other pressures.

PSII-herbicides are monitored at a greater range of sites and more frequently in the MMP than relatively more hydrophobic chemicals such as the organophosphate insecticide chlorpyrifos. Unlike the PSII-herbicides the concentration estimates for chlorpyrifos at inshore GBR sites in the Wet Tropics exceed the GBRMPA Guideline in at least one monitoring period. This finding indicates the importance of monitoring for a broader range of chemicals such as chlorpyrifos which although present at lower concentrations than PSII herbicides can also have significantly lower Guideline values.

2 INTRODUCTION

The Great Barrier Reef Marine Park (GBRMP) off the coast of Queensland covers an area of approximately 344, 400 km^2 and was listed as a World Heritage Area in 1981. The protection of this nationally and internationally treasured ecosystem and iconic natural resource is a priority for both the Commonwealth and Queensland State governments and the wider domestic and international community. In recognition of this immense value a dedicated regulatory authority the Great Barrier Reef Marine Park Authority (GBRMPA) was established in 1975 to manage the Great Barrier Reef Marine Park (GBRMP). Although this level of protection and management has ensured that the inner and outer reefs of the GBR are less degraded in comparison to coral reef ecosystems worldwide (Pandolfi et al. 2003) many of the factors which will influence the resilience and hence preservation of these ecosystems for future generations have their origin beyond the boundaries of the marine park (Hughes et al. 2003; GBRMPA 2009a). The degradation of these ecosystems and their capacity to adapt to change would be exacerbated by a decline in water quality.

One of the dominant contributors to declining water quality within the GBR are terrestrial discharge derived inputs of elevated nutrients, sediments and agricultural chemicals from adjacent catchments (Furnas 2003; Brodie et al. 2008; Brodie and Waterhouse 2009; Packett et al. 2009; van Dam et al. 2010). Extensive monitoring of water bodies within these adjoining catchments has revealed a broad range of agricultural chemicals (herbicides and insecticides) at often elevated concentrations (Mitchell et al. 2005; Lewis et al. 2007; Davis et al. 2008; Rohde et al. 2008; Bainbridge et al. 2009a; Packett et al. 2009). These catchment contributions to the GBR lagoon may be exacerbated by flood plume events (Devlin and Schaffelke 2009; Brodie et al. 2010) with the extent of these plume bands extending out to 50 km (Devlin and Brodie 2005) and 100 km (Rohde et al. 2008) from the coast.

There are differences in the relative risk estimated for different Natural Resource Management Regions which have been both significantly developed and that define the GBR catchment area (Wet Tropics, Burdekin, Mackay Whitsunday, Fitzroy and Burnett Mary). These risks may be related to dominant agricultural land use within these regions. Priority agricultural chemicals identified in all regions are photosystem II herbicides (Brodie and Waterhouse 2009) which may be detected more frequently and at relatively high concentrations (Davis et al. 2008; Lewis et al. 2009). These herbicides including the triazines (i.e. atrazine, simazine, ametryn and prometryn) triazinone (hexazinone) and the urea based (diuron and tebuthiuron) have a common mode of action inhibiting photosynthesis through the photosystem II pathway (Bengtson-Nash et al. 2005a). There exists the potential for these herbicides to impact seagrass (Haynes et al. 2000), mangroves (Duke et al. 2005), tropical benthic microalgae (Magnusson et al. 2010) and corals (Jones and Kerswell 2003; Jones et al. 2003; Jones 2005; Negri et al. 2005). Notably synergistic effects between sedimentation stress and trace levels of the PSII herbicide diuron on the photosynthetic activity and recovery of crustose coralline algae have been demonstrated (Harrington et al. 2005).

Significantly these herbicides have been detected in both rivers in adjoining catchments and at inshore reef locations in both dry and wet seasons using passive sampling techniques (Shaw and Mueller 2005; Shaw et al. 2010) and have been traced at extremely elevated concentrations in river water plumes from catchments (Davis et al. 2008) to the GBR lagoon using grab sampling techniques (Rohde et al. 2008; Bainbridge et al. 2009a; Lewis et al. 2009; Devlin et al. 2010). It is important to note that a flood plume sampled along the same transect nine days apart in the Mackay Whitsunday Region (Pioneer River to Whitsunday Islands) indicates biologically significant concentrations (Haynes et al. 2000) which decline by a factor of two within this period (Lewis et al. 2009). The utility of passive samplers to detect a wider range of herbicides in rivers discharging to the GBR and to identify the presence of a range of insecticides such as chlorpyrifos and diazinon in rivers and nearshore waters (Shaw et al. 2010) has demonstrated their applicability to more completely identify the agricultural chemicals to which these ecosystems are potentially exposed, across concentration ranges spanning several orders of magnitude. These sampling techniques offer cost effective monitoring tools which are particularly suited to monitoring both temporal and spatial variation in chronic exposure in the often remote locations encountered on the GBR (Shaw and Mueller 2005). It is important to note however that time integrated estimates derived using passive sampling techniques and acute (short duration) exposure estimates will differ and offer quite different risk assessment information within these ecosystems. It is advisable to consider all available information within specific regions rather than just time integrated estimates at a limited number of specific sites within these regions to more completely characterize the risk.

The Reef Rescue Marine Monitoring Program (MMP) was established in 2005 to assess any improvement in water quality in the Great Barrier Reef (GBR) and the status of key ecosystems. The MMP is a component of the Paddock to Reef Integrated Monitoring, Modelling and Reporting Program, designed to evaluate and report on progress towards the Reef Water Quality Protection Plan (Reef Plan) and Reef Rescue goals and targets. The “immediate” goal of the Reef Plan is to halt and reverse the decline in water quality entering the GBR by 2013. Annual monitoring of inshore reef sites of the GBR and several rivers discharging into nearshore waters has been conducted by Entox since 2005. The principal objective of the monitoring activities conducted by Entox as part of MMP Project 3.7.8 during the 2009 – 2010 monitoring year is to:

“Determine time integrated baseline concentrations of specific organic chemicals in water with the aim to evaluate long term trends in pesticide concentrations along inshore waters of the GBR”

Time integrated estimates of concentration in water are derived using passive sampling techniques. The information from this monitoring will assist in overall assessment of inshore marine water quality, risk assessment and the evaluation of remedial activities undertaken to improve water quality within the GBR lagoon in order to inform management of the GBR by the GBRMPA. This component of the MMP encourages community ownership of the Reef Rescue through direct participation of community groups, tourist operators and agencies. Volunteers contribute to these monitoring efforts by receiving, deploying/retrieving and returning the passive samplers to Entox for subsequent extraction and analysis. This active participation of volunteers within the program is made possible by training by GBRMPA and/or Entox staff in Standard Operating Procedures to ensure the quality of the data obtained from these deployments.

Monitoring has been conducted at sites within five major Natural Resource Management Regions (Cape York, Wet Tropics, Burdekin, Mackay Whitsunday, and Fitzroy). Monitoring of river systems was discontinued within this project within the current monitoring year (2009 -2010) and is now undertaken more comprehensively by the Department of Environment and Resource Management as a component of the Paddock to Reef Program. As a result of this pesticide and herbicide monitoring and other water quality monitoring conducted as components of Reef Rescue (and Reef Plan) an annual Great Barrier Reef Water Quality Report Card will be derived in October 2010 with the baseline reporting year being the previous monitoring year (2008-2009).

To date the most frequently detected and abundant agricultural chemicals detected at inshore reef sites over the last five sampling years include the PS-II herbicides: diuron, atrazine, hexazinone, and tebuthiuron. In the 2008-2009 baseline reporting year a PS-II Herbicide Equivalent Index was introduced which provides a mode of action based integrative assessment of PSII herbicide equivalent concentration. This equivalent concentration incorporates both the relative potency and the relative abundance of individual PSII herbicides within each sampling period (Bengtson-Nash et al. 2005a; Escher et al. 2006; Muller et al. 2008; Shaw et al. 2009b) and is consistent with the use of diuron equivalencies to assess PSII activity in environmental samples using bioanalytical methods (Bengtson-Nash et al. 2005b). The PSII-HEq Index Categories subsequently refined by GBRMPA for 2009-2010 and presented within this report provide a metric for reporting purposes across the GBR. The reporting parameter for PSII herbicides in the GBR will be the maximum PSII-HEq concentration within each monitoring year.

3 METHODOLOGY

Time integrated concentrations in water for specific organic chemicals are estimated using passive sampling techniques. These samplers accumulate chemicals from water via passive diffusion. The passive sampling techniques which are utilized in the MMP include:

- SDB-RPS Empore^{TM} Disk (ED) based passive samplers for relatively hydrophilic organic chemicals with relatively low octanol-water partition coefficients (logK_{OW}) such as the PSII herbicides (example: diuron).
- Polydimethylsiloxane (PDMS) and Semipermeable Membrane Devices (SPMDs) passive samplers for organic chemicals which are relatively more hydrophobic (higher log K_{OW}) such as chlorpyrifos.

These techniques are described in more detail in the “Reef Rescue Marine Monitoring Program: Quality Assurance/Quality Control Methods and Procedures Manual” and in previous reports (Kennedy et al. 2010; RRRC 2010).

3.1 Target Chemicals & Limits of Reporting

The chemicals targeted for analysis in the different passive samplers and the limits of reporting (LOR) are indicated in Table 2. This list of target chemicals was derived through consultation with GBRMPA with the criteria being:

- Detected in recent studies
- Recognised as a potential risk
- Analytical affordability and within the current analytical capabilities of Queensland Health Forensic and Scientific Services (QHFSS).
- Likelihood of accumulation in one of the passive samplers (exist as neutral species in the environment).

Empore disc sampler extracts are analysed using liquid chromatography mass spectrometry (LCMS) run in positive analysis mode. It should be noted that the analysis of bromacil was specifically requested from 2009-2010. Being run only in positive analysis mode excludes the detection of specific hydrophilic organic chemicals such as 2,4-D, MCPA, mecoprop, and picloram which would only be detected in negative analysis mode. These chemicals may not however be particularly suited to sampling using this specific passive sampler as speciation information compiled for all analytes targeted for aquatic analysis by QHFSS indicate that these would be present predominantly as negatively charged species. PDMS and SPMD sampler extracts are analysed using gas chromatography mass spectrometry (GCMS). While certain chemicals are specifically targeted through the MMP, a broader suite of chemicals are analysed for and these are indicated in Table 29 Appendix A. LOR for other non-target chemicals quantified in the MMP are provided in Table 30 Appendix A.

The LOR for the LCMS and GCMS instrumental data produced for this report have been defined by Queensland Health Forensic and Scientific Services laboratory as follows: The LORs are determined by adding a very low level amount of analyte to a matrix and injecting 6-7 times into the analytical instrument. The standard deviation of the resultant signals is obtained and a multiplication factor of 10 is applied to obtain the LOR. A further criterion for the LOR is that the analyte value should exceed 3 times the mass detected in the blank. Actual LOR for a given deployment may vary from those indicated in Table 2.

Table 2. Specific organic chemicals specified under the MMP for analysis in different passive sampler extracts and the Limits of Reporting (LOR) for these analytes.

Organic compounds	LOR (ng.L^{-1})		
	SPMD	PDMS	ED
Ametryn		<10	<0.3
Atrazine		<10	<0.3
Bifenthrin		<1	
Bromacil			<0.3
Chlordane	<0.1	<0.5	
Chlorfenvinphos		<2	
Chlorpyrifos	<0.03	<0.5	
Desisopropylatrazine		<25	<0.3
DDT	<0.08	<0.5	
Diazinon	<5	<5	
Dieldrin	<0.2	<0.5	
Diuron		<25	<0.3
Endosulphan	<1.9	<5	
Fenamiphos		<5	
Fenvalerate		<0.5	
Fluometuron		<30	<0.3
Hexachlorobenzene	<0.09	<0.5	
Heptachlor	<0.07	<0.5	
Hexazinone		<25	<0.3
Lindane	<0.5	<5	
Metolachlor		<10	<0.3
Oxadiazon		<0.5	
Prometryn		<5	<0.3
Pendimethalin	<0.4	<0.5	
Phosphate-tri-n-butyl		<3	
Propazine		<10	
Propiconazole		<2	
Propoxur		<25	
Prothiophos	<0.09	<0.5	
Simazine		<30	<0.3
Tebuconazole		<5	
Tebuthiuron		<25	<0.3
Trifluralin		<0.5	

3.2 Sampling Sites

Passive samplers were routinely deployed at twelve current inshore reef sites (Figure 4) in 2009-2010 and two inshore reef sites and two river sites which were discontinued late in 2009-2010. The current sites include three new pesticide monitoring sites which were incorporated into the MMP in 2009-2010. These were Green Island in the Wet Tropics Region and Inner Whitsunday-Pioneer Bay-Inner Whitsunday and Sarina Inlet in the Mackay Whitsunday Region. The discontinued inshore reef sites included Pixies Garden in the Cape York Region and Daydream Island – Inner Whitsunday in the Mackay Whitsunday Region. The two river sites which were discontinued included the Tully River in the Wet Tropics Region and the Pioneer River in the Mackay Whitsunday Region. As mentioned previously, these and other river sites will now be monitored more comprehensively through the Paddock to Reef Program. Sites were discontinued for budgetary reasons with the criteria used to exclude specific sites being:

- Little data availability
- Problems with site organization
- Better sites available in the same region while representing the same type of exposure

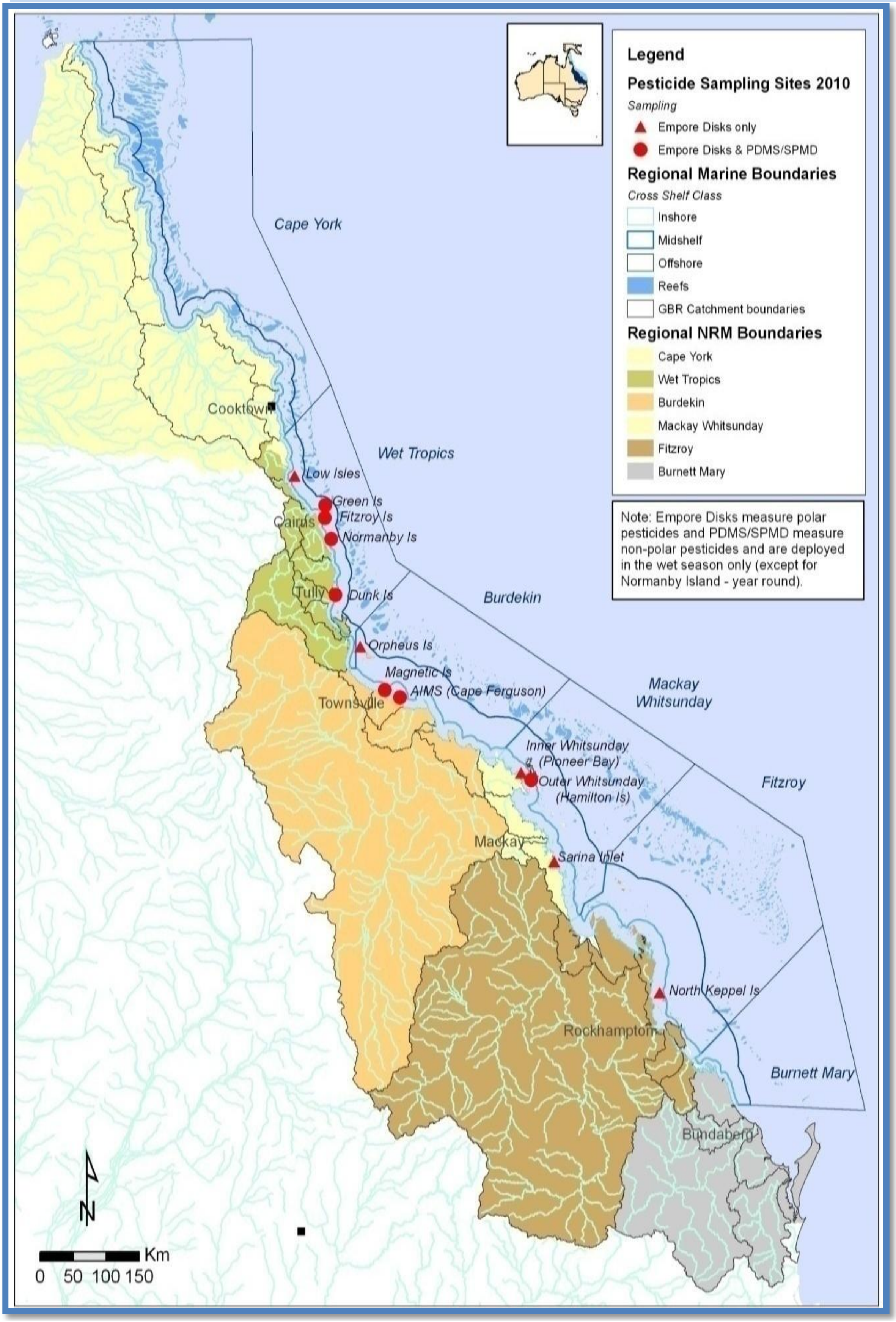

Figure 4 Locations of current inshore reef monitoring sites where time integrated sampling of pesticides was undertaken during 2009 – 2010.
(sourced from Jane Waterhouse of C_2O Consulting)

A brief monitoring history with respect to all of these sites (current and discontinued) is provided in Table 32 Appendix C.

3.3 Sampling Periods

The monitoring year for pesticide sampling is from May 2009 to April 2010. The 2009-2010 monitoring year is divided into "Dry 09" (May 2009 to October 2009) and "Wet 09-10" (November 2009 – April 2010) periods for reporting purposes. Within each dry period samplers are deployed for two months (maximum of three periods) and within each wet period samplers are deployed for one month (maximum of six monitoring periods). The maximum number of samples which should be obtained from each location within each monitoring year is nine. The sampling records for all sites in 2009-2010 are illustrated in Table 33 Appendix C.

3.4 Types of Sampling at each Location in Dry and Wet Periods

The types of sampling conducted for all sites are indicated with a "cross" in Table 3 with discontinued sites shaded grey.

Table 3 The types of passive samplers deployed at each sampling site in either dry or wet sampling periods in 2009-2010

Region	Site	EDs		PDMS		SPMD	
		Dry	Wet	Dry	Wet	Dry	Wet
Cape York	Pixies Garden	×	×				
Wet Tropics	Low Isles	×	×				
	Green Island	×	×		×		
	Fitzroy Island	×	×		×		
	Normanby Island	×	×	×	×	×	×
	Dunk Island	×	×		×		
	Tully River	×	×	×	×	×	×
Dry Tropics	Orpheus Island	×	×				
	Magnetic Island	×	×		×		
	Cape Cleveland	×	×		×		
Mackay - Whitsunday	Pioneer Bay – Inner Whitsunday	×	×				
	Daydream Island –Inner Whitsunday	×	×				
	Outer Whitsunday	×	×		×		
	Pioneer River	×	×	×	×	×	×
	Sarina Inlet	×	×				
Fitzroy	North Keppel Island	×	×				

3.5 Deployment of Passive Samplers

During a typical deployment when all types of samplers were utilized, two replicate EDs were deployed in a Chemcatcher housing (Kingston et al. 2000) and two PDMS (Smedes 2007) (and two SPMDs (Huckins et al. 2000) in the case of Normanby Island) were deployed in a marine grade stainless steel deployment cage as illustrated in Figure 5.

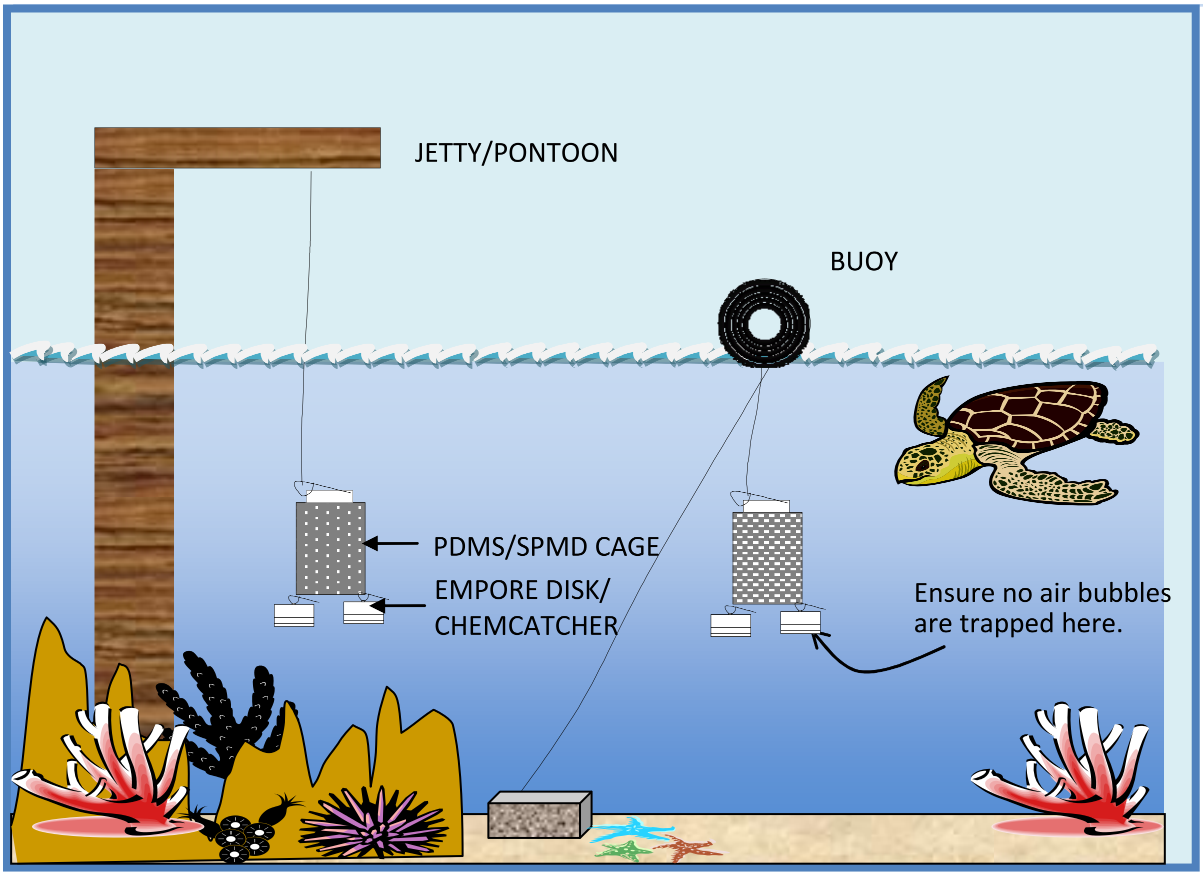

Figure 5 **Schematic for the deployment of both Empore discs and PDMS/SPMDs passive samplers in aquatic environments**

3.6 Replication & Blanks

All ED samples were extracted and one replicate analysed for each location. All replicate sample extracts were stored at 1 mL in glass vials in freezers with selected replicates (10 %) subsequently analysed. All PDMS and SPMD samplers were extracted and replicates from each island site were combined to form one analysed sample per site to increase the concentration of accumulated chemicals. Replicates from the river sites were extracted and analysed separately.

3.6.1 Normalised Differences

The reproducibility of replicate passive samples in estimating C_W was determined using normalised difference (ND) (replicates =2). The normalised difference between two samples A and B was calculated according to Equation 1.

$$ND\% = \frac{|value\ a - value\ b|}{((value\ a + value\ b)/2)} \times 100$$ **Equation 1**

Mean normalized differences samples where pesticides were detected in both replicates were 4 % for PDMS and SPMD samplers and 33 % for ED samplers in 2009 – 2010.

Laboratory blanks of each passive sampler type were prepared in parallel with samplers for each deployment, stored (< 4 ^{o}C) during deployments and subsequently extracted simultaneously with each set of deployed samplers. No target analytes were detected in blank EDs in 2009-2010. Cypermethrin was detected in PDMS laboratory blanks and exposed samples for a single deployment and was excluded for this specific monitoring period.

3.7 Internal and Recovery Standards

An internal standard (250 ng of D_{10}-Simazine) was added to each ED sampler prior to extraction. A recovery standard (100 ng of D_5-atrazine) was subsequently added to each sample just prior to analysis. A percentage recovery of internal standard was determined for each sample and these were used to account for losses during sample processing. Internal standards are not used for recovery correction of the amounts accumulated by the PDMS or SPMD samplers. However all stages of sampler processing are subject to method development and an evaluation of the recoveries for this procedure typically range from 65 – 100 %. The amounts detected in PDMS and SPMD samplers are corrected for known procedural losses during sampler processing such as the use of gel permeation chromatography to purify sample extracts (50 %), prior to estimating the concentration in water.

3.8 Estimating the Concentration in Water using Passive Sampling Techniques

Passive sampling techniques provide a time averaged estimate of the concentrations in water of analytes detected in samplers after a defined exposure period in the environment. These concentration estimates are derived using the concentration of analytes sequestered in the sampler within this exposure period and calibration data obtained in laboratory or field studies (Stephens et al. 2005; Booij et al. 2007; Shaw et al. 2009a; Shaw and Müller 2009; Stephens et al. 2009). This calibration data is typically comprised of sampling rates (volume of water sampled per day).

Passive samplers initially accumulate chemicals from the environment in a time integrated manner (linear uptake). Eventually, equilibrium is achieved between the concentration in the sampler (C_S) and the concentration in water (C_W). The equations used to estimate C_W when sampling is either time integrated or during equilibrium phase sampling are provided in equations 2 and 3 respectively.

$$C_W = \frac{C_S \; M_S}{R_S \; t} = \frac{N_S}{R_S \; t}$$ **Equation 2**

$$C_W = \frac{C_S}{K_{SW}}$$ **Equation 3**

Where:

C_W = the concentration of the compound in water (ng.L^{-1})
C_S = the concentration of the compound in the sampler (ng.g^{-1})
M_S = the mass of the sampler (g)
N_S = the amount of compound accumulated by the sampler (ng)
R_S = the sampling rate (L.day^{-1})
t = the time deployed (days)
K_{SW} = the sampler –water partition coefficient (L.g^{-1})

The duration of the deployment period can be a critical factor in determining whether time integrated sampling or equilibrium phase sampling are occurring for a given analyte in a given sampler. During the dry season monitoring period EDs were routinely deployed in a 2-disc configuration to increase the capacity of the sampling phase and hence theoretically the time required to achieve equilibrium. Time integrated sampling is assumed for these samplers in all monitoring periods and Equation 2 used to derive Cw. A sampling rate of 0.08 $L.day^{-1}$ has been assumed for all target chemicals in ED samplers since monitoring commenced in 2005. This sampling rate is equivalent to the sampling rate of diuron in this sampler at nominal flow velocity of 0.14 $m.s^{-1}$, determined in a tank calibration study previously (Shaw et al. 2009a).

For SPMD and PDMS passive samplers all pesticides accumulated in the passive sampler with log $K_{OW} \leq 4$ are assumed to be in equilibrium phase sampling in both wet and dry sampling periods and C_W determined using Equation 3. Conversely all chemicals with log $K_{OW} > 4$ are assumed to be in kinetic phase sampling and Equation 2 applied to determine C_W. For chemicals that have exceeded the kinetic phase this may result in an underestimation of the time averaged concentration. However, this case is most likely to arise within extended dry season deployments when fewer pesticides are detected and concentrations are typically low compared to wet season periods, any such underestimations are unlikely to be significant. Concentrations in water estimated using SPMDs were determined using a calibration spreadsheet provided by Jim Huckins of the United States Geological Survey who developed this sampler (Huckins et al. 1993; Huckins et al. 2000). This spreadsheet accounts for the influence of water temperature during the deployment period. The sampling rates for pesticides within this spreadsheet per SPMD range from 1.0 to 6.9 $L.day^{-1}$ with an average of 3.5 $L.day^{-1}$. Calibration data for PDMS sampler were obtained from studies conducted at Entox. The sampling rates for pesticides in PDMS range from 1.0 to 5.6 $L.day^{-1}$ with an average R_S of 2.8 $L.day^{-1}$. However if Rs values were not available for specific chemicals they have been extrapolated from other chemicals with similar physico-chemical properties. Further calibration studies are currently underway at Entox in a collaborative research project with the Department of Environment & Resource Management. The purpose of this research is to specifically calibrate these samplers for pesticides relevant to the GBR catchment monitoring program and which are in the current QHFSS GCMS analysis run. Estimated concentrations in water should be considered semi-quantitative in the interim for these samplers (Shaw et al. 2010).

In order to achieve meaningful results with passive sampling techniques, it is necessary to understand the techniques and their limitations and consider site specific factors that may influence the uptake of chemicals into samplers in-situ. It should be noted that the uptake of chemicals into the sampler is expected to be primarily via the dissolved phase. Consequently the total concentration in water (C_W) may be underestimated for extremely hydrophobic chemicals or chemicals which partition significantly into suspended particulate matter. Furthermore, an assumption is made that chemicals are not degraded in the passive samplers. However, for passive samplers deployed in shallow and very clean water, degradation may be an issue for compounds susceptible to photo-transformation. When samplers are deployed for extended periods both reversibility of sorption and degradation may be confounding factors which influence estimated water concentrations.

3.8.1 Data Processing

Data received from QHFSS in ng/sampler for ED, SPMD and PDMS samples were used for the calculation of C_W (concentrations in water) using either Equations 2 or 3. Minimum, mean and maximum values were then determined for each location. It should be noted that in order to determine these statistics for each location that non-detects were assigned an arbitrary value of zero to be consistent with previous reporting years.

3.9 Water Quality Guideline Trigger Values

Table 4. Water quality guideline trigger values available for specific pesticides and herbicides (and transformation product)

Chemical	GBRMPA[a]		ANZECC & ARMCANZ[b]	
	ng.L^{-1}	Notes	ng.L^{-1}	Notes
Organochlorine Pesticides				
Chlordane			30	99 % species protection; Fresh water
			80	95 % species protection
Dieldrin			10*	Low reliability; Fresh water
			10*	Low reliability; Marine water
Dinitroaniline Herbicides				
Trifluralin			2600	99 % species protection; Freshwater
Organophosphate Pesticides				
Chlorpyrifos	0.5	99 % species protection; High reliability	0.5	99 % species protection; Marine water
	9	95 % species protection; High reliability	9	95 % species protection; Marine water
			0.04	99 % species protection; Fresh water
			10	95 % species protection; Fresh water
Diazinon	0.03	Low reliability	0.03	99 % species protection; Fresh water
			10	95 % species protection; Fresh water
Choracetanilide herbicides				
Metolachlor			20*	Low reliability; Freshwater
			20*	Low reliability; Marine
Triazine or Triazinone Herbicides				
Atrazine	600	99 % species protection; Moderate reliability	700	99 % species protection; Fresh water
	1400	95 % species protection; Moderate reliability	1300	95 % species protection; Fresh water
Hexazinone	1200	Low reliability		
Simazine	200	Low reliability	200	99 % species protection; Freshwater
			3200	95 % species protection; Fresh water
Ametryn	500	99 % species protection; Moderate reliability		
	1000	95 % species protection; Moderate reliability		
Urea Herbicides				
Diuron	900	99 % species protection; Moderate reliability	200 *	Low reliability ; Fresh water
	1600	95 % species protection; Moderate reliability	200 *	Low reliability ; Marine water
Tebuthiuron	20	Low reliability	20	99 % species protection; Fresh water
			2200	95 % species protection; Fresh water
Transformation Product				
3,4-dichloroaniline			85000	99 % species protection; Marine water

[a] Sourced from Table 26 & Table 27 of the GBRMPA Guidelines (GBRMPA 2009b); Please note the 99 % species protection GBRMPA Guideline for chlorpyrifos 0.5 ng.L^{-1} is incorrect (5 ng.L^{-1}) in the 2009 document and will be corrected in a revised edition (C. Honchin GBRMPA pers. comm.); [b] Sourced from Table 3.4-1 of the ANZECC &

ARMCANZ guidelines (ANZECC and ARMCANZ 2000); "*" indicates values which are Interim Working Levels rather than Guidelines as indicated in Chapter 8.3.7 Volume 2 of the ANZECC & ARMCANZ Guidelines.

In order to interpret the potential significance of time integrated estimates of concentrations in water these estimates were compared with available Water Quality Guideline Trigger Values (Guidelines). Guidelines have been developed by both the GBRMPA (GBRMPA 2009b) and as part of the National Water Quality Management Strategy for fresh and marine waters (ANZECC and ARMCANZ 2000). A selection of relevant Guidelines and Interim Working Levels, are provided in Table 4.

Guidelines which are protective of 99 % of species are ideal for water bodies of high ecological value like the GBR World Heritage Area (GBRMPA 2009b). Study sites included within this monitoring program include river mouths in catchment areas which potentially contribute to pesticide loadings to inshore reefs of the GBR. In this case trigger values which offer less protection (95 % of species) may also be considered for these areas. In certain cases only freshwater guidelines (ANZECC & ARMCANZ) or "low reliability" Guidelines or "interim working levels" (IWLs) rather than Guideline values are available for assessing the concentrations of specific chemicals. In many cases no Guideline values are available to the assess the concentrations of specific chemicals.

3.10 Calculation of PSII-Herbicide Equivalent Concentrations (PSII-HEq)

For the purpose of this work we propose the use of relative potency factors for relevant herbicides that are routinely found in the environment in order to estimate the inhibition of PSII as a function of the suite of chemicals present in these waters. Specifically we assume that PSII-herbicides act additively (Escher et al. 2006; Muller et al. 2008; Magnusson et al. 2010) and the PSII-HEq ($ng.L^{-1}$) based on those herbicides detected can be predicted for each location using Equation 4.

$$\text{PSII-HEq} = \sum C_i \times REP_i \qquad \text{Equation 4}$$

Where C_i is the concentration of the chemical "i" in the water and REP_i is the relative potency of chemical "i" with respect to the reference chemical diuron. REP values for the chemicals of interest were collated from relevant laboratory studies and are provided in Table 5. For this initial determination of 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 REP values (Table 5) giving equal weight to EC_{50} and EC_{20} values. These initial consensus values were developed and applied to determine PSII-HEq in the baseline reporting year 2008-09 and have not been updated for the sake of consistency however it should be acknowledged that more data will continue to be published (Magnusson et al. 2010) and it is likely that these values would benefit from review and updating in the future.

Table 5. PSII-Herbicide relative potency factors for different herbicides and selected degradation products. Preliminary summary of available data that are used for calculating PSII-HEq concentrations from data obtained in passive samplers.

PSII Herbicides	Relative potency (range)			Relative potency (mean based on various EC)			
	Zooxanthellae (Corals) [a]	P. tricornutum[bcd]	C. vulgaris[bde]	Zooxanthellae (Corals) [a]	P. tricornutum[bcd]	C. vulgaris[bde]	Mean/ Preliminary consensus REP
diuron	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
hexazinone	0.2-0.26	0.27-0.82	0.17-0.95	0.23	0.46	0.44	0.38
atrazine	0.05-0.06	0.1-0.4	0.15 -0.3	0.05	0.22	0.21	0.16
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
prometryn			1-1.1			1.05	1.05
terbuthylazine			0.3			0.3	0.3
desethyl-atrazine			0.01-0.2			0.105	0.11
desisopropyl-atrazine			0.003			0.003	0.003
flumeturon			0.04			0.04	0.04

[a](Jones and Kerswell 2003);[b] (Muller et al. 2008); [c] (Bengtson-Nash et al. 2005a); [d] (Schmidt 2005); [e] Macova et al., unpublished data (Entox)

3.11 PS-II Herbicide Index

For the interpretation of the PSII-herbicide data reported as PSII-HEq an index has been compiled (Table 6) in consultation with the GBRMPA as a metric to report across the MMP. This index uses published scientific evidence with respect to the effects of the reference PSII herbicide diuron and is summarized for each index category in Table 31 Appendix B. These index criteria have been slightly modified from those indicated in the baseline reporting year 2008-2009 (Kennedy et al. 2010).

Table 6 PSII-Herbicide Index developed as a metric for reporting of PSII herbicides across the Reef Rescue Marine Monitoring Program

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. This concentration represents a level at which 99 per cent of tropical marine plants and animals are protected, using diuron as the reference chemical.

For categories 4 – 2:

- 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.

3.12 Outline of Data Presentation

The data for this report is presented in several sections. These include:

1. Summary Results for 2009-2010
2. Spatial Distribution of PSII herbicides and other pesticides 2009-2010
3. Temporal and Seasonal Trends Across All Monitoring Years
4. Regional Summaries for 2009-2010
5. Discussion/GBR Wide Summary 2009-2010
6. Recommendations for Future Work

More detailed results for each site are presented in further detail in Appendix D.

4 SUMMARY RESULTS 2009-2010

Table 7 The regional range in concentrations (ng.L^{-1}) of herbicides (triazine, phenyl urea, triazinone, dinitroaniline, chloracetanilide) and the organophosphate insecticide chlorpyrifos detected at monitoring sites in the inshore GBR in 2009-2010. The PSII-HEq range for these sites and the PSII-HEq Index Category for PSII-HEq Max are also provided. Sites where no monitoring is undertaken for chemicals other than PSII herbicides are shaded light grey. Concentration estimates which exceed GBRMPA Guidelines are indicated in red.

Region	Site	Triazine-PSII Herbicide	Triazine-PSII Herbicide	Urea-PSII Herbicide	Triazinone-PSII Herbicide	Triazine-PSII Herbicide	Urea-PSII Herbicide	PSII-HEq		Organophosphate Insecticide	Dinitroaniline Herbicide	Chloracetanilide Herbicide
		Ametryn	Atrazine	Diuron	Hexazinone	Simazine	Tebuthiuron	Range	Index	Chlorpyrifos	Pendimethalin	Metolachlor
Cape York	Pixies Garden[D]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5			
Wet Tropics	Low Isles	n.d	n.d.– **0.90**	n.d.-**5.7**	n.d.-**2.6**	n.d.	n.d.-**0.30**	n.d.-**6.7**	5			
	Green Is[N]	n.d	n.d.-**1.6**	n.d.-**6.2**	n.d.-**2.2**	n.d.	n.d.-**0.90**	n.d.-**7.4**	5	n.d-**0.69**	n.d.	n.d.
	Fitzroy Is	n.d	n.d.-**2.6**	**0.90-12**	n.d.-**9.5**	n.d.	n.d.-**1.9**	**0.94-16**	4	n.d.-**0.56**	n.d.	n.d.
	Normanby Is	n.d	n.d.-**1.5**	n.d.-**3.6**	n.d-**1.9**	n.d.	n.d.-**0.93**	n.d.-**4.0**	5	n.d.-**0.72**	n.d.-**1.1**	n.d.
	Dunk Is	n.d	n.d.-**3.0**	**0.57-5.9**	n.d.-**2.6**	n.d.	n.d.-**1.6**	**0.57-7.1**	5	n.d.-**0.69**	n.d.	n.d.
Burdekin	Orpheus Is	n.d.	n.d.-**2.2**	**1.5-100***	n.d.-**0.86**	n.d.	n.d.-**2.8**	**2.1-100**	3			
	Magnetic Is	n.d.	n.d.-**5.1**	n.d.-**6.9**	n.d.-**1.8**	n.d.-**1.5**	n.d.-**4.7**	**0.88-8.8**	5	n.d.	n.d.	n.d.
	Cape Cleveland	n.d.-**0.10**	n.d.-**13**	n.d.-**6.7**	n.d.-**0.61**	n.d.-**0.36**	n.d.-**2.2**	**0.036-9.1**	5	n.d.	n.d.	**5.8**
Mackay -Whitsunday	Outer Whitsunday	n.d.	n.d.-**11**	n.d.-**27**	n.d.-**15**	n.d.	n.d.-**0.64**	n.d.-**35**	4	n.d.	n.d.	n.d.
	Daydream Island – Inner Whitsunday[D]	n.d.	**0.59-3.1**	**1.5-51**	**0.50-15**	n.d.	n.d.-2.2	**1.7-57**	3			
	Pioneer Bay-Inner Whitsunday[N]	n.d.	n.d.-**1.1**	**3.6-43**	n.d.-**11**	n.d.	n.d.-**0.90**	**3.6-43**	4			
	Sarina Inlet[N]	n.d.-**2.3**	n.d.-**170**	n.d.-**429**	n.d.-**91**	n.d.	n.d.-**0.71**	**0.58-495**	2			
Fitzroy	North Keppel Is	n.d.	n.d.-**8.4**	n.d.-**6.4**	n.d.-**2.1**	n.d.	n.d.-**14**	n.d.-**8.7**	5			

"N" and "D" denote sites which were either new or discontinued in 2009-2010

The range in estimated concentrations of PSII herbicides and other pesticides for 2009-2010 for inshore GBR sites are indicated in Table 7. PSII herbicides have been detected at all inshore GBR sites except Pixies Garden in the Cape York Region in 2009-2010. There were no exceedances of GBRMPA Guidelines for these individual PSII herbicides. The PSII-HEq Max Index ranged from “5” in the Cape York and Fitzroy Regions (both one site only), from “5”-“4” in the Wet Tropics Region, from “5” – “3” in the Burdekin Region, and from “4 – 2” in the Mackay Whitsunday Region.

The organophosphate insecticide chlorpyrifos (0.56 – 0.72 ng.L^{-1}) was detected at all sites in the Wet Tropics Region where monitoring occurred. These concentrations all exceed the GBRMPA Guideline for Chlorpyrifos of 0.5 ng.L^{-1} for 99 % species protection. In addition, the dinitroaniline herbicide pendimethalin (1.1 ng.L^{-1}) was detected at Normanby Island in the Wet Tropics and the chloracetanilide herbicide metolachlor (5.8 ng.L^{-1}) was detected at Cape Cleveland in the Burdekin Region. This concentration of metolachlor does not exceed the ANZECC & ARMCANZ low reliability Interim Working Level (IWL) for marine waters. There were no other pesticides detected at either Magnetic Island in the Burdekin Region or at the Outer Whitsunday site in the Mackay Whitsunday Region in 2009-2010.

The range in estimated concentrations of PSII herbicides and other pesticides (herbicides, insecticides, and fungicides) for the Tully and Pioneer Rivers are provided in Tables 8 and 9 respectively. The PSII-HEq Max in the Tully and Pioneer Rivers have PSII-HEq Index Categories of “4” and “1” respectively. Monitoring was discontinued at both sites within 2009-2010. The maximum concentration of atrazine in the Pioneer River is equivalent to the ANZECC & ARMCANZ Guideline (99 % freshwater) of 0.7 µg.L^{-1}. The IWL for diuron of 0.2 µg.L^{-1} is exceeded by the maximum concentration of diuron in this river.

Table 8 The range in concentration in water (ng.L^{-1}) of PSII herbicides at the two river sites in 2009-2010. The PSII-HEq range for these sites and the PSII-HEq Index Category for PSII-HEq Max are also provided. Concentrations which exceed ANZECC & ARMCANZ Guideline or IWL values indicated in red.

Region	Site	Triazine-PSII Herbicide	Triazine-PSII Herbicide	Urea-PSII Herbicide	Triazinone-PSII Herbicide	Triazine-PSII Herbicide	Urea-PSII Herbicide	PSII-HEq	
		Ametryn	Atrazine	Diuron	Hexazinone	Simazine	Tebuthiuron	Range	Index
Wet Tropics	**Tully River[D]**	n.d. – **1.1**	**3.1-17**	**3.0-22**	**4.0-14**	n.d.-**5.1**	n.d.	**5.5-32**	4
Mackay Whitsunday	**Pioneer River[D]**	n.d.-**3.7**	**0.26-690**	**0.62-761***	**0.27-232**	n.d.-**22**	n.d.	**0.77-970**	1

* Interim Working Level (IWL) as no Guideline value established; “D” indicates sites discontinued in 2009-2010

The estimated concentrations of chlorpyrifos and diazinon in the Tully River, and the maximum chlorpyrifos concentration in the Pioneer River exceeded ANZECC & ARMCANZ Guidelines in 2009-2010. The maximum chlorpyrifos concentration in the Tully River in the Wet Tropics is higher than that in the Pioneer River by a factor of 17. The 99 % species protection Guideline for freshwater was only exceeded once in the Pioneer River while in the Tully River this Guideline was exceeded in all sampling periods with at least one period exceeding the 95 % species protection Guideline for freshwater. The estimated diazinon concentrations in the Tully River all exceed the 95 % species protection Guideline. Concentrations of other pesticides detected in 2008-2009 are also provided in Table 9. It is however problematic to interpret differences between monitoring years as sampling was discontinued within the current wet season at both sites.

Table 9 The range in concentration in water (ng.L^{-1}) of other herbicides, insecticides and fungicides at the two river sites in 2009-2010 compared to the maximum concentration estimated in 2008-2009. Concentrations which exceed the ANZECC & ARMCANZ Guidelines are indicated in red.

Class	Chemical	Tully River		Pioneer River	
		2008-2009 Max	2009-2010 Range	2008-2009 Max	2009-2010 Range
Pyrethroid insecticide/acaricide	Bifenthrin	**1.5**	n.d.	n.d.	n.d.
Organochlorine insecticide	Chlordane trans	**1.2**	n.d.	n.d.	n.d.
Organophosphate insecticide/acaricide	Chlorfenvinfos	n.d.	n.d.	6.6	n.d.
Aromatic fungicide	Chlorothalonil	**115**	n.d.		n.d.
Organophosphate insecticide/acaricide/nematicide	Chlorpyrifos	**26**	**2.4-12**	**2.1**	**0.25-0.69**
Organophosphate insecticide/acaricide	Diazinon	**62**	**46-55**	**6.1**	n.d.
Organochlorine insecticide	Dieldrin	**0.85**	n.d.	**3.7**	**0.87-2.9**
Arylphenoxypropionic herbicide	Haloxyfop-methyl	n.d.	**0.63**	**n.d.**	n.d.
Chloracetanilide herbicide	Metolachlor	n.d.	n.d.	**42**	**n.d.**
Dinitroaniline herbicide	Pendimethalin	**12**	**0.85-5.4**	**1.3**	**0.36-7.3**
Chlorotriazine herbicide	Propazine	n.d.	n.d.	**24**	n.d.
Conazole fungicide	Propiconazole	**12**	**11-19**	**6.8**	n.d.
Organophosphate insecticide	Prothiofos	**4.1**	**0.19-2.0**	n.d.	n.d.
Conazole fungicide	Tebuconazole	**7.5**	**13-22**	n.d.	n.d.
Methylthiotriazine herbicide/algaecide	Terbutryn	n.d.	n.d.	**3.2**	n.d.
Dinitroaniline herbicide	Trifluralin	n.d.	n.d.	**0.50**	n.d.

5 SPATIAL DISTRIBUTIONS OF PESTICIDES 2009-2010

Spatial differences in the relative abundance (higher concentration) and detection of PSII herbicides are illustrated in Figure 6 for the inshore GBR sites (inshore waters and reefs) and Figure 7 for the Tully and Pioneer Rivers. Other pesticides (insecticides, herbicides and fungicides) detected at sites where PDMS sampling was undertaken are illustrated in Figure 8. All concentrations are the maximum concentration in water for each compound at each site in 2009-2010.

