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environmental toxicology

Monitoring of organic chemicals in the Great Barrier Reef Marine Park and selected tributaries using time integrated monitoring tools (2008-2009)

Reef Rescue Marine Monitoring Plan: Projects 3.7.1b, 3.7.2b, 3.7.8

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Executive Summary

This monitoring program was designed to collect annual data for assessing trends and changes in pesticide and herbicide levels at sites on the Great Barrier Reef (GBR) as part of the Reef Rescue Marine Monitoring Program. This information will subsequently be incorporated into an overall assessment of inshore marine water quality within the GBR. Routine monitoring was carried out at 13 inshore reef sites (project 3.7.8) and two river mouth sites (project 3.7.2b). In addition a limited number of samples were collected during flood events (project 3.7.2b) and during coral spawning (project 3.7.1b).

Routine sampling occurs monthly during the wet season (November to April) and for two month periods during the dry season (May to October). Ninety per cent of all samplers sent for deployment were returned for analysis. Flood event sampling was undertaken at two river mouth sites. Samplers were also deployed for toxicological testing at 12 inshore coral spawning sites. This report details results from May 2008 to April 2009 sampling and offers some comparison to results from routine monitoring conducted in the previous three periods - 2005/06, 2006/07 and 2007/08. Temporal comparisons were made for sites monitored continuously during all periods.

For this report, routine marine and river mouth monitoring sites have been assessed against a preliminary overall herbicide rating system based on herbicide equivalent (HEq) concentrations. In addition to discussion of levels of relevant pesticides, sites are rated from *very low* through to *very high* depending on the overall toxic effect of herbicides detected. Similarly, pesticide levels at each site are also expressed in terms of whether any individual contaminant has exceeded its trigger value as listed in the *Water Quality Guidelines for the Great Barrier Reef Marine Park 2009* (GBRMPA 2009).

Routine monitoring showed the pesticide profile at all inshore reef sites is dominated by diuron, atrazine and hexazinone. Other chemicals that can be detected regularly included simazine and tebuthiuron. For eight inshore reef sites diuron was detected at the highest