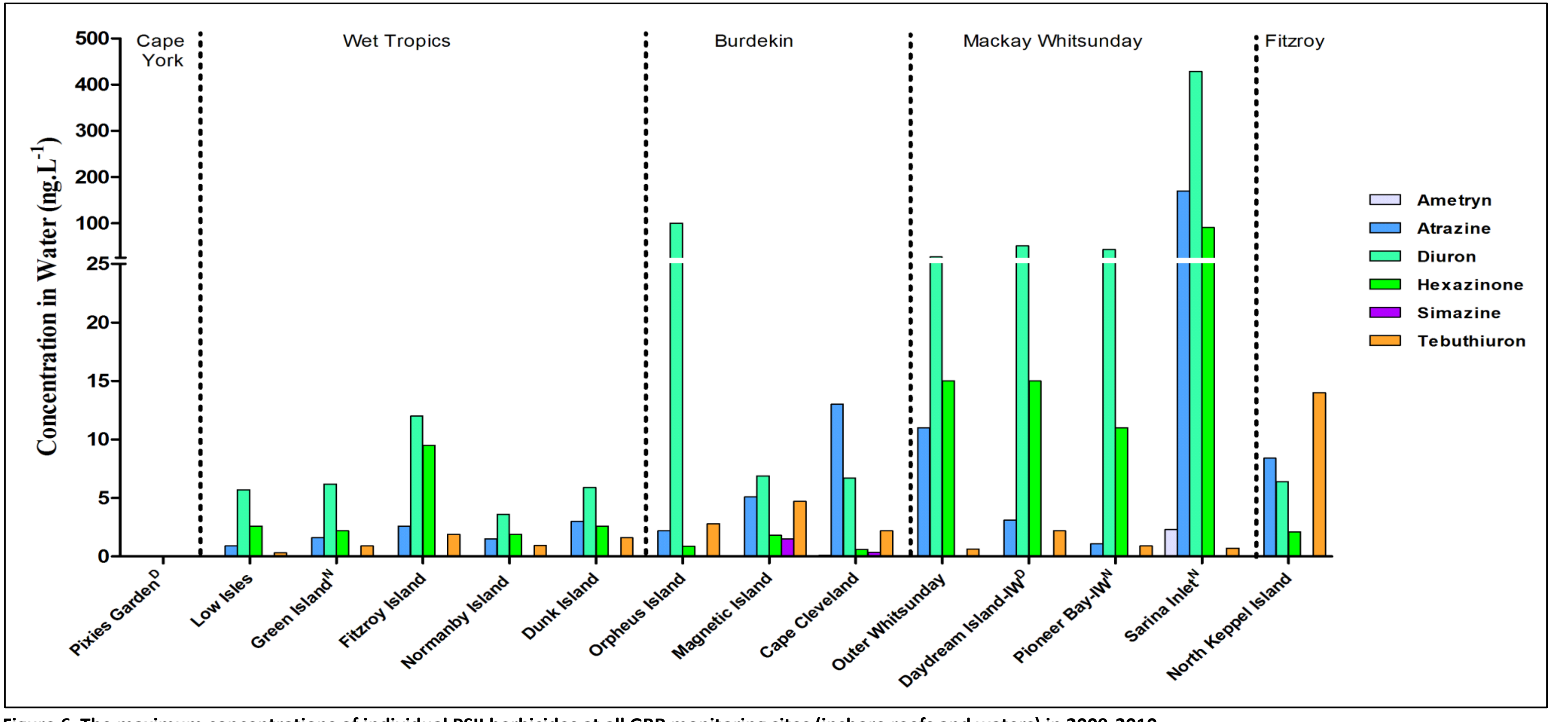

Figure 6 The maximum concentrations of individual PSII herbicides at all GBR monitoring sites (inshore reefs and waters) in 2009-2010.
“D” indicates discontinued sites, while “N” indicates new sites in 2009-2010

These profiles (Figure 6 and 7) indicate that diuron has typically occurred at the highest concentration at most sites in 2009-2010. The exceptions are Cape Cleveland in the Burdekin Region where the maximum atrazine concentration is higher than that of diuron and North Keppel Island in the Fitzroy Region where both the maximum concentration of atrazine and tebuthiuron are higher than that of diuron. Maximum hexazinone concentrations in the Wet Tropics and in the Mackay Whitsunday Regions are typically less than that of diuron but higher than atrazine. In comparison, in the Burdekin and Fitzroy Regions hexazinone maximum concentrations are typically less than those of atrazine or tebuthiuron.

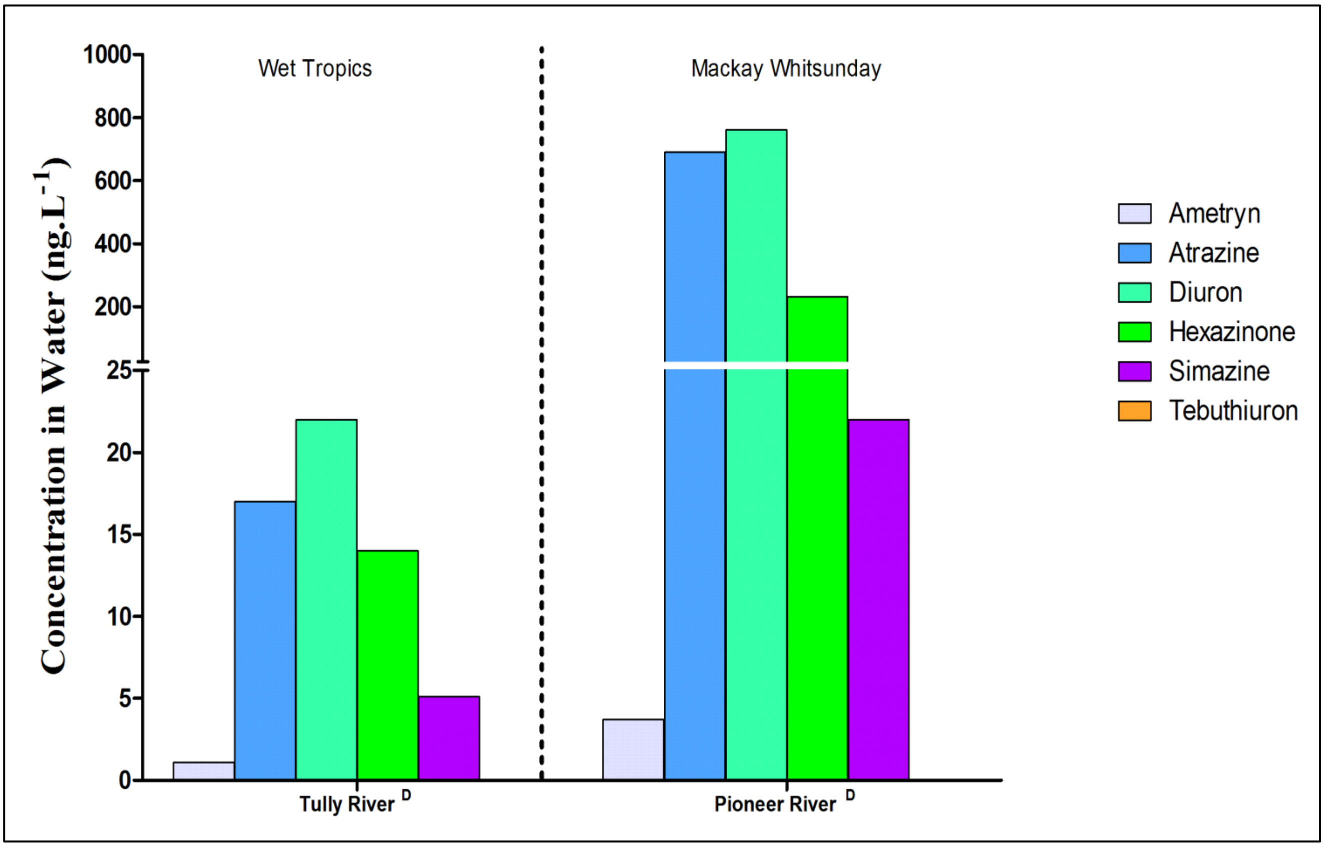

Figure 7 Maximum concentrations of individual PSII herbicides in the Tully and Pioneer Rivers in 2009-2010
"D" indicates discontinued site in 2009-2010

Notably, tebuthiuron was not detected in either the Tully or Pioneer Rivers in 2009-2010 although monitoring was discontinued within the current wet season at both sites. The maximum concentration profiles in these Rivers are remarkably similar in terms of the relative concentration of individual PSII herbicides with diuron > atrazine > hexazinone > simazine > ametryn. However the maximum concentrations of each individual PSII herbicide is higher in the Pioneer River than in the Tully River. The maximum concentrations in the Pioneer River were higher by a factor of 3, 41, 35, 17 and 4 for ametryn, atrazine, diuron, hexazinone and simazine respectively.

A broader range of herbicides, insecticides and fungicides were detected using PDMS sampling in the Tully River than in the Pioneer River in 2009-2010 (Figure 8) . For example, diazinon, haloxyfop methyl, prothiofos, propiconazole and tebuconazole were detected only in the Tully River. Chlorpyrifos was detected in both rivers but at a higher maximum concentration in the Tully River. However, pendimethalin was detected at higher concentrations in the Pioneer River and dieldrin was detected only in the Pioneer River. Chlorpyrifos was also detected at all GBR sites in the Wet Tropics Region. Apart from the Rivers, pendimethalin was detected only at Normanby Island in the Wet Tropics Region of the GBR. Metolachlor was not detected in either river in 2009-2010 but was detected at Cape Cleveland in the Burdekin Region.

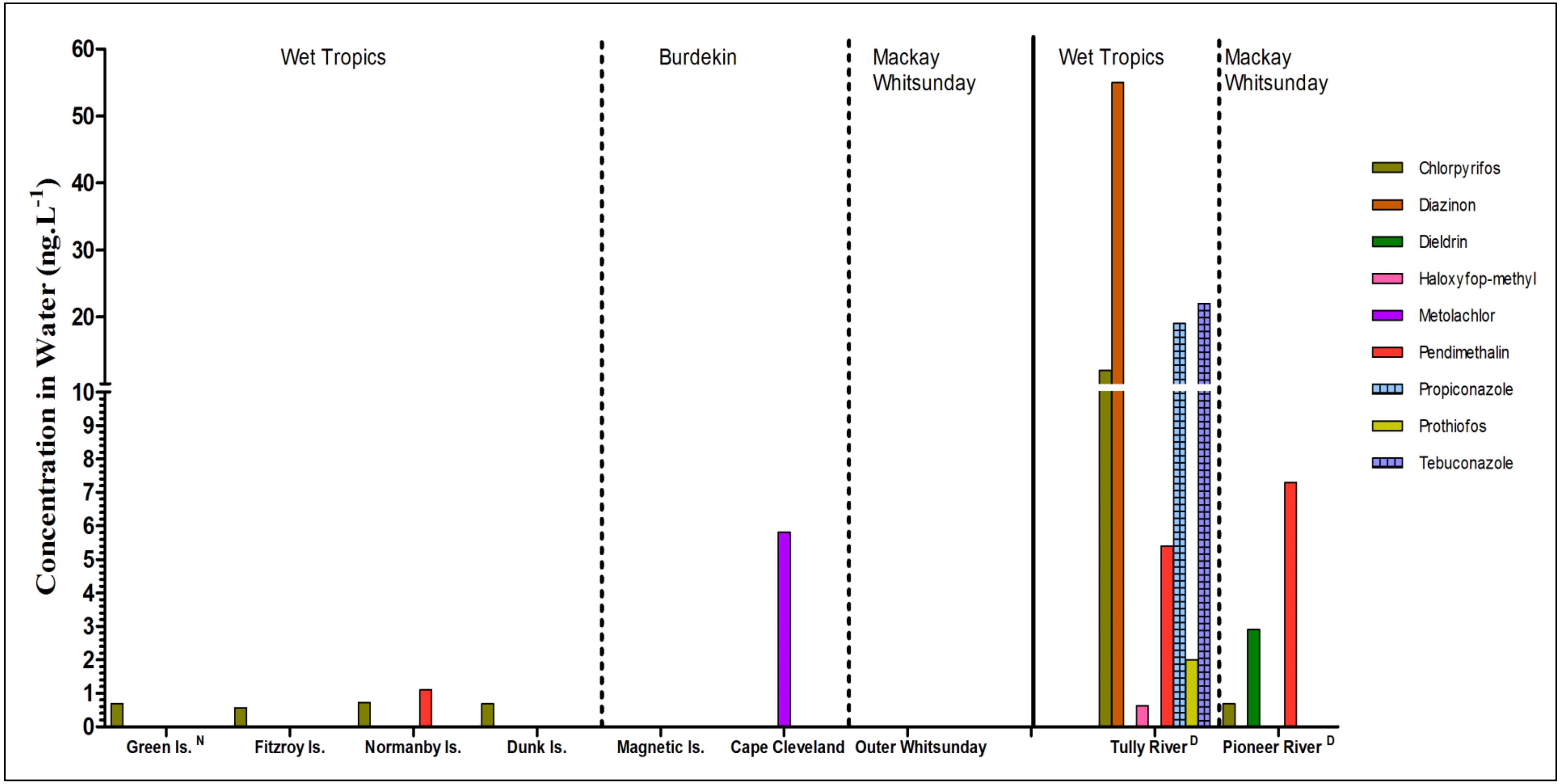

Figure 8 Maximum concentrations of other insecticides, herbicides and fungicides for all GBR (inshore reefs and waters) and River sites where PDMS sampling occurred in 2009-2010
“D” indicates discontinued sites and “N” indicates new sites in 2009-2010

6 TEMPORAL & SEASONAL TRENDS

For all temporal trend plots in this section time averaged concentration estimates are indicated as a separate point for each month even though this may represent only a single deployment across multiple months particularly during the dry seasons. Any gaps in the sampling record are indicated by a gap in the connecting line between these points. Where replicate samplers have been analysed for each point, the point represents the mean and error bars represent standard deviations. These trend plots are illustrated for PSII herbicides and PSII-HEq for all locations and relationships between PSII-HEq and discharge from adjacent rivers are made where possible. In addition temporal trends in the concentrations of a broad range of pesticides (insecticides, herbicides and fungicides) are provided for the Tully and Pioneer Rivers, since a broader range of compounds are more frequently detected using PDMS sampling in these rivers.

6.1 Cape York Region

6.1.1 Pixies Garden - discontinued

PS-II Herbicides: September 2006 – March 2010

Passive sampling has been used to estimate the concentrations of PS-II Herbicides at the Pixies Garden site since September 2006 with a total of 19 time averaged monitoring events in this period. The temporal profile for this location(Figure 9) indicates the dominance of diuron at this site with concentrations typically < 2 ng.L^{-1} and most detections occurring in the wet seasons in each monitoring year. Other herbicides detected at this site in previous years include hexazinone, atrazine (and breakdown product desethyl atrazine), and simazine.

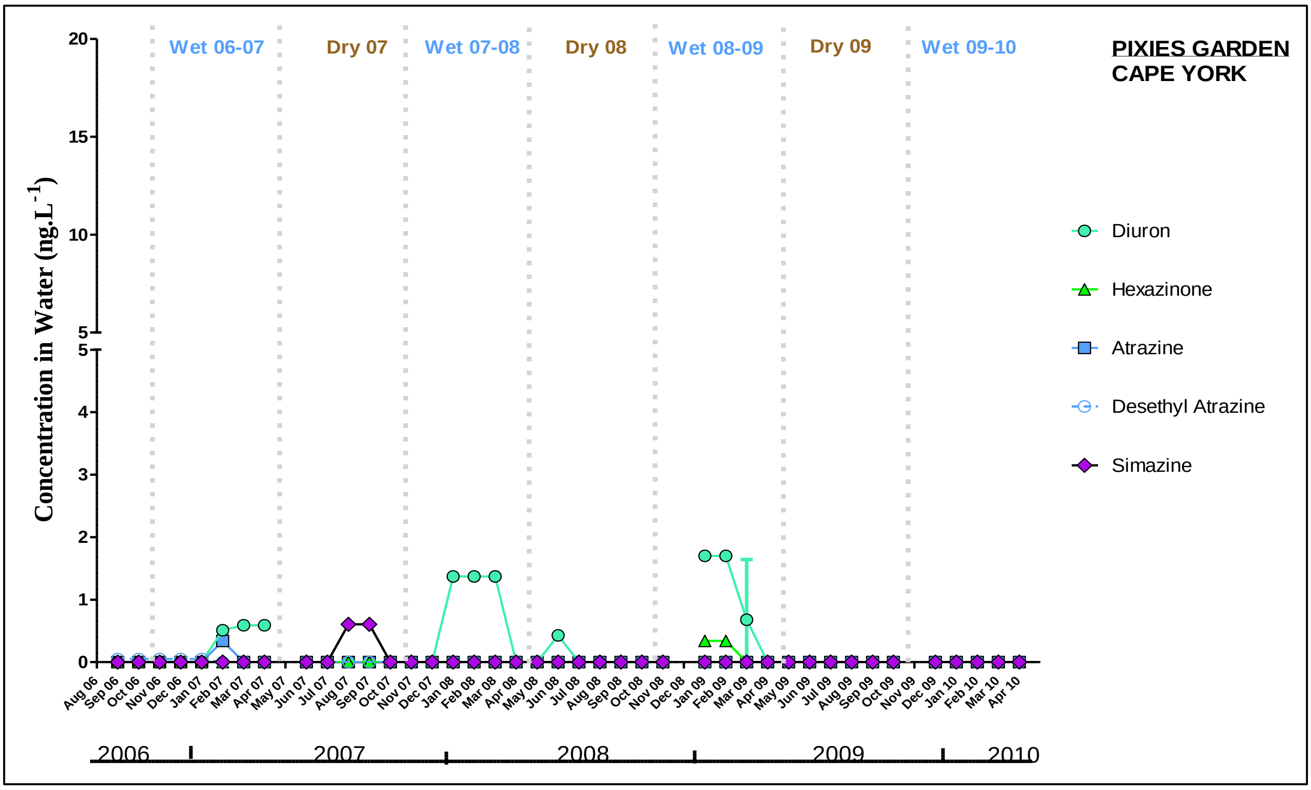

Figure 9 Time averaged PSII herbicide concentrations for Pixies Garden in the Cape York Region across wet and dry seasons 2006-2010

The PSII-HEq for the Pixies Garden site between September 2006 and March 2010 are illustrated in Figure 10. There is a slight increase in the PSII-HEq evident between each wet season period between “Wet 06-07” and “Wet 08-09” and a subsequent decrease in the current “Wet 09-10” period with no PSII herbicides detected. Sampling was discontinued within this latest "Wet 09-10" period. The maximum PSII-HEq for the previous three wet seasons were 0.59, 1.4 and 1.8 ng.L^{-1} respectively. The initial 2006-07 wet season maximum (March –April – 28 days) may not however be typical because of the inclusion of one monitoring period from September 2006 to January 2007 (130 days) in the initial part of the wet season where samplers were deployed for a period beyond those considered suitable for the application of these techniques. In this case the last two wet seasons which were reasonably well captured (more frequent shorter duration monitoring) have relatively consistent PSII-HEq. These PSII-HEq are all relatively low (< 2 ng.L^{-1}) within the range of Category "5" (≤ 10 ng.L^{-1}) of the PSII-HEq Index.

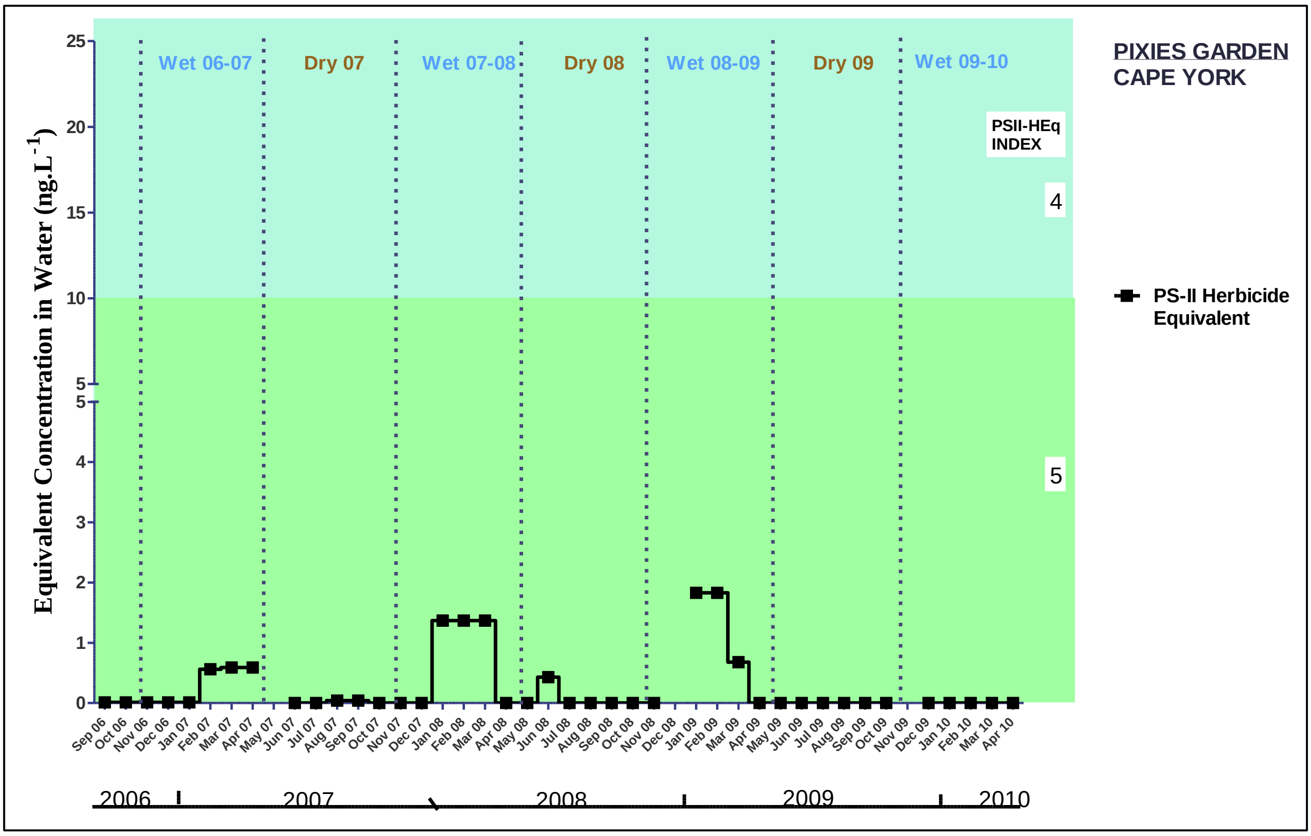

Figure 10 The influence of wet or dry season on the PSII-HEq for the Pixies Garden monitoring site in the Cape York Region between 2006 and 2010

6.2 Wet Tropics Region

6.2.1 Low Isles

PS-II Herbicides: August 2005 – March 2010

The most notable feature of the profiles for Low Isles between 2005 and 2010 (Figure 11) are the relative consistency of the spikes in the levels of the dominant herbicide diuron in the wet seasons in 2006-2007, 2007-2008, 2008-2009 and 2009-2010. The presence of simazine at this location in the three previous wet seasons is not evident in the current 2009-2010 wet season. The consistent levels of diuron are reflected in the consistent PSII-HEq for this site (Figure 12) with only one sampling period (March 2006) increasing the maximum HEq for this site into PSII-HEq Index Category " 4" (10 < HEq ≤ 50 ng.L^{-1}).

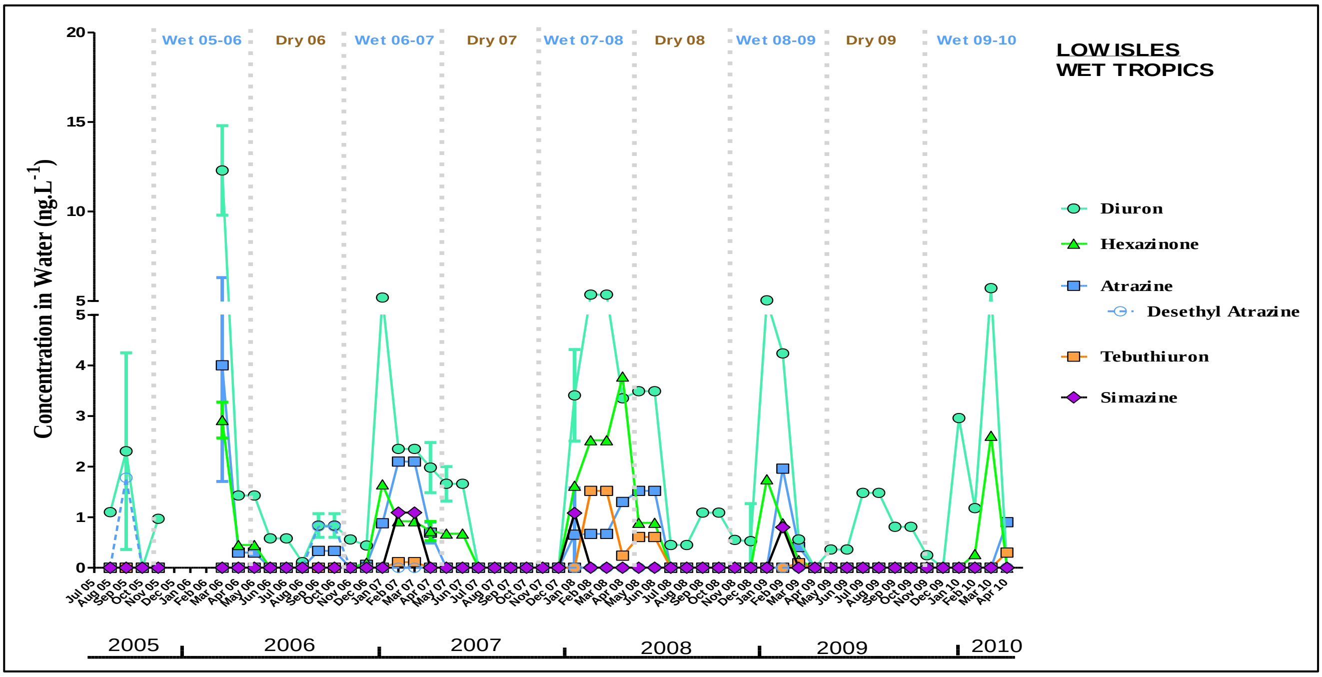

Figure 11 Time averaged PSII herbicide concentrations for Low Isles in the Wet Tropics Region across wet and dry seasons between 2005 and 2010

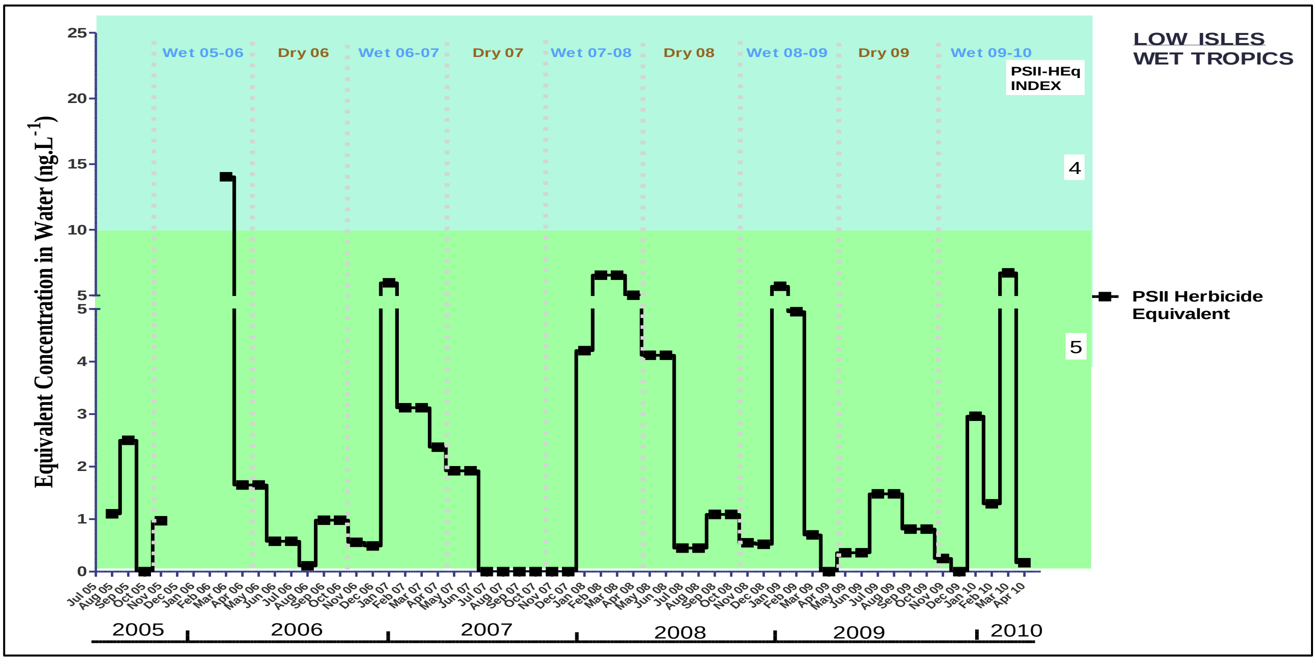

Figure 12 Time averaged concentrations at Low Isles expressed as PSII-Herbicide Equivalent concentrations across wet and dry seasons between 2005 and 2010 with PSII Herbicide Index categories "4" and "5" (≤ 10 ng.L^{-1}) indicated

Relationships between temporal and seasonal PSII-HEq profiles and discharge in the Daintree and Mossman Rivers

The Low Isles site is approximately 15 km southeast (heading 132.60 degrees) of the mouth of the Daintree River and 17 km northeast (heading 71.70 degrees) of the Mossman River. The highest PSII-HEq for the Low Isles site in the "Wet 05-06" sampling period coincides with the highest annual freshwater discharge for the Daintree River in 2005/06 (Table 10) and an PSII-HEq index of "4". The latest 2009/10 year also indicates river flows exceeding median annual flows but the PSII-HEq is relatively consistent with 2006/07 (below median) and 2007/08 (also above median). Discharges from the Mossman River have not been included for this location but may also be relevant.

Table 10 Annual freshwater discharge (ML) for the Daintree River in proximity to the Low Isles sampling site. Shaded cells highlight years for which river flow exceeded the median annual discharge as estimated from available long-term time series for each river.

River	2005/06	2006/07	2007/08	2008/09	2009/10	Long term median
Daintree	1,253,555	715,530	874,013	423,711*	1,147,846	777,014

* Incomplete gauging record; Sourced from Table A1-2 (Schaffelke et al. 2010)

Table 11 Monthly discharges (ML) for the Daintree and Mossman Rivers available for 2009 -2010 from DERM Stations 108002A and 109001A

River	Jun 09	Jul 09	Aug 09	Sep 09	Oct 09	Nov 09	Dec 09	Jan 10	Feb 10	Mar 10	Apr 10
Daintree	22,400	15,415	11,469	6,572	4,201	17,892	9,680	145,421	198,059	366,933	303,542
Mossman	10,516	6,584	1,434*		2,684*	16,993	11,206	37,228	51,842	11,534*	68,732
Total	32,916	22,000	12,902	6,572	6,885	34,885	20,887	182,649	249,901	378,467	372,274

 * Incomplete gauging record

In the 2009-2010 the first significant increase (>100,000 ML) in monthly discharge occurred in January 2010, which coincides with the first spike in PSII-HEq for the Low Isles site. The maximum total monthly discharge from the Daintree and Mossman Rivers (Table 11) for 2009-2010 occurred in March 2010 which also coincides with the maximum PSII-HEq estimate of 6.7 ng.L^{-1} (Figure 13).

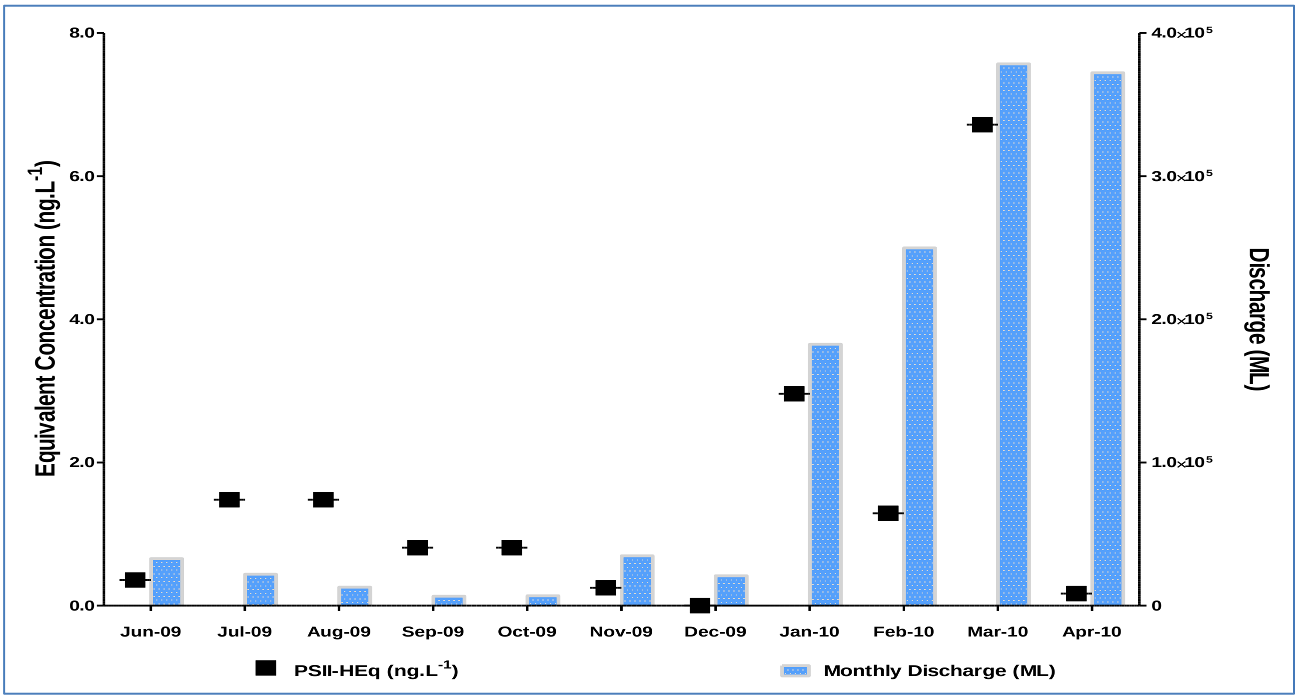

Figure 13 Total monthly discharges from the Daintree and Mossman Rivers together with monthly PSII-HEq for the Low Isles site in 2009-2010

6.2.2 Green Island

PS-II Herbicides: June 2009 – April 2010

The concentrations of all PSII herbicides were < 1 $ng.L^{-1}$ across most of 2009-2010 (Figure 14) with increases beginning to be apparent in the wet 09-10 sampling period. These increase were observed from January (diuron), February (hexazinone) and March (atrazine) 2010 with tebuthiuron detected only when the maximum concentrations for all herbicides were recorded in April 2010. The diuron concentration increased by a factor of nine between March 2010 and April 2010 increasing from 0.73 to 6.2 $ng.L^{-1}$. The maximum PSII-HEq (7.4 $ng.L^{-1}$) for April 2010 (Figure 15) approaches the top of the Category "5" (≤ 10 $ng.L^{-1}$) PSII-HEq Index range.

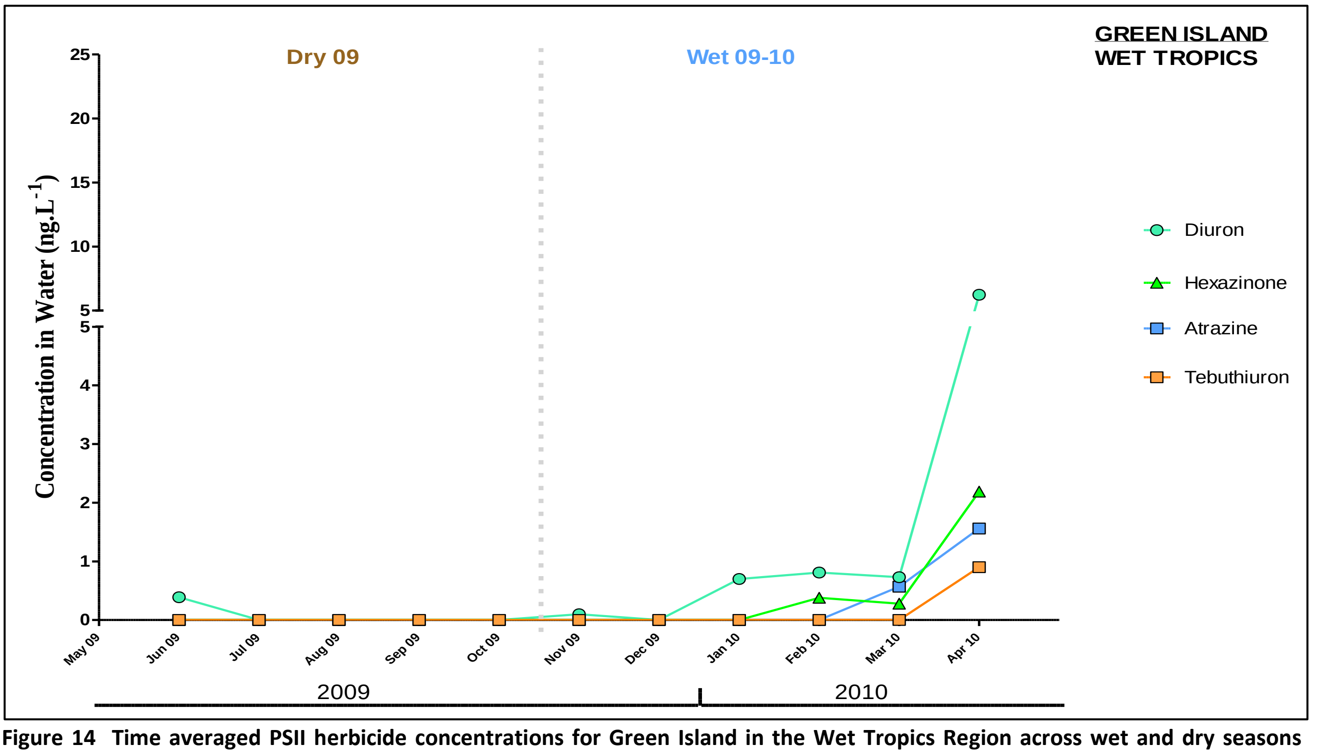

Figure 14 Time averaged PSII herbicide concentrations for Green Island in the Wet Tropics Region across wet and dry seasons between 2009 and 2010

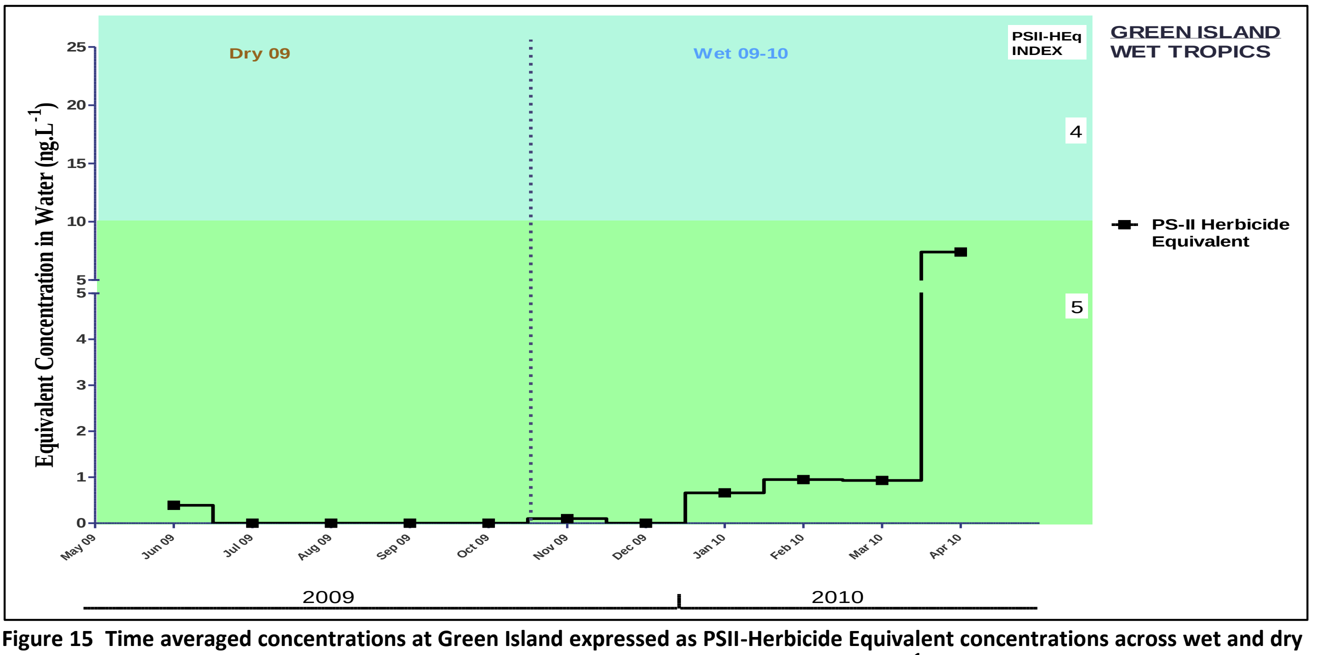

Figure 15 Time averaged concentrations at Green Island expressed as PSII-Herbicide Equivalent concentrations across wet and dry seasons between 2005 and 2010 with PSII Herbicide Index categories "4" and "5" (≤ 10 $ng.L^{-1}$) indicated

Relationships between temporal and seasonal PSII-HEq profiles and freshwater discharge in the Barron River

The Green Island site is located approximately 24 km northeast (heading 62.37 degrees) of the Barron River mouth. Long term median annual flow were not exceeded in this river in 2009-2010 (Table 12).

Table 12 Annual freshwater discharge (ML) for the Barron River in proximity to the Green Island sampling site. Shaded cells highlight years for which river flow exceeded the median annual flow as estimated from available long-term time series for each river.

River	2008/09	2009/10	Long term median
Barron	781,081	539,064	692,447

Sourced from Table A1-2(Schaffelke et al. 2010)

In 2009-2010 (Table 13) the first significant increase (>100,000 ML) in monthly discharge occurred in January 2010, which coincides with the first wet season increases in PSII-HEq observed in January 2010. The maximum monthly discharge (179, 068 ML) was however observed in January 2010, while the PSII-HEq Max was not observed until April 2010 once monthly discharge had declined to 64,339 ML (Figure 16).

Table 13 Monthly discharges (ML) for the Barron River available for 2009 -2010 from DERM Station 110001D

River	Jun 09	Jul 09	Aug 09	Sep 09	Oct 09	Nov 09	Dec 09	Jan 10	Feb 10	Mar 10	Apr 10
Barron	29,047	26,370	24,988	7,632	5,932	6,378	6,572	179,068	100,709	72,985	64,339

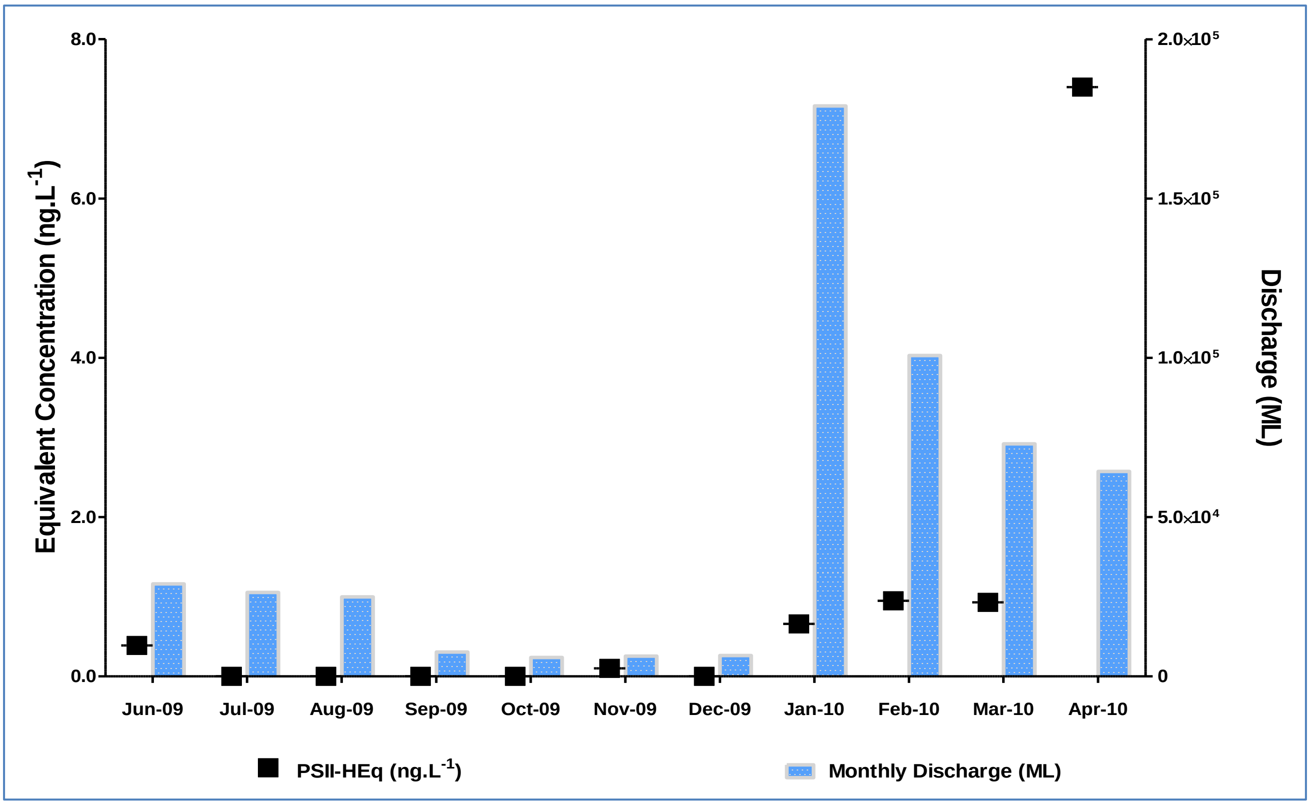

Figure 16 Monthly total discharges from the Barron River together with monthly PSII-HEq for the Green Island site in 2009-2010

6.2.3 Fitzroy Island

PSII Herbicides: July 2005 – April 2010

The seasonal profiles for Fitzroy Island (Figure 17) reveal the dominance of diuron and the consistent presence of this herbicide in both wet and dry seasons, with elevated levels occurring typically in the wet season, with the exception of a dry season spike between June and July 2007. This dry season spike in diuron was accompanied by a slight increase in the levels of atrazine and hexazinone from April – May 2007. The other PSII herbicides consistently detected are again atrazine, hexazinone, tebuthiuron and simazine. However simazine was not detected in this latest 2009-2010 wet season which was also the case at the Low Isles site in this monitoring period. One notable feature of this profile is the apparent increase in the levels of hexazinone between 2005 and 2010 from 1.5 to 10 ng.L^{-1}. The seasonal PSII-HEq profiles for Fitzroy Island between 2005 and 2006 (Figure 18) indicate an apparent increase in equivalent concentrations in the 2008-2009 and 2009-2010 wet seasons compared with the previous three wet seasons. Due to its relative abundance and relative potency diuron is the dominant contributor to the PSII-HEq and therefore this profile mirrors the concentration of diuron seasonally. Fitzroy Island PSII-HEq are more consistently Category "5" with peaks in diuron levels contributing to Category "4" ((10 < HEq ≤ 50 ng.L^{-1}) maximums during each monitoring year over the last three years.

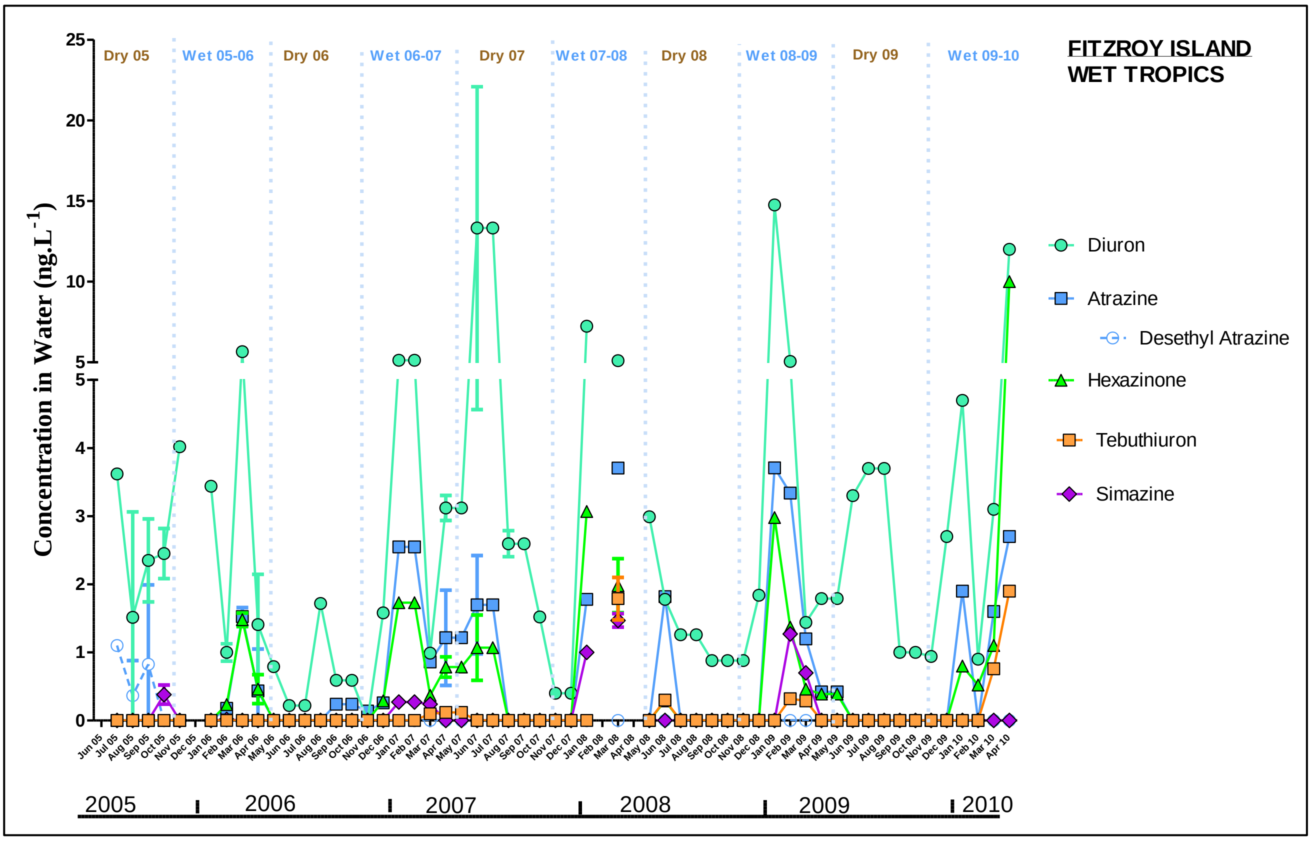

Figure 17 Time averaged PSII herbicide concentrations for Fitzroy Island in the Wet Tropics Region across wet and dry seasons between 2005 and 2010

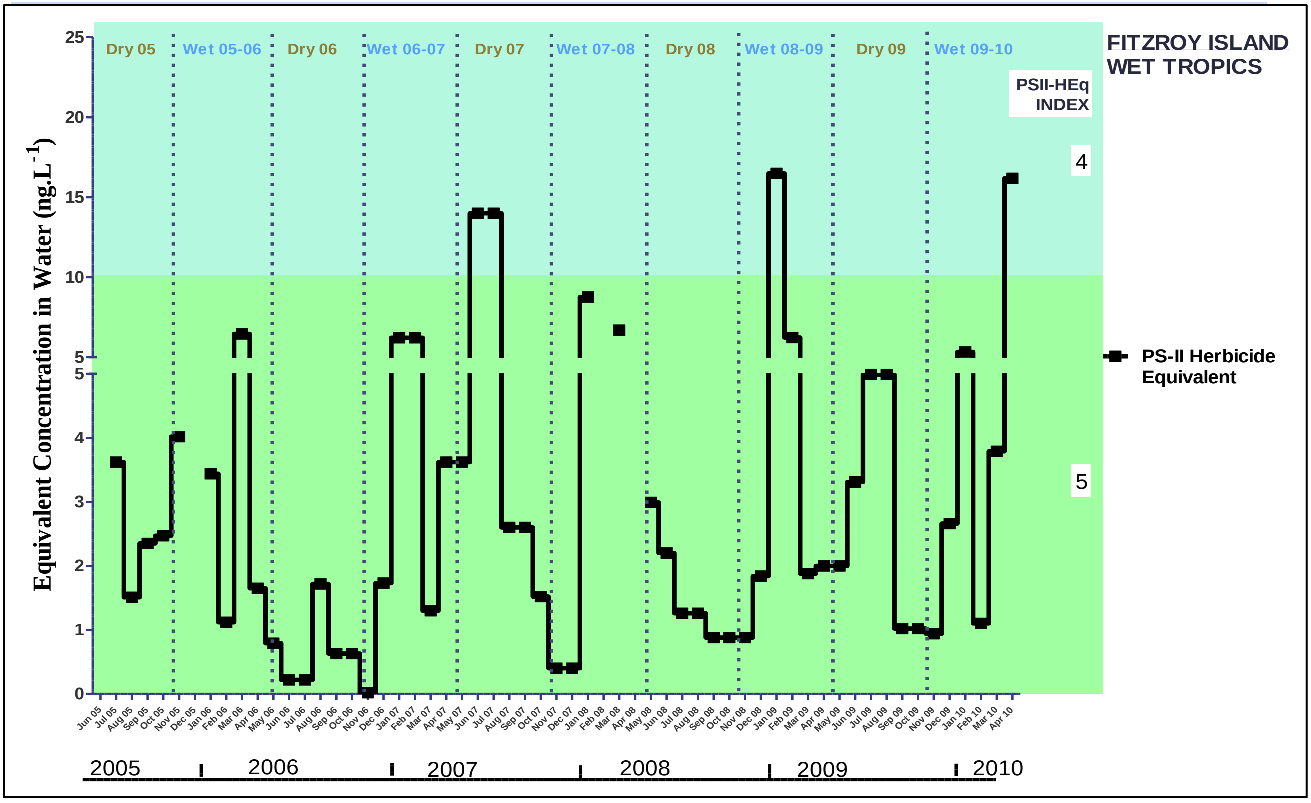

Figure 18 Time averaged concentrations at Fitzroy Island expressed as PSII-Herbicide Equivalent concentrations across wet and dry seasons between 2005 and 2010 with PSII Herbicide Index categories "4" and "5" (≤ 10 ng.L^{-1}) indicated

Relationships between temporal and seasonal PSII-HEq profiles and freshwater discharge in the Barron and Russell-Mulgrave Rivers

The Fitzroy Island site is approximately 25 km southwest (heading 107.95 degrees) of the Barron River Mouth and 32 km northeast (heading 3.22 degrees) of the Russell-Mulgrave River Mouth. Annual discharges in 2009/10 from both the Barron and Mulgrave Rivers (Table 14) did not exceed median annual flows while the Russell River median was exceeded and has been consistently exceeded between 2005/06 and 2009/10. The annual discharge from the Russell River is typically higher than the other rivers in most years. In 2005/06 and 2007/8 discharges from all rivers were above the median.

Table 14 Annual freshwater discharge (ML) for the Barron River, Mulgrave and Russel Rivers in proximity to the Fitzroy Island sampling site. Shaded cells highlight years for which river flow exceeded the median annual discharge as estimated from available long-term time series for each river.

River	2005/06	2006/07	2007/08	2008/09	2009/10	Long Term Median
Barron	745,779	471,359	1,582,470	781,081	539,064	692,447
Mulgrave	1,014,701	757,914	938,122	689,845	602,261	719,625
Russell	1,299,019	1,276,654	1,075,370	1,213,227	1,624,432	1,049,894
TOTAL	**3,059,499**	**2,505,927**	**3,595,962**	**2,684,153**	**2,765,757**	

* Incomplete gauging record; Sourced from Table A1-2 (Schaffelke et al. 2010)

The total discharge for each monitoring year has been plotted against the PSII-HEq max (ng.L^{-1}) in each year and the proportion of total discharge accounted for by both the Barron River and the Russell-Mulgrave Rivers combined (Figure 19). There is no clear relationship between total discharge from these three river systems combined and the PS-II HEq max in these years. In particular in the last two monitoring years (2008-09 and 2009-10) total discharges have been lower compared to 2007-08 but PSII-HEq Max has remained

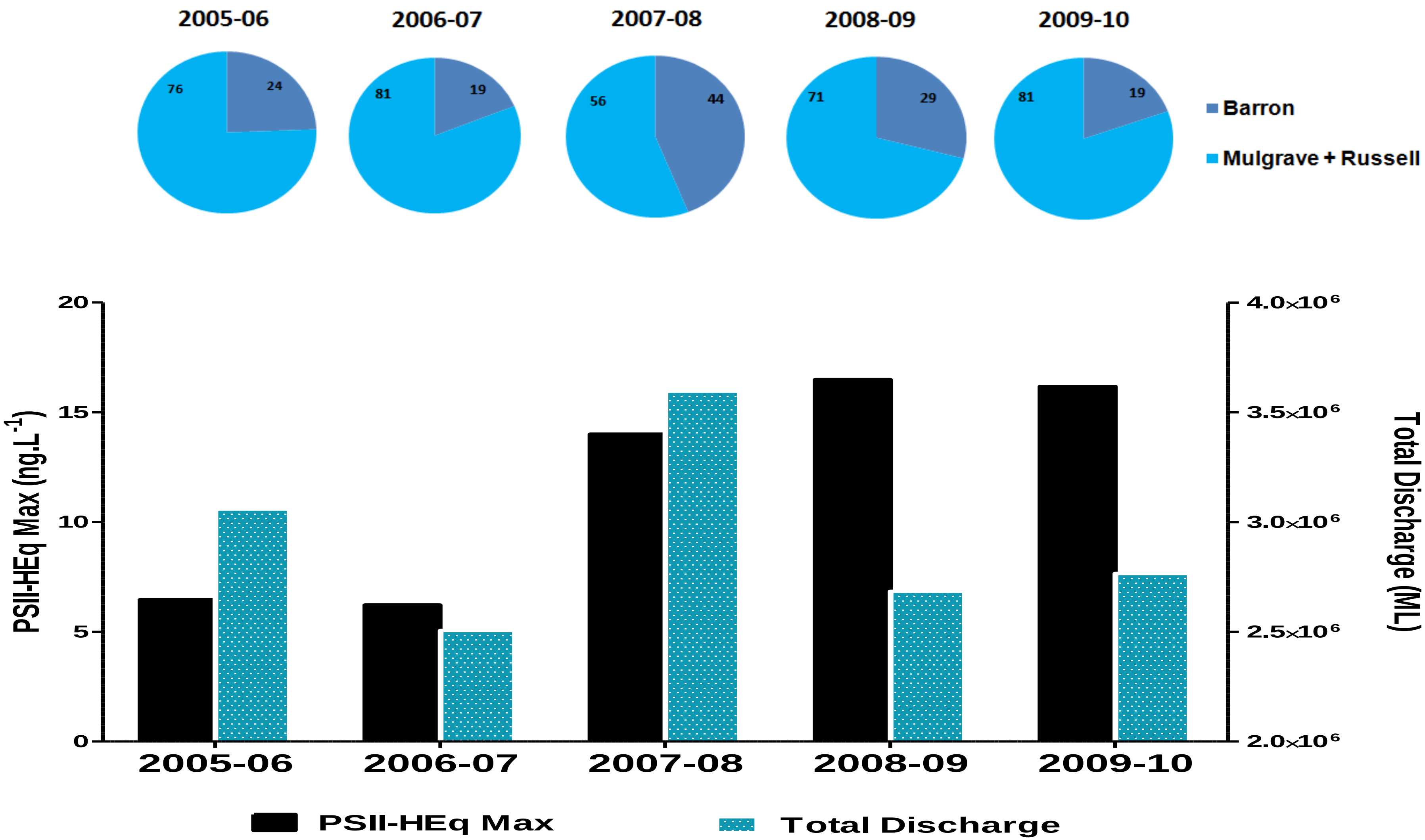

Figure 19 Fitzroy Island PSII herbicide equivalent maximum (left y-axis) in each reporting year together with total discharge from all three river systems combined in each year (right y-axis). The percentage of total discharge attributable to either the Barron River or Russell-Mulgrave Rivers combined in each monitoring year is also illustrated using pie charts.

relatively high. The maximum discharge observed in 2007-08 does have one of the higher PS-II HEq max but it is not the highest value observed while the Barron River was the dominant contributor to discharge in this year. It is interesting to note that the relative contributions of Russell-Mulgrave Rivers(81 %) and the Barron River (19 %) to total discharge is consistent in the 2006-07 and 2009-10 monitoring years but PSII-HEq was a factor of 3 times higher in 2009-10. It is apparent that some knowledge of PS-II herbicide loads, and plume extent in these systems is required to interpret these relationships completely at the Fitzroy Island site.

The complexity of these relationships is further illustrated within the monthly discharges for 2009-2010 (Table 15) when plotted as total discharge (ML) against monthly PSII-HEq (Figure 20). In general the lowest monthly discharges in September and October 2009 are associated with the lowest PSII-HEq estimates and the maximum discharge in April 2010 is associated with the PSII-HEq Max for this monitoring year. However within this monitoring year there are periods within which discharge increases yet PSII-HEq decreases. It does appear that discharges > 100,000 ML beginning in January 2010 for each river are associated with a peak in PSII-HEq in January 2010 but this is not maintained within subsequent months (February and March 2010) until a maximum is again observed in April 2010. The timing of peak discharges within each month and with respect to each other would also influence whether there are any lag times in the influence of these (dilution or enhanced delivery) on concentration in each month.

Table 15 Monthly discharges (ML) for the Barron, Mulgrave and Russell Rivers available for 2009 -2010 from DERM Stations 110001D, 111007A and 111101D

River	Jun 09	Jul 09	Aug 09	Sep 09	Oct 09	Nov 09	Dec 09	Jan 10	Feb 10	Mar 10	Apr 10
Barron	29,047	26,370	24,988	7,632	5,932	6,378	6,572	179,068	100,709	72,985	64,339
Mulgrave	29,431	17,661	14,221	9,326	7,228	27,459	12,048	98,967	70,762	129,959	126,754
Russell	43,192	18,527	15,118	7,982	6,653	49,407	12,107	162,217	123,056	205,116	279,054

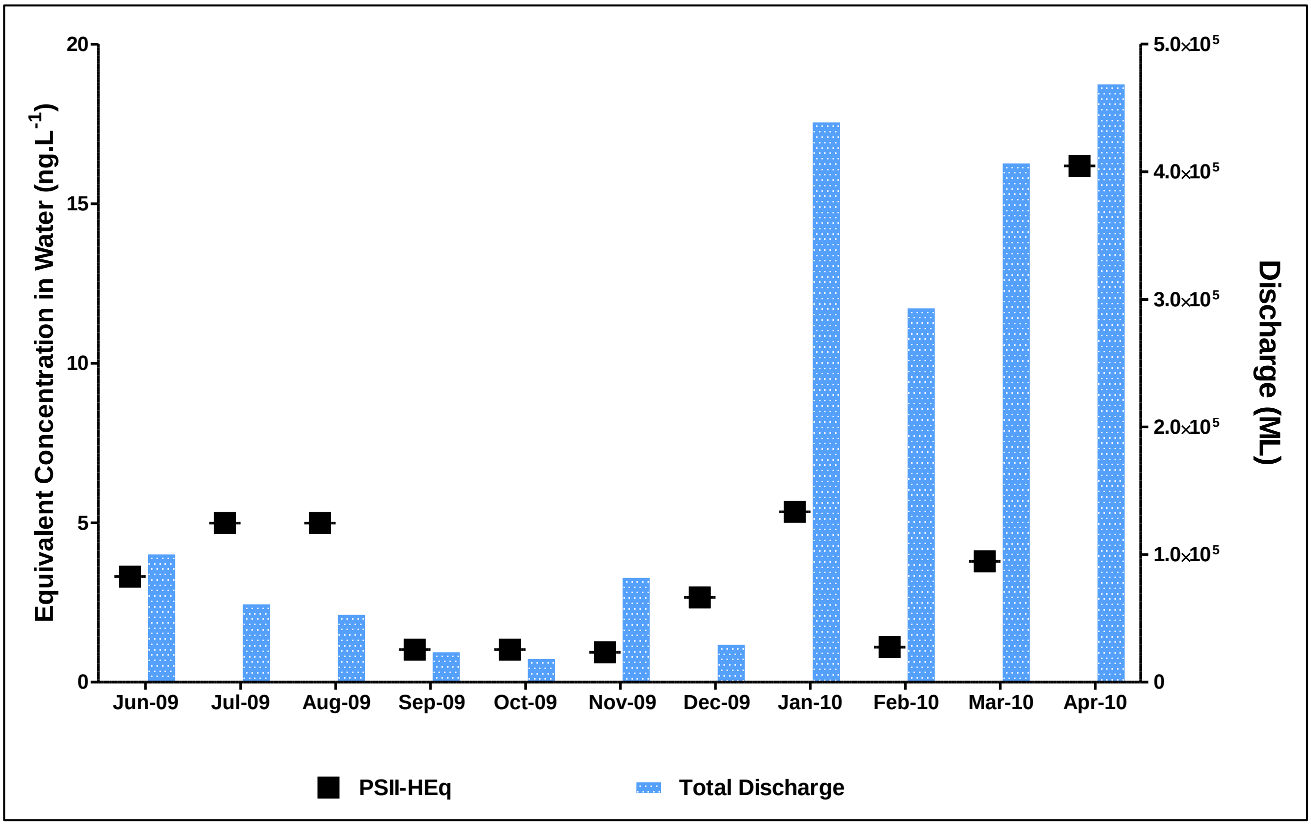

Figure 20 Monthly total discharges from the Mulgrave, Russell and Barron Rivers together with monthly PSII-HEq for the Fitzroy Island site in 2009-2010.

6.2.4 Normanby Island

PSII Herbicides: July 2005 – April 2010

The temporal profile for Normanby Island between 2005 and 2010 (Figure 21) indicates the dominance of diuron and the relative abundance of all PSII herbicides in the wet season with few detections in dry season monitoring periods. The maximum levels of diuron in this latest 2009-2010 wet season are somewhat lower than the previous three wet seasons. The PSII-HEq Index for this site (Figure 22) is more consistently Category "5" with a maximum of Category "4" during the wet season in 07-08.

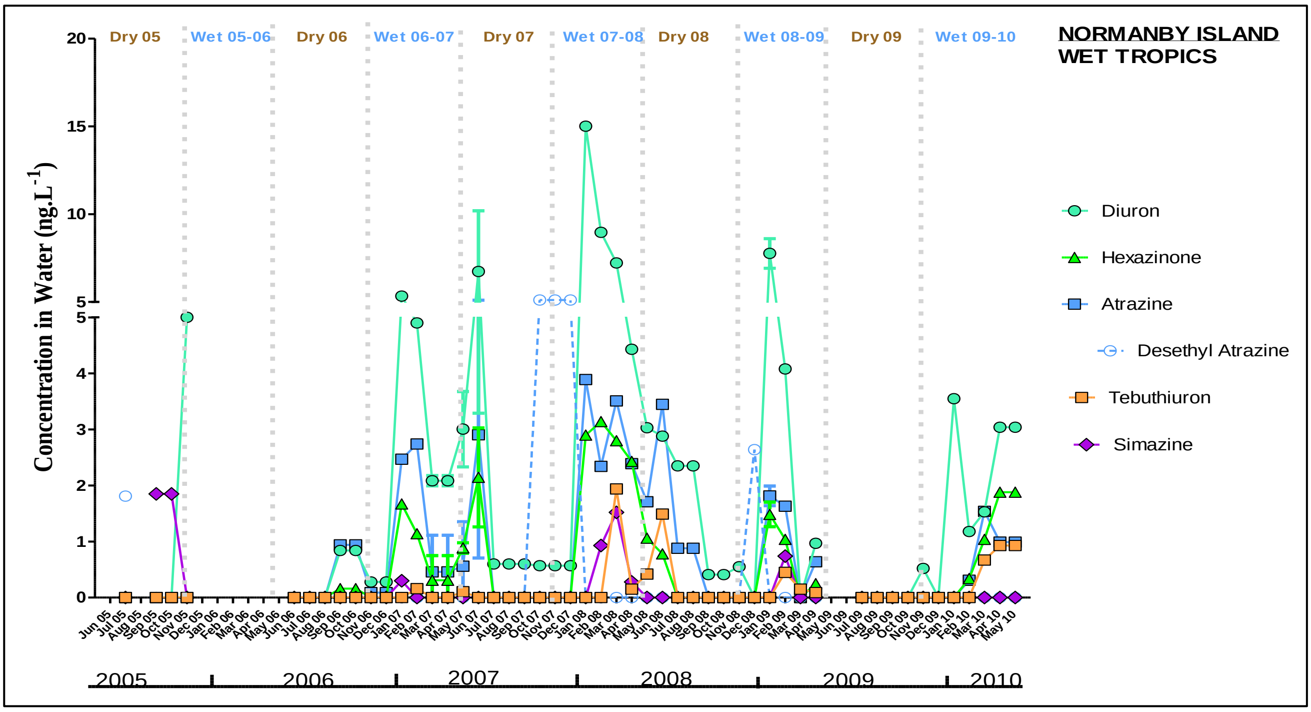

Figure 21 Time averaged PSII herbicide concentrations for Normanby Island in the Wet Tropics Region across wet and dry seasons between 2005 and 2010

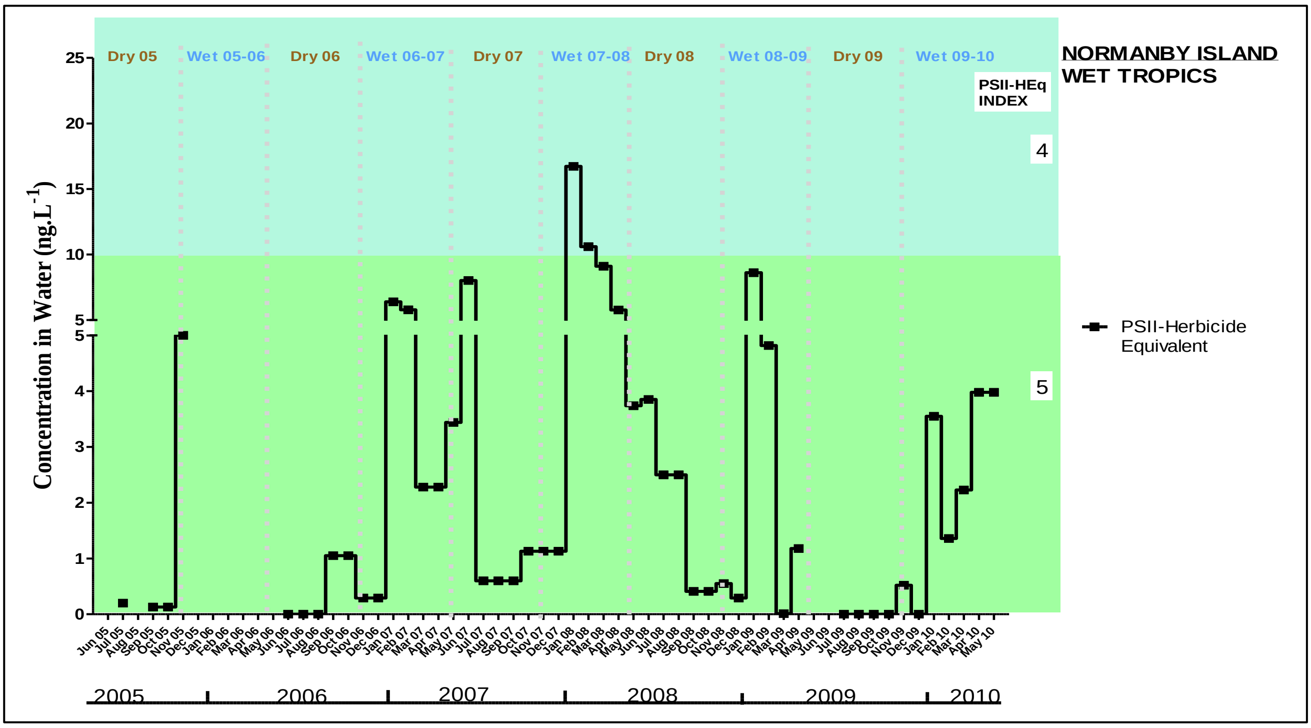

Figure 22 Time averaged concentrations at Normanby Island expressed as PSII-Herbicide Equivalent concentrations across wet and dry seasons between 2005 and 2010 with PSII Herbicide Index categories "4" and "5" (≤ 10 $ng.L^{-1}$) indicated

Relationships between temporal and seasonal PSII-HEq profiles and freshwater discharge in the Russell-Mulgrave Rivers

The Normanby Island site is approximately 11 km East (heading 78.80 degrees) of the mouth of the Mulgrave and Russell Rivers. The monitoring year with the highest PSII-HEq (2007/08) of 17 ng.L^{-1} is not associated with the maximum discharge observed in 2005/06 (refer Table 14 above), however the wet season in 2005/06 was not sampled. The Mulgrave River contributed a higher proportion (47 %) to total discharge in the year (2007/8) when the highest PSII-HEq has been observed.

The monthly discharges for these rivers (refer Table 15 above) in 2009-2010 were combined to estimate total monthly discharge. The total monthly discharge is plotted against monthly PSII-HEq for this monitoring year in Figure 23. It is interesting to compare this figure for Normanby Island with the same plot for Fitzroy Island (Figure 20) to the north which may also be influenced by discharge from these rivers. The PSII-HEq for Fitzroy Island are in general higher with contributing herbicides detected more consistently throughout the year. However, both sites indicate an increase in PSII-HEq in January 2010, a decrease into February 2010 and subsequent increases in March 2010, with the maximum PSII-HEq for both sites occurring in April 2010.

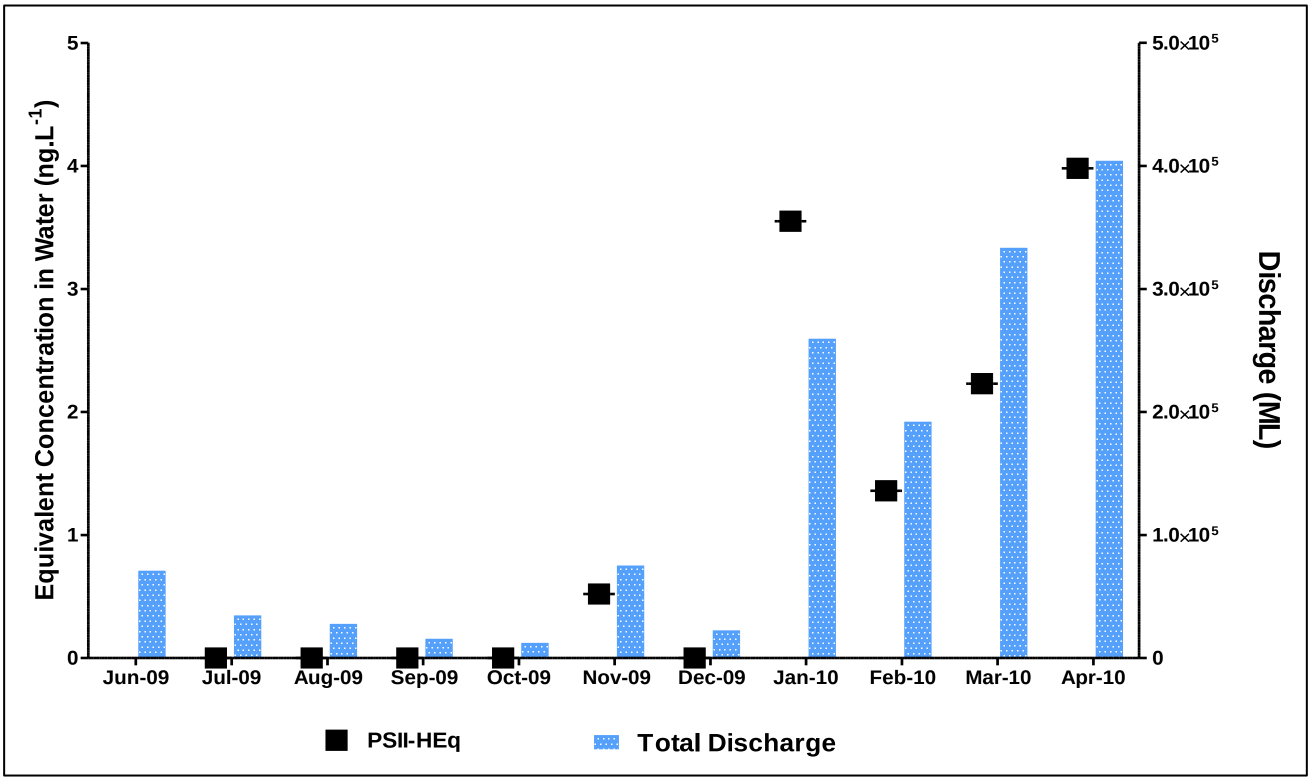

Figure 23 Monthly total discharges from the Russell-Mulgrave Rivers together with monthly PSII-HEq for the Normanby Island site in 2009-2010

6.2.5 Dunk Island & Tully River

Dunk Island is located approximately 13 km northeast (heading 39.28 degrees) of the Tully River mouth. Both Dunk Island and The Tully River have been routine pesticide monitoring sites since 2007, with the Tully River site discontinued in January 2010. Due to the proximity of these sites and the potential contribution of PSII herbicide and pesticide loads in the Tully River to the Dunk Island site the results from these locations will be discussed in combination.

Pesticides and Industrial Chemicals in the Tully River: March 2007 – January 2010

The temporal profiles for the Tully River site (Figure 24) reveal that diazinon, prothiofos and chlorpyrifos (organophosphate insecticides), propiconazole and tebuconazole (conazole fungicides), pendimethalin (dinitroaniline herbicide) and the personal insect repellent DEET (since Dry 08) have been the most frequently detected chemicals at this location through time. Interestingly there is no clear trend associated with dry or wet sampling periods for this river site, although specific pesticides such as tebuconazole and chlorpyrifos do have higher concentrations in wet sampling periods.

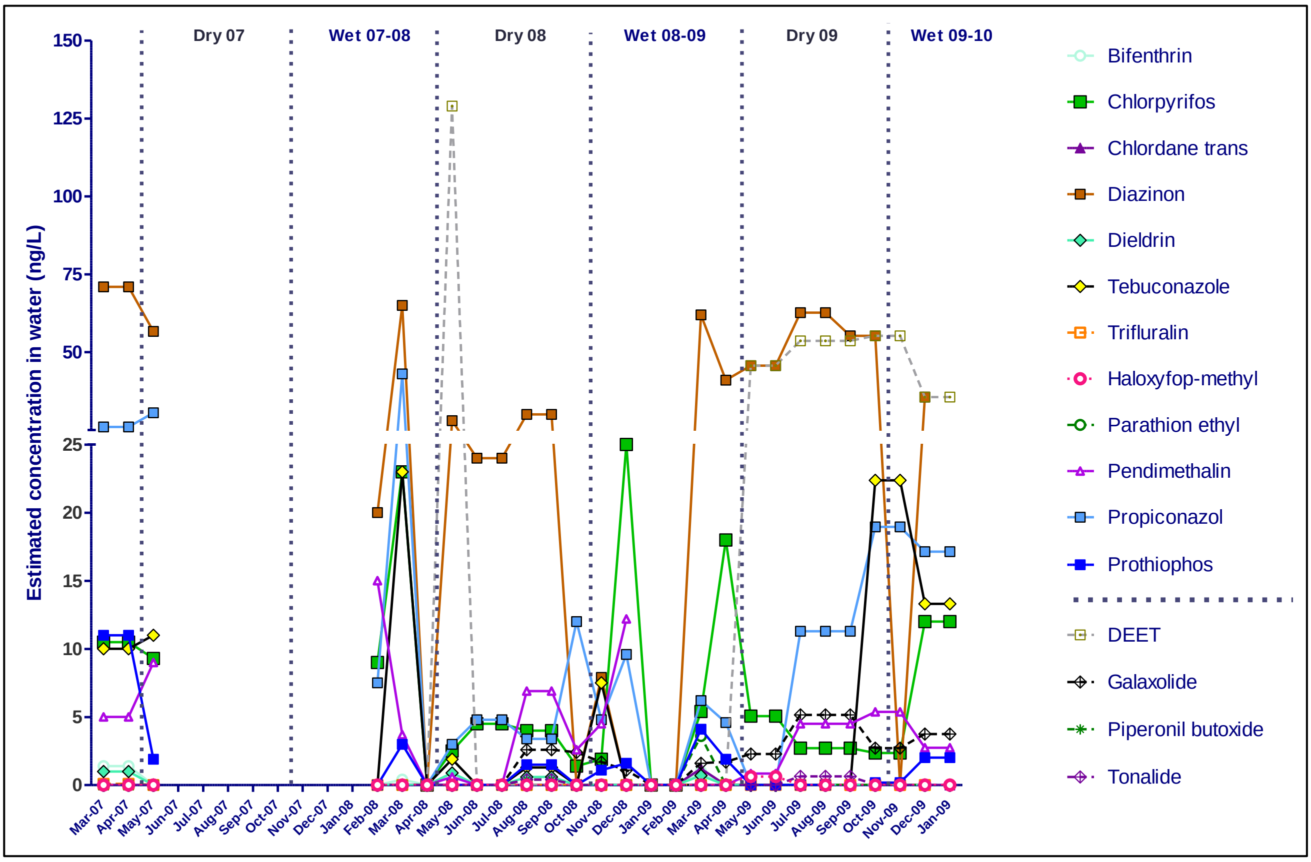

Figure 24 Time averaged pesticide concentrations determined using PDMS sampling for the Tully River in the Wet Tropics Region across wet and dry seasons between 2007 and 2010

PSII Herbicides: March/April 2007– April 2010

Since monitoring began at the Dunk Island site only two wet seasons (Wet 08-09 and 09-10) have been captured with more than a single monitoring period and both of these have incomplete monitoring within these periods. One dry season (Dry 09) has been monitored comprehensively (no gaps in sampling record) and this occurred in the latest monitoring year (Figure 25). Diuron has been the only chemical detected in the dry season at this location which is consistent with previous dry season monitoring using the same sampling techniques in October 2004 which detected only diuron (Shaw et al. 2010). Whilst acknowledging these gaps in the record, the results available indicate the dominance of diuron in all periods monitored. Interestingly, in the wet seasons the highest concentrations of diuron, hexazinone and tebuthiuron occur in the month prior to the highest concentrations of atrazine. Simazine has only been detected once at this location in the single April 2007 monitoring period in Wet 06-07.

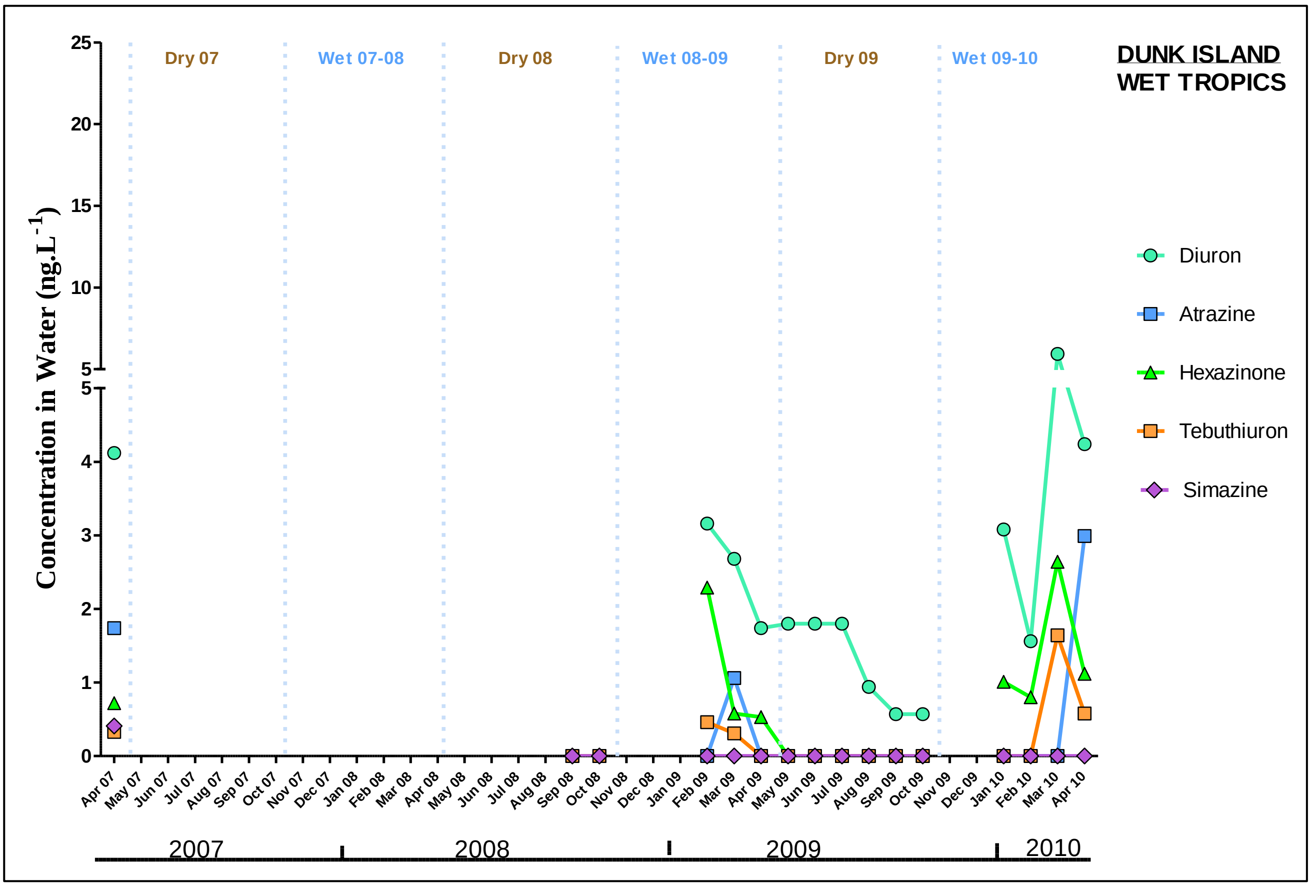

Figure 25 Time averaged PSII herbicide concentrations for Dunk Island in the Wet Tropics Region across wet and dry seasons between 2007 and 2010

Flood plume monitoring during wet season events in April 2006 (4 samples) and February 2007 (nine samples) in a transect from the Tully River mouth to Dunk Island found that seven of these samples had diuron concentrations > 100 ng.L^{-1} but < the GBRMPA Guideline (900 ng.L^{-1}) at least 15 km from the river mouth, while atrazine could also be detected as far as Dunk Island (Bainbridge et al. 2009a). There are no concurrent time integrated estimates using passive sampling for this period. Tully River flood plumes can extend out into the Coral Sea and impact significant proportions of seagrass meadows and coral reefs in the Tully marine area with relatively high frequency with the areal extent determined by both discharge volume and wind direction (Devlin and Schaffelke 2009). Monitoring conducted in January and February 2009 assessing Tully River flood plumes as a component of MMP Project 3.7.2 b have detected (> 10 ng.L^{-1}) diuron, atrazine and hexazinone and simazine residues in January and diuron and hexazinone in February (Devlin et al. 2010). Concurrent time integrated estimates in February 2009 are < 10 ng.L^{-1} for diuron and hexazinone while no monitoring was conducted in January 2009. Similarly elevated concentrations have been observed in flood plume waters extending to Dunk Island between 2005 and 2008 (Lewis et al. 2009). All of this data indicates that acute exposures during flood plume events may be at least an order of magnitude higher than time integrated estimates, although with limited concurrent sampling it is difficult to quantify the extent of this variation completely. Significantly higher concentrations have been estimated within the Tully River itself in the wet season in February 2008 (Figure 26). Together this data illustrates the importance of a complete monitoring record to adequately assess and compare risks associated with PSII exposure within regions.

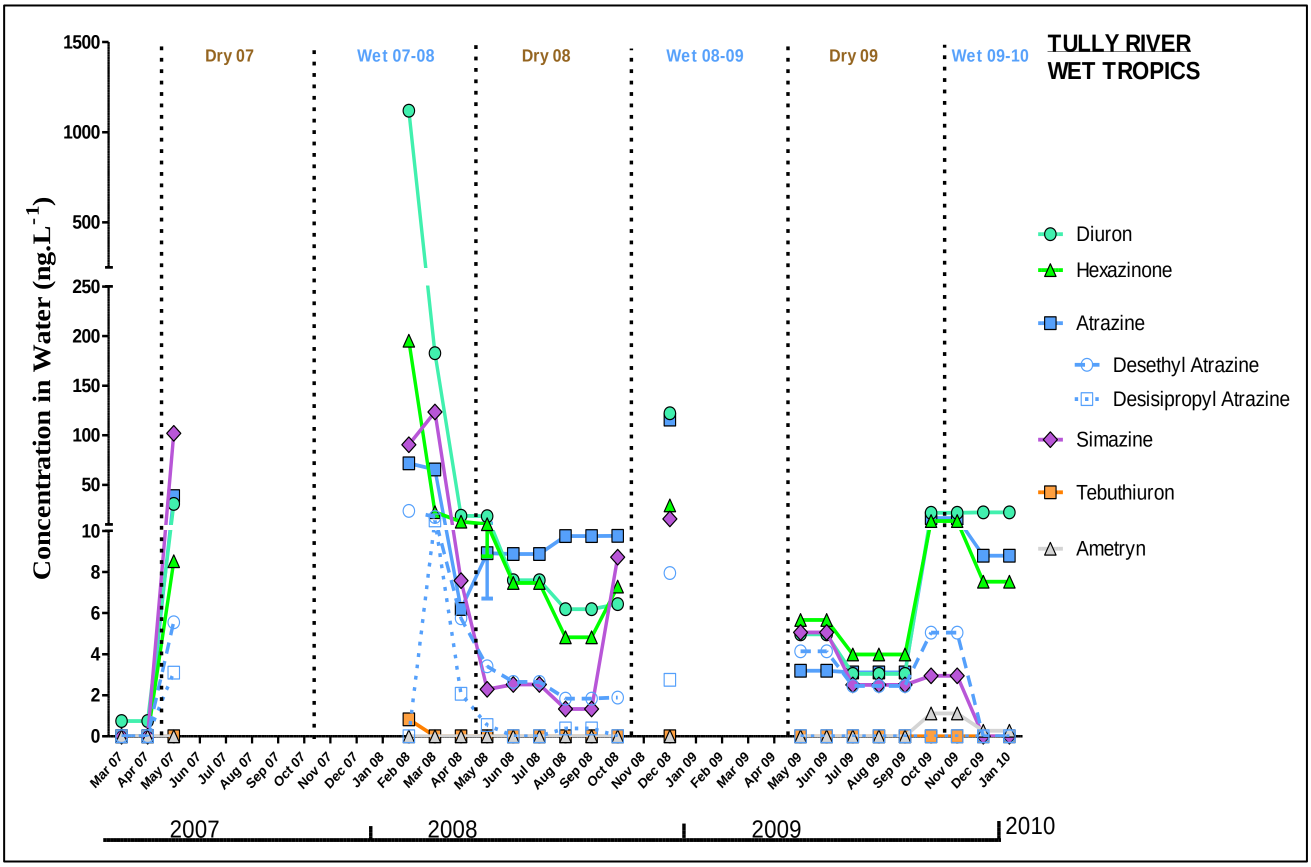

Figure 26 Time averaged PSII herbicide concentrations for the Tully River site in the Wet Tropics Region across wet and dry seasons between 2007 and 2010.

The temporal and seasonal PSII-HEq profiles for Dunk Island and the Tully River between 2007 and 2010 are illustrated in Figure 27. These combined profiles indicate that co-occurring sampling has occurred infrequently at these location with the exception of the Dry 09 monitoring period. Within this period there is reasonable agreement between the trends in the PSII-HEq. These profiles indicate that while the Dunk Island site has only indicated an index of category 5 between 2007-2010, the Tully River has a PSII-HEq Max of category 1 (> 900 $ng.L^{-1}$) within the Wet 07-08 within this period. No concurrent monitoring results are available for the Dunk Island site within this period.

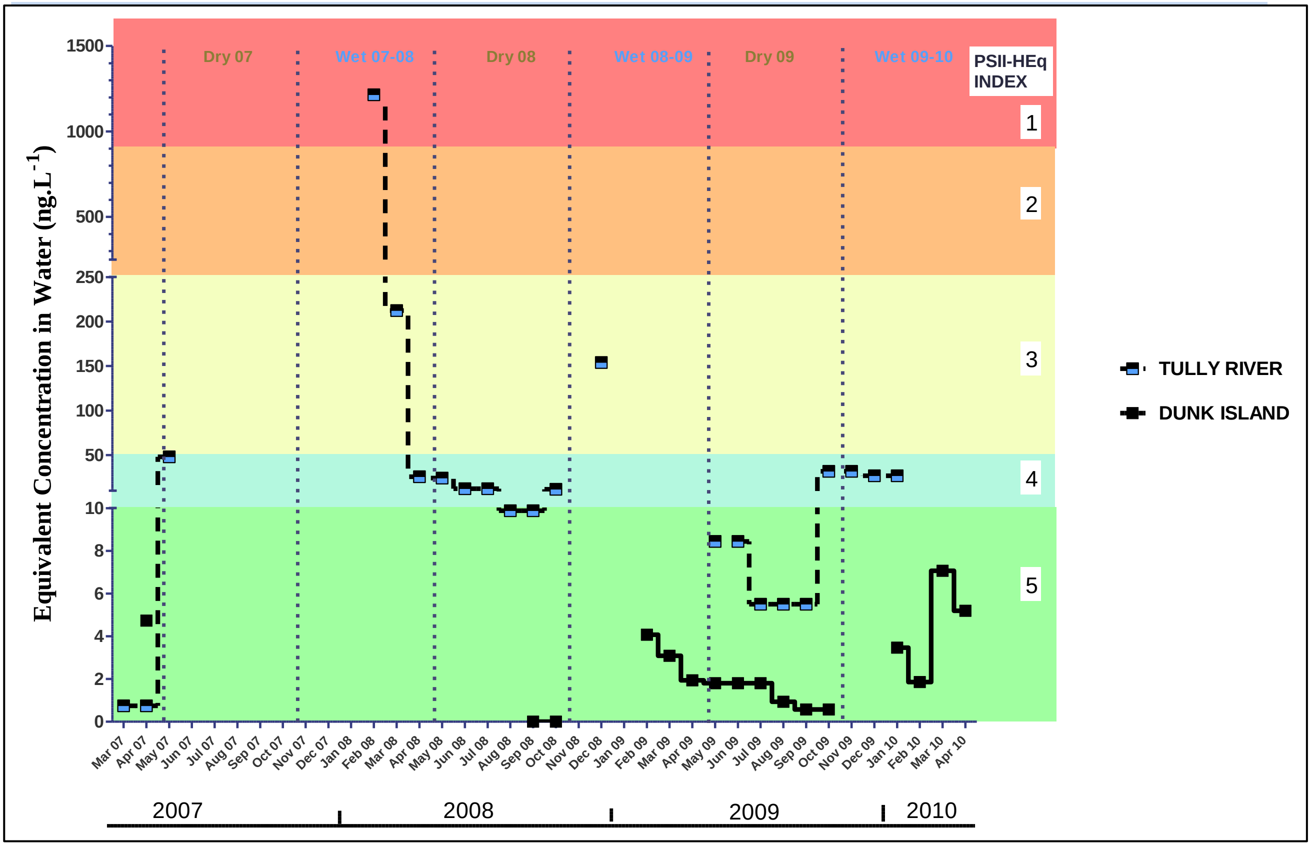

Figure 27 Time averaged concentrations at Dunk Island and the Tully River expressed as PSII-Herbicide Equivalent concentrations across wet and dry seasons between 2007 and 2010 with PSII Herbicide Index categories "1" (> 900 ng.L^{-1}) through to "5" (< 10 ng.L^{-1}) indicated.

Relationships between temporal and seasonal PSII-HEq profiles with respect to freshwater discharge in the Tully River

The annual freshwater discharge in the Tully River (Table 16) in 2009-2010 has not exceeded median annual discharge and the PSII-HEq for the Tully River are either Category "5" (dry season) or Category "4" (Wet season) while Dunk Island was consistently Category 5 in both seasons. Above median discharges were recorded in 2007/08 which coincides with the peak in Category "1" PSII-HEq in the river in that year.

Table 16 Annual freshwater discharge (ML) for the Tully River in proximity to the Dunk Island sampling site. Shaded cells highlight years for which river flow exceeded the median annual discharge as estimated from available long-term time series for this river.

River	2007/08	2008/09	2009/10	Long Term Median
Tully	3,232,667	3,769,840	2,507,335	3,128,458

* Incomplete gauging record; Sourced from Table A1-2 (Schaffelke et al. 2010)

The monthly discharge in the Tully River in the 2009-2010 is indicated with respect to monthly PSII-HEq estimates for both the Tully River and Dunk Island in Figure 28. The profiles indicate that PSII-HEq concentrations in the Tully River are higher within the October-November and December-January sampling period. Unfortunately there are no concurrent concentration estimates available for November and December at Dunk Island with monthly estimates only available from January to April 2010. In general the peak discharge periods from January to April 2010 are associated with the higher PSII-HEq estimates at Dunk Island. The PSII-HEq concentrations in the Tully River are higher in June 2009 than in July to September 2009 while discharge is declining. These concentrations increase within the October-November sampling period with a concurrent discharge increase from October to November. The PSII-HEq decreases slightly in the December-January period while discharge within these months continues to increase.

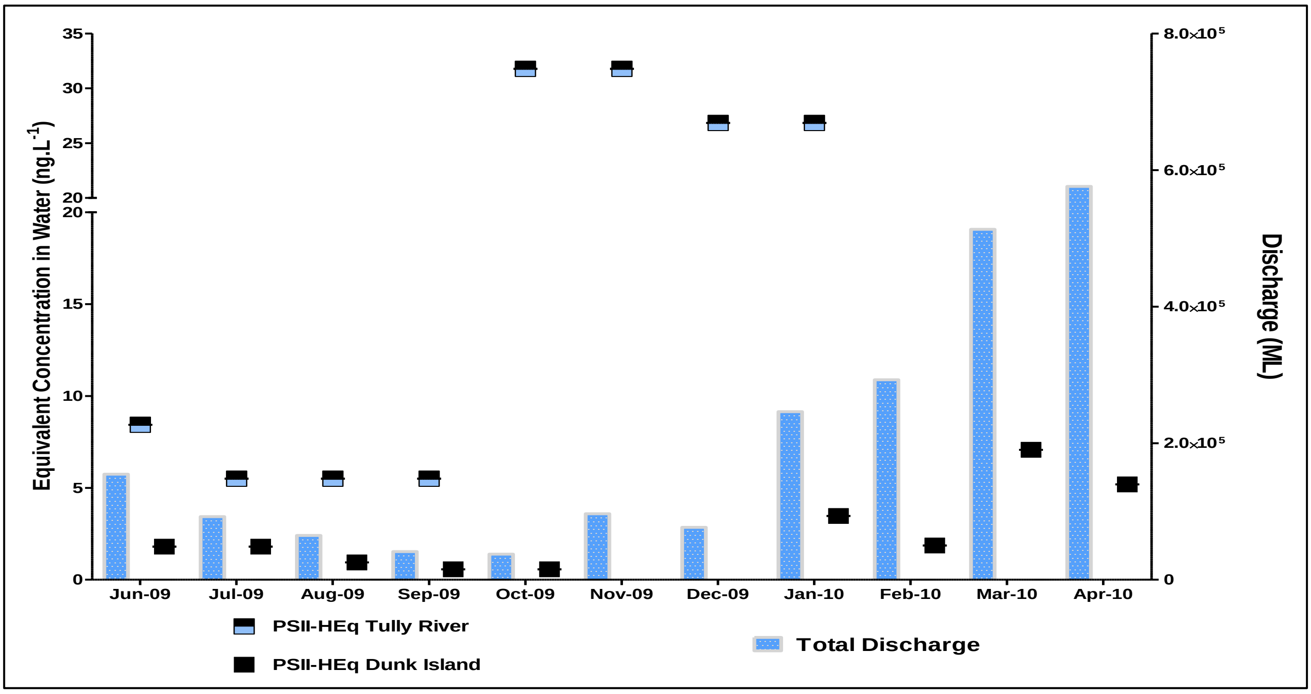

Figure 28 Total monthly discharge in the Tully River in 2009-2010 together with monthly PSII-HEq for the Tully River and Dunk Island.

6.3 Burdekin Region

6.3.1 Orpheus Island

PSII Herbicides: July 2005– May 2010

The Orpheus Island site has been monitored since July 2005 (Figure 29) although the site has some gaps in the sampling record within various monitoring years. There is a relatively large gap in the sampling record in 2009-2010 in the wet season between November 2009 and February 2010, which makes interpretation of the site in 2009-2010 problematic. Through time however, there does appear to be an increase in the number of different PSII herbicides detected, from diuron only in wet 05-06 and wet 06-07 to diuron, atrazine, tebuthiuron and hexazinone in later years since wet 07-08. These profiles indicate that the time averaged concentrations of PSII herbicides are typically < 5 ng.L^{-1} at this location which has indicated a PSII-HEq Index of Category "5" (Figure 30). This emphasizes how unusual the peak in diuron is that was observed in the current dry season (2009) wherein no other PSII herbicides apart from 0.24 ng.L^{-1} for atrazine have co-occurred. This may indicate that a more localized source of diuron other than agricultural land use and subsequent runoff from adjacent catchment areas may be implicated for this period. Diuron is also registered for use in Australia in antifoulant paints (Jones et al. 2003) and diuron residues have been detected in marine environments associated with the use of these chemicals for these purposes (Boxall et al. 2000). To date none of the monitoring years has a complete sample record in both wet and dry seasons which makes any inference with respect to seasonal differences difficult.

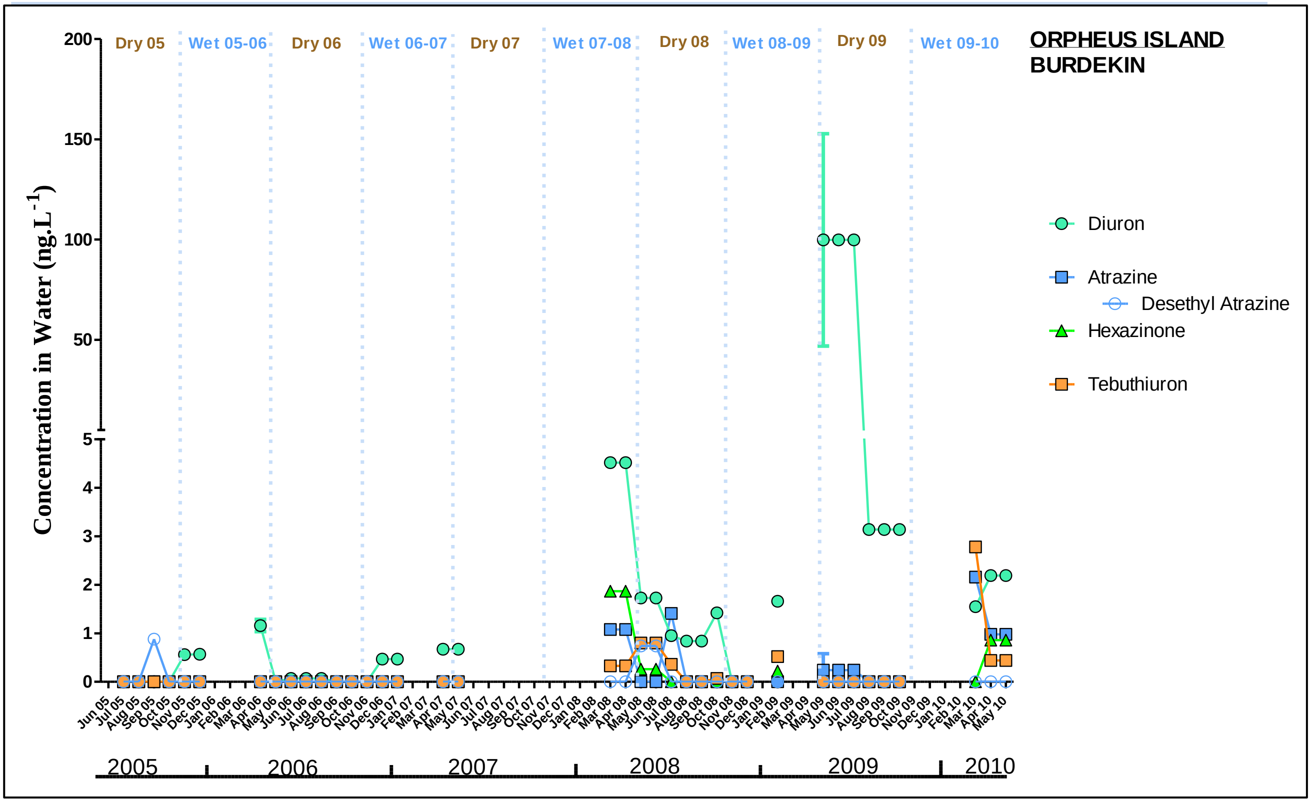

Figure 29 Time averaged PSII herbicide concentrations for Orpheus Island in the Burdekin Region across wet and dry seasons between 2005 and 2010.

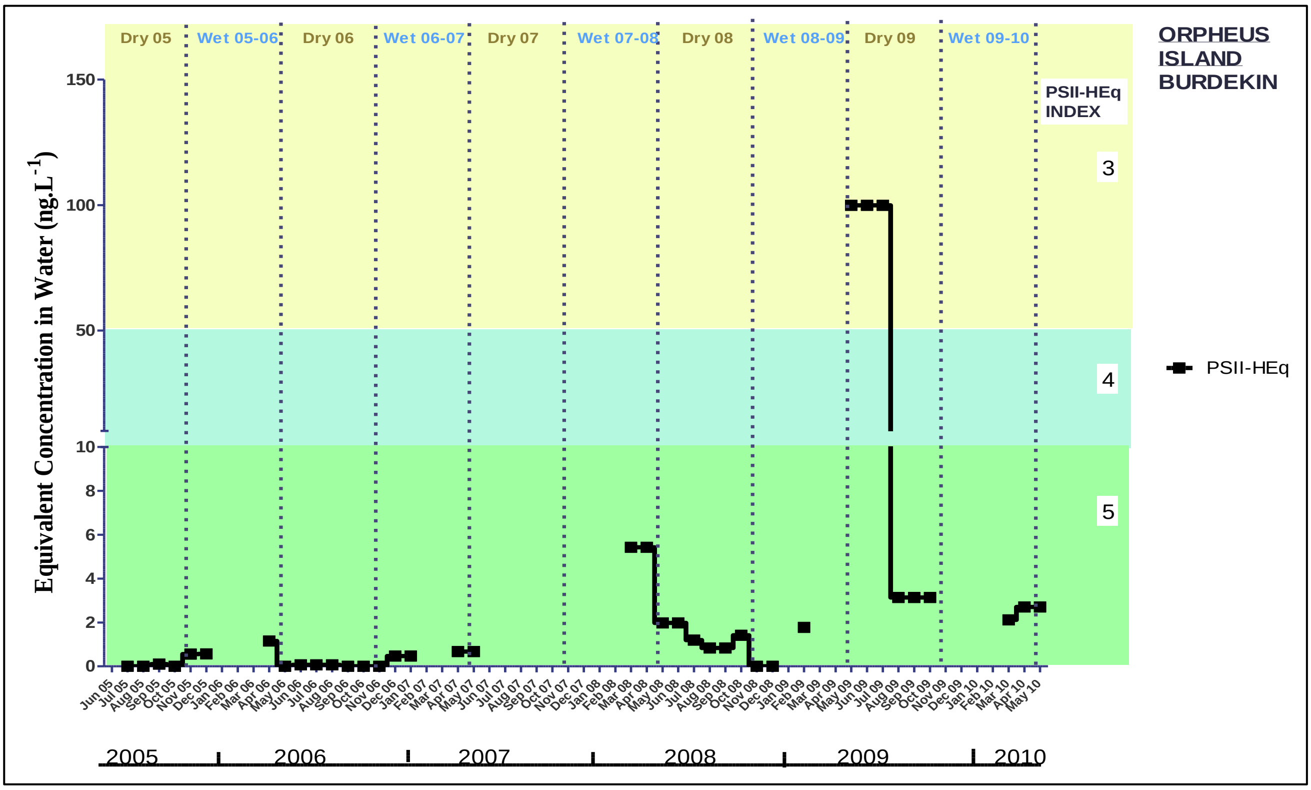

Figure 30 Time averaged concentrations at Orpheus Island in the Burdekin Region expressed as PSII-Herbicide Equivalent concentrations across wet and dry seasons between 2005 and 2010 with PSII Herbicide Index categories "3" (50 < HEq < 250), "4" (10 < HEq ≤ 50) and "5" (< 10 $ng.L^{-1}$) indicated.

Relationships between temporal and seasonal profiles and discharge in the Herbert River

The gauging record for the Herbert River in 2009-2010 was incomplete. Due to gaps in the sampling record for this location no comparison with discharge will be made.

6.3.2 Magnetic Island

PSII Herbicides: August 2005– April 2010

The profile for the Magnetic Island site (Figure 31) indicates differences in the relative abundance of other PS-II herbicides such as atrazine and tebuthiuron with respect to diuron which is typically the most dominant PSII-herbicide at sites in the Wet Tropics Region for example. This is consistent with atrazine being the compound discharged at highest loads from sub-catchments in the Burdekin Region (Davis et al. 2008). The peak concentrations of atrazine are higher than the concentrations of diuron during "wet06-07", "wet 07-08", "dry 08", "wet 08-09" and relatively analogous in the latest "wet 09-10" monitoring periods. Decreases in the concentrations of atrazine, diuron and tebuthiuron were apparent between "wet 07-08" and "wet 08-09" but have increased between "wet 08-09" and "wet 09-10". The concentration maximum of 4.7 ng.L^{-1} for tebuthiuron in particular in the current "wet 09-10" monitoring year is notable with respect to all other periods. Another notable feature of this profile is the spike in atrazine and diuron concentrations in the dry 08 monitoring period of the previous monitoring year. Apart from this spike in concentrations in a single dry season, dry season concentrations are typically lower than wet season concentrations.

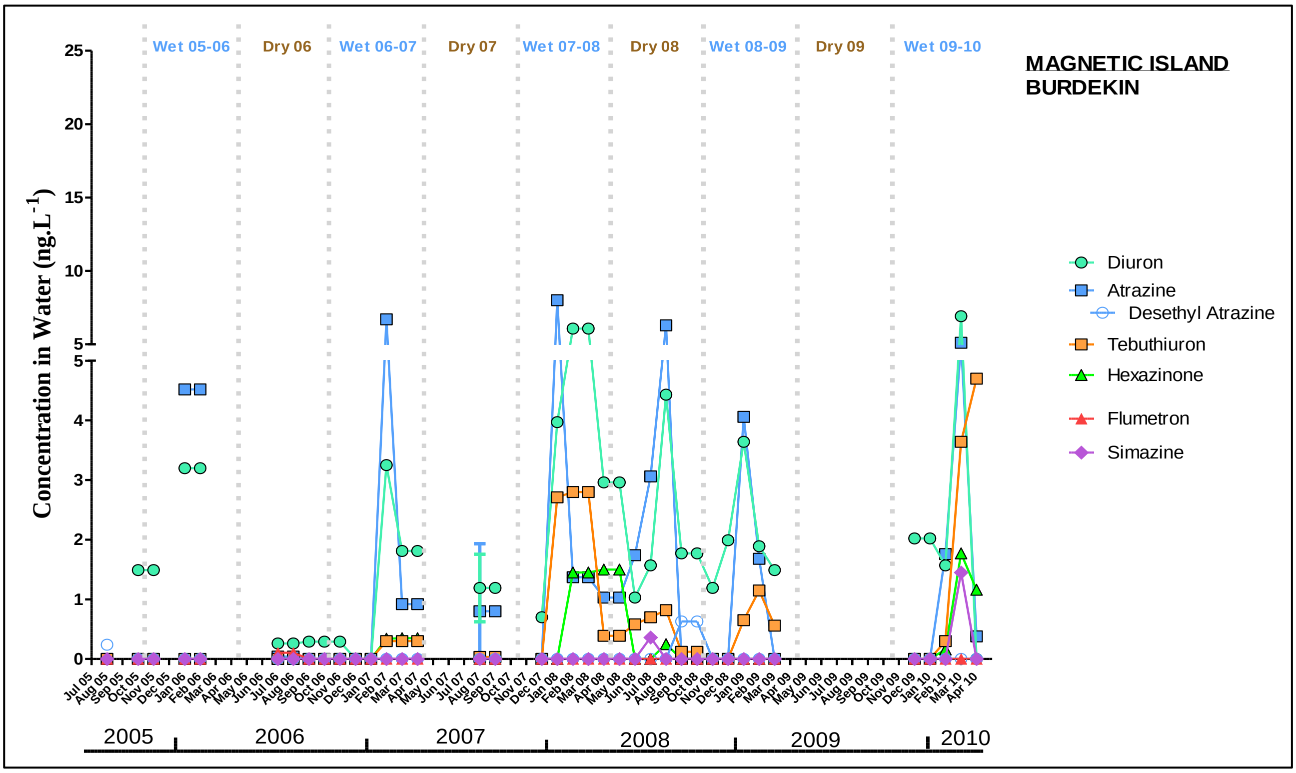

Figure 31 Time averaged PSII herbicide concentrations for Magnetic Island in the Burdekin Region across wet and dry seasons between 2005 and 2010.

Burdekin River flood plumes can extend north as far as Hinchinbrook Island in the Wet Tropics with medium to high exposures indicated offshore of the Burdekin and moving past Magnetic Island (Devlin et al. 2010). No PSII herbicides were detected in flood plume monitoring in January and February 2009. This is consistent with time integrated estimates < 10 ng.L^{-1} in these months. Risk contouring maps for PS-II herbicides profiles based on event monitoring do not indicate that Magnetic Island is significantly impacted in these events although plumes from the Ross River indicate a risk contour of between 0.01 – 0.4 µg.L^{-1} adjacent to

Magnetic Island for atrazine (Lewis et al. 2009). The minimum and maximum ranges of this contour were defined by the detection limit of atrazine in 1 L grab samples and the (draft) Guideline value for atrazine on the GBR (GBRMPA 2008) respectively.

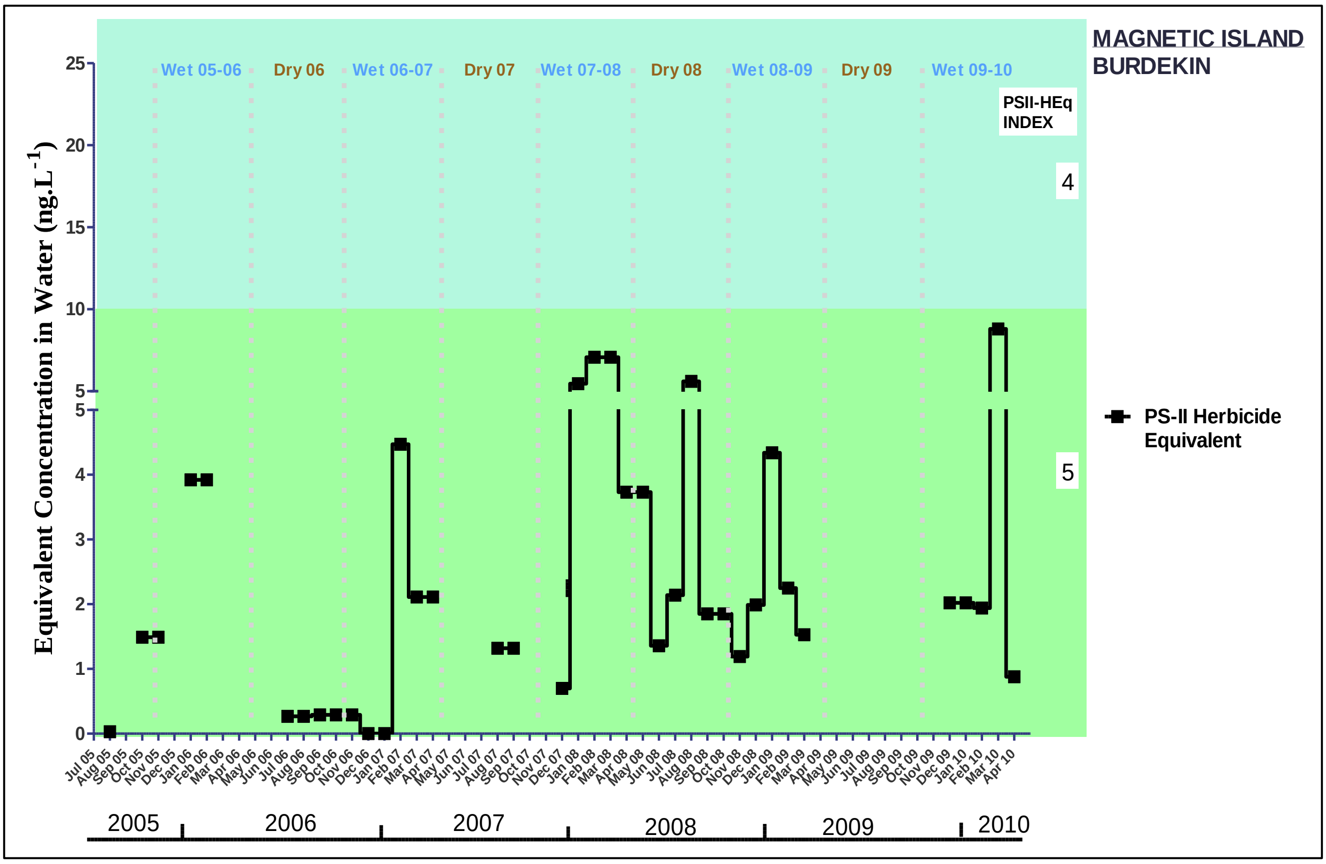

Figure 32 Time averaged concentrations at Magnetic Island in the Burdekin Region expressed as PSII-Herbicide Equivalent concentrations across wet and dry seasons between 2005 and 2010 with PSII Herbicide Index categories "4" (10 < HEq ≤ 50) and "5" (≤ 10 ng.L^{-1}) indicated.

Although PSII herbicides such as atrazine and tebuthiuron can be present at higher concentrations at this location, the trend in the PSII-HEq (Figure 32) is comparable to the trend in the concentration of diuron, since both atrazine and tebuthiuron are less potent PSII herbicides. The latest wet season period has the highest PSII-HEq (8.8 ng.L^{-1}) of all periods monitored since 2005. All PSII-HEq since monitoring commenced have been within PSII-HEq Index Category "5" (≤ 10 ng.L^{-1}).

Relationships between temporal and seasonal PSII-HEq profiles and discharge in the Burdekin River

Annual freshwater discharges 2005/06 to 2009/10 and monthly discharge 2009-2010 for the Burdekin River are provided in Tables 17 and 18 respectively. Annual freshwater discharges from the Burdekin have exceeded long term median annual discharge since 2006/07. Gauging data in the Ross River is poor (Stephen Lewis pers. comm.) and has not been considered in this assessment.

Table 17 Annual freshwater discharge (ML) for the Burdekin River which may impact the Magnetic Island sampling site. Shaded cells highlight years for which river flow exceeded the median annual discharge as estimated from available long-term time series for each river.

River	2005/06	2006/07	2007/08	2008/09	2009/10	Long Term Median
Burdekin	2,191,850	9,170,162	27,970,750	30,090,023	7,845,420	5,957,450

* Incomplete gauging record; Sourced from Table A1-2 (Shchaffelke et al. 2010)

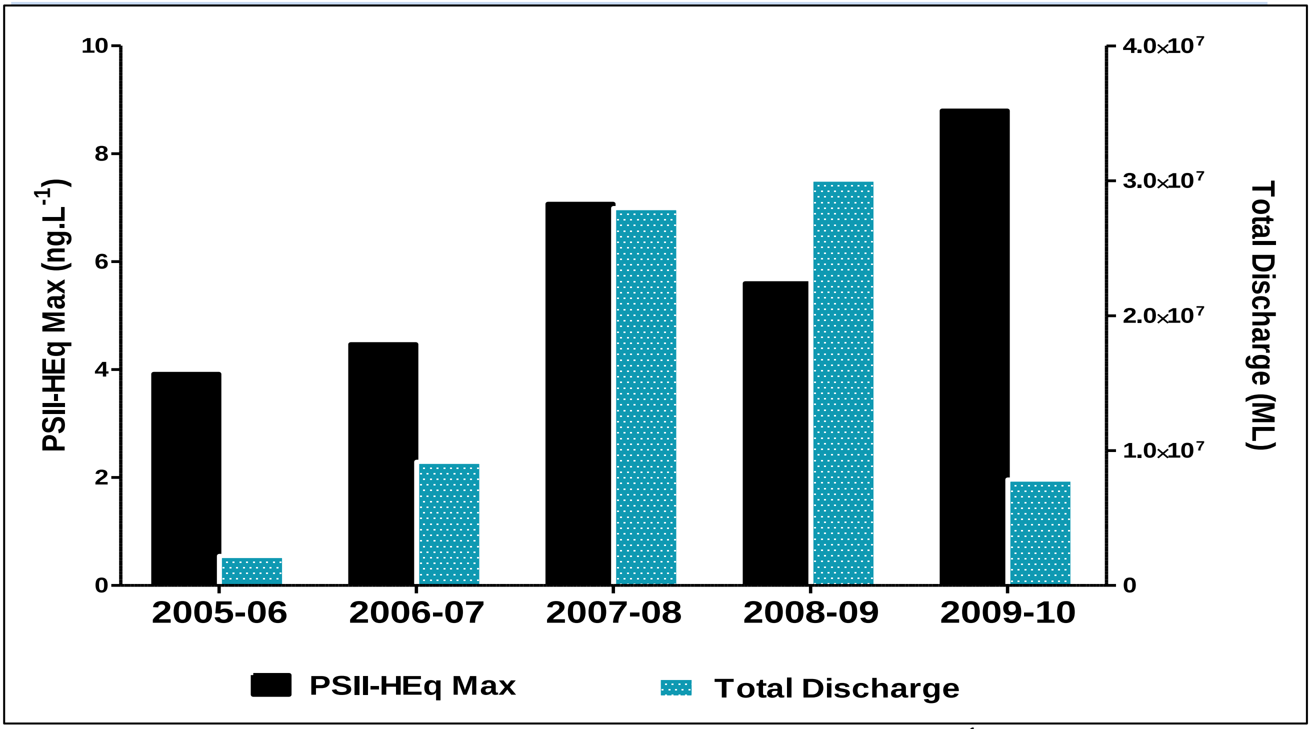

Figure 33 Total Discharge (ML) from the Burdekin River with respect to PSII-HEq Max (ng.L^{-1}) at the Magnetic Island site in monitoring years between 2005 and 2010.

There is no relationship apparent between years with maximum total discharge in the Burdekin River and the observed PSII-HEq Max recorded in each monitoring year at Magnetic Island (Figure 33). In particular the year with the highest PSII-HEq Max 2009-10 has relatively lower (although still above median) total discharge. The year with below median total discharge (2005-06) does however have the lowest observed PSII-HEq Max. It should be noted that in 2008-2009 the PSII-HEq Max was observed within the dry season.

The PSII-HEq Max within 2009-2010 was observed in March 2010, while elevated discharge levels commenced in January 2010 (Table 18). With no monitoring results for the dry season at Magnetic Island it is problematic to assess these profiles.

Table 18 Monthly discharges (ML) for the Burdekin River available for the 2009 -2010 monitoring year from DERM Station 120006B

River	Jun 09	Jul 09	Aug 09	Sep 09	Oct 09	Nov 09	Dec 09	Jan 10	Feb 10	Mar 10	Apr 10
Burdekin	40,576	30,272	29,319	31,820	48,261	49,732	61,593	222,019	3,380,229	3,358,945	587,620

6.3.3 Cape Cleveland

PSII Herbicides: December 2007 - April 2010

The most notable feature of the profiles (Figure 34) at Cape Cleveland are the consistent spikes in concentration in the wet seasons in each monitoring year and the relative abundance of atrazine at this site. This is consistent with monitoring in the Haughton River and Barratta Creek in the Burdekin Region which suggest that atrazine is discharged at the highest loads (Davis et al. 2008). The maximum concentration of atrazine since monitoring began was 20 $ng.L^{-1}$ in the "07-08" wet season. The subsequent "dry 08" monitoring season also had relatively elevated concentrations with respect to dry 09. Relatively low levels of diuron (< 1 $ng.L^{-1}$) were detected within this period and this is reflected within the PSII-HEq profile (Figure 35) for this dry 08 season being relatively low in spite of the spike in atrazine levels and the detection of other herbicides such as hexazinone and tebuthiuron within this period. PSII-HEq Max in the "wet 07-08" period were Category "4" while subsequent wet season spikes have been Category "5" albeit at the higher end of this range within the latest "wet 09-10" monitoring period.

Risk contour mapping based on event monitoring indicate that the Cape Cleveland site is likely to be impacted by tebuthiuron (0.01 – 0.02 $\mu g.L^{-1}$), atrazine (0.01 – 0.4 $\mu g.L^{-1}$) and diuron (0.01 – 0.1 $\mu g.L^{-1}$) (Lewis et al. 2009). Flood plume monitoring from the Haughton River and Barratta Creek on the 3rd February 2007 detected atrazine (< 0.01 – 0.08 $\mu g.L^{-1}$) and diuron (< 0.01 – 0.08 $\mu g.L^{-1}$) with one sample collected off Cape Cleveland indicating concentrations of atrazine and diuron of 0.03 and 0.02 $\mu g.L^{-1}$ respectively (Davis et al. 2008). Time integrated passive sampling estimates for February 2008 indicate concentrations of atrazine, diuron and tebuthiuron of 20, 6.7 and 2.2 $ng.L^{-1}$ respectively.

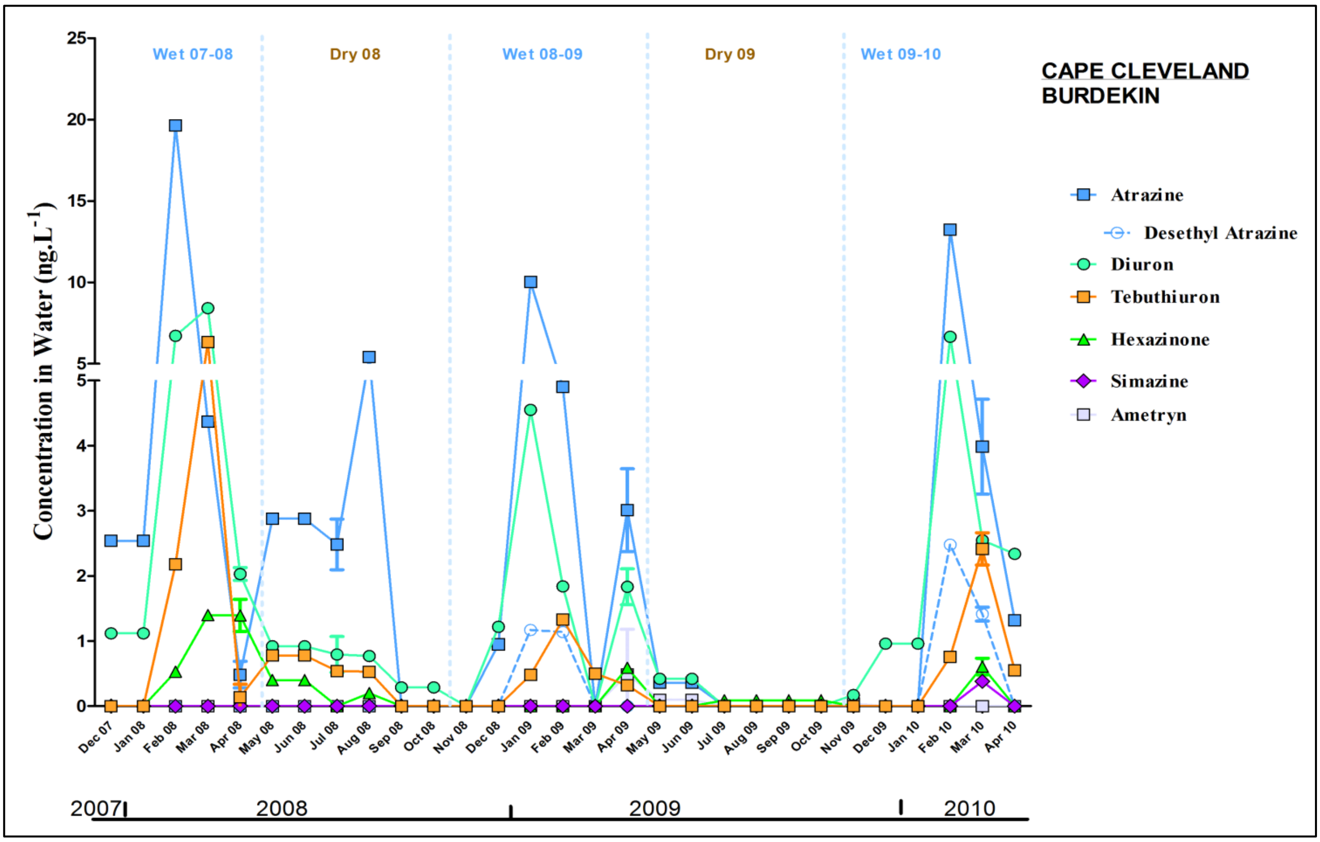

Figure 34 Time averaged PSII herbicide concentrations for Cape Cleveland in the Burdekin Region across wet and dry seasons between 2007 and 2010.

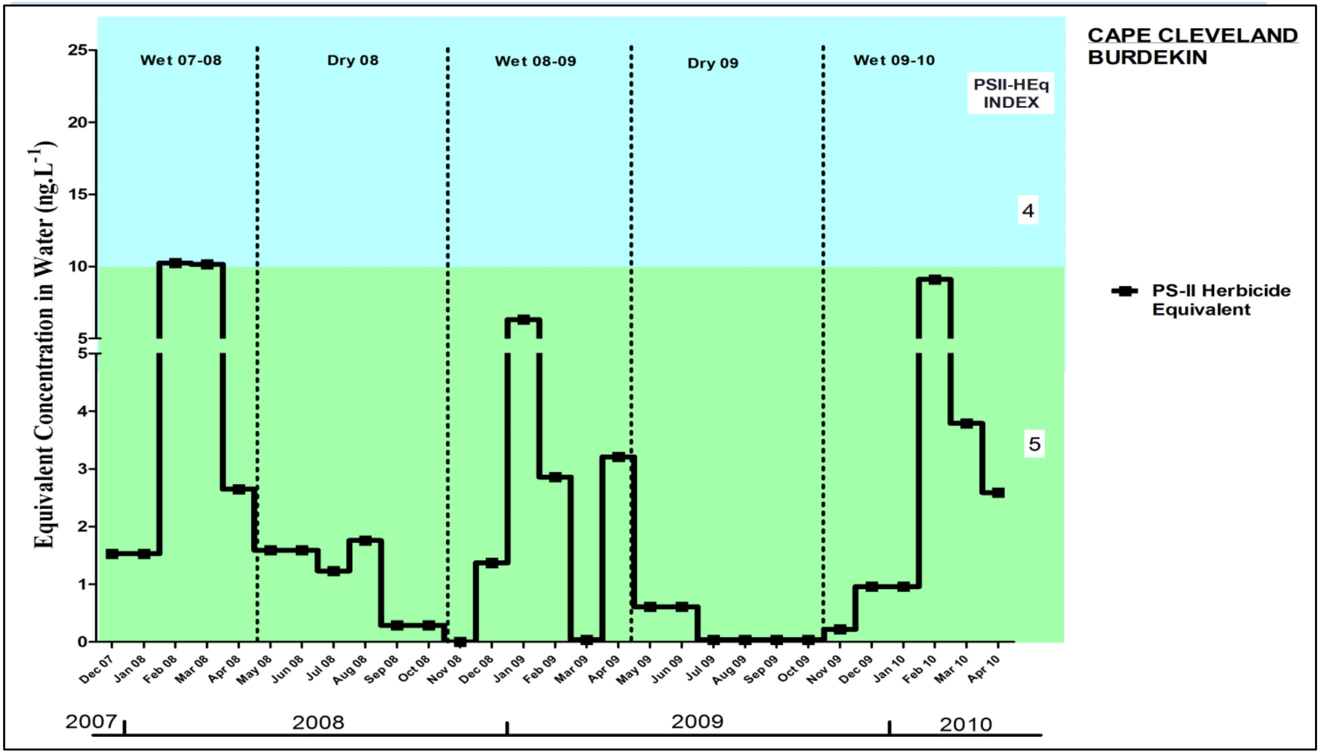

Figure 35 Time averaged concentrations at Cape Cleveland in the Burdekin Region expressed as PSII-Herbicide Equivalent concentrations across wet and dry seasons between 2007 and 2010 with PSII Herbicide Index categories "4" (10 < HEq ≤ 50) and "5" (≤ 10 ng.L^{-1}) indicated.

Relationships between temporal and seasonal PSII-HEq profiles and freshwater discharge from the Haughton River.

The Cape Cleveland site is located approximately 16 km northeast of the mouth of the Haughton River. Monthly PSII-HEq were plotted (Figure 36) against monthly discharge in the Haughton River (Table 24). The month with the highest monthly discharge was January 2010 while the PSII-HEq Max was observed for the February 2010 sampling period. However the February 2010 sampler was deployed on the 20th January 2010 and 98 % of the total discharge for January (298,499 ML) occurred between the 20th and the 31st January 2010. This indicates that the peak discharge from the Haughton River is in fact showing very good agreement with the timing of PSII-HEq Max at the Cape Cleveland site. Gauging records in March and April are incomplete so the declines in discharge with PSII-HEq may not be quite as great as indicated in this Figure.

Table 19 Monthly discharges (ML) for the Burdekin River in 2009-2010 from DERM Station 119003A

River	Jun 09	Jul 09	Aug 09	Sep 09	Oct 09	Nov 09	Dec 09	Jan 10	Feb 10	Mar 10	Apr 10
Haughton	3,275	2,231	3,016	3,693	4,426	4,513	9,539	301,678	158,687	41,691*	21,785*

*Incomplete gauging records

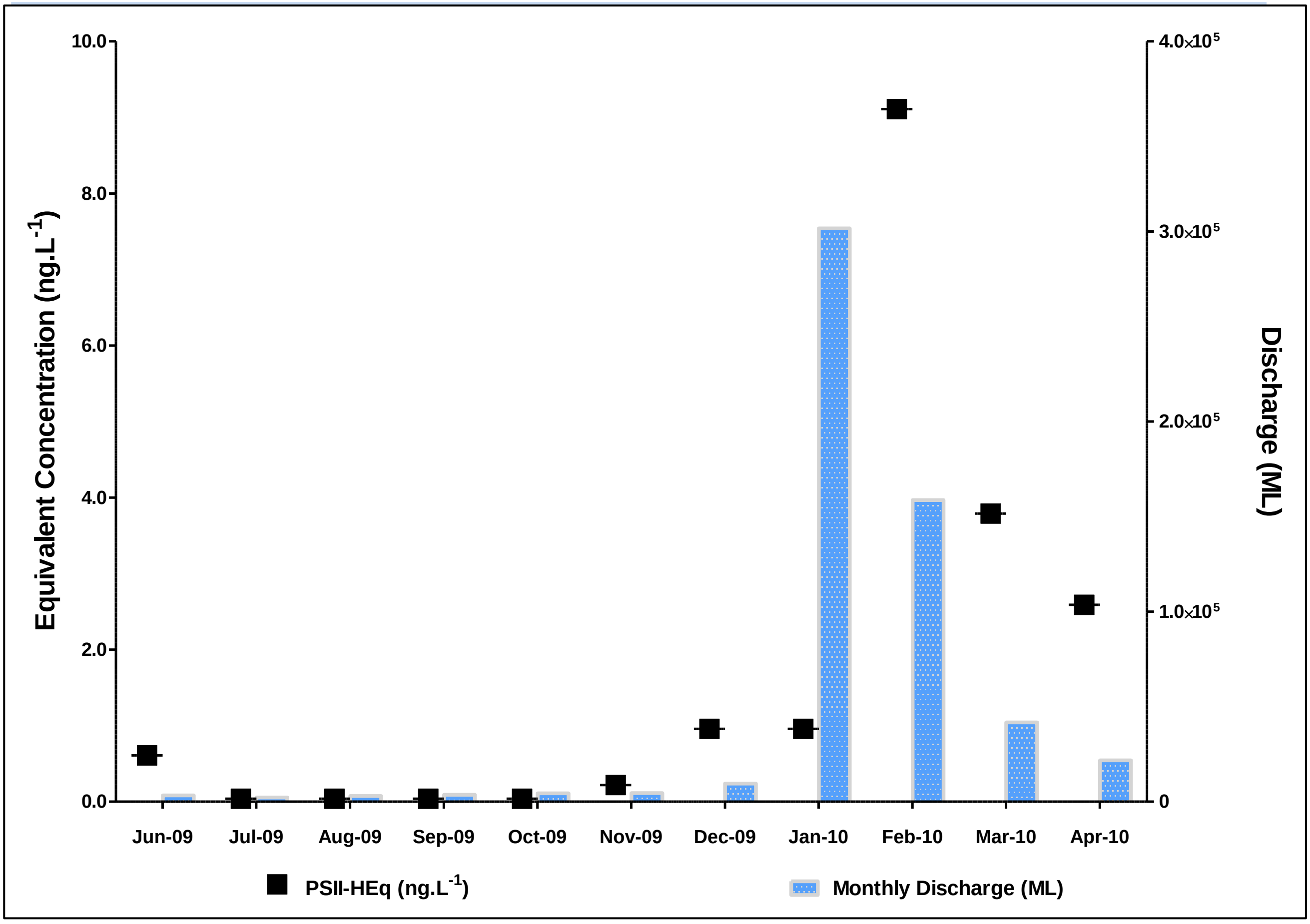

Figure 36 Total monthly discharge in the Haughton River in 2009-2010 together with PSII-HEq at Cape Cleveland.

6.4 Mackay Whitsunday Region

6.4.1 Outer Whitsunday

PSII Herbicides: November 2006 - April 2010

The monitoring record for the Outer Whitsunday site in the Mackay Whitsunday Region (Figure 37) since November 2006 indicates multiple gaps in the sampling record. The only wet season where the monitoring record is complete is the initial "Wet 06-07" period. PSII herbicides detected at this site include diuron which is typically the dominant herbicide in most monitoring periods as well as hexazinone, atrazine and tebuthiuron with ametryn (February 2007) and the atrazine transformation product desethylatrazine (November-December 2007) also detected.

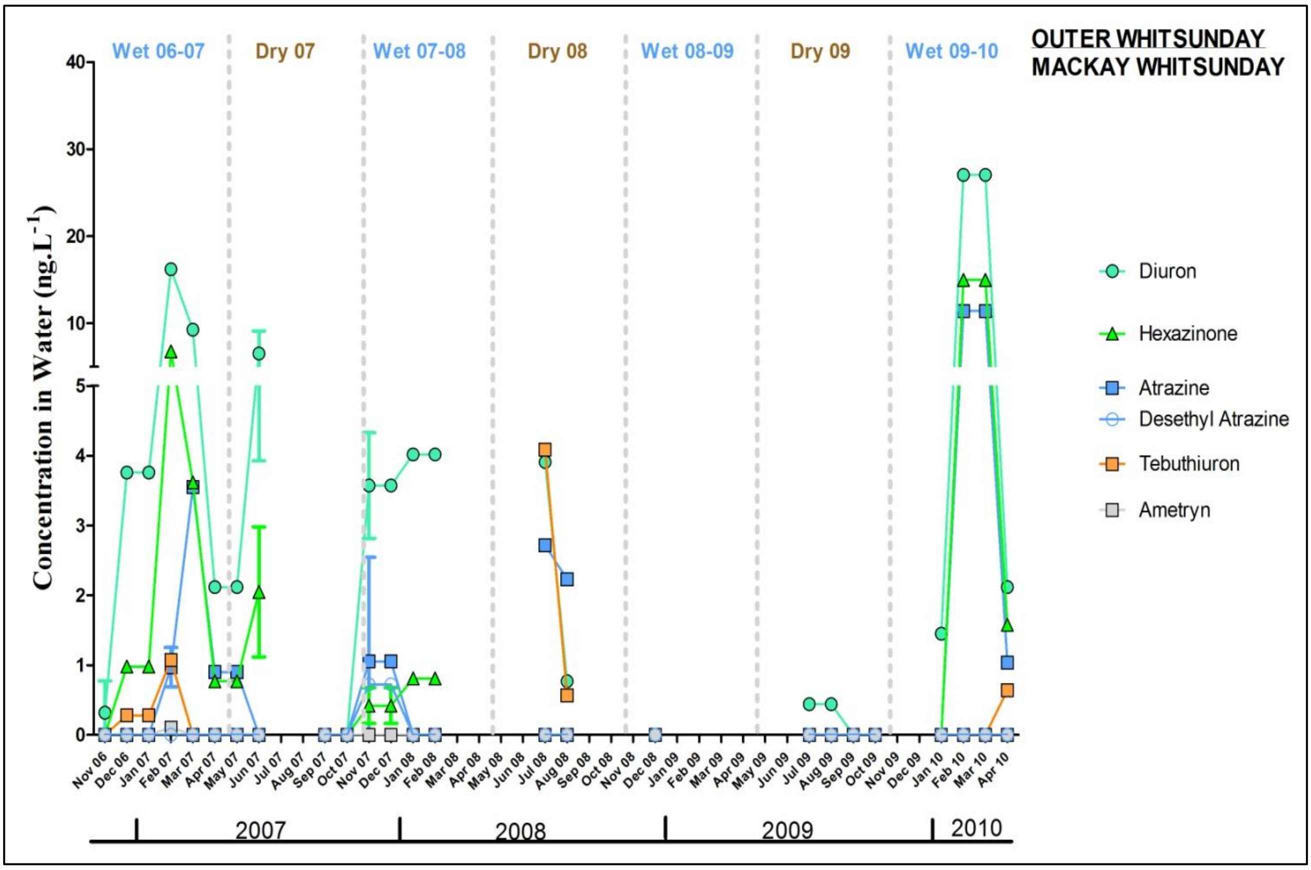

Figure 37 Time averaged PSII herbicide concentrations for Outer Whitsunday in the Mackay Whitsunday Region across wet and dry seasons between 2006 and 2010.

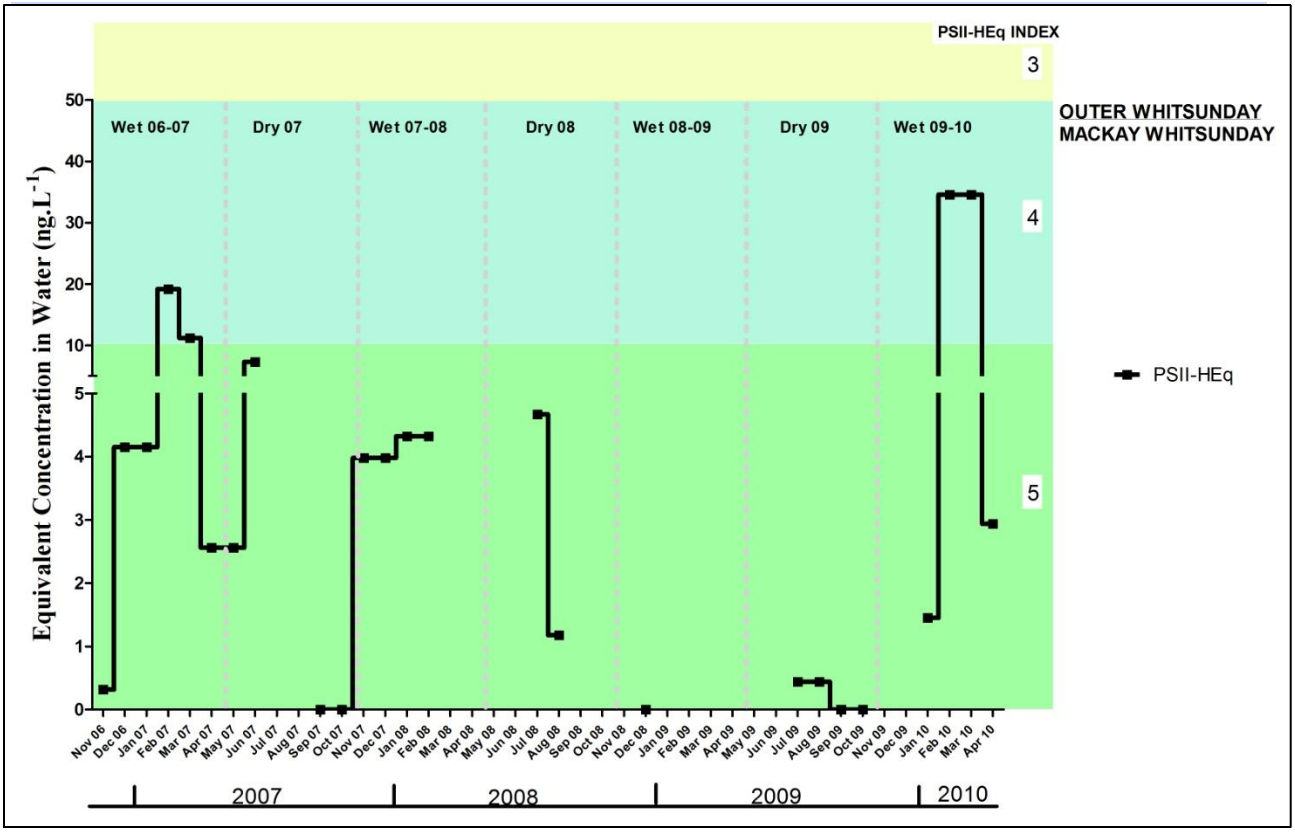

Figure 38 Time averaged concentrations at Outer Whitsunday in the Mackay Whitsunday Region expressed as PSII-Herbicide Equivalent concentrations across wet and dry seasons between 2006 and 2010 with PSII Herbicide Index Categories "3" (50 < HEq < 250 ng.L^{-1}), "4" (10 < HEq ≤ 50 ng.L^{-1}) and "5" (≤ 10 ng.L^{-1}) indicated.

There are two PSII-HEq Max occurring in Category "4" of the PSII-HEq in "Wet 06-07" (19 ng.L^{-1}) and "Wet 09-10" (35 ng.L^{-1}) as illustrated in Figure 38. These are mid to high range values within this Category. The previous monitoring year 2008-2009 was very poorly characterized with only two dry season periods (July and August 2008) and one wet season period (December 2008 with trace levels of diuron only) sampled. The PSII-HEq Max in the previous monitoring year was derived from July 2008 during the dry season when diuron was not the dominant herbicide. The concentrations of diuron, hexazinone and atrazine within the current 2009-2010 wet period have been the highest levels monitored at this site. Due to the poor monitoring record it is however impossible to indicate any potential trends at this location.

6.4.2 Daydream Island

PSII Herbicides: November 2006 - February 2010

The only periods within the temporal profile for Daydream Island where consecutive wet and dry periods have been monitored consecutively was between "Wet 06-07" and "Dry 07"(Figure 39). The dry season period in that case does indicate the presence of the same PSII herbicides (diuron, hexazinone, atrazine and tebuthiuron) with similar relative abundance albeit at lower levels than observed during the wet monitoring period. Subsequent dry periods ("Dry 08" and "Dry 09") and at least one wet period "Wet 07-08" have either one single month with monitoring or no monitoring record. It is unlikely that true seasonal variation has been adequately captured and little confidence can be placed in the maximum values for individual herbicides observed since monitoring commenced.

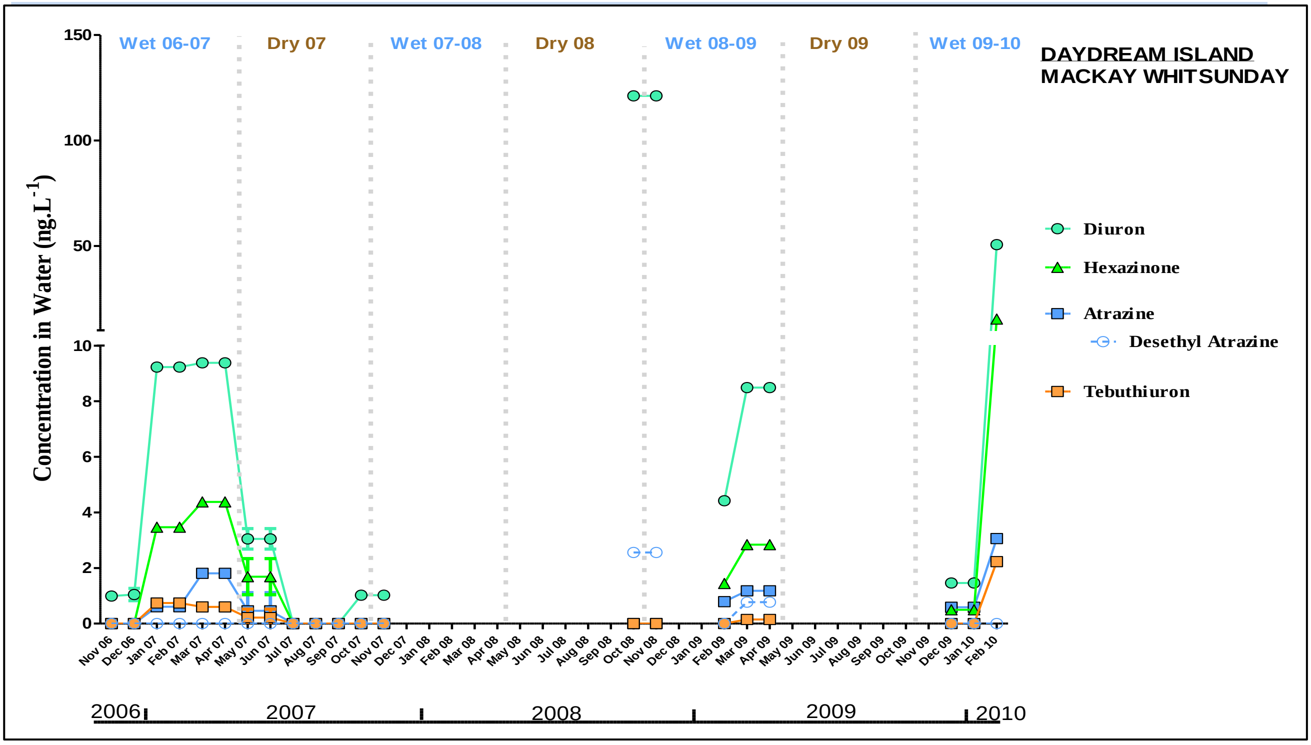

Figure 39 Time averaged PSII herbicide concentrations for Daydream Island (Inner Whitsunday) in the Mackay Whitsunday Region across wet and dry seasons between 2006 and 2010.

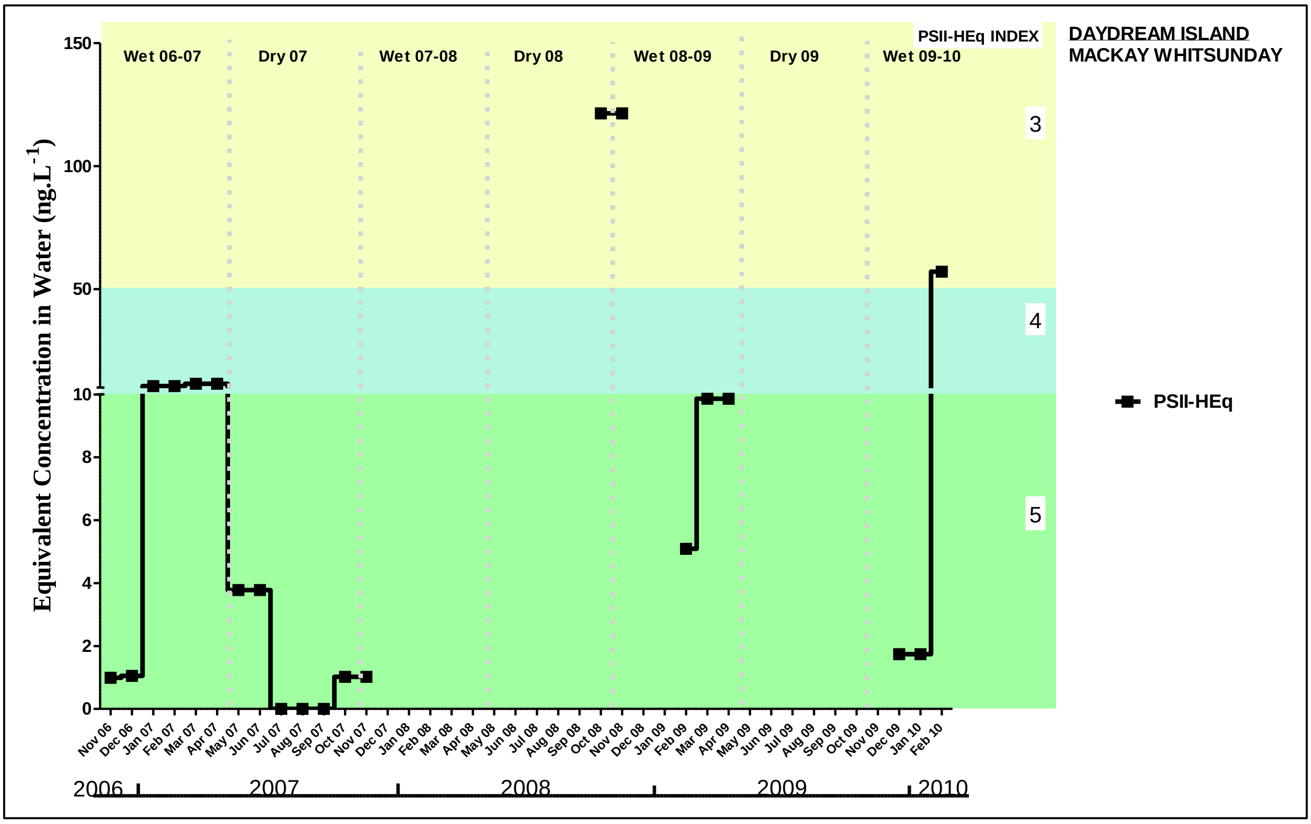

Figure 40 Time averaged concentrations at Daydream Island (Inner Whitsunday) in the Mackay Whitsunday Region expressed as PSII-Herbicide Equivalent concentrations across wet and dry seasons between 2006 and 2010 with PSII Herbicide Index Categories "3" (50 < HEq < 250), "4" (10 < HEq ≤ 50) and "5" (≤ 10 ng.L^{-1}) indicated.

While PSII-HEq Max at the Outer Whitsunday site have been in the mid-high range of Category "4", the PSII-HEq profile for the Daydream Island site (Figure 40) indicates at least two monitored periods with a PSII-HEq Index Category of "3". Any comparison of these sites within the Whitsunday Islands area is compromised by incomplete monitoring records at both locations. These observations of biologically relevant concentrations indicated by time integrated sampling techniques which are more typically indicated for inshore coastal sites, at a site in the Whitsunday Islands which relies so heavily on reef generated tourism , are concerning. More extensive monitoring within this area should be a priority to more adequately characterize the risk to reefs in these waters.

The O'Connell river discharges into Repulse Bay just south of the Whitsunday Islands. Plumes from the O'Connell River can be guided north around Cape Conway and extend into the Whitsunday Islands while plumes from the Pioneer River may extend out into the ocean and head south east or can be pushed north towards the Whitsunday Islands under the influence of strong southerly winds (Rohde et al. 2008; Lewis et al. 2009; Devlin et al. 2010). Herbicides including diuron, atrazine, hexazinone and tebuthiuron and ametryn have been detected in these plume waters and can demonstrate a conservative mixing profile which declines across the salinity gradient due to dilution with sea water with the level of mixing significantly influencing concentrations in different events (Rohde et al. 2008).

Relationships between temporal and seasonal PSII HEq profiles at Outer Whitsunday and Daydream Island and annual freshwater discharge in the O'Connell River

Since the monitoring record is so incomplete annual discharge will not be compared with PSII-HEq Max within each monitoring year. River flow exceeded median annual flow in2009-2010 and for all previous years from 2006/07 onwards.

Monthly discharges for the O'Connell River which enters Repulse Bay to the south of the Proserpine River in 2009-2010 are provided in Table 20. The contribution of the Proserpine River has not been considered in this assessment although its contribution may be lessened by the Peter Faust Dam (Stephen Lewis pers. com.).

Table 20 Monthly discharges (ML) for the O'Connell River available for the 2009 -2010 monitoring year from DERM Station 1240001B

River	Jun 09	Jul 09	Aug 09	Sep 09	Oct 09	Nov 09	Dec 09	Jan 10	Feb 10	Mar 10	Apr 10
O'Connell	1,521	839	286	160	70	92	43	50,864	91,177	55,309	9,115

PSII-HEq (ng.L^{-1}) for the Outer Whitsunday and Daydream Island sites are indicated with respect to monthly discharge (ML) in the O'Connell River in Figure 41. The PSII-HEq Max for the Whitsunday Region observed at Daydream Island co-occurs with the maximum monthly discharge from the O'Connell River in February 2010. Similarly PSII-HEq Max for the Outer Whitsunday site was observed in February- March 2010 during the peak February discharge and the next highest discharge in March 2010.

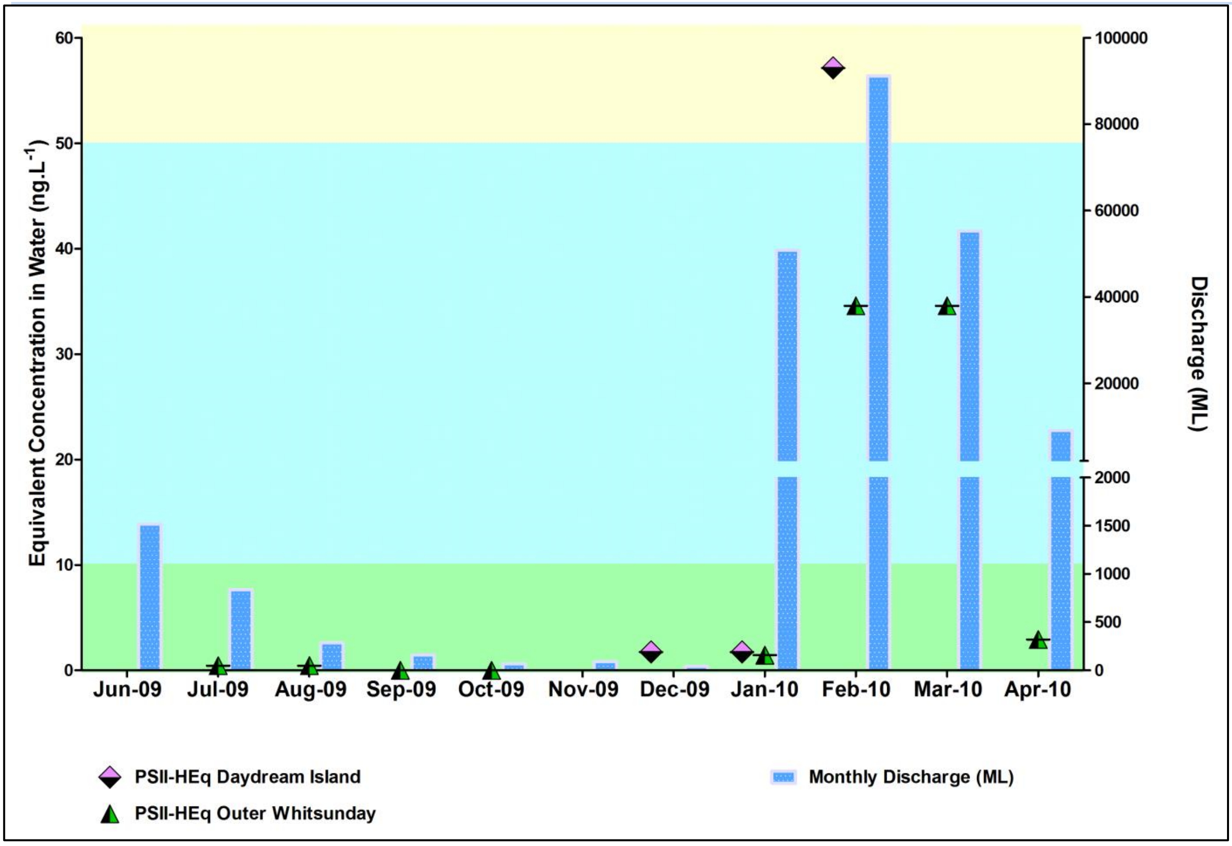

Figure 41 Total monthly discharge in the O'Connell River in the 2009-2010 monitoring year together with PSII-HEq for Daydream Island and Outer Whitsunday.

6.4.3 Pioneer Bay

PSII Herbicides: June 2009 - April 2010

The temporal profile (Figure 42) in 2009-2010 reveals the dominance and relative consistency of the concentration of diuron in both dry and wet periods when sampling occurred. The concentration of diuron is more consistently > 10 ng.L^{-1} at this location. Significantly, there is a gap in the monitoring record in the early part of the wet season (November 2009 to January 2010). In contrast all other PSII herbicides detected demonstrate a peak in concentration in March 2010. The PSII herbicide profile and the relatively consistent diuron concentration profile is reflected in the PSII-HEq profile (Figure 43) which indicates that the site is at least more consistently Category "4" than Category "5" in 2009-2010. More complete monitoring is required across the entire monitoring year to characterize this site.

Figure 42 Time averaged PSII herbicide concentrations for Pioneer Bay (new Inner Whitsunday) in the Mackay Whitsunday Region across wet and dry seasons between 2009 and 2010.

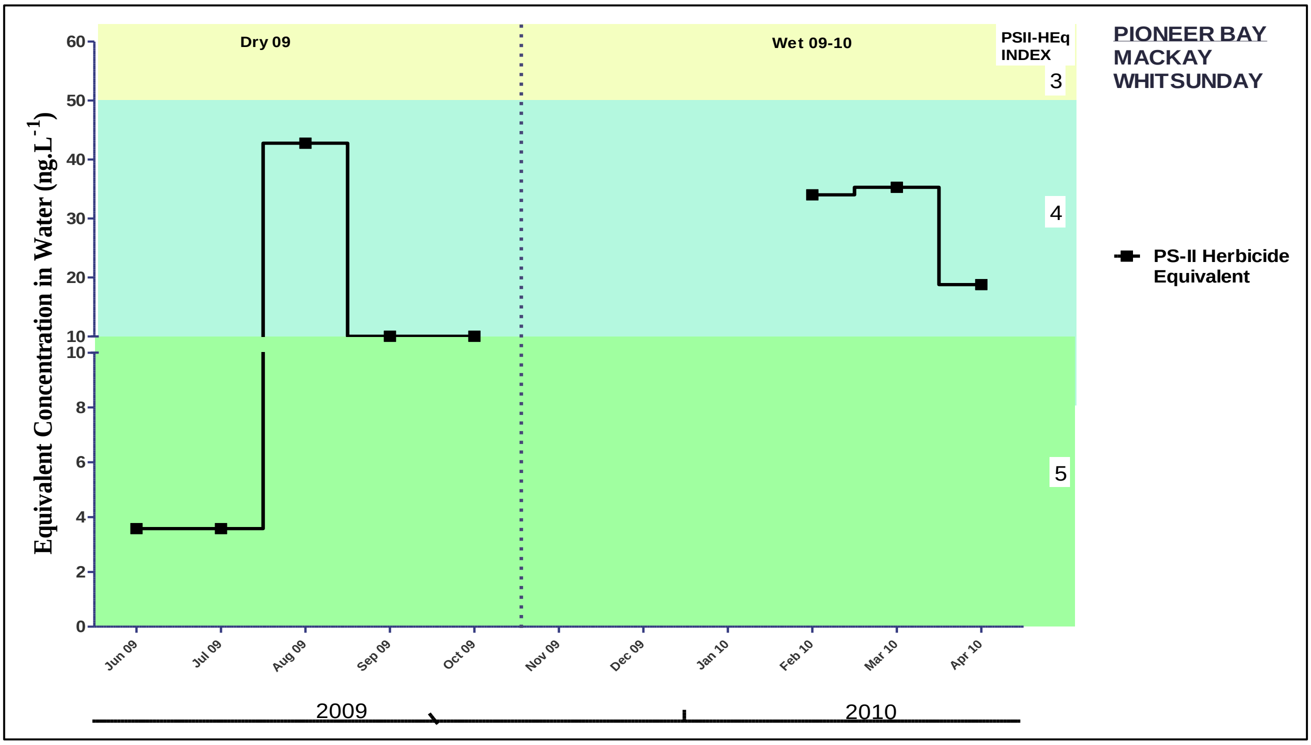

Figure 43 Time averaged concentrations at Pioneer Bay (new Inner Whitsunday) in the Mackay Whitsunday Region expressed as PSII-Herbicide Equivalent concentrations across wet and dry seasons between 2006 and 2010 with PSII Herbicide Index Categories "3" (50 < HEq < 250 ng.L^{-1}), "4" (10 < HEq ≤ 50 ng.L^{-1}) and "5" (≤ 10 ng.L^{-1}) indicated.

6.4.4 Pioneer River

Pesticides and Industrial Chemicals (PDMS) : November 2006 –December 2009.

Pesticides have been continuously monitored at the Pioneer River site using PDMS since November 2006 (Figure 44). More pesticides and herbicides are typically detected in wet than dry season sampling periods in the Pioneer River. The more frequently detected pesticides are metolachlor (chloracetanilide herbicide), propazine (chlorotriazine herbicide), pendimethalin and trifluralin (dinitroaniline herbicides), dieldrin (organochlorine/cyclodiene insecticide), and chlorpyrifos (organophosphate insecticide). There are few pesticides detected in the latest Dry 09 period and sampling was discontinued within the latest Wet 09-10 period. Notably metolachlor was not detected in 2009-2010 to date.

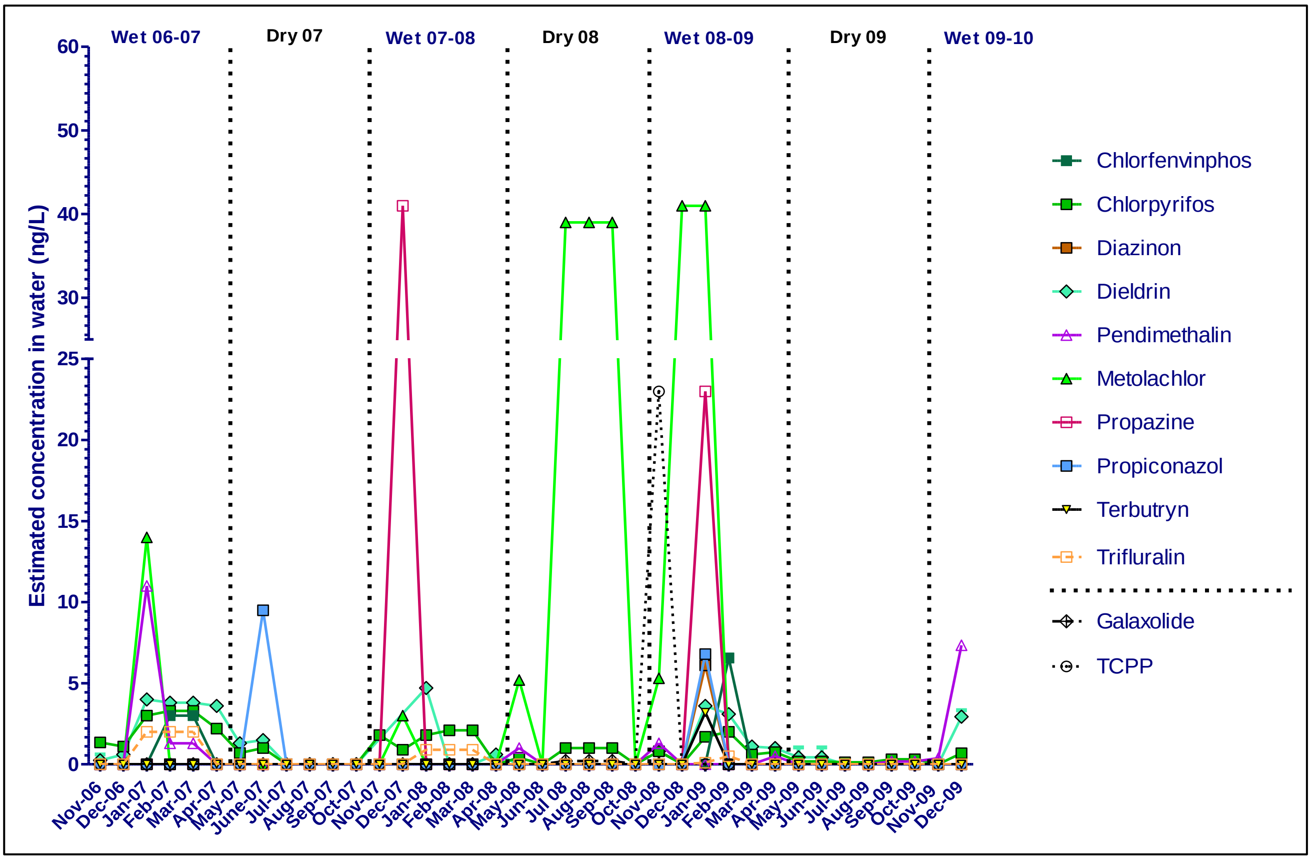

Figure 44 Time averaged pesticide concentrations determined using PDMS sampling for the Pioneer River in the Mackay Whitsunday Region across wet and dry seasons between 2007 and 2010

PSII Herbicides: November 2005 – December 2010

The temporal profiles for the Pioneer River between Wet 05-06 and Wet 09-10 (Figure 45) are characterized by marked peaks in the concentrations of diuron, atrazine and hexazinone in all wet season sampling periods. A larger range of different herbicides and transformation products have been detected at this site than all other locations.

The temporal profiles in PSII herbicides expressed as PSII-HEq (Figure 46) indicate that every wet season sampling period in all monitoring years has demonstrated at least one PSII HEq Index Category “1”. These wet periods also frequently demonstrate an Index of Category “2”. The dry season sampling periods are more frequently Category “4” across all monitoring years although the latest dry season sampling period (Dry 09) has been more consistently Category “5”.

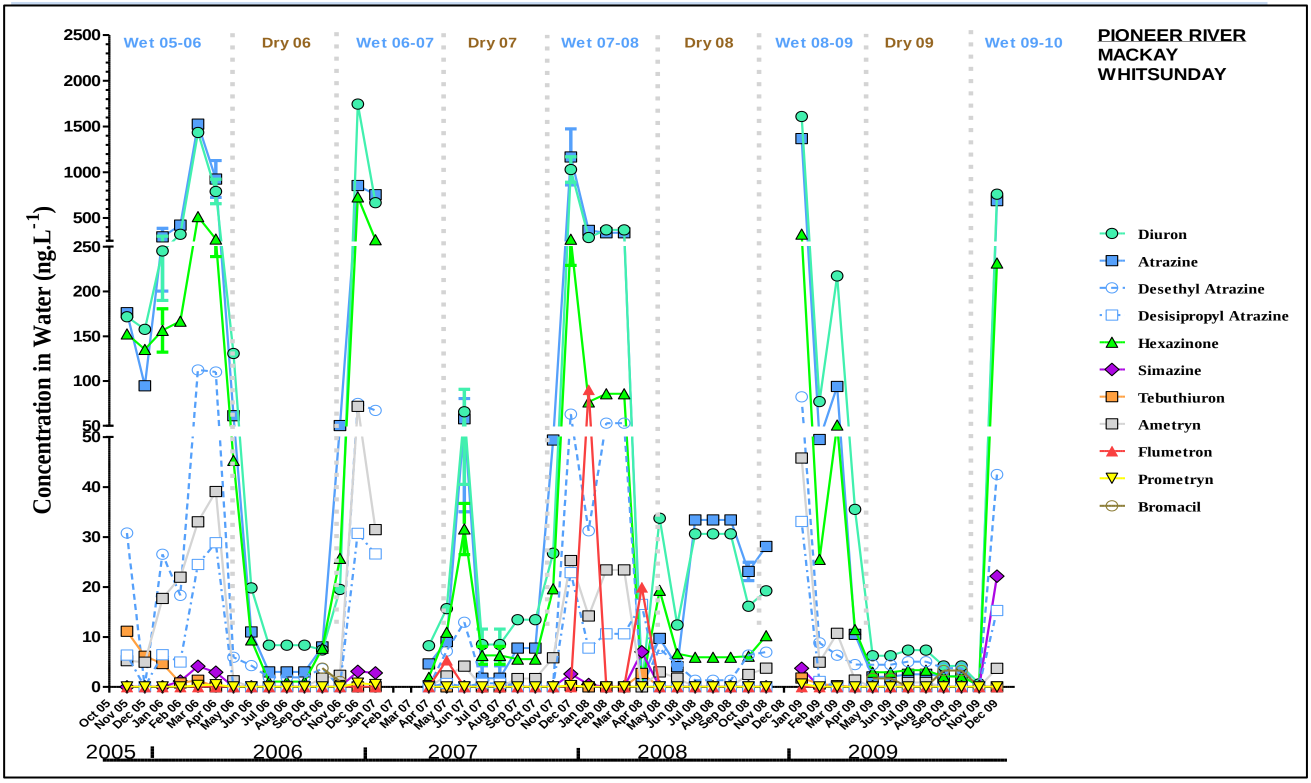

Figure 45 Time averaged PSII herbicide concentrations for the Pioneer River in the Mackay Whitsunday Region across wet and dry seasons between 2005 and 2010.

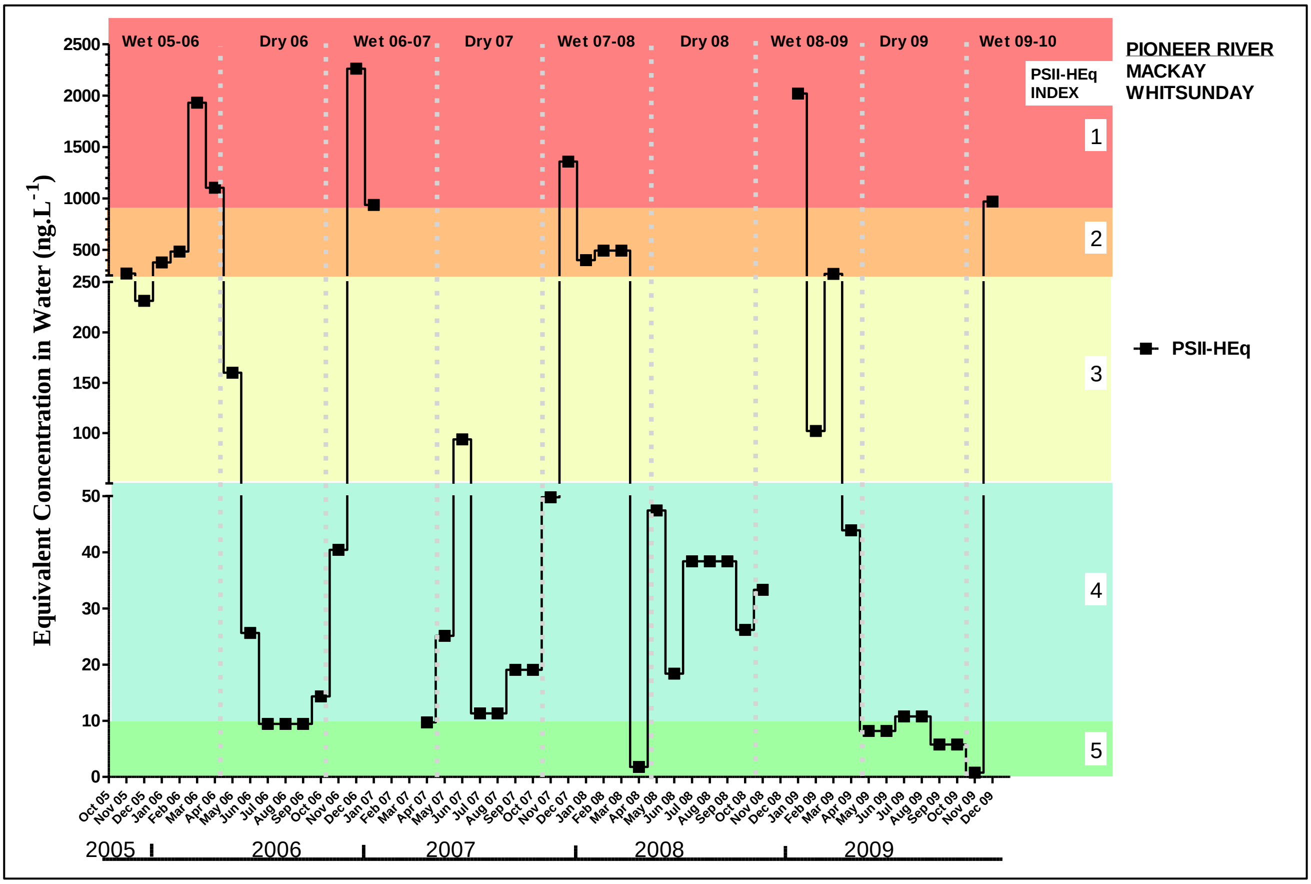

Figure 46 Time averaged concentrations at the Pioneer River in the Mackay Whitsunday Region expressed as PSII-Herbicide Equivalent concentrations across wet and dry seasons between 2006 and 2010 with PSII Herbicide Index Categories “1” (HEq > 900 ng.L^{-1}), “2” (250 ≤ HEq ≤ 900 ng.L^{-1}) , “3” (50 < HEq < 250 ng.L^{-1}), “4” (10 < HEq ≤ 50 ng.L^{-1}) and “5” (≤ 10 ng.L^{-1}) indicated.

6.4.5 Sarina Inlet

PSII Herbicides: June 2009 – April 2010

The temporal profile for the Sarina Inlet site (Figure 47) reveals an evident seasonal influence with more herbicides detected and at significantly higher levels in the "Wet 09-10" period compared with the preceding "Dry 09" period when only diuron and hexazinone were detected. This profile is reflected in the PSII-HEq temporal profile in Figure 48 where PSII-HEq Index Categories increase from Category "5" during the dry period and the first month of the wet period (November 2009) to a PSII-HEq Index Max Category of "2" when the concentrations of all PSII herbicides increased in December 2009. An Index Category of "3" is indicated across January and February 2010, before PSII herbicide levels decline later in the wet season and the Index Category reduces back to "5". For three months within 2009-2010 (December 2009 to February 2010) time integrative concentration estimates indicate that the Sarina Inlet site was either Category "3" or higher.

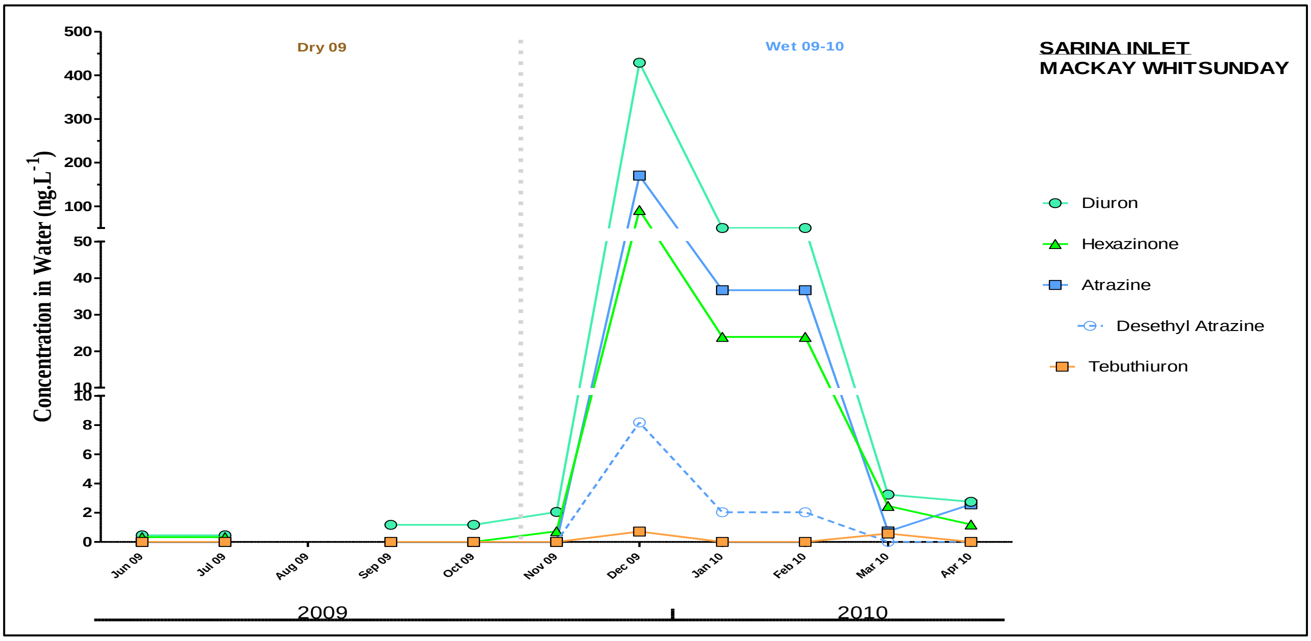

Figure 47 Time averaged PSII herbicide concentrations for Sarina Inlet in the Mackay Whitsunday Region across wet and dry seasons between 2005 and 2010.

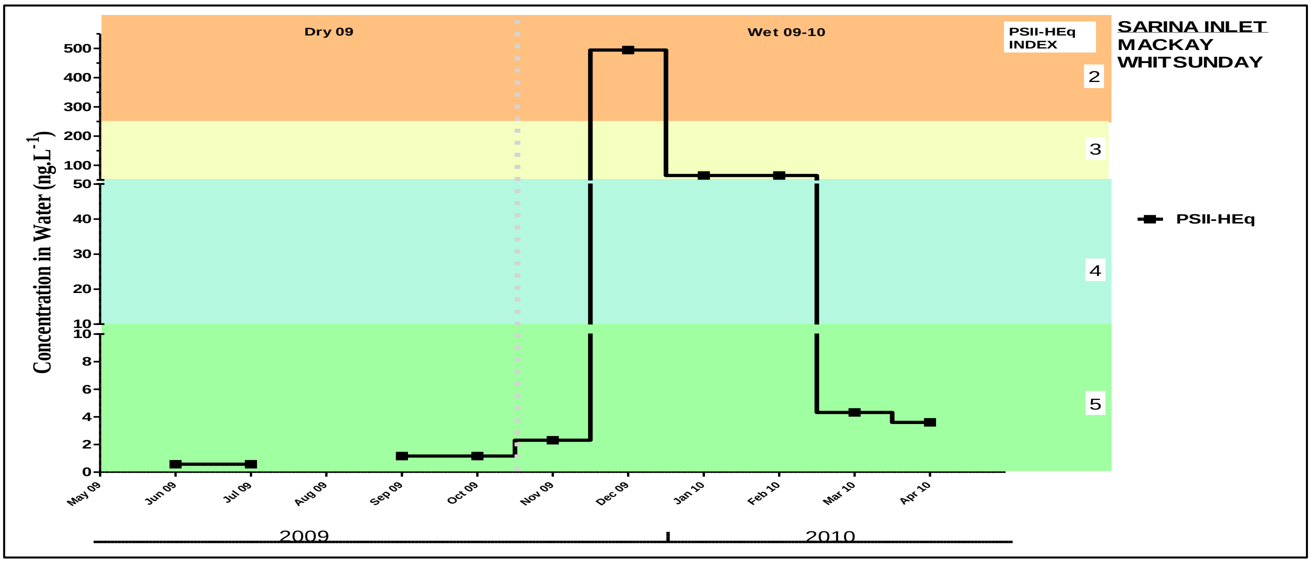

Figure 48 Time averaged concentrations at the Sarina Inlet site in the Mackay Whitsunday Region expressed as PSII-Herbicide Equivalent concentrations across dry and wet seasons between 2009 and 2010 with PSII Herbicide Index Categories "2" (250 ≤ HEq ≤ 900 ng.L^{-1}) , "3" (50 < HEq < 250 ng.L^{-1}), "4" (10 < HEq ≤ 50 ng.L^{-1}) and "5" (≤ 10 ng.L^{-1}) indicated.

Relationships between temporal and seasonal PSII-HEq profiles at Sarina Inlet and freshwater discharge in Sandy Creek

Plane Creek drains into Sarina Inlet however gauge monitoring data was not available for this creek so discharge data for Sandy Creek to the north of this Inlet has been used as indicative of discharge at this location. Total monthly discharge (ML) for Sandy Creek (Table 21) is plotted against PSII-HEq for this location in Figure 49.

Table 21 Monthly discharges (ML) for Sandy Creek for 2009 -2010 from DERM Station 126001A

Creek	Jun 09	Jul 09	Aug 09	Sep 09	Oct 09	Nov 09	Dec 09	Jan 10	Feb 10	Mar 10	Apr 10
Sandy	715	610	387	302	229	660	4,024	93,463	157,158	32,463	6,032

*Incomplete gauging records

This profile indicates that the peak in PSII-HEq in December 2009, may be associated with a “first” flush effect rather than the dominant flow events beginning in January. This effect has been observed previously within creeks and rivers in this region (Rohde et al. 2008).

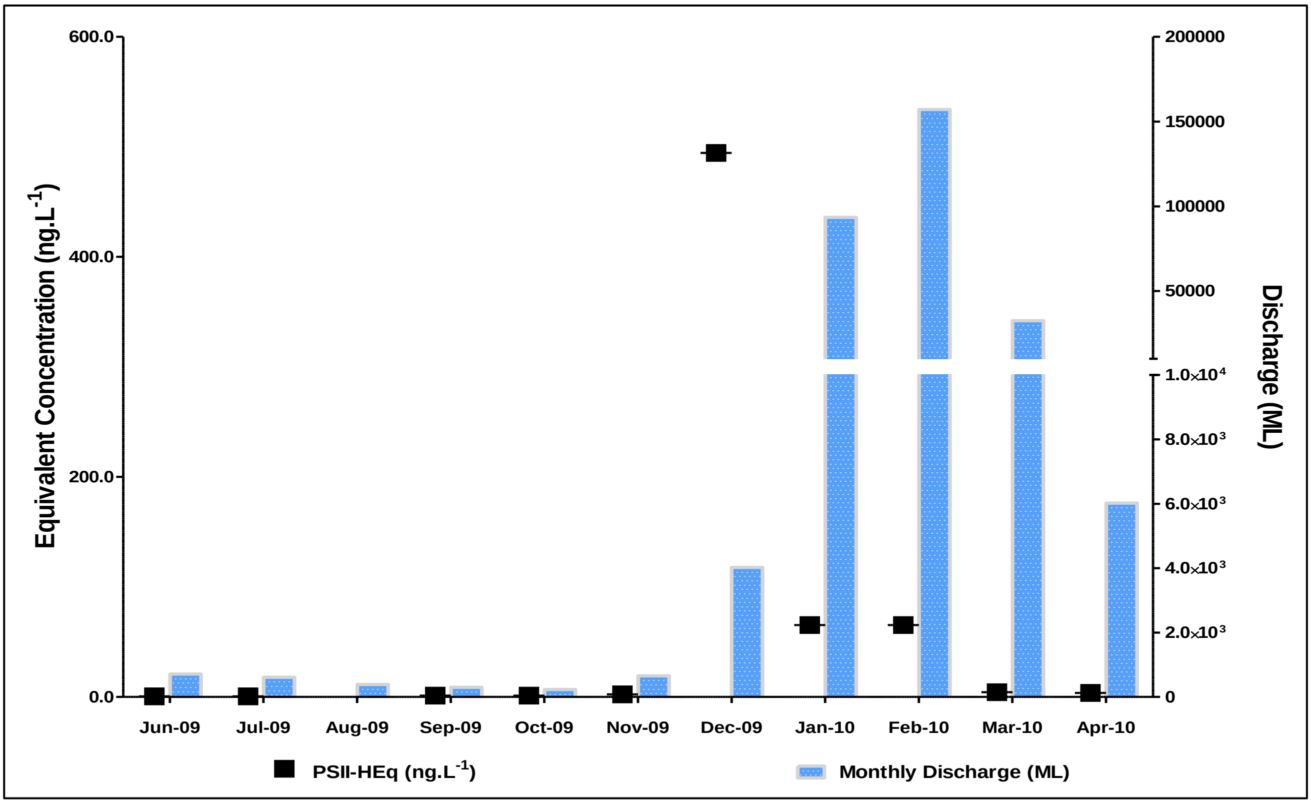

Figure 49 Total monthly discharge in Sandy Creek in 2009-2010 together with PSII-HEq for Sarina Inlet.

6.5 Fitzroy Region

6.5.1 North Keppel Island

Sampling has been conducted at the North Keppel Island site in the Fitzroy Region since August 2005. This region is only represented by a single site.

PSII Herbicides: August 2005 – April 2010

The temporal profile for North Keppel Island (Figure 50) since monitoring commenced in 2005 indicates that diuron has been the most frequently detected PSII herbicide with concentrations typically ≤ 2 $ng.L^{-1}$. The last two wet season sampling periods which were reasonably well monitored at this site (Wet 07-08 and Wet 09-10) have been relatively notable in that elevated concentrations of atrazine and tebuthiuron (Wet 07-08) and elevated concentrations of atrazine, tebuthiuron, diuron and hexazinone (Wet 09-10) have been observed. Hexazinone in particular has not been detected at this site previously until the 2009-2010 wet season.

The influence of the differential PSII herbicides detected in these two wet periods is illustrated with respect to PSII-HEq profiles in Figure 51. PSII-HEq are typically in the low range of Category "5" of the Index. The influence of increasing concentrations of tebuthiuron and atrazine in Wet 07-08 has resulted in a slight increase in PSII-HEq (3 $ng.L^{-1}$), however in the latest wet season when the level of diuron has also increased the PSII-HEq has increased to 8.7 $ng.L^{-1}$ which is in the higher range in Category "5". There are quite a few gaps in the sampling record at North Keppel Island including little sampling in the interim wet season (Wet 08-09), which makes any conclusions about how unusual these observations may be quite difficult.

Flood plume monitoring (five samples) from the Fitzroy River in 2008-2009 have detected atrazine, (and atrazine transformation products desethyl- and desisopropyl atrazine), tebuthiuron and metolachlor. Tebuthiuron exceeded the GBRMPA Guideline in every sample and the plumes were observed up to 50 km from the coast in proximity to the Keppel Group (Devlin et al. 2010). This was a below median flow discharge year for the Fitzroy River but the compounds detected are similar to those indicated by passive sampling to affect this site. The exceptions being that diuron was not detected in grab samples and that metolachlor would normally be detected using PDMS sampling and these samplers are not used at this location. As indicated previously the entire wet season was not monitored in this lower discharge year using passive samplers. More integrated monitoring is required to assess differences in these acute and chronic exposure estimates.

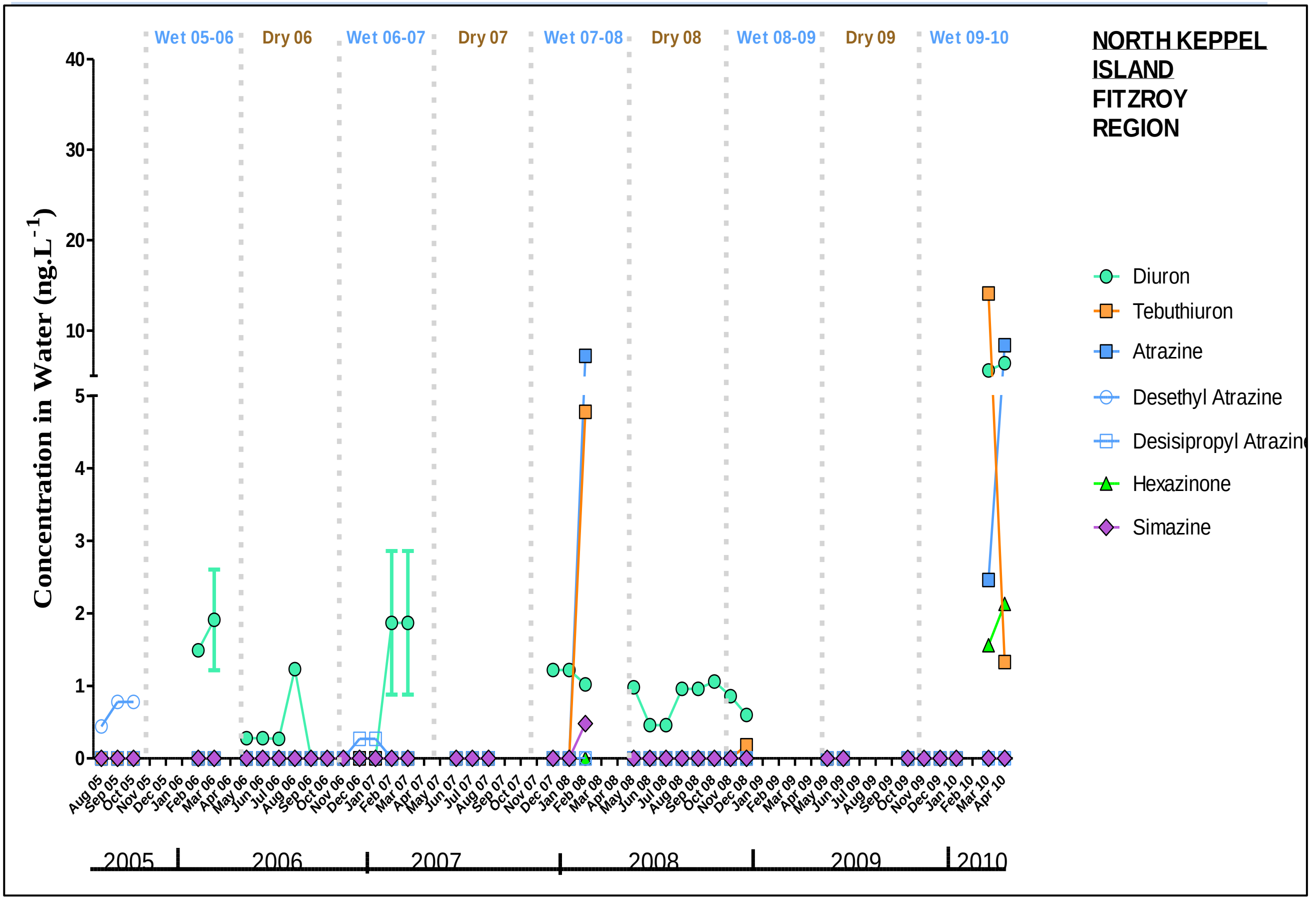

Figure 50 Time averaged PSII herbicide concentrations for North Keppel Island in the Fitzroy Region across wet and dry seasons between 2005 and 2010.

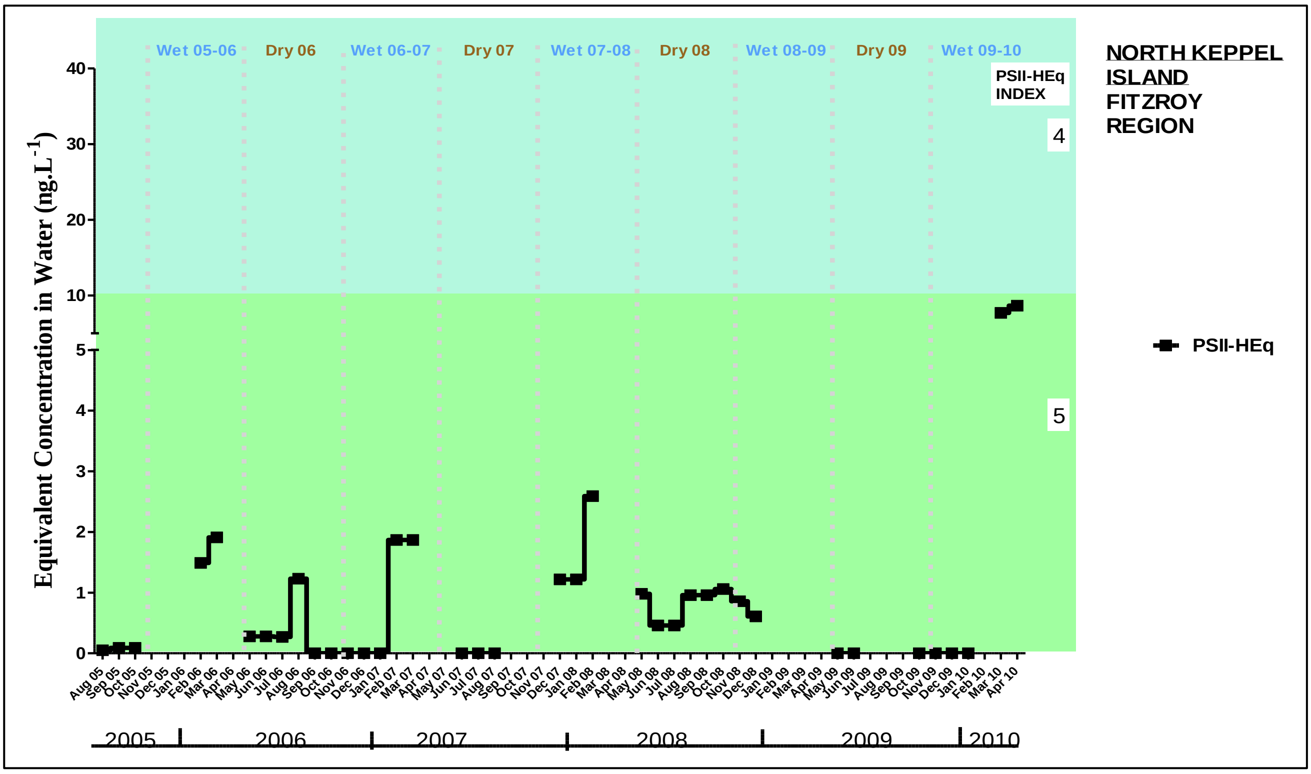

Figure 51 Time averaged concentrations at the North Keppel Island site in the Fitzroy Region expressed as PSII-Herbicide Equivalent concentrations across dry and wet seasons between 2009 and 2010 with PSII Herbicide Index Categories "4" (10 < HEq ≤ 50 ng.L^{-1}) and "5" (≤ 10 ng.L^{-1}) indicated.

Grab sample concentrations across peak flows in the Fitzroy River in the wet season of 2009-2010 (Figure 52) indicate that hexazinone has been more consistently detected than diuron during peak flows. Similarly longer term data for the maximum concentrations of these herbicides in the Fitzroy River (Figure 53) seem to indicate an apparent increase in the concentration of hexazinone between 2008 and 2010.

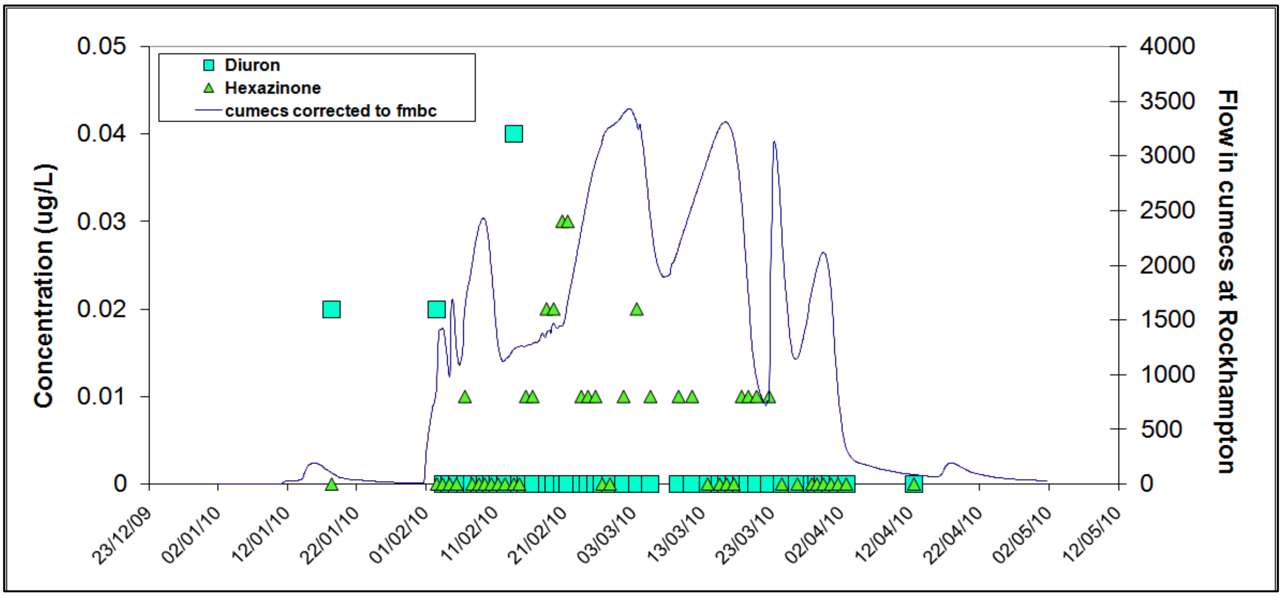

Figure 52 Concentrations of hexazinone and diuron monitored during periods of peak flow in the Fitzroy River in 2010. (Source: Bob Packett of the Department of Environment and Resource Management)

Figure 53 Variation in the maximum concentrations of PSII herbicides in the Fitzroy River with time (Source: Bob Packett of the Department of Environment and Resource Management)

Total event loads have been calculated for specific PSII herbicides in the Fitzroy River between 1994 and 2008 (Packett et al. 2009). Interestingly the relative magnitude of herbicide loads in the Fitzroy River in the Jan-Feb 2008 event were: atrazine (2153 kg) > tebuthiuron (1081 kg) > simazine (82 kg) > diuron (12 kg) which show quite good agreement with the relative magnitude of these PSII herbicide concentrations at North Keppel Island in February 2008. The herbicides detected in this region reflect dominant agricultural land uses of cropping and grazing (tebuthiuron) and rainfall/runoff/flooding originating from these lands within the Fitzroy River Basin (Packett et al. 2009).

Relationships between temporal and seasonal PSII-HEq profiles at North Keppel Island and freshwater discharge in the Fitzroy River

The annual discharge from the Fitzroy River within each monitoring year is provided in Table 22. Above median flows were observed in the Fitzroy River in 2007/08 and 2009/10. These are also the years where elevated concentrations of PSII-Herbicides have been observed at North Keppel Island.

Table 22 Annual freshwater discharge (ML) for the Fitzroy River in proximity to the North Keppel Island sampling site. Shaded cells highlight years for which river flow exceeded the median discharge as estimated from available long-term time series for each river.

River	2005/06	2006/07	2007/08	2008/09	2009/10	Long Term Median
Fitzroy	677,845	886,272	12,051,412	2,192,808	10,677,915	2,708,440

* Incomplete gauging record; Sourced from Table A1-2 (Schaffelke et al. 2010)

Table 23 Monthly discharges (ML) for the Fitzroy River available for the 2009 -2010 monitoring year from DERM Station 130005A

River	Jun 09	Jul 09	Aug 09	Sep 09	Oct 09	Nov 09	Dec 09	Jan 10	Feb 10	Mar 10	Apr 10
Fitzroy	2,616	124	0	0	0	0	0	110,540	4,331,191	5,5,902,239	293,113

Monthly discharge (ML) from the Fitzroy River in 2009-2010 are provided in Table 23. These are also plotted against PSII-HEq in Figure 54. The highest PSII-HEq occur in March 2010 and April 2010. The first significant increase in monthly discharge occurred just prior to these months (February 2010). The PSII-HEq Max is actually observed in April 2010 once monthly discharge had decreased significantly suggesting that there is a lag time between both the onset of peak discharge and peak concentrations.

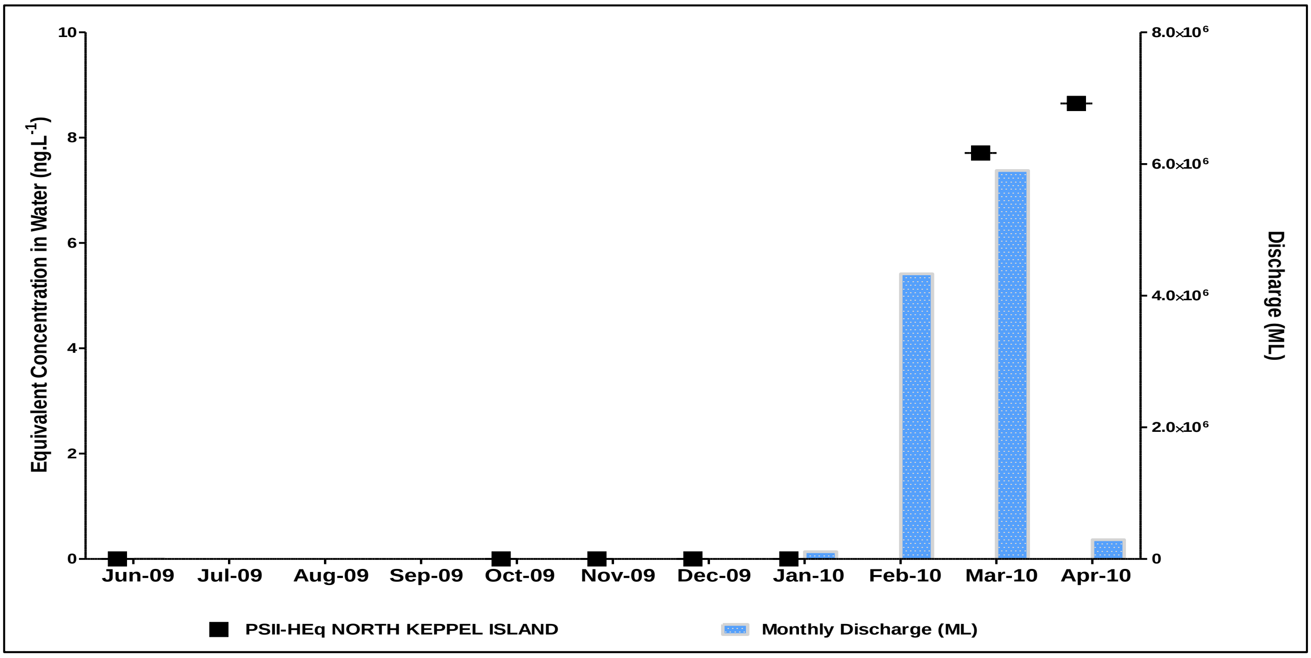

Figure 54 Total monthly discharge in the Fitzroy River in 2009-2010 together with monthly PSII-HEq at North Keppel Island.

7 REGIONAL SUMMARIES

7.1 Cape York Regional Summary

No PSII herbicides were detected in the 2009-2010 monitoring period for the Pixies Garden site discontinued from January 2010. PSII-HEq Max in the baseline reporting year (2008-2009) and 2009-2010 are illustrated in Figure 55. The PSII Herbicide Index for the Cape York Region based on the Pixies Garden site (2006-2010) is "5" with all PSII-HEq being ≤ 10 $ng.L^{-1}$ across all monitoring periods (Figure 56). All PSII-HEq are typically within the lower range of the Category "5" Index Category with maximum values in the wet seasons typically < 2 $ng.L^{-1}$. Diuron has been the most frequently detected PSII-herbicide at this site.

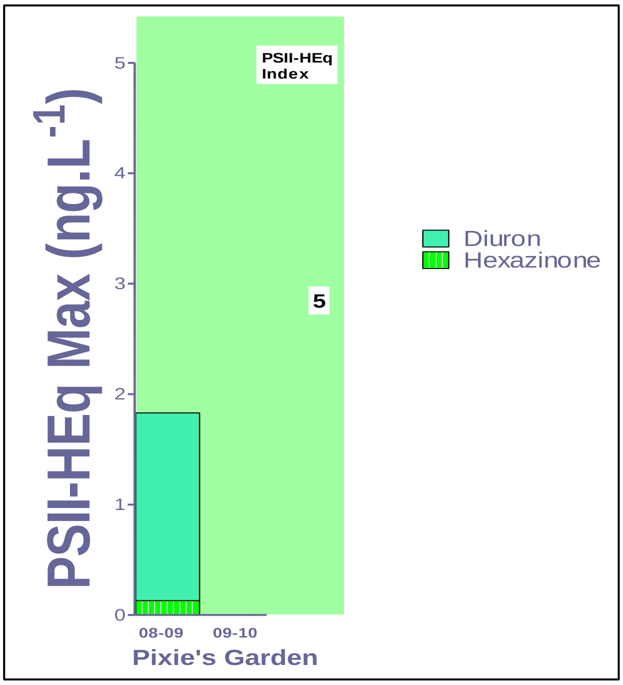

Figure 55 The relative contribution of different PSII herbicides to PSII-HEq Max ($ng.L^{-1}$) in the baseline reporting year (2008-2009) and (2009-2010 for Pixies Garden in the Wet Tropics Region

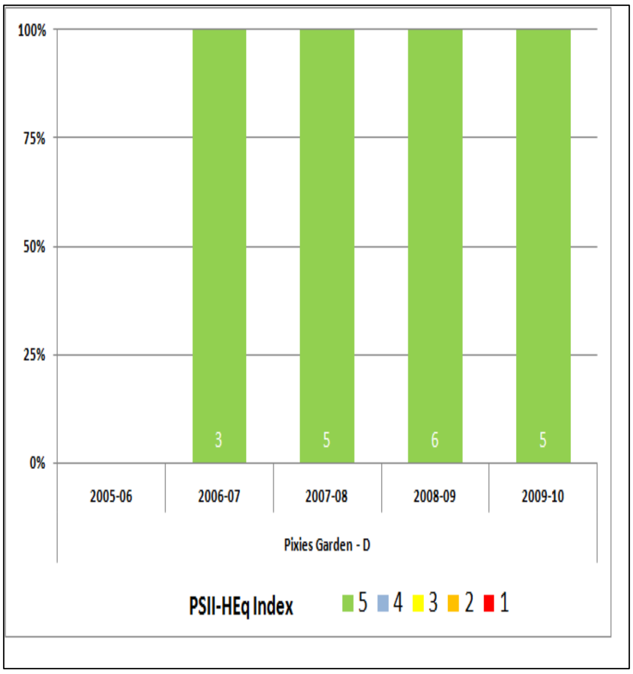

Figure 56 The proportion of all measurements within each monitoring year between 2005 and 2010 which are classified into Categories "1" (HEq > 900 $ng.L^{-1}$) to "5" (HEq ≤ 10 $ng.L^{-1}$) of the PSII-HEq Index for Pixies Garden in the Cape York Region.
"D" indicates discontinued in 2009-2010

7.2 Wet Tropics Regional Summary

Sampling sites within the wet tropics region in 2009-2010 included Low Isles, Green Island, Fitzroy Island, Normanby Island, Dunk Island and the Tully River (discontinued February 2010).

A range of industrial chemicals including polycyclic synthetic musks used in detergents such as galaxolide (all sites) and tonalide (Fitzroy Island) and the flame retardant tris(1-chlor-2-propyl)phosphate (TCPP) (Normanby Island) were detected using PDMS in 2009-2010. Chlorpyrifos, pendimethalin and the personal insect repellent *N*,*N*-diethyl-*meta*-toluamide (DEET) were detected in PDMS samples from inshore reef sites in the Wet Tropics Region in 2009-2010 (Table 24). These chemicals were also detected at several sites in 2008-2009: pendimethalin at Fitzroy Island (0.90 $ng.L^{-1}$) and Dunk Island (1.2 $ng.L^{-1}$); chlorpyrifos at Normanby Island (0.30 $ng.L^{-1}$) and Dunk Island (0.70 $ng.L^{-1}$) and DEET at Normanby Island (31 $ng.L^{-1}$). Fipronil which was detected at Dunk Island (0.30 $ng.L^{-1}$) in 2008-2009 was not detected in 2009-2010.

Chlorpyrifos concentrations estimated for inshore GBR sites (Table 24) exceed the GBRMPA Guideline of 0.5 $ng.L^{-1}$ in 2009-2010. Notably there were exceedances of the ANZECC & ARMCANZ Guidelines for the two organophosphate insecticides (chlorpyrifos (2.4 – 12 $ng.L^{-1}$) and diazinon (46 – 55 $ng.L^{-1}$)) at the Tully River site in 2009-2010. The maximum concentration of chlorpyrifos in the Tully River (12 $ng.L^{-1}$) was observed in a December 2009 – January 2010 sampling period which is consistent with the timing of chlorpyrifos detection at Dunk Island and all other Islands in the Wet Tropics Regions where chlorpyrifos was detected. The maximum concentration in the Tully River was a factor of 17 times higher than was estimated at Dunk Island.

Table 24 The concentration of pesticides and the personal insect repellent DEET ($ng.L^{-1}$) for inshore reef sites in the Wet Tropics Region where PDMS sampling occurred.

	Chlorpyrifos		Pendimethalin		DEET	
Green Island	0.70	January 2010				
Fitzroy Island	0.56	January 2010				
Normanby Island	0.72	January 2010	1.1	May-June 2009	25	March 2010
Dunk Island	0.69	January 2010			40	January 2010

A broad range of other chemicals were detected in the Tully River for which no Guidelines are available. These include an aryloxyphenoxypropionic herbicide (haloxyfop-methyl: 0.63 $ng.L^{-1}$), a dinitroaniline herbicide (pendimethalin: 0.85 – 5.4 $ng.L^{-1}$), two conazole fungicides (propiconazole: 11 – 19 $ng.L^{-1}$ and tebuconazole: 13 – 22 $ng.L^{-1}$), and another organophosphate insecticide (prothiofos: 0.19 – 2.0 $ng.L^{-1}$).

The reporting parameter for PSII herbicides (PSII-HEq Max) are provided for each location for 2009-2010 in Table25 and illustrated with respect to the baseline reporting year (2008-2009) in Figure 57. There were no exceedances of the GBRMPA Guidelines for individual PSII herbicides in 2009-2010.

Table 25 PSII-HEq Max and the PSII-HEq Index Category for these values for all Wet Tropics Sampling sites in the current 2009-2010 monitoring year

Site	PSII-HEq Max 2009-2010 ($ng.L^{-1}$)	PSII-HEq Index Category
Low Isles	6.7	Category 5
Green Island	7.4	Category 5
Fitzroy Island	16	Category 4
Normanby Island	4.0	Category 5
Dunk Island	7.1	Category 5
Tully River	32	Category 4

The inshore reef site with the highest PSII-HEq Max in both the baseline reporting year and 2009-2010 is Fitzroy Island with maximum values in Index Category "4" (10 < HEq ≤ 50) in both years. The dominant contributors to PSII-HEq in the Wet Tropics Region are diuron, hexazinone and atrazine. Normanby Island PSII-HEq is lower in 2009-2010 while Dunk Island is higher. The Tully River site has lower PSII-HEq than 2008-2009, with monitoring discontinued within the wet season.

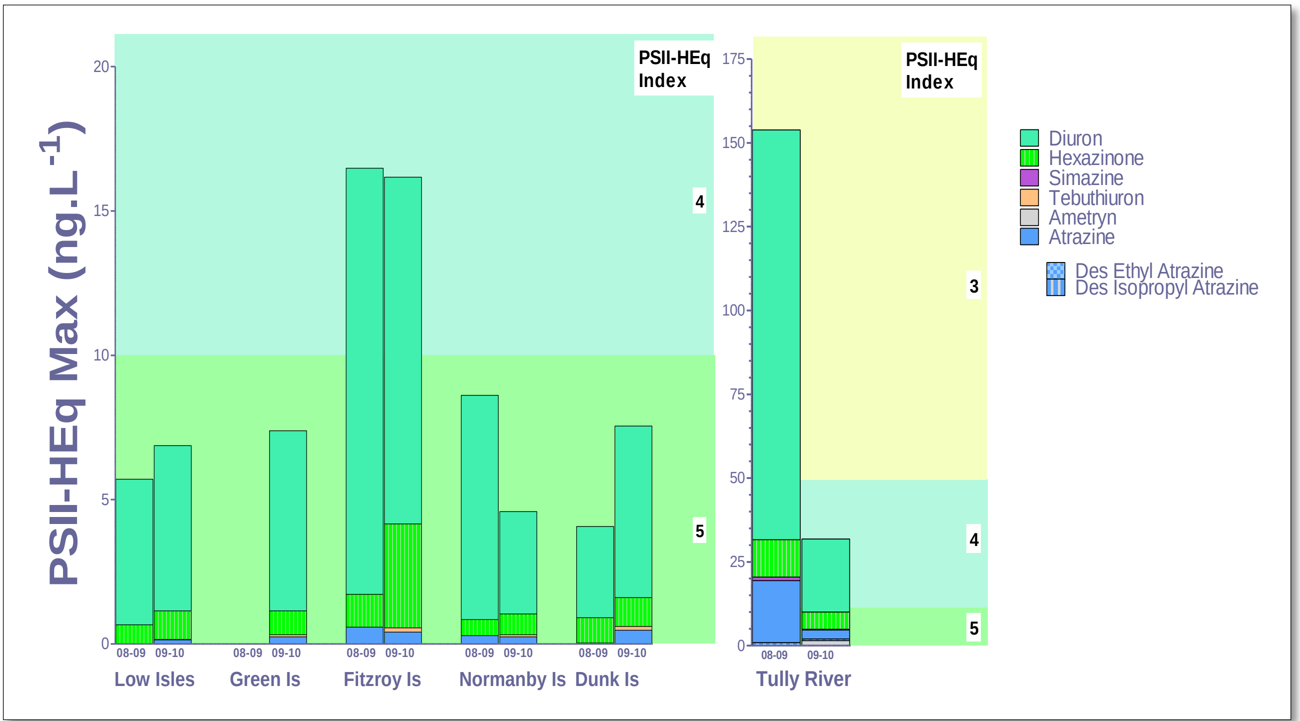

Figure 57 The relative contribution of different PSII herbicides to PSII-HEq Max (ng.L^{-1}) in the baseline reporting year (2008-2009) and 2009-2010 for all sites in the Wet Tropics Region.

The proportion of PSII-HEq within each Index Category across all monitoring years are illustrated in Figure 58. Fitzroy Island has a greater proportion of PSII-HEq in Category "4" within the last three monitoring years compared with 2005-2006 and 2006-2007 (all Category "5"). All other inshore reef sites are more consistently Category "5" sites with only a single monitoring year including Category "4" for Low Isles (2005-2006) and Normanby Island (2007-2008). The Green Island site which commenced within 2009-2010 has all PSII-HEq in Category "5". Dunk Island (2006-2010 with no monitoring in 2007-2008) has consistently been a Category "5" site. The PSII-HEq Index within the Tully River is more variable with a greater or equivalent proportion of all PSII-HEq being Category "4" than Category "5" in the last three monitoring years and also a proportion of all results being Category "3" or even Category "1" in 2007-2008.

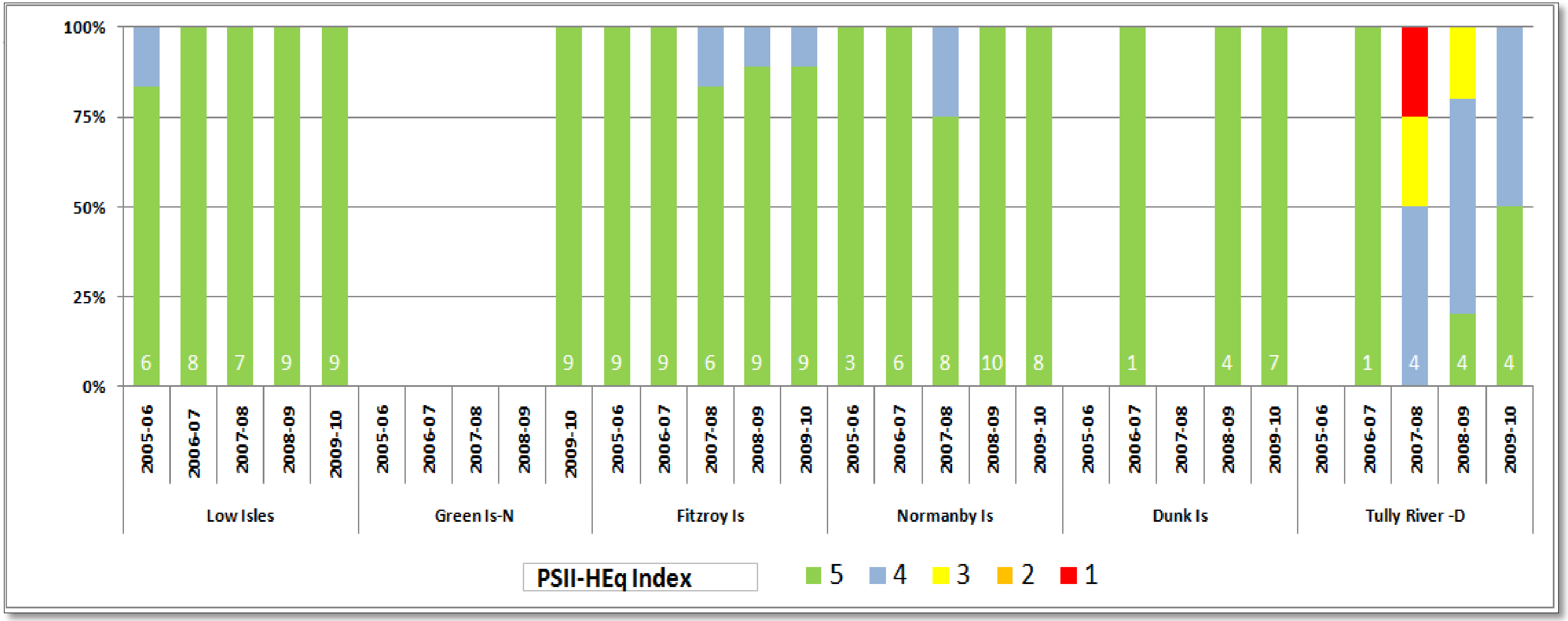

Figure 58 The proportion of all measurements within each monitoring year between 2005 and 2010 which are classified into Categories "1" (HEq > 900 ng.L^{-1}) to "5" (HEq ≤ 10 ng.L^{-1}) of the PSII-HEq Index for Low Isles, Green Island, Fitzroy Island, Normanby Island, Dunk Island and Tully River in the Wet Tropics Region.
"N" and "D" indicate new and discontinued sites respectively

7.3 Burdekin Regional Summary

Sampling sites in the Burdekin Region in 2009-2010 include Orpheus Island, Magnetic Island (Picnic Bay) and Cape Cleveland. The only pesticides detected in the Burdekin Region (Magnetic and Cape Cleveland) using PDMS samplers in the 2009-2010 was metolachlor (5.8 ng.L^{-1}) during a single sampling period at Cape Cleveland. This concentration does not exceed the ANZECC & ARMCANZ IWL of 20 ng.L^{-1} for metolachlor in marine waters. The Haughton River in the Burdekin River has been shown to discharge relatively high loads of metolachlor previously and discharge from this river can impact this site (Davis et al. 2008).

Table 26 PSII-HEq Max and the PSII-HEq Index Category for these values for all Burdekin Region sampling sites in the current 2009-2010 monitoring year

Site	PSII-HEq Max 2009-2010 (ng.L^{-1})	PSII-HEq Index Category
Orpheus Island	100	Category 3
Magnetic Island	8.8	Category 5
Cape Cleveland	9.1	Category 5

Atrazine was frequently the dominant PSII herbicide detected at Cape Cleveland and Magnetic Island which is consistent with relative discharge loads in rivers in this region (Davis et al. 2008). The reporting parameter for PSII herbicides (PSII-HEq Max) are provided for each location for 2009-2010 in Table 26 and illustrated with respect to the baseline reporting year (2008-2009) in Figure 59. There were no exceedances of the GBRMPA (2009) Guidelines for individual PSII herbicides in 2009-2010. All sites within this region have higher PSII-HEq Max in 2009-2010 than in 2008-2009. The maximum for Orpheus Island was almost totally caused by a spike in the concentration of diuron occurring within the dry season. Diuron and atrazine are the dominant contributors to PSII-HEq Max at Magnetic Island and Cape Cleveland. Hexazinone has also contributed a greater proportion to these values at these sites during 2009-2010 compared to 2008-2009.

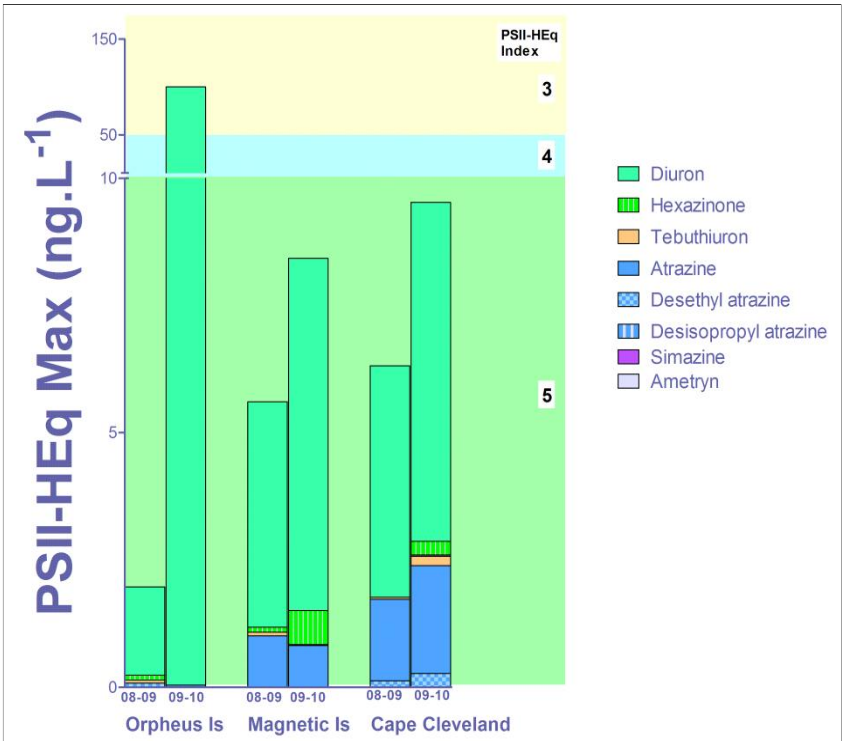

Figure 59 The relative contribution of different PSII herbicides to PSII-HEq Max (ng.L^{-1}) in the baseline reporting year (2008-2009) and 2009-2010 for all sites in the Burdekin Region.

The proportion of PSII-HEq within each Index Category across all monitoring years are illustrated in Figure 60. These indicate that the most frequent Index Category for all sites in the Burdekin Region is Category "5" One single period at Orpheus Island in 2009-2010 during the dry season indicated a time averaged diuron concentration of 100 $ng.L^{-1}$ while the only other herbicide detected in this event was atrazine (< 1 $ng.L^{-1}$) which has resulted in a Category "3". This type of profile with no concomitant increase in the levels of other herbicides is perhaps indicative of more localized sources of diuron within this period. It should be further noted that the monitoring record for Orpheus Island is not continuous within most years. Since monitoring commenced at Cape Cleveland in 2007-08, the PSII-HEq Index has been more consistently Category "5" than Category "4".

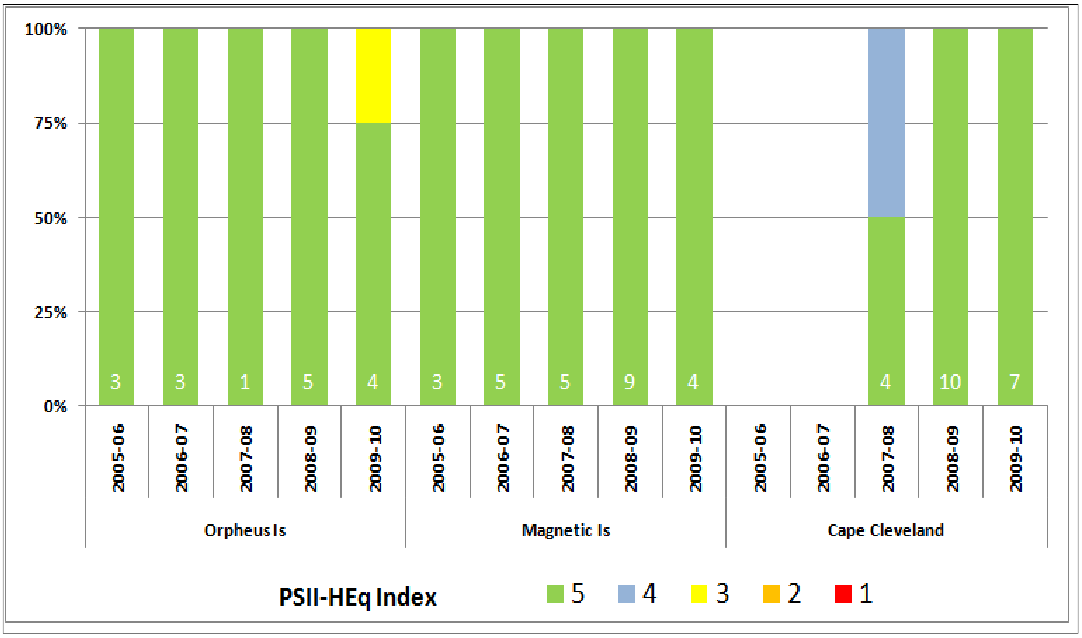

Figure 60 The proportion of all PSII-HEq measurements within each monitoring year between 2005 and 2010 which are classified into Categories "1" (HEq > 900 $ng.L^{-1}$) to "5" (HEq ≤ 10 $ng.L^{-1}$) of the PSII-HEq Index for Orpheus Island, Magnetic Island and Cape Cleveland.

7.4 Mackay Whitsunday Regional Summary

Sites within the Mackay Whitsunday Region in 2009-2010 included Outer Whitsunday, Daydream Island, Pioneer Bay, Sarina Inlet and the Pioneer River. Of these sites Outer Whitsunday, Pioneer Bay and Sarina Inlet are current sites while Daydream Island and the Pioneer River were discontinued within 2009-2010. PDMS sampling only occurred at Outer Whitsunday and in the Pioneer River. No pesticides were detected at Outer Whitsunday in 2009-2010 using PDMS, while chlorpyrifos, dieldrin and pendimethalin had maximum concentration estimates of 0.69, 2.9 and 7.7 ng.L^{-1} respectively in the Pioneer River. This maximum chlorpyrifos concentration exceeds ANZECC & ARMCANZ Guidelines for 99 % species protection in marine and freshwaters.

The reporting parameter for PSII herbicides (PSII-HEq Max) are provided for each location for 2009-2010 in Table 27 and illustrated with respect to the baseline reporting year (2008-2009) in Figure 61. Sites within this region have a wide range of Index Categories from “4” to “1” which is in contrast to the Burdekin Region (“5” to “3”), Wet Tropics Region (“5 to “4”) and Cape York Region (“5”). When the discontinued sites (Pioneer River and Daydream Island) are excluded this range is “4 to 2”. The PSII herbicides which contribute most significantly to PSII-HEq in the region are diuron, atrazine and hexazinone.

Table 27 PSII-HEq Max and the PSII-HEq Index Category for these values for all Mackay Whitsunday Region sampling sites in 2009-2010

Site	PSII-HEq Max 2009-2010 (ng.L^{-1})	PSII-HEq Index Category
Outer Whitsunday	35	Category 4
Daydream Island	57	Category 3
Pioneer Bay	43	Category 4
Sarina Inlet	495	Category 2
Pioneer River	970	Category 1

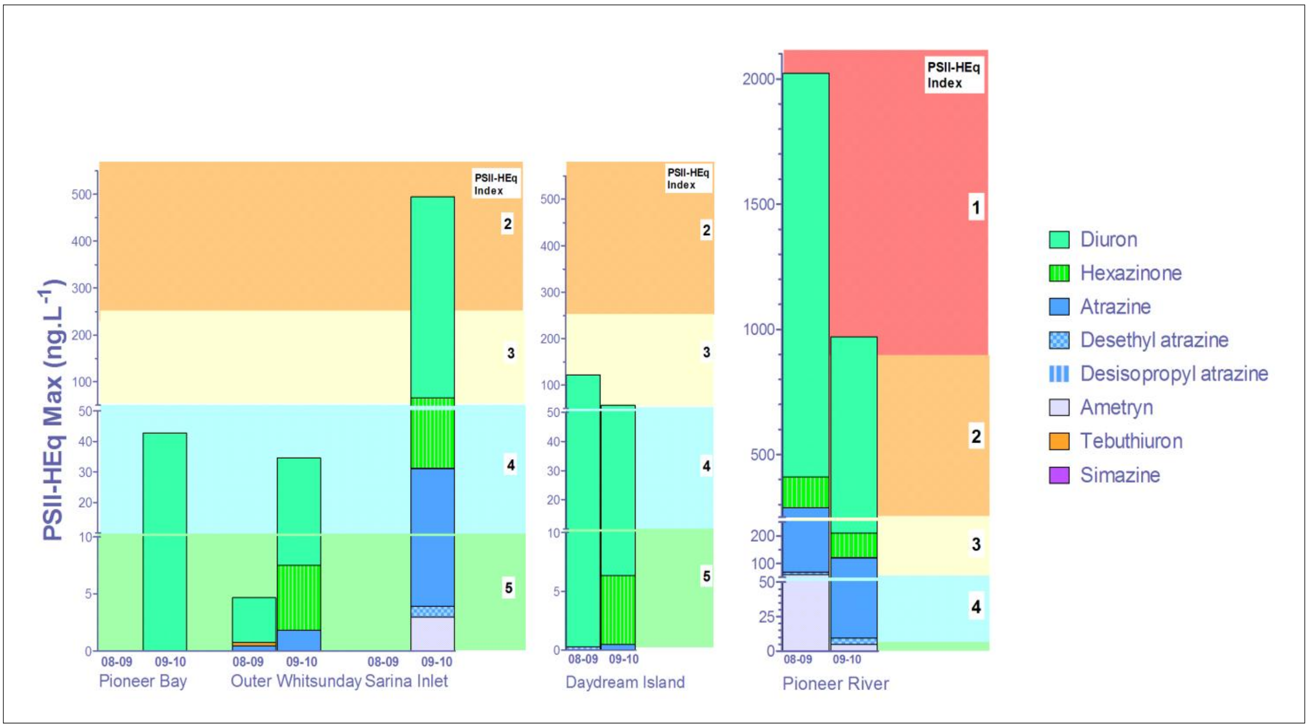

Figure 61 The relative contribution of different PSII herbicides to PSII-HEq Max (ng.L^{-1}) in the baseline reporting year (2008-2009) and 2009-2010 for all sites in the Mackay Whitsunday Region

The maximum atrazine (690 ng.L^{-1}) and diuron (761 ng.L^{-1}) concentrations in the Pioneer River were the only exceedances for PSII herbicides in the Mackay Whitsunday Region of ANZECC & ARMCANZ Guideline (0.7 µg.L-1) or IWL (0.2 µg.L^{-1}) values for these compounds respectively.

The proportion of PSII-HEq within each Index Category across all monitoring years are illustrated in Figure 62. These contain the two new sites Pioneer Bay and Sarina Inlet which are inshore sites in relative proximity to the coast. Pioneer Bay is more consistently Category “4” while Sarina Inlet has a higher proportion of Category “5” with both Category “3” and “2” sampling periods occurring within the west season of 2009-2010. The quality of the sampling record has not been good for the Whitsunday Island sites with between 3 – 5 and 2 -4 monitoring periods per year at Outer Whitsunday and Daydream Islands respectively since monitoring began. Trend evaluation at these sites based on these figures is therefore not advisable. It is however interesting to note that Category “3”Index have been observed at the Daydream Island site in the past two monitoring years. The Pioneer River site has a relatively good sampling record between2005 and 2010. This river has had between 11 and 33 % of Category “1” sampling periods in each year. Monitoring at more sites within this region with an emphasis on selecting and retaining locations which can return more reliable monitoring data is suggested to more completely characterize the risk of exposure to PSII-herbicides within this region. Greater integration with flood plume monitoring studies in this area would enhance our understanding of both acute and chronic exposures within this region.

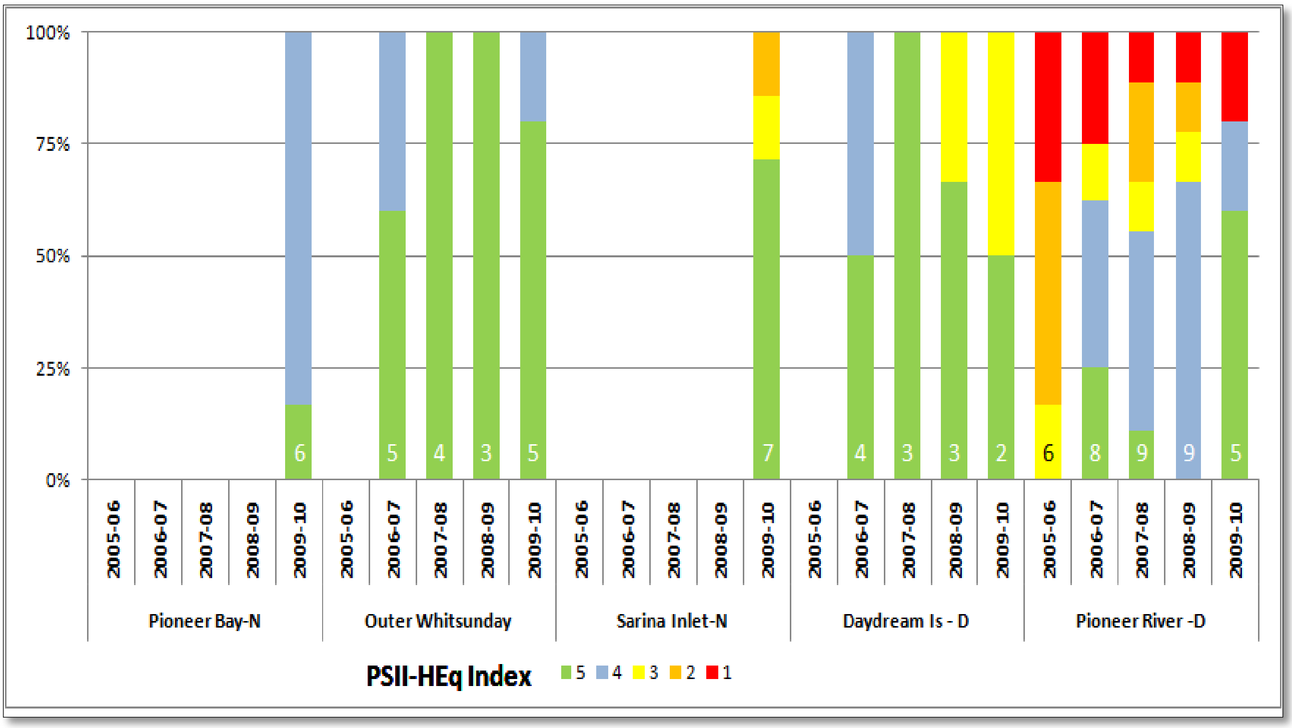

Figure 62 The proportion of all PSII-HEq measurements within each monitoring year between 2005 and 2010 which are classified into Categories “1” (HEq > 900 ng.L^{-1}) to “5” (HEq ≤ 10 ng.L^{-1}) of the PSII-HEq Index for Pioneer Bay, Outer Whitsunday, Daydream Island and the Pioneer River in the Mackay Whitsunday Region.
“N” and “D” indicate new and discontinued sites in 2009-2010 respectively”

7.5 Fitzroy Regional Summary

North Keppel Island is the only site in the Fitzroy Region. This site had a PSII-HEq Max of 8.7 ng.L^{-1} in the 2009-2010 which indicates a Category "5" PSII-HEq Index for this location (Table 28).

Table 28 PSII-HEq Max and the PSII-HEq Index Category for these values for North Keppel Island in 2009-2010

Site	PSII-HEq Max 2009-2010 (ng.L^{-1})	PSII-HEq Index Category
North Keppel Island	8.7	Category 5

The reporting parameter for PSII herbicides (PSII-HEq Max) are provided for North Keppel Island in 2009-2010 (8.7 ng.L^{-1}) and the baseline reporting year 2008-2009 (1.1 ng.L^{-1}) in Figure 63. The dominant PSII herbicide contributing to PSII-HEq in both years is diuron with atrazine, hexazinone and tebuthiuron also contributing to the observed maximum in the current year. The monitoring record in the wet season of the previous monitoring year was not complete however.

The increase in PSII-HEq in 2009-2010 may be attributed to above median discharge in the Fitzroy River with respect to the previous year and increasing concentrations of diuron. This was the first year that the PSII herbicide hexazinone (1.6 – 2.1 ng.L^{-1}) has been detected at North Keppel Island. The maximum concentrations of both atrazine (8.4 ng.L^{-1}) and tebuthiuron (14 ng.L^{-1}) exceed the maximum concentration of diuron (6.4 ng.L^{-1}) in 2009-2010. The maximum concentration estimated for tebuthiuron occurred in the month just prior (March 2010) to PSII-HEq Max (April 2010) when the maximum concentrations of diuron and atrazine occurred. The North Keppel Island site has been a consistently Category "5" (Figure 64) site within the PSII-HEq Index since 2005 which is similar to Pixies Garden in the Cape York Region.

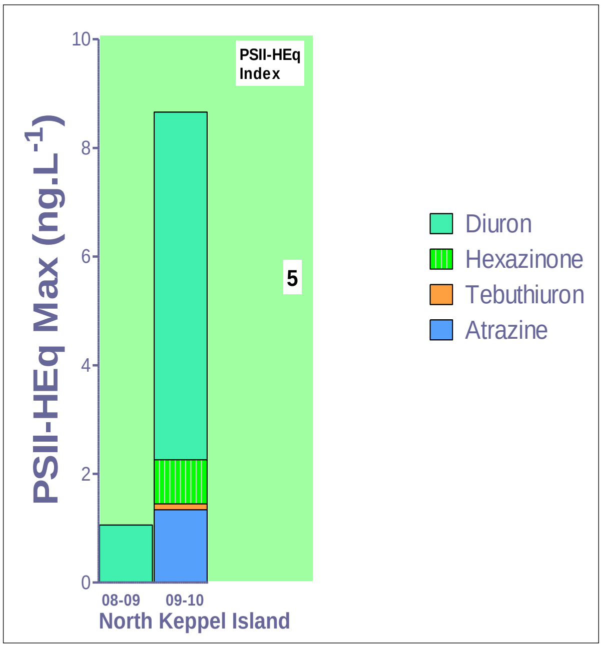

Figure 63 The relative contribution of different PSII herbicides to PSII-HEq Max (ng.L^{-1}) in the baseline reporting year (2008-2009) and 2009-2010 for North Keppel Island in the Fitzroy Region

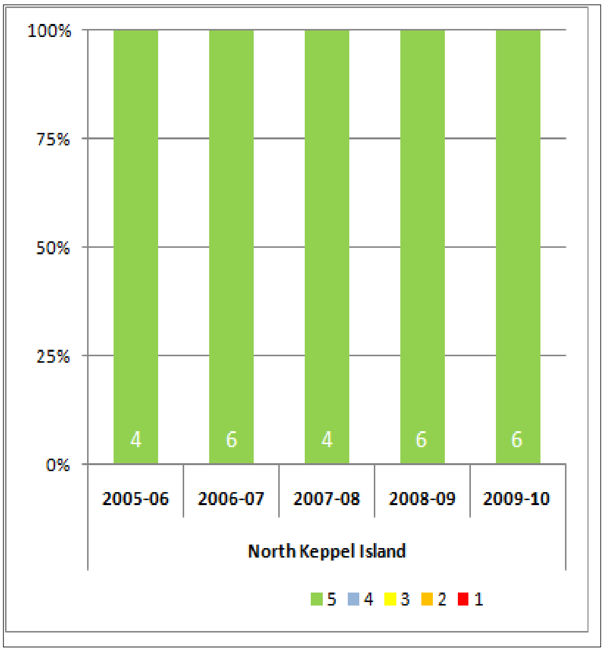

Figure 64 The proportion of all PSII-HEq measurements within each monitoring year between 2005 and 2010 which are classified into Categories "1" (HEq > 900 ng.L^{-1}) to "5" (HEq ≤ 10 ng.L^{-1}) of the PSII-HEq Index for North Keppel Island in the Fitzroy Region.

8 DISCUSSION

8.1 GBR Regional Summary 2009-2010

PSII-HEq Max determined for all sampling sites in 2009–2010 where PSII herbicides were detected (Figure 65) indicate regional differences in the exposure of inshore waters of the GBR. PSII herbicides were not detected at Pixies Garden in the Cape York Region in 2009-2010. The maximum value is used as a reporting parameter since it represents the worst case exposure to PSII herbicides for each location and demonstrates the highest potential for effects on the PSII-HEq Index. These regional PSII-HEq Max when assessed against the PSII-HEq Index ranged from Categories “5” (Cape York), “5 – 4” (Wet Tropics), “5 – 3” (Burdekin), “4 – 1” (Mackay Whitsunday) and “5” (Fitzroy). In the previous reporting year both the Cape York and Fitzroy Regions to the north and south of the GBR respectively had the lowest levels of PSII herbicides. PSII-HEq Max has increased by a factor of 8 at North Keppel Island in the Fitzroy Region in 2009-2010. This increase is associated with above median discharge in the Fitzroy River in 2009-2010 and increased concentrations of diuron and hexazinone with respect to all previous years of monitoring. However the monitoring record in the previous year was incomplete in the wet season. Both of these regions have only been represented by one site within these regions.

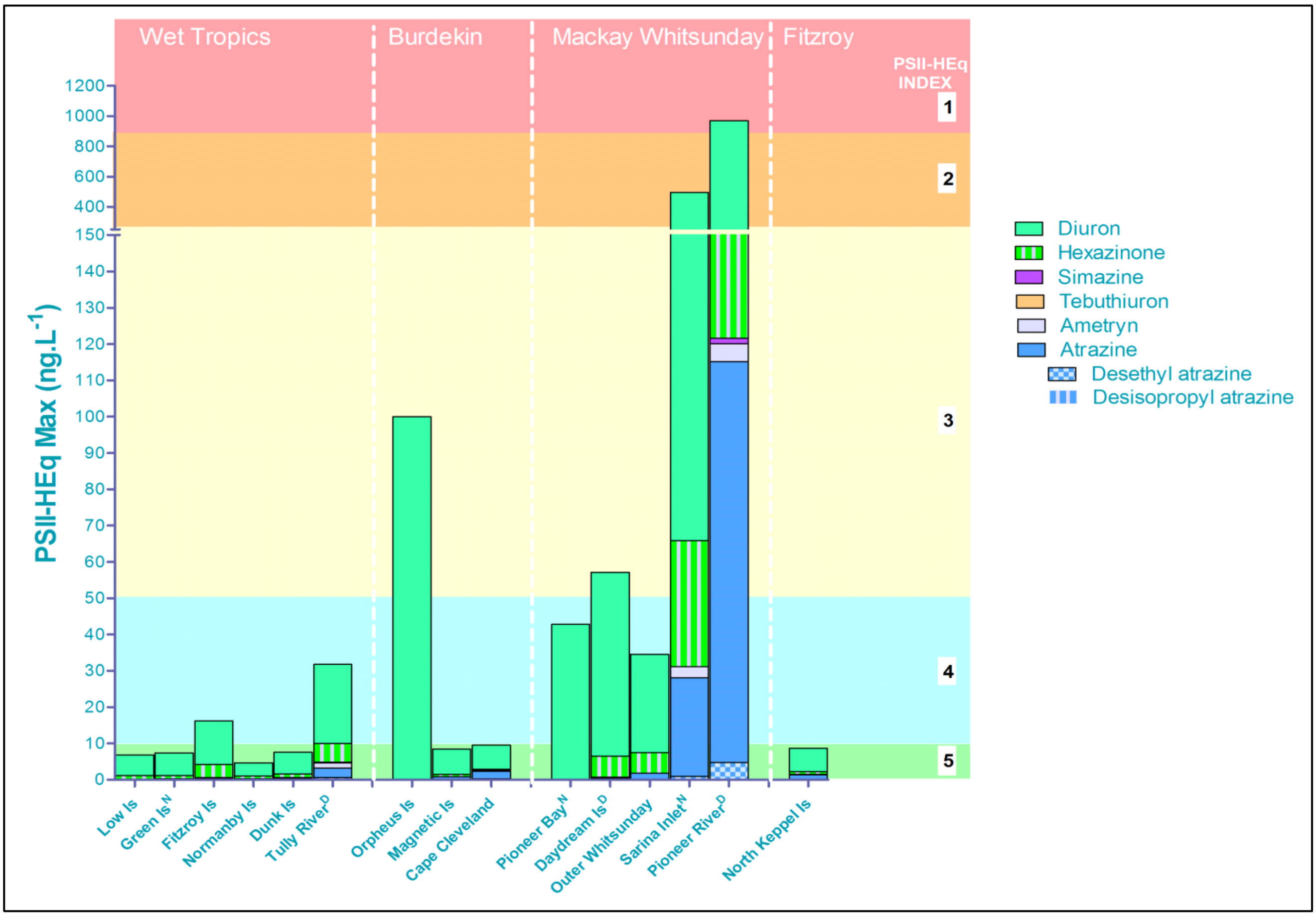

Figure 65 PSII-HEq Max (ng.L^{-1}) in the 2009-2010 monitoring year for all sites in the Wet Tropics, Burdekin and Mackay Whitsunday and Fitzroy Regions

The Mackay Whitsunday Region has been identified as a High Risk region previously (Brodie and Waterhouse 2009) and in terms of PSII herbicides this is reflected in higher PSII-HEq Max than all other regions in 2009-2010. This is in spite of the relatively poor sampling record for sites in the Whitsunday Islands group (Daydream Island and Outer Whitsunday). Approximately 56 % of the catchment area of this region is used for agricultural production with sugar cane and cattle grazing being the dominant activities. Two near shore sites (Pioneer Bay and Sarina Inlet) were commenced in this region in 2009-2010. Concentrations estimated at Sarina Inlet to the south indicate higher potential for biological effects than concentrations monitored at Pioneer Bay to the north of the region with a Category "2" PSII-HEq Max. Although concentrations in Pioneer Bay are more consistently Category "4" in dry season monitoring compared to Sarina Inlet with Category "5". The Pioneer River within this region had a Category "1" PSII-HEq Max, and the concentrations of PSII herbicides can be up to several orders of magnitude higher than most other locations including the Tully River (up to a factor of 40) in the Wet Tropics Region on a consistent basis. Seagrass cover in areas of the Mackay Whitsunday Region such as Hamilton Island and Sarina Inlet have been in decline since 2005, while in Pioneer Bay to the north the trend is more variable (McKenzie et al. 2010). The PSII-HEq Max at sites including Sarina Inlet (Category "2") and Daydream Island (Category "3") when assessed against the Index indicate the potential for effects on diatoms, seagrass and corals in the Mackay Whitsundays.

The dominant contributor to PSII-HEq at all locations is the phenyl urea herbicide diuron. This assessment reflects both its relative abundance in all regions in 2009-2010 and its potency as an inhibitor of the photosystem II pathway. Hexazinone (triazinone herbicide) and atrazine (chlorotriazine herbicide) are also relatively dominant contributors albeit to a lesser extent than diuron and this contribution varies on a regional basis, with hexazinone contributing to a greater extent in the Wet Tropics and Mackay Whitsunday Regions. These PSII herbicides which contribute the most to PSII-HEq (diuron, atrazine and hexazinone) have demonstrated a strong land use signal in waterways draining catchments with under sugar cane cultivation (> 10 %) (Lewis et al. 2009). Maximum diuron concentrations at current inshore GBR sites in the MMP ranged from 3.6 – 12 $ng.L^{-1}$, 6.7 – 100 $ng.L^{-1}$, 27 – 429 $ng.L^{-1}$ and 6.4 $ng.L^{-1}$ in the Wet Tropics, Burdekin, Mackay Whitsunday and Fitzroy (one site) Regions respectively.

Diuron is a pre- and post-emergent herbicide widely used in sugarcane production and some tropical fruit crops and is also to control weeds and algae around water bodies and in antifoulant paints. The Australian Pesticides and Veterinary Medicines Authority (APVMA) is currently conducting a review of diuron and released preliminary findings of this review in 2005. These preliminary findings included that "environmental exposure from uses of diuron at current label rates on sugarcane, cotton, citrus and horticultural crops (apples, pears, bananas, pawpaw, coffee, grapes and pineapples) is likely to have an unacceptable environmental impact" (APVMA 2005). The risks to reef ecosystems as a whole of exposure to mixtures of PSII herbicides and the potential for synergistic effects with concomitant changes in other water quality parameters (Harrington et al. 2005) remain largely uncharacterized. The time integrated concentration estimates for these individual PSII-herbicides in 2009-2010 at inshore GBR sites have not exceeded GBRMP Guidelines. However potentially biologically relevant concentrations of PSII herbicides expressed as PSII-HEq higher than Category "5" (> 10 $ng.L^{-1}$) have been determined at inshore GBR sites in the Wet Tropics, Burdekin and Mackay Whitsunday Regions in 2009-2010. The only exceedance of Guidelines (99 % ANZECC & ARMCANZ) for PSII herbicides was observed for atrazine (0.7 $\mu g.L^{-1}$) in the Pioneer River in December 2009.

The relative abundance of individual PSII herbicides can exhibit variation across sites in the different regions of the GBR. These differences may be related to dominant agricultural land use within these regions (Lewis et al. 2009; Packett et al. 2009). Notably, atrazine is frequently the dominant herbicide detected at sites in the Burdekin Region (Magnetic Island and Cape Cleveland) or can be the dominant herbicide during discharge events at North Keppel Island in the Fitzroy Region. However the highest maximum concentrations of atrazine have been determined at sites in the Mackay Whitsunday Region (i.e. Sarina Inlet 170 $ng.L^{-1}$). Maximum concentrations of tebuthiuron were observed in the Burdekin Region (2.2 – 4.7 $ng.L^{-1}$) and at North Keppel Island (14 $ng.L^{-1}$) in the Fitzroy Region which had the highest concentration in 2009-2010. The GBRMPA Guideline for tebuthiuron of 20 $ng.L^{-1}$ was approached at this location. Tebuthiuron is used to control tree regrowth and woody weeds on grazing lands and has been found predominantly downstream of grazing lands (Lewis et al. 2009). Hexazinone maximum concentrations ranges are higher in the Wet Tropics Region (2.2 – 9.5 $ng.L^{-1}$) and in the Mackay Whitsundays (11 -91 $ng.L^{-1}$). Ametryn was detected only at Cape

Cleveland (0.10 ng.L^{-1}) and Sarina Inlet (2.3 ng.L^{-1}) at inshore GBR sites in 2009-2010. Simazine was detected only at Magnetic Island and Cape Cleveland in the Burdekin region. All of the above assessments only consider current sites and not discontinued sites such as the Rivers and Daydream Island.

The concentrations of PSII herbicides can increase between 1 and 2 orders of magnitude between dry and wet sampling periods or are detected only in wet sampling periods within a given monitoring year. Any assessment of long term trends within regions is complicated by observed relationships between peak discharge events (i.e. flow variability (Bainbridge et al. 2009b)) within specific monitoring years which may influence PSII-HEq Max in each year. When rainfall is concentrated in specific areas of catchments where dominant land use differs in these regions this can also contribute to variability in loads in these regions (Packett et al. 2009). Both specific catchment related events such as these and gaps in the monitoring record at sampling sites will need to be considered in order to properly assess both short term variation and long term trends. It is also important to recognize that more localized sources may be impacting sites which can result in non-catchment derived increases which may obscure relationships between catchment derived loads and herbicide residues monitored on the GBR. For example the PSII-HEq Max for the Orpheus Island site in the Burdekin Region in 2009-2010 was derived from a spike in the concentration of diuron alone which is perhaps indicative of a more localized point source rather than a diffuse runoff derived source from adjacent catchments.

Limited monitoring (fewer sites) of more relatively hydrophobic chemicals is undertaken within the MMP. Chlorpyrifos concentrations estimated at several inshore reef sites in the Wet Tropics Region (Green Island, Fitzroy Island, Normanby Island and Dunk Island) exceed the GBRMPA Guideline (0.5 ng.L^{-1}) in 2009-2010. These were all observed during January 2010 while ANZECC & ARMCANZ (99 %) Guidelines were consistently exceeded in the Tully River (12 ng.L^{-1}) with the maximum concentration occurring in the December 2009-January 2010 sampling period. Diazinon concentrations in the Tully River (46-55 ng.L^{-1}) also exceed ANZECC & ARMCANZ guidelines. Chlorpyrifos concentrations in the Pioneer River 0.25 – 0.69 ng.L^{-1} were lower but also exceed the 99 % species protection freshwater guideline. A larger range of insecticides, herbicides and fungicides were detected in the Tully River than in the Pioneer River in 2009-2010.

8.2 Uncertainties in Monitoring Results & Reporting Metric for PSIIs

Passive samplers can be used to estimate either a time integrated or equilibrium phase concentration of chemicals in water. Time integrated concentration estimates are similar to an event mean concentration across the deployment period while equilibrium phase estimates will fluctuate in response to changes in the concentration in water. Sampling rates (volume of water sampled per day) are required to estimate the concentration in water from the amount of chemical accumulated in a passive sampler during linear phase sampling (time integrated). These sampling rates are typically determined in laboratory calibration studies where the samplers are deployed under constant concentration conditions and at a defined flow velocity (or several flow velocities) and for a limited number of chemicals. Constant concentrations and defined flow rates are rarely encountered under field conditions. Limited studies have been conducted to model or evaluate the performance of passive sampler derived concentration estimates under varying concentration scenarios (Shaw and Müller 2009; Hawker 2010). In spite of these uncertainties concentration estimates derived using passive samplers show reasonable agreement with grab samples taken during deployment periods on the GBR (Shaw et al. 2010). This type of co-sampling (passive + grab sampling) is often undertaken to validate laboratory derived calibration data such as sampling rates. It is important to recognise however that grab samples also have their own inherent limitations associated with sampling frequency (Ort et al. 2010; Rabiet et al. 2010) and sample handling which may create artefacts in the concentration profiles but may also be limited by issues with sensitivity of detection. The monitoring results derived for the MMP would benefit. from improvements in and validation of the calibration data used to derive the concentration in water. Individual PSII herbicide concentrations estimated using passive sampling techniques were converted to PSII-HEq using a relatively limited relative potency dataset (preliminary consensus values) with respect to the reference PSII herbicide diuron. This relative potency dataset will continue to increase and our understanding of the effects of exposure to mixtures of PSII herbicides in association with other stressors will continue to improve. It is likely that this Index would benefit from scientific review and revision in the future.

9 FURTHER WORK

There are a range of areas which require further work. Several of these relate to quantifying the level of uncertainty in passive sampler derived concentration estimates. Concentrations in water are estimated using sampling rates. Sampling rates are available for relatively few chemicals within the different samplers and are often assumed based on similar physico-chemical properties. In order to address this issue a number of steps are currently being taken to derive chemical specific sampling rates in different passive samplers. These include:

i. A collaborative research project with DERM to derive compound specific sampling rates for chemicals of interest in GBR catchments for PDMS samplers.
ii. An Australian Research Council funded project which develops and calibrates aquatic passive samplers for emerging contaminants.
iii. A case study which applies passive flow monitors (PFMs) as an in-situ calibration device to account for the influence of flow on sampling rates (Appendix E).

Some preliminary integration of temporal and seasonal PSII herbicide concentrations and discharge data in adjacent catchments has been undertaken in this report. It is however necessary to also integrate information with respect to loads within these discharges and also the influence and extent of flood plume events in different years. This may not always be possible until the following monitoring year. More cohesive integration of different components of the MMP such as data with respect to terrestrial runoff (flood plumes) and other water quality parameters is required for this project. This integration would provide not only information with respect to plume extent but would also allow for an appropriate comparison of both event sampling (several "grab" samples, multiple locations, often only one day of sampling) and time integrated passive sampler (single monthly and two monthly deployments at fixed locations) derived concentration estimates at the same locations and within the same sampling periods. This information could be used to obtain a more complete understanding of how acute and chronic exposures differ at these sampling sites.

Some of this integration may be achieved in the 2010 – 2011 monitoring year through the following projects either underway or being planned in collaboration with other MMP providers including the (i) Australian Centre for Tropical and Freshwater Research , James Cook University and also with (ii) CSIRO. These projects include:

i. Honours project commencing in 2011 which will integrate passive sampling with grab sampling in terrestrial runoff events/flood plume waters. This project will provide both analytical and bioanalytical (effect based) assessments of these waters using both sampling techniques.
ii. Relationships between remote sensing derived water quality parameters (Brando et al. 2010) and time integrated PSII herbicide concentrations at sites within the GBR.

The first of these projects is in the planning stages while the second project is already underway and an preliminary assessment of results was presented at a recent conference. This work appears promising in that statistically significant relationships are indicated between herbicide concentrations and specific water quality parameters at different sites in the GBR. Together these projects will help advance our understanding of how reefs are exposed to PSII herbicides (chronic vs. acute exposures) together with other water quality parameters, quantify the differences between these two monitoring techniques in-situ and measure effects relating to these exposures.

10 APPENDIX A: ANALYTE LIST FOR GCMS ANALYSIS & ADDITIONAL LORS (NON-TARGET CHEMICALS)

Table 29 GCMS analyte list for PDMS extracts with cells shaded grey to indicate chemicals which are not calibrated within the fraction collected during gel permeation (size exclusion) chromatography of extracts and cells shaded blue to indicated industrial chemicals/personal care products which may also be reported along with pesticides in the MMP results

ACEPHATE	DICHLORVOS	METHAMIDOPHOS
ALDRIN	DICLOFOP METHYL	METHIDATHION
AMETRYN	DICOFOL o,p	METHOMYL
AMITRAZ	DICOFOL p,p bd	METHOPRENE
ATRAZINE	DIELDRIN	METHOXYCHLOR
AZINPHOS ETHYL	DIMETHOATE	METOLACHLOR
AZINPHOS METHYL	DIMETHOMORPH E,Z	METRIBUZIN
BENALAXYL	DIOXATHION	MEVINPHOS z+E
BENDIOCARB	DISULFOTON	MOLINATE
BIFENTHRIN	Diuron bd	MONOCROTOPHOS
BIORESMETHRIN	ENDOSULFAN alpha	MUSK KETONE
BITERTANOL	ENDOSULFAN beta	MUSK XYLENE
BROMACIL	ENDOSULFAN ETHER	NICOTINE
BROMOPHOS ETHYL	ENDOSULFAN LACTONE	NONACHLOR cis
CADUSAPHOS	ENDOSULFAN SULPHATE	NONACHLOR trans
CAPTAN	ENDRIN	OMETHOATE
CARBARYL	ENDRIN ALDEHYDE	OXADIAZON
CARBOPHENOTHION	ETHION	OXYCHLOR
CHLORDANE cis	ETHOPROP	OXYDEMETON METHYL
CHLORDANE trans	ETRIMIPHOS	OXYFLUORFEN
CHLORDENE	FAMPHUR	PARATHION ETHYL
CHLORDENE EPOXIDE	FENAMIPHOS	PARATHION METHYL
CHLORDENE, 1-HYDROXY	FENCHLORPHOS	PENDIMETHALIN
CHLORDENE, 1-OH-2,3-EPOXY	FENITROTHION	PERMETHRIN isomers
CHLORFENVINPHOS e+Z	FENTHION ETHYL	PHENOTHRIN isomers
CHLOROTHALONIL	FENTHION METHYL	PHORATE
CHLORPYRIFOS	FENVALERATE isomers	PHOSMET
CHLORPYRIFOS ME	FIPRONIL	PHOSPHAMIDON peak1 **200**
CHLORPYRIFOS OXON	FLUAZIFOP BUTYL	PHOSPHAMIDON peak2 **800**
COUMAPHOS	FLUOMETURON	PHOSPHATE TRI-n-BUTYL
CYFLUTHRIN isomers	FLUVALINATE isomers	PIPERONYL BUTOXIDE
CYHALOTHRIN isomers	FURALAXYL	PIRIMICARB
CYPERMETHRIN isomers	GALOXOLIDE	PIRIMIPHOS METHYL
DCPP isomers	HALOXYFOP 2-EtOEt	PROCYMIDONE
DDD o,p	HALOXYFOP METHYL	PROFENOPHOS
DDD p,p	HCB	PROMETRYN
DDE o,p	HCH-a	PROPAGITE
DDE pp	HCH-b	PROPANIL
DDT o,p	HCH-d	PROPAZINE
DDT p,p	HEPTACHLOR	PROPICONAZOL isomers
DEET	HEPTACHLOR EPOXIDE	PROPOXUR
DELTAMETHRIN isomers	HEXAZINONE	PROTHIOPHOS
DEMETON-S-METHYL	IPRODIONE	PYRAZAPHOS
DESETHYLATRAZINE	ISOPHENOPHOS	ROTENONE
DESISOPROPYLATRAZINE *900*	LINDANE (HCH-g)	SIMAZINE
DIAZINON	MALATHION	SULPROFOS

DICHLOROANILINE 3,4	METALAXYL	TCEP
TEBUTHIURON		
TEBUCONAZOLE		
TCPP		
TEMEPHOS		
TEP		
TERBUPHOS		
TERBUTHYLAZINE		
TERBUTRYN		
TETRACHLORVINPHOS		
TETRADIFON		
TETRAMETHRIN isomers		
THIABENDAZOLE		
TONALID		
TRANSFLUTHRIN		
TRIADIMEFON		
TRIADIMENOL ISOMERS		
TRIALLATE		
TRIFLURALIN		
VINCLOZALIN		

Table 30 Limits of reporting for chemicals which are reported but not specifically targeted under the MMP

Organic compounds	LOR ng.L^{-1}		
	SPMD	PDMS	ED
Galaxolide		<0.5	
Tonalide		<0.5	
DEET		<25	
Fipronil		<0.5	
Chlorothalonil			
Cypermethrin		<0.5	
Haloxyfop methyl		<0.5	
Piperonyl Butoxide		<10	
Permethrin		<0.5	
TCPP		<10	
Terbutryn			
3,4-dichloroaniline		<10	

11 APPENDIX B: SUPPORTING LITERATURE FOR DERIVATION OF PSII-HEQ INDEX

Table 31 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 a metric for reporting purposes

			Supporting Literature with Respect to the Reference Chemical Diuron				
Category	**PSII-HEq Range (ng.L^{-1})**	**Description**	**Species**	**Effects Concentration (ng.L^{-1})**	**Endpoint**	**Toxicity measure**	**Reference**
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	**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
			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	↓	LOEC	Negri *et al* 2005

		animals are protected, using diuron as the reference chemical.			Metamorphosis		
			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. banksii	1650	↓ photosynthesis	EC50	Seery *et al* 2006
			Red Algae				
			P. onkodes	2900	↓ photosynthesis	LOEC	Harrington *et al* 2005
			Diatoms				
			Navicula sp	2900	↓ photosynthesis	IC50 Acute, 6 m	Magnusson *et al* 2006
			P. tricornutum	3300	↓ photosynthesis	I50	Schreiber *et al* 2002
			Mangroves				
			A. marina	1100	Health	NOEC	Duke *et al* 2003, 2005
			A. marina	1500	Reduced health	LOEC	Duke *et al* 2003, Bell & Duke 2005
			A. marina	2000	Dieback/	Mortality	Duke et al 2003, Bell & Duke

					absence		2005
			A. marina	1500	Reduced health	LOEC	Duke *et al* 2003, Bell & Duke 2005

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Organisms and comments	**Toxicity (ug.L^{-1}) test substance (95% CL)**	**Year reported**	**US EPA category**
Fish			
M. cephalus (striped mullet) tech. (95%) static	6300 (NR) 48h, acute	1986	S
C. variegates (Sheephead minnow) 99% active constituent; static	6700 (NR) 96h, acute NOEC = 3600	1986	Core
Invertebrates			
M. bahia (Mysid shrimp) 99% active constituent; static	LC50 = 110 96h, acute NOEC = 1000	1987	Core
M. bahia (Mysid shrimp) 96.8% active constituent; early life stage; static	28d LOEC = 110 560 NOEC = 270	1992	Core
P. aztecus (Brown shrimp) 95% active constituent; flow through	LC50 = 1000 48h acute	1986	S
C. virginica (Eastern oyster) 96.8% active constituent; flow through	EC50 = 4800 96h, acute NOEC = 2400	1991	Core
C. virginica (Eastern oyster) 96.8% active constituent; flow through	EC50 = 3200 96h acute	1986	Core
Algae			
D. tertiolecta 95% active constituent; static	EC50 = 20 240h chronic	1986	S
Platmonas sp 95% active constituent; static	EC50 = 17 72h chronic	1986	S
P. cruentum (red algae) 95% active constituent; static	EC50 = 24	1986	S

	72h chronic		
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

12 APPENDIX C: SITE HISTORY & DEPLOYMENT DETAILS

Table 32 Sampling history for sites monitored with passive samplers together with the number of samplers* sent and deployed and the number of samples subsequently analysed for each location.

Region	Site	Volunteer	Sent	Deployed	Analysed	Sampling History
Cape York	Pixies Garden	Mike Ball Dive Expeditions	6	6	5	Established 2006, location changed September 2007, discontinued after April 2010
Wet Tropics	Low Isles	Quicksilver Connections (transport & logistics) & Low Isles Caretakers (deployment)	9	9	9	Established 2005; Current site
	Green Island	Green Island Resort	9	9	9	Established 2009
	Fitzroy Island	Raging Thunder Pty Ltd (transport, logistics); Fitzroy Island Resort (deployment)	10	10	10	Established 2005
	Normanby Island	Frankland Island Cruise & Dive	9	9	8	Established 2005
	Dunk Island	Mission Beach/Dunk Island Water Taxi	8	8	7	Established 2007; discontinued and re-established September 2008
	Tully River	Cardwell Shire Council	5	4	4	Established 2007, discontinued after January 2010
Burdekin	Orpheus Island	Orpheus Island Research Station, Orpheus Island Resort (May 2009-February 2010)	4	4	4	Established 2005; discontinued 2007; re-established 2008; Orpheus Island research stations re-established by GBRMPA March 2010.
	Magnetic Island	GBRMPA/REEF Safari Diving	7	5	4	Established 2005, GBRMPA established REEF Safari Diving in deployment role in February 2010.
	Cape Cleveland	GBRMPA/AIMS	7	7	7	Established 2007
Mackay Whitsunday	Outer Whitsunday	Hamilton Island Resort	8	7	5	Established 2006; GBRMPA have retrained site personnel
	Daydream Island-IW	QPWS/GBRMPA/Whitsunday Moorings	5	4	2	Established 2006; Difficulties maintaining site personnel. Discontinued from March 2010
	Pioneer Bay-IW	Whitsunday Moorings	7	6	6	Established 2009
	Sarina Inlet	Sarina Bait Supplies	9	9	7	Established 2009
	Pioneer River	DERM	7	7	5	Established 2005; Discontinued in January 2010.
Fitzroy	North Keppel Island	North Keppel Island Education Centre	7	7	6	Established 2005

IW = Inner Whitsunday; *These numbers relate only to ED samplers which are deployed throughout the year

Table 33 Passive sampler deployments* at all sites during 2009-2010, where concentrations in water could be determined. The length of each of these deployment periods (days), along with any gaps in the sampling record and an indication of when sites were discontinued or new sites were commenced are also provided.

REGION	SAMPLINGSITE	08-09	CURRENT 2009-2010 MONITORING YEAR												10-11
			DRY						WET						
		APR-09	MAY-09	JUN-09	JUL-09	AUG-09	SEP-09	OCT-09	NOV-09	DEC-09	JAN-10	FEB-10	MAR-10	APR-10	MAY-10
CAPE YORK	Pixies			56		63		63			46			80	
WET TROPICS	Low Isles			55		61		67	25	31	33	30	28	35	
	Green			42 NEW		57		61	34	27	31	32	29	28	
	Fitzroy		44	47		63		67	24	30	33	30	27	27	
	Normanby			58					81	31	25	29	34	30	
	Dunk				70	53		60			34	29	33	23	
	Tully R			53			73		72		50				
BURDEKIN	Orpheus				83			93					20		58
	Magnetic										50	33	29	34	
	Cape Cleveland			63				126	23		41	35	41	43	
MACKAY WHITSUNDAY	Outer Whitsunday					71		53			46		39	45	
	Daydream										49	29			
	Pioneer Bay				60 NEW	52		52				29	41	23	
	Sarina Inlet				78 NEW			50	32	37		36	42	29	
	Pioneer River			50		67		58							
FITZROY	North Keppel			58					81	31	25		34	30	

DRY SEASON PERIOD	
WET SEASON PERIOD	
GAP IN SAMPLING RECORD	
DISCONTINUED IN 2009-2010	

* ED samplers deployed for all periods indicated; PDMS may only deployed in the wet season at specific sites (refer Table 3)

13 APPENDIX D: SITE SPECIFIC RESULTS 2009-2010

Please refer to Table 3 for a description of the type of sampling which occurred at each site in 2009-2010

13.1 Cape York Region

13.1.1 Pixies Garden

ED Sampling Results for PS-II Herbicides

Empore^{TM} disks were deployed and analysed in five separate periods in 2009-2010. These included three dry season periods attributed to May through to October 2009 and two wet season period attributed to December 2009 - January 2010 and February - March 2010. No PSII herbicides were detected in these samples. Diuron (3/6 periods) and hexazinone (1/6 periods) were detected in the previous 2008-2009 monitoring season where the maximum PSII-HEq was 1.8 ng.L^{-1} during a wet season monitoring period.

13.2 Wet Tropics Region

13.2.1 Low Isles

ED Sampling Results for PS-II Herbicides

Empore^{TM} disks were deployed and analysed in nine separate periods in 2009-2010 (Table 34). These included three dry season deployments between May and October 2009 and six wet season deployments between November 2009 and April 2010. The most frequently detected and dominant PSII herbicide at Low Isles was diuron with a mean concentration in water of 1.4 ng.L^{-1}. Diuron was also the only PSII herbicide detected in the dry season at this site. The maximum concentrations in water all occurred in the wet season in 2010 for all PSII herbicides detected (diuron, atrazine, hexazinone, and tebuthiuron). The maximum concentrations of diuron (5.7 ng.L^{-1}) and hexazinone (2.6 ng.L^{-1}) were determined in March 2010, while the maximum (and only) concentrations for atrazine (0.90 ng.L^{-1}) and tebuthiuron (0.30 ng.L^{-1}) were determined in April 2010. Interestingly diuron and hexazinone were not detected in this April 2010 monitoring period while atrazine and tebuthiuron were detected only in this period. The maximum PSII-HEq was 6.7 ng.L^{-1} in 2009-2010 which is consistent with the maximum of 5.7 ng.L^{-1} reported for the 2008-2009 monitoring year. These PSII-HEq suggest a Herbicide Index Category of “5” for Low Isles with all estimates ≤ 10 ng.L^{-1}.

Table 34 Summary statistics for PSII herbicides at Low Isles in the Wet Tropics Region 2009-2010 reported as concentrations in water (ng.L^{-1})

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE
						PSII-HEq Index
Atrazine	9/1	n.d.	0.10	n.d.	0.90	<
Diuron	9/7	n.d.	1.4	1.5	5.7	<
Hexazinone	9/2	n.d.	0.32	n.d.	2.6	<
Tebuthiuron	9/1	n.d.	0.034	n.d.	0.30	<
PSII-HEq	9/(8)	n.d.	1.6	1.5	6.7	Category 5

13.2.2 Green Island

PDMS Sampling Results

PDMS samplers were deployed and analysed for five separate deployments in the wet season between December 2009 and April 2010. The organophosphate insecticide chlorpyrifos was detected at Green Island Table 35) in January 2010 with an estimated concentration in water of 0.69 ng.L^{-1} which exceeds the GBRMPA Guideline of 0.5 ng.L^{-1} for 99 % species protection in marine waters. The only other chemical detected was galaxolide a polycyclic synthetic musk used in detergents.

Table 35 Concentrations (ng.L^{-1})of pesticides and industrial chemicals detected at the Green Island site in 2009-2010 compared with maximum concentrations in 2008-2009

Pesticides	Samples/detects	Range 09-10	Max 08-09	GBRMPA GUIDELINE
Chlorpyrifos	5/1	0.69	-	>
Industrial				
Galaxolide	5/3	0.45 -0.78	-	-

ED Sampling Results for PS-II Herbicides

Empore^{TM} disks were deployed and analysed in nine separate periods in 2009-2010. These included three dry season periods from June to October 2009 and six wet season periods from November 2009 to April 2010. Diuron (Table 36) was the most frequently detected herbicide (6/8 periods) with concentrations ranging from non-detect (July-August, September-October, December) to 6.2 ng.L^{-1} in the April 2010. The maximum concentrations of all other herbicides detected only in the wet season including atrazine (1.6 ng.L^{-1}), hexazinone (2.2 ng.L^{-1}) and tebuthiuron (0.90 ng.L^{-1}) also occurred in April 2010. The maximum PSII-HEq for the 2009-2010 monitoring year was 7.4 ng.L^{-1} which suggests an PSII-HEq index category of "5" (≤ 10 ng.L^{-1}) for Green Island.

Table 36 Summary statistics for PSII herbicides at Green Island in the Wet Tropics Region 2009-2010 reported as concentrations in water (ng.L^{-1})

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE
						PSII-HEq Index
Atrazine	9/2	n.d.	0.24	n.d.	1.6	<
Diuron	9/6	n.d.	0.99	0.39	6.2	<
Hexazinone	9/3	n.d.	0.32	n.d.	2.2	<
Tebuthiuron	9/1	n.d.	0.10	n.d.	0.90	<
PSII-HEq	9/(6)	n.d.	1.2	0.39	7.4	Category 5

13.2.3 Fitzroy Island

PDMS Sampling Results

PDMS samplers were deployed and analysed during five deployments in the wet season from November 2009 to April 2010. The range in concentration of individual pesticides and industrial chemicals detected in these samples in the 2009-2010 compared with maximum concentrations in the previous monitoring year are indicated in Table 37 . The concentration of chlorpyrifos at Fitzroy Island is relatively similar to the single concentration estimate at Green Island with both detections occurring in January 2010 and exceeding the GBRMPA Guideline for 99 % species protection. Tonalide, another polycyclic synthetic musk was detected in both the current and previous monitoring year. TCPP (Tris(1-chlor-2-propyl)phosphate) a flame retardant used in polyurethane foams was also detected.

Table 37 Concentrations (ng.L^{-1}) of pesticides and industrial chemicals detected at the Fitzroy Island site in 2009-2010 compared with maximum concentrations in 2008-2009

Pesticides	Samples/detects	Range 09-10	Max 08-09	GBRMPA GUIDELINE
Chlorpyrifos	5/1	0.56	n.d.	>
Pendimethalin	5/0	n.d.	0.90	-
Industrial				
Galaxolide	5/3	0.27 – 0.96	n.d.	-
Tonalide	5/1	0.63	0.86	-
TCPP	5/0	n.d.	30	-

Pesticides detected previously at this site include chlorpyrifos (0.30 ng.L^{-1}) in November 2006, and propxur (450 ng.L^{-1}) in March 2008.

ED Sampling Results for PS-II Herbicides

Empore™ disks were deployed and analysed in ten separate periods in 2009-2010. These included one period which covered both "dry and wet periods" from April to May 2009, three dry season periods from May to October 2009 and six wet season periods from November 2009 to April 2010. Diuron was detected in all monitoring periods with concentrations in water ranging from 0.90 to 12 ng.L^{-1}, with a mean concentration of 3.5 ng.L^{-1} (Table 38). The mean and maximum concentrations for diuron in 2008-2009 were 3.8 and 15 ng.L^{-1} respectively. Atrazine, hexazinone and tebuthiuron were also detected in 2009-2010 but only in the wet season. The maximum concentrations of these herbicides were 2.6, 9.5 and 1.9 ng.L^{-1} respectively. The maximum PSII-HEq for this site was 16 ng.L^{-1} which is Category "4" (10 < HEq ≤ 50 ng.L^{-1}) on the Index. This maximum value is equivalent to the PSII-HEq max reported for this site in the 2008-2009 monitoring year.

Table 38 Summary statistics for PSII herbicides at Fitzroy Island in the Wet Tropics Region 2009-2010 reported as concentrations in water (ng.L^{-1})

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE
						PSII-HEq Index
Atrazine	10/4	n.d.	0.65	n.d.	2.6	<
Diuron	10/10	0.90	3.5	5.0	12	<
Hexazinone	10/5	n.d.	1.2	n.d.	9.5	<
Tebuthiuron	10/2	n.d.	0.26	n.d.	1.9	<
PSII-HEq	10	0.94	4.1	5.0	16	Category 4

13.2.4 Normanby Island

PDMS & SPMD Sampling Results

PDMS samplers were deployed for three dry season deployments from May to October 2009 and six wet season deployments between November 2009 and May 2010. The organophosphate insecticide chlorpyrifos and the dinitroaniline herbicide pendimethalin were detected at Normanby Island in 2009-2010 (Table 39). SPMD samplers deployed at Normanby Island detected only chlorpyrifos. The personal insect repellent DEET was detected in March 2010 at levels consistent with the previous monitoring year. Industrial chemicals detected in the current year include galaxolide in all monitoring periods and the flame retardant TCPP in March 2010.

Table 39 Concentrations (ng.L^{-1})of pesticides and industrial chemicals detected at the Normanby Island site in 2009-2010 compared with maximum concentrations in 2008-2009

Pesticides	Samples/detects	Range 09-10	Max 08-09	GBRMPA GUIDELINE
Chlorpyrifos	9/1	0.72	0.30	<
Pendimethalin	9/1	1.1	n.d.	-
Industrial/Personal Care				
DEET	9/1	25	31	-
Galaxolide	9/9	0.14 – 0.56	4.0	-
TCPP		27	18	-

Pesticides detected previously at this location include diazinon 31 ng.L^{-1}, trifluralin 0.90 ng.L^{-1} (July-August-September 2007) and propoxur 96 ng.L^{-1} (January 2008).

ED Sampling Results for PS-II Herbicides

Empore™ disks were deployed and analysed in eight separate periods in 2009-2010. These included two dry season deployments between July to August and September to October 2009 and six wet season deployments between November 2009 and April 2010 (continued into May 2010). PSII herbicides were not detected during either of the dry season deployments and in the December 2009 wet season deployment. Diuron (Table 40) was the most frequently detected PS-II herbicide at Normanby Island with a mean concentration of 1.2 ng.L^{-1} and a maximum concentration of 3.6 ng.L^{-1} being observed during January 2010. The maximum concentration of atrazine (1.5 ng.L^{-1}) was observed in March 2010 while the maximum concentrations of hexazinone (1.9 ng.L^{-1}) and tebuthiuron (0.93 ng.L^{-1}) both occurred in April-May 2010. The maximum PS-II HEq of 4.0 ng.L^{-1} was observed in April-May 2010 when all of these PSII herbicides were detected and the concentration of diuron was 3.0 ng.L^{-1}. Similar to results at Low Isles and Fitzroy Island, simazine was not detected in 2009-2010.

Table 40 Summary statistics for PSII herbicides at Normanby Island in the Wet Tropics Region 2009-2010 reported as concentrations in water (ng.L^{-1})

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE
						PSII-HEq Index
Atrazine	8/3	n.d.	0.35	n.d.	1.5	<
Diuron	8/5	n.d.	1.2	n.d.	3.6	<
Hexazinone	8/3	n.d.	0.41	n.d.	1.9	<
Tebuthiuron	8/2	n.d.	0.20	n.d.	0.93	<
PSII-HEq	8/5	n.d.	1.5	n.d.	4.0	Category 5

13.2.5 Dunk Island & Tully River

PDMS Sampling Results

PDMS samplers were deployed and analysed at Dunk Island in four separate wet season monitoring periods between January and April 2010. The Tully River site was also monitored during two dry season periods between May and September 2009, one period with monitoring in both wet and dry periods and one wet season periods between December 2009 and January 2010. Chlorpyrifos (Table 41) was the only pesticide detected (0.69 ng.L^{-1}) in 2009-2010 (January 2010) at Dunk Island. This concentration exceeds the 99 % species protection GBRMPA Guideline. The concentration and timing of the detection of chlorpyrifos is consistent with all other inshore reef sites in the Wet Tropics Region where PDMS sampling occurred.

Fipronil and pendimethalin were not detected in 2009-2010 compared with 2008-09. The personal insect repellent DEET was detected in January 2010 (40 ng.L^{-1}), while the polycyclic synthetic musk galaxolide was more consistently detected.

Chlorpyrifos (2.4 – 12 ng.L^{-1}) was consistently detected in all monitoring periods at the Tully River (Table 42) at estimated concentrations which exceed ANZECC & ARMCANZ 95 % species protection Guidelines for freshwater (0.01 μg.L^{-1}) in at least one period (Dec-Jan 09), while the 99 % Guideline was exceeded in all periods. Chlorpyrifos was the only compound detected in co-deployed SPMD samplers in the Tully River. Diazinon (46 -55 ng.L^{-1}) exceeds both the 99 % (0.04 ng.L^{-1}) and the 95 % (10 ng.L^{-1}) Guidelines in all periods. Notably, diazinon was not detected at Dunk Island while the maximum concentration of chlorpyrifos in the Tully River was a factor of 17 times greater than the maximum concentration observed at Dunk Island.

Table 41 Concentrations (ng.L^{-1}) of pesticides and industrial chemicals detected at the Dunk Island site in the 2009-2010 monitoring year compared with maximum concentrations in the previous 2008-2009 year

Pesticides	Samples/detects	Range 09-10	Max 08-09	GBRMPA GUIDELINE
Chlorpyrifos	4/1	0.69	0.70	>
Fipronil	4/0	n.d.	0.30	-
Pendimethalin	4/0	n.d.	1.2	-
Industrial/Personal Care				
DEET	4/1	40	n.d.	-
Galaxolide	4/2	0.41 – 0.85	0.50	-
TCPP		n.d.	20	-

Table 42 Concentrations (ng.L^{-1}) of pesticides and industrial chemicals detected at the Tully River site in the 2009-2010 monitoring year compared with maximum concentrations in the previous 2008-2009 year

Pesticides	Samples/detects	Range 09-10 (ng/L	Max 08-09 (ng/L)	GBRMPA /ANZECC & ARMCANZ GUIDELINES
Bifenthrin	4/0	n.d.	1.5	-
Chlordane *trans*	4/0	n.d.	1.2	-/<
Chlorothalonil	4/0	n.d.	115	-
Chlorpyrifos	4/4	2.4 - 12	26	> / >
Diazinon	4/4	46 - 55	62	> / >
Dieldrin	4/0	n.d.	0.85	-
Haloxyfop-methyl	4/1	0.63	n.d.	-
Pendimethalin	4/4	0.85 - 5.4	12	-
Propiconazole	4/3	11 - 19	12	-
Prothiofos	4/2	0.19 - 2.0	4.1	-
Tebuconazole	4/2	13 - 22	7.5	-
Industrial/Personal Care				
DEET	4/0	n.d.	129	-
Galaxolide	4/4	2.3 - 5.2	2.6	-
Piperonyl butoxide	4/0	n.d.	0.40	-
Tonalide	4/1	0.65	0.40	-

Other pesticides detected using PDMS samplers in 2009-2010 include aryloxyphenoxypropionic herbicide (haloxyfop-methyl), dinitroaniline herbicide (pendimethalin), conazole fungicides (propiconazole and tebuconazole), and the organophosphate insecticide prothiofos. No Guidelines are available to assess these concentrations against.

ED Sampling for PSII Herbicides

Empore™ disks were deployed and analysed in seven separate periods at Dunk Island in 2009-2010 (Table 43). These included three dry season deployments from May to October 2009 and five wet season deployments between November 2009 and April 2010. Diuron and hexazinone were the most frequently detected PSII herbicides at the Dunk Island site in 2009-2010. Diuron was the only herbicide detected in both wet and dry seasons with a mean and maximum concentration in water of 2.6 ng.L^{-1} and 5.9 ng.L^{-1} respectively. The mean concentration of diuron was slightly higher than the mean concentration of 1.9 ng.L^{-1} in the previous 2008-09 monitoring year.. The PSII-HEq for Dunk Island ranged from 0.57 to 7.1 ng.L^{-1} which indicates a PSII Herbicide Index category of "5" (≤ 10 ng.L^{-1}) for this location. The maximum PSII-HEq in the previous monitoring year (2008-09) was lower (4.1 ng.L^{-1}) in comparison to 2009-2010. All time averaged concentration estimates for PS-II herbicides were beneath the GBRMPA Guidelines in 2009-2010.

Table 43 Summary statistics for PSII herbicides at Dunk Island in the Wet Tropics Region 2009-2010 reported as concentrations in water (ng.L^{-1})

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE
						PSII-HEq Index
Atrazine	7/1	n.d.	0.43	n.d.	3.0	<
Diuron	7/7	0.57	2.6	1.8	5.9	<
Hexazinone	7/4	n.d.	0.80	n.d.	2.6	<
Tebuthiuron	7/2	n.d.	0.32	n.d.	1.6	<
PSII-HEq	7/(7)	0.57	3.0	1.8	7.1	Category 5

Table 44 Summary statistics for PSII herbicides at the Tully River monitoring site in the Wet Tropics Region 2009-2010 reported as concentrations in water (ng.L^{-1})

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE/ ANZECC & ARMCANZ GUIDELINE
						PSII-HEq Index
Ametryn	4/2	n.d.	0.35	n.d.	1.1	</-
Atrazine	4/4	3.1	7.9	3.2	17	</<
Desethyl atrazine	4/3	n.d.	2.9	4.1	5.0	-
Diuron	4/4	3.0	13	5.0	22	</<*
Hexazinone	4/4	4.0	7.7	5.7	14	</-
Simazine	4/3	n.d.	2.6	5.1	5.1	</-
PSII-HEq	4/(4)	5.5	18	8.4	32	Category 4

* Interim Working Level (IWL) as no Guideline derived

Concentration estimates for the 2009-2010 monitoring year reveal interesting differences between the Dunk Island site and the Tully River site (Table 44). Tebuthiuron has been detected at Dunk Island but not in the Tully River, however the detections at Dunk Island occurred in March and April 2010 after sampling was discontinued in the Tully River. In addition ametryn, an atrazine transformation product (desethyl atrazine) and simazine have also been detected in the Tully River but not at Dunk Island. For PSII herbicides detected at both locations (atrazine, diuron, hexazinone) on average the maximum levels were a factor or 5 times higher in the Tully River than at Dunk Island. This is reflected in the different categories indicated for PSII-HEq Max at these locations of category" 5" for Dunk Island and category "4" for Tully River within the 2009-2010 monitoring year. Despite the elevated levels in the Tully River with respect to Dunk Island, the time averaged estimates obtained using passive samplers at this location indicate no exceedances of GBRMPA Guidelines in 2009-2010.

13.3 Burdekin Region

13.3.1 Orpheus Island

ED Sampling Results for PS-II Herbicides

Empore^{TM} disks were deployed and analysed in four separate periods in 2009-2010. These included two dry season deployments between May and October 2009, one wet season deployment in March 2010 and one deployment in both wet and dry seasons from April to May 2010. Atrazine (Table 45) and diuron were detected more frequently in these periods being the only PSII herbicides detected in both wet and dry monitoring periods , with diuron detected in all periods. This monitoring year was notable for Orpheus Island due to a spike in the level of diuron during the dry season resulting in a range in concentration from 1.5 to 100 ng.L^{-1}, with a mean of 27 ng.L^{-1}. This has resulted in a PSII-HEq Index Category "3" for this PSII-HEq Max. In spite of this result there were no exceedances of GBRMPA Guidelines in 2009-2010.

Table 45 Summary statistics for PSII herbicides at Orpheus Island in the Burdekin Region 2009-2010 reported as concentrations in water (ng.L^{-1})

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE
						PSII-HEq Index
Atrazine	4/3	n.d.	0.85	0.24	2.2	<
Diuron	4/4	1.5	27	100	100	<
Hexazinone	4/1	n.d.	0.21	n.d.	0.86	<
Tebuthiuron	4/2	n.d.	0.80	n.d.	2.8	<
PSII-HEq	4/(4)	2.1	27	100	100	Category 3

13.3.2 Magnetic Island

PDMS Sampling Results

PDMS were deployed during four wet season periods between December 2009 and April 2010. No pesticides were detected in these samples in 2009-2010 (Table 46). The only organic chemical detected at Magnetic Island was the polycyclic synthetic musk galaxolide at < 1 $ng.L^{-1}$.

Table 46 Concentrations ($ng.L^{-1}$) of pesticides and industrial chemicals detected at the Magnetic Island site in 2009-2010 compared with maximum concentrations in the previous 2008-2009 year

Pesticides	Samples/detects	Range 09-10	Max 08-09	GBRMPA GUIDELINE
Chlorpyrifos	4/0	n.d.	n.d.	<
Metolachlor	4/0	n.d.	4.2	-
Pendimethalin	4/0	n.d.	1.1	-
Industrial/Personal Care				
DEET	4/0	n.d.	34	-
Galaxolide	4/3	0.19 - 0.42	0.9	-
TCPP	4/0	n.d.	24	-

ED Sampling Results for PS-II Herbicides

Empore™ disks were deployed and analysed in four separate periods in 2009-2010. All of these periods were within the wet season attributed to months from December 2009 to April 2010. Atrazine, tebuthiuron and diuron are the dominant PSII herbicides at Magnetic Island (Table 47) and were detected frequently, with mean concentrations of 1.8, 2.6 and 2.2 $ng.L^{-1}$ respectively. The maximum concentrations of these PSII herbicides in 2009-2010 were 5.1, 6.9 and 4.7 $ng.L^{-1}$. These maximum values were observed in March 2010 for atrazine and diuron and in April 2010 for tebuthiuron. Hexazinone was also detected frequently but at lower concentrations with a mean of 0.77 $ng.L^{-1}$ and a maximum of 1.8 $ng.L^{-1}$. Unlike sampling locations in the Wet Tropics Region and Orpheus Island further north in the Burdekin Region, simazine has been detected in 2009-2010 albeit at < 1 $ng.L^{-1}$ and only in one monitoring period. There were no exceedances of the GBRMPA Guidelines for these herbicides within 2009-2010 and the PSII-HEq Max (8.8 $ng.L^{-1}$) indicates a PSII-HEq Index Category "5" (≤ 10 $ng.L^{-1}$). This maximum represents an increase with respect to the previous 2008-2009 monitoring year where PSII-HEq Max was 5.6 $ng.L^{-1}$ and was observed in the dry season.

Table 47 Summary statistics for PSII herbicides at Magnetic Island in the Burdekin Region 2009-2010 reported as concentrations in water ($ng.L^{-1}$)

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE PSII-HEq Index
Atrazine	4/3	n.d.	1.8	-	5.1	<
Diuron	4/3	n.d.	2.6	-	6.9	<
Hexazinone	4/3	n.d.	0.77	-	1.8	<
Simazine	4/1	n.d.	0.36	-	1.5	<
Tebuthiuron	4/3	n.d.	2.2	-	4.7	<
PSII-HEq	4/(4)	0.88	3.4	-	8.8	Category 5

13.3.3 Cape Cleveland

PDMS Sampling Results

PDMS were deployed during four wet season periods between December 2009 and April 2010. The only pesticide detected in 2009-2010 was metolachlor (5.8 $ng.L^{-1}$) during the February 2009 monitoring period. The ANZECC & ARMCANZ IWL for metolachlor in marine waters (20 $ng.L^{-1}$) was not exceeded. Industrial compounds detected included galaxolide (< 1 $ng.L^{-1}$) and the flame retardant TCPP (Table 48). Both chlorpyrifos and pendimethalin were detected in the previous monitoring year. Monitoring in creeks and rivers 2005-2008 in the Tully-Murray, Burdekin-Townsville and Mackay Whitsunday Regions detected only metolachlor in streams draining sugar cane and horticulture in the Burdekin-Townsville Region (Lewis et al. 2009). The Haughton River in the Burdekin Region has been shown to discharge relatively high loads of metolachlor and to impact this site during flood plumes (Davis et al. 2008).

Table 48 Concentrations ($ng.L^{-1}$) of pesticides and industrial chemicals detected at the Cape Cleveland site in 2009-2010 compared with maximum concentrations in the previous 2008-2009 year

Pesticides	Samples/detects	Range 09-10	Max 08-09	GBRMPA GUIDELINE
Chlorpyrifos	4/0	n.d.	0.40	<
Metolachlor	4/1	5.8	13	-
Pendimethalin	4/0	n.d.	0.9	-
Industrial/Personal Care				
Galaxolide	4/2	0.23 – 0.40	0.40	-
TCPP	4/1	10	19	-

ED Sampling Results for PS-II Herbicides

Empore™ disks were deployed and analysed in seven separate periods in 2009-2010. These included two dry season deployments and five wet season deployments. Atrazine, diuron and tebuthiuron were the most frequently detected herbicides at this site (Table 49), with mean concentrations of 2.6, 1.8 and 0.51 $ng.L^{-1}$ respectively. The maximum concentrations of these PSII herbicides were 13, 6.7 and 2.2 $ng.L^{-1}$ respectively. The Cape Cleveland site is quite similar to the site at Magnetic Island in the Burdekin with respect to the concentration of atrazine often exceeding those of diuron. Ametryn, hexazinone, simazine and the atrazine transformation product desethyl atrazine were also detected but less frequently and at relatively low concentrations in the case of the herbicides. Simazine (0.38 $ng.L^{-1}$) was detected only in a single sampling period (March 2010) which was also the case at the Magnetic Island site. There were no exceedances of the GBRMPA Guidelines in 2009-2010. PSII-HEq ranged from 0.036 during an excessively extended monitoring period (4 months during the dry season) when only hexazinone was detected to a PSII-HEq Max of 9.1 $ng.L^{-1}$ which indicates a PSII-HEq Category of "5" for this location. PSII-HEq Max in the previous monitoring year (2008-2009) was slightly lower at 6.3 $ng.L^{-1}$.

Table 49 Summary statistics for PSII herbicides at Cape Cleveland in the Burdekin Region 2009-2010 reported as concentrations in water (ng.L^{-1})

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE
						PSII-HEq Index
Ametryn	7/2	n.d.	0.020	0.10	0.10	<
Atrazine	7/4	n.d.	2.6	0.36	13	<
Desethyl atrazine	7/2	n.d.	0.56	n.d.	2.5	
Diuron	7/6	n.d.	1.8	0.42	6.7	<
Hexazinone	7/2	n.d.	0.10	0.095	0.61	<
Simazine	7/1	n.d.	0.054	n.d.	0.36	<
Tebuthiuron	7/3	n.d.	0.51	n.d.	2.2	<
PSII-HEq	7/(7)	0.036	2.4	0.61	9.1	Category 5

13.4 Mackay Whitsunday Region

13.4.1 Outer Whitsunday

PDMS Sampling Results

PDMS were deployed during four sampling periods between December 2009 and April 2010. No pesticides were detected in these samplers during 2009-2010. The only chemical detected (Table 50) was galaxolide (0.16-0.45 ng.L^{-1}).

Table 50 Concentrations (ng.L^{-1}) of industrial chemicals detected at the Outer Whitsunday site in 2009-2010 compared with maximum concentrations in 2008-2009

Industrial Chemicals	Samples/detects	Range 09-10	Max 08-09	GBRMPA GUIDELINE
Galaxolide	4/4	0.16 – 0.45	0.60	-
TCPP	4/0	n.d.	11	-

ED Sampling Results for PS-II Herbicides

Empore™ disks were deployed and analysed in five separate periods in 2009-2010. These included two dry season deployments attributed to periods between July and October 2009 and three wet season deployments between January and April 2010. PSII herbicides were not detected at this site during the September –October dry season monitoring period in 2009. Diuron (Table 51) was the only PSII herbicide detected in the dry season at Outer Whitsunday in the July-August monitoring period and was the most frequently detected herbicide with a mean concentration of 6.2 ng.L^{-1} and a maximum concentration of 27 ng.L^{-1} being determined in February-March 2010 during the wet season. Other PSII herbicides detected but at low frequency were atrazine, hexazinone and tebuthiuron with maximum concentrations of 11, 15 and 0.64 ng.L^{-1} respectively. There were no exceedances of GBRMPA Guidelines in 2009-2010 and the PSII-HEq Max of 35 ng.L^{-1} indicates a PSII-HEq Index Category of “4” for this location. With a low number of sampling events and considerable gaps within the sampling record in the monitoring year including at the commencement of the wet season this is a low reliability site categorization. It was a similar case for this site in the baseline reporting year (2008-2009) with results from only three samples being used to classify this site and a lower PSII-HEq Max of 4.7 ng.L^{-1}. The PSII herbicides detected in the previous monitoring year were diuron, atrazine and tebuthiuron with no hexazinone detected in that year.

Table 51 Summary statistics for PSII herbicides at Outer Whitsunday in the Mackay Whitsunday Region 2009-2010 reported as concentrations in water ($ng.L^{-1}$)

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE
						PSII-HEq Index
Atrazine	5/2	n.d.	2.5	n.d.	11	<
Diuron	5/4	n.d.	6.2	0.44	27	<
Hexazinone	5/2	n.d.	3.3	n.d.	15	<
Tebuthiuron	5/1	n.d.	0.13	n.d.	0.64	<
PSII-HEq	5/44	n.d.	7.9	0.44	35	Category 4

13.4.2 Daydream Island

ED Sampling Results for PS-II Herbicides

Empore™ disks were deployed and analysed in two separate periods in 2009-2010. Both of these periods were within the wet period with concentrations of PSII herbicides attributed to December 09 – January 10 and to February 2010. The Daydream Island site was discontinued as the "Inner Whitsunday" site from March 2010. The maximum concentrations of PSII herbicides were observed within the February 2010 period, where diuron and hexazinone were the dominant herbicides detected with maximum concentrations of 51 $ng.L^{-1}$ and 15 $ng.L^{-1}$ respectively (Table 52). The concentrations of these two herbicides increased by a factor of 35 and 31 between adjacent wet season periods, while the concentration of atrazine increased by a factor of 5 (0.59 to 3.1 $ng.L^{-1}$). The PSII-HEq ranged from 1.7 $ng.L^{-1}$ (Category 5) to 57 $ng.L^{-1}$ (Category "3") across these two periods. The PSII-HEq Max in the baseline reporting year (2008-2009) was 121 $ng.L^{-1}$ (Category "3") which was then reported as occurring within the dry season (August-September 2009). All data across the entire program have subsequently been cross-checked against all deployment dates and the period when this sampler was actually deployed was from the end of the dry period (October 2009) and into the commencement of the wet period (November 2009). The data record in this previous monitoring year was similarly poor (3 successful deployments) with significant gaps in the sampling record.

Table 52 Summary statistics for PSII herbicides at Daydream Island in the Mackay Whitsunday Region 2009-2010 reported as concentrations in water ($ng.L^{-1}$)

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE
						PSII-HEq Index
Atrazine	2/2	0.59	1.8	-	3.1	<
Diuron	2/2	1.5	26	-	51	<
Hexazinone	2/2	0.50	7.9	-	15	<
Tebuthiuron	2/1	n.d.	1.1	-	2.2	<
PSII-HEq	2/(2)	1.7	29	-	57	Category 3

13.4.3 Pioneer Bay – Inner Whitsunday

ED Sampling Results for PS-II Herbicides

Empore™ disks were deployed and analysed in six separate periods in 2009-2010. These included three dry season periods between June and October 2009 and three wet season periods between February and April 2010. The PSII herbicides detected at this location (Table 53) are consistent with those detected at sites in the Whitsunday Islands (atrazine, diuron, hexazinone and tebuthiuron). Diuron was the dominant PSII herbicide at Pioneer Bay and was detected in all dry and wet season periods in 2009-2010. No other PSII herbicides were detected in the dry season period. The concentration of diuron ranged from 3.6 $ng.L^{-1}$ to 43 ng.L^{-1}. The maximum diuron concentration was observed during the dry period in August 2009. The highest observed concentration during the wet period was 33 ng.L^{-1} in February 2010. Hexazinone was the next most frequently detected PSII herbicide with concentrations ranging from 1.7 – 11 ng.L^{-1} during the wet season. Atrazine and tebuthiuron were detected only once (March 2010) in all six periods. The PSII-HEq Max of 43 ng.L^{-1} was accounted for solely by the equivalent concentration of diuron in August 2009 and which indicates an Index Category of "4". There were no exceedances of the GRMPA Guidelines in 2009-2010.

Table 53 Summary statistics for PSII herbicides at Pioneer Bay in the Mackay Whitsunday Region 2009-2010 reported as concentrations in water (ng.L^{-1})

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE
						PSII-HEq Index
Atrazine	6/1	n.d.	0.18	n.d.	1.1	<
Diuron	6/6	3.6	23	43	43	<
Hexazinone	6/3	n.d.	3.2	n.d.	11	<
Tebuthiuron	6/1	n.d.	0.15	n.d.	0.90	<
PSII-HEq	6/(6)	3.6	24	43	43	Category 4

13.4.4 Pioneer River

PDMS Sampling Results 2009-2010

PDMS were deployed during three dry season periods between May and October 2009 and two wet season periods between November and December 2009. Pesticides detected in 2009-2010 (Table 54) were chlorpyrifos, dieldrin, and pendimethalin. The maximum concentrations of these pesticides were observed in the December 2009 monitoring period with chlorpyrifos exceeding the GBRMPA and ANZECC & ARMCANZ Guidelines for 99 % species protection in marine (0.0005 µg.L^{-1}) and freshwaters (0.00004 µg.L^{-1}) in this period. Interestingly 3,4-dichloroaniline was also detected in the December 2009 sampling period. This compound is used as an intermediate industrial chemical in the synthesis of certain herbicides and is a breakdown product of phenylcarbamates, phenylurea and acylanilide herbicides (IHCP and ECB 2006).

Table 54 Concentrations (ng.L^{-1})of pesticides and industrial chemicals detected at the Pioneer River site in 2009-2010 compared with maximum concentrations in 2008-2009

Pesticides	Samples/detects	Range 09-10	Max 08-09	GBRMPA /ANZECC & ARMCANZ GUIDELINES
Chlorfenvinphos	5/0	n.d.	6.6	-
Chlorpyrifos	5/4	0.25 – 0.69	2.1	>/>
Diazinon	5/0	n.d.	6.1	<
Dieldrin	5/2	0.87 – 2.9	3.7	-/<*
Metolachlor	5/0	n.d.	42	-/<*
Pendimethalin	5/2	0.36 – 7.3	1.3	-
Propazine	5/0	n.d.	24	-
Propiconazole	5/0	n.d.	6.8	-
Terbutryn	5/0	n.d.	3.2	-
Trifluralin	5/0	n.d.	0.50	-/<*
Industrial/Personal Care				
3,4-Dichloroaniline	5/1	70	n.d.	-/<
Galaxolide	5/0	n.d.	0.80	-
TCPP	5/0	n.d.	23	-

* Interim Working Level (IWL) as no Guideline value derived

ED Sampling Results for PS-II Herbicides (and Bromacil)

Empore™ disks were deployed and analysed in five separate periods in 2009-2010. These included three dry season periods between May and October 2009 and two wet season periods between November and December 2009, when sampling was subsequently discontinued at this site. PSII herbicides were detected in all monitoring periods (Table 55) including ametryn, atrazine (and transformation products desethyl- and desisopropyl- atrazine), diuron, hexazinone and simazine. No tebuthiuron was detected in 2009-2010. The uracil herbicide bromacil was also detected twice in the dry sampling period. This herbicide is not typically targeted in the MMP although it has been within this current year. This herbicide was detected only in the Pioneer River in 2009-2010. The most frequently detected PSII herbicides in 2009-2010 were atrazine, diuron and hexazinone which were detected in all monitoring periods. The time averaged maximum concentration of atrazine (690 ng.L^{-1}) exceeds the moderately reliable 99 % species protection Guideline established by GBRMPA (0.6 µg.L^{-1}) and is equivalent to the 99 % species protection Guideline for freshwater established by ANZECC & ARMCANZ (0.7 µg.L^{-1}). The maximum concentration of diuron (761 ng.L^{-1}) is the highest concentration reported in this current year of monitoring although it does not exceed the GBRMP Guideline of 0.9 µg.L^{-1} but does exceed the ANZECC & ARMCANZ IWL for diuron of 200 ng.L^{-1}. Hexazinone levels were similarly elevated (232 ng.L^{-1}) but also did not exceed the low reliability GBRMPA Guideline (1.2 µg.L^{-1}). All of these maximum concentrations were observed in the current wet season during the December 2009 monitoring period (and the last monitoring period for this site). The concentrations of atrazine, desethyl atrazine, diuron and hexazinone which were detected in all sampling periods range over approximately three orders of magnitude. The PSII-HEq ranged from 0.77 to 970 ng.L^{-1} in 2009-2010 which indicates a PSII-HEq Max Index Category of “1” (> 900 ng.L^{-1}) which was the only Category “1” within 2009-2010. PSII-HEq Max (2022 ng.L^{-1}) in the baseline reporting year (2008-2009), observed in January 2009 was also Category “1” at this location.

Table 55 Summary statistics for PSII herbicides and the uracil herbicide bromacil at the Pioneer River site in the Mackay Whitsunday Region 2009-2010 reported as concentrations in water (ng.L^{-1})

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE/ANZECC & ARMCANZ PSII-HEq Index
Ametryn	5/3	n.d.	0.93	0.89	3.7	</-
Atrazine	5/5	0.26	139	2.5	690	>/=
Desethyl atrazine	5/5	0.026	11	5.0	42	-
Desisopropyl atrazine	5/1	n.d.	3.1	n.d.	15	-
Diuron	5/5	0.62	156	7.3	761	</>*
Hexazinone	5/5	0.27	48	3.3	232	</-
Simazine	5/1	n.d.	4.4	n.d.	22	</<
PSII-HEq	5/(5)	0.77	199	11	970	Category 1
Bromacil	5/2	n.d.	1.0	3.3	3.3	-

*Interim Working Level (IWL) as no Guideline value derived

13.4.5 Sarina Inlet

ED Sampling Results for PS-II Herbicides

Empore™ disks were deployed and analysed in seven separate periods in 2009-2010. These included two dry season periods and five wet season periods between November 2009 and April 2010. The most frequently detected PSII herbicides were diuron, hexazinone and atrazine (Table 56). Diuron was the only herbicide detected in all monitoring periods while hexazinone and diuron were the only herbicides detected in both the wet and dry sampling periods. The maximum concentrations of all PSII herbicides were detected in the wet period during December 2009 which was also when maximum concentrations were observed in the Pioneer River in Mackay to the North of this sampling site. The diuron concentrations ranged from 0.46 to 429 ng.L^{-1} which again represents approximately three orders of magnitude higher concentrations during the wet period. The maximum concentrations of atrazine and hexazinone were 170 and 91 ng.L^{-1} respectively. The Sarina Inlet site differs from the Pioneer River in that the concentrations are somewhat lower, although tebuthiuron was detected at the Sarina Inlet site and not in the Pioneer River while simazine was detected in the Pioneer River but not at Sarina Inlet. Simazine has been associated with both relatively urban and sugar cane waterways although it is not used in the sugarcane industry (Davis et al. 2008; Lewis et al. 2009). The relative proportions of PSII herbicides are consistent with previous monitoring in both Plane Creek and Sandy Creeks which may influence concentrations at this site with diuron > atrazine > hexazinone >> ametryn and tebuthiuron (Rohde et al. 2008).

Table 56 Summary statistics for PSII herbicides at Sarina Inlet in the Mackay Whitsunday Region 2009-2010 reported as concentrations in water (ng.L^{-1})

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE
						PSII-HEq Index
Ametryn	7/1	n.d.	0.33	n.d	2.3	<
Atrazine	7/4	n.d.	30	n.d	170	<
Desethyl atrazine	7/2	n.d.	4.8	n.d	8.2	
Diuron	7/7	0.46	70	1.2	429	<
Hexazinone	7/6	n.d.	17	0.33	91	<
Tebuthiuron	7/2	n.d.	0.18	n.d	0.71	<
PSII-HEq	7/(7)	0.58	82	12	495	Category 2

13.5 Fitzroy Region

13.5.1 North Keppel Island

ED Sampling Results for PS-II Herbicides

Empore^{TM} disks were deployed and analysed in six separate periods in 2009-2010. These included one dry season periods between May and June 2009, one period with monitoring in both dry and wet periods (October – November 2009) and four wet periods between December 2009 and April 2010 with a gap in the monitoring record between July and September 2009 (dry) and in February 2010 (wet). PSII herbicides were detected only in two sampling periods during March and April 2010 (Table 57). This is in contrast to the previous monitoring year where diuron was detected in all monitoring periods (6). Diuron, atrazine, hexazinone and tebuthiuron were detected at this site in 2009-2010, compared with only diuron and tebuthiuron (1 period) in the previous monitoring year. The maximum concentrations for atrazine, diuron and hexazinone were 8.4, 6.4 and 2.1 ng.L^{-1} respectively and these occurred in April 2010. In contrast the tebuthiuron maximum concentration was 14 ng.L^{-1} and this occurred in the previous sampling period (March 2010). PSII HEq Max in 2009-2010 was 8.7 ng.L^{-1} (April 2010) compared with 1.1 ng.L^{-1} in the previous monitoring year (2008-2009). There were no exceedances of the GBRMPA Guidelines for individual chemicals in 2009-2010, however the maximum time integrated concentration of tebuthiuron is approaching the GBRMPA low reliability GUIDELINE of 0.02 µg.L^{-1}. This was the maximum tebuthiuron concentration observed at all sites in 2009-2010.

Table 57 Summary statistics for PSII herbicides at North Keppel Island in the Fitzroy Region 2009-2010 reported as concentrations in water (ng.L^{-1}).

Pesticides	Samples/detects	Min	Mean	Max Dry	Max	GBRMPA GUIDELINE
						PSII-HEq Index
Atrazine	6/2	n.d.	1.8	n.d.	8.4	<
Diuron	6/2	n.d.	2.0	n.d.	6.4	<
Hexazinone	6/2	n.d.	0.62	n.d.	2.1	<
Tebuthiuron	6/2	n.d.	2.6	n.d.	14	<
PSII-HEq	6/(2)	n.d.	2.7	n.d.	8.7	Category 5

14 APPENDIX E: PFM CASE STUDY

Concentrations in water estimated using passive sampling techniques in this report have been derived using assumed sampling rates. These estimates may not account for different compound specific sampling rates (Shaw et al. 2009a; Shaw and Müller 2009) or account for environmental factors such as flow conditions which influence the magnitude of sampling rates in-situ. Passive flow monitors (PFMs) (O'Brien et al. 2009) were co-deployed with passive samplers in order to provide an in-situ calibration technique for the influence of flow on sampling rate. Alternative means of in-situ calibration such as the use of performance reference compounds are not a viable option for these samplers (Shaw et al. 2009a). The elimination of plaster from these PFMs at nominal flow rates in tank calibration studies conducted at Entox have been related to compound specific sampling rates in both EDs and PDMS passive samplers (O'Brien et al. 2010 submitted a; O'Brien et al. 2010 submitted b). This section will provide a brief comparative assessment of concentrations in water estimated using ED samplers for three sites in 2009-2010 using both PFM-derived water velocities combined with compound specific sampling rates, versus an assumed (diuron based) sampling rate of 0.08 $L.day^{-1}$. Compound specific sampling rates may be predicted for atrazine and prometryn based on the elimination of plaster from the PFM. Further compound specific sampling rates are then predicted relative to atrazine based on a review of published calibration studies where atrazine sampling rates have been determined in conjunction with sampling rates for other compounds (Shaw et al. 2009a; Shaw and Müller 2009; Stephens et al. 2009; Vermeissen et al. 2009). This comparison is only preliminary in the sense that a more complete assessment would require the concentration in water to be monitored with traditional sampling techniques to validate these estimates.

14.1 PSII-HEq Estimated Using Two Methods

Three sites (Fitzroy Island, Normanby Island, and Pioneer River) were selected for this comparative assessment as PSII herbicides are consistently detected with peaks in concentration in the wet season when flows may be higher and reliable PFM data has been returned. PFMs have been co-deployed with passive samplers since 2007, however only data obtained during 2009-10 has been used for this comparison. Figure 66 shows PS-II HEq concentrations for Fitzroy Island estimated using both techniques between May 2009 and April 2010.

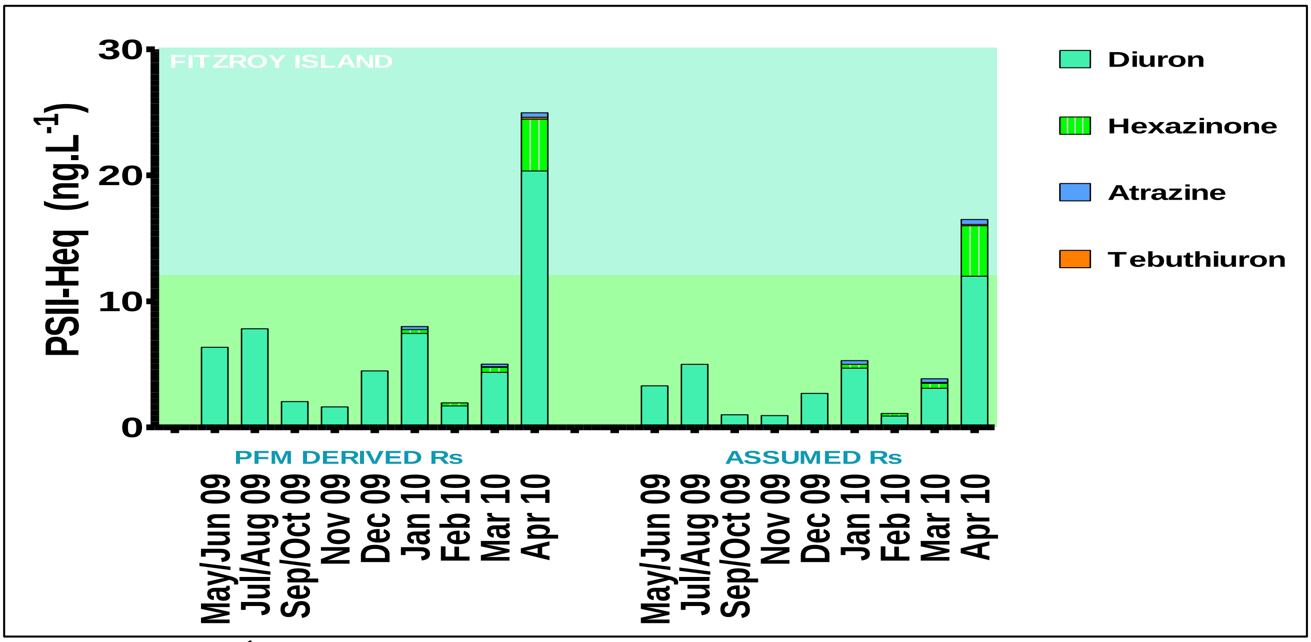

Figure 66 PSII-HEq ($ng.L^{-1}$) for Fitzroy Island in 2009-2010 based on either PFM derived or assumed sampling rates (Rs)

Concentrations estimated using PFM derived sampling rates are higher in each sampling period at Fitzroy Island by a factor of between 1.3 - 2. However the PSII-HEq derived have not resulted in any change to the PSII-HEq Index categories for individual concentration estimates. The increase in the PSII-HEq Max is largely driven by increases in the diuron concentration estimated with PFM derived sampling rates. It should be noted that the relatively low to average nominal flow velocities have been estimated Fitzroy Island (0.8 – 0.14 $m.s^{-1}$) In theory lower flows will increase the thickness of the water side boundary lower and subsequently increase the "resistance" to mass transfer and ultimately the uptake of chemicals into the sampler. This results in lower volumes of water being sampled (lower sampling rates R_S – $L.day^{-1}$) and higher concentration estimates.

Figure 67, which provides a similar comparison for the Normanby Island site indicates less variation between PSII-HEq concentrations determined using the two methods being relatively equivalent, varying by factors of between 1.0 and 1.2 (average 1.1).

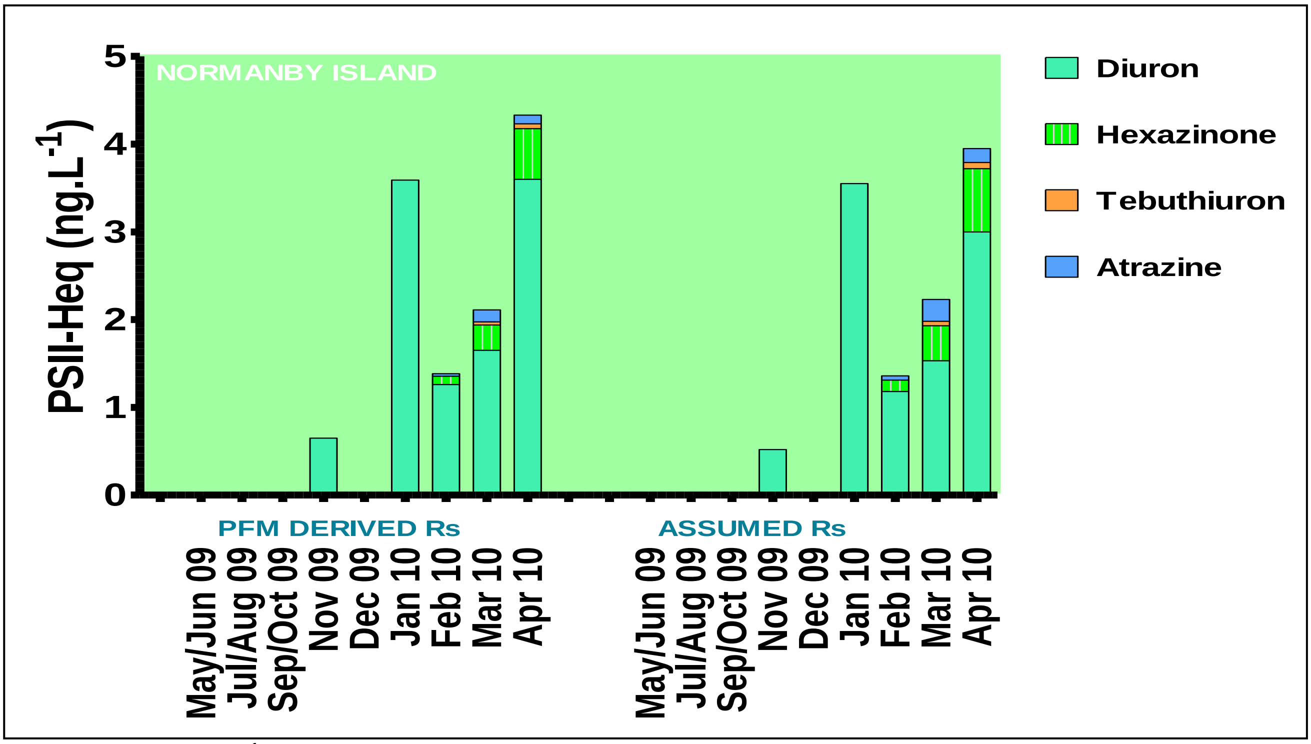

Figure 67 PSII-HEq ($ng.L^{-1}$) for Normanby Island in 2009-2010 monitoring year based on either PFM derived or assumed sampling rates (Rs)

The Normanby Island site is characterized by a generally higher PFM derived nominal flow velocity (0.15 – 0.3 $m.s^{-1}$) estimates in 2009-2010. All chemicals detected at Normanby, except for diuron, had a reduced contribution to the overall PSII-HEq when calculated using PFM derived compound specific sampling rates. The contribution of diuron to the PSII-HEq was almost identical using both methods except for the November 2009 and April 2010 sampling periods, when the nominal flow velocities estimated for this location were lowest. Overall, the two methods are in very good agreement in relation to PSII-HEq with a PSII-HEq Index Category of "5" using both methods.

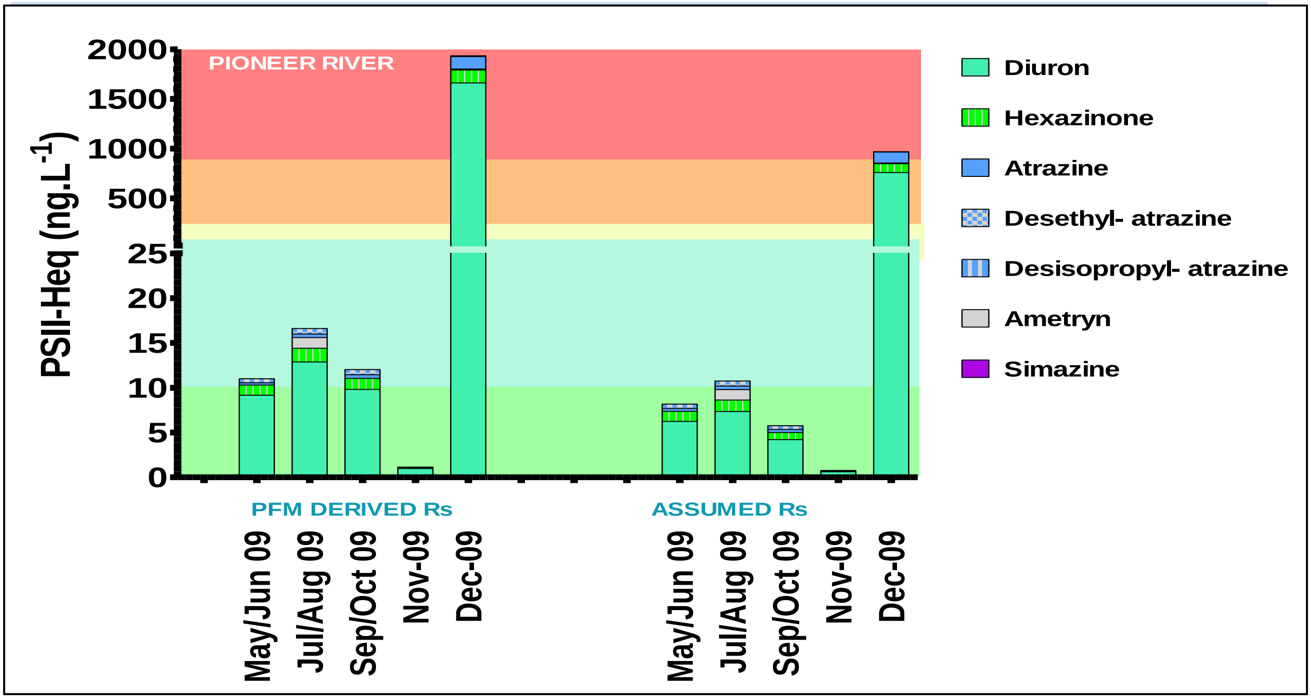

Figure 68 PSII-HEq for Pioneer River in from May – December 2009 based on based on either PFM derived or assumed sampling rates (Rs)

The variation in concentration estimates derived in the Pioneer River range from a factor of 1.3 to 1.8 (average 1.6) which is similar to that observed at Fitzroy Island. However these differences result in higher PSII-HEq Index categories in dry season monitoring periods (from Category "5" to "4") and a marked increase in PSII-HEq Max in December 2009 within Category "1". This is largely driven by differences in concentration estimates for diuron which is the dominant contributor to PSII-HEq, when nominal flow velocity estimates are lower.

In summary, these results indicate that the assumed sampling rate applied in the MMP more consistently estimate lower concentrations than PFM derived sampling rates. In most cases this has not influenced PSII-HEq Index Categories for these monitoring periods. However this disparity may be significant where diuron concentrations are relatively high. Further work is required to validate these different concentration estimates in the field using independent concentration estimates and to ensure that PFMs calibrated in tank studies are responding to actual flow velocities in the field appropriately. It is anticipated that much of this validation data will be provided through the Paddock to Reef monitoring of river sites, where both passive sampling (co-deployed with PFMs) and grab sampling concentration estimates will be determined in conjunction with actual flow measurements in these systems. Validating these estimates in inshore reef locations may prove more problematic in the short term.

15 APPENDIX F: DERM ACKNOWLEDGEMENT FOR USE OF FLOW DATA

Based on or contains data provided by the State of Queensland (Department of Environment and Resource Management). In consideration of the State permitting use of this data you acknowledge and agree that the State gives no warranty in relation to the data (including accuracy, reliability, completeness, currency or suitability) and accepts no liability (including without limitation, liability in negligence) for any loss, damage or costs (including consequential damage) relating to any use of the data. Data must not be used for direct marketing or be used in breach of the privacy laws.

Ownership: The State of Queensland as represented by the Department of Environment and Resource Management (DERM) is the owner of the intellectual property rights in and to the data or has the right to make this data available under licence arrangements. External contributors to data are listed on the website www.derm.qld.gov.au/products

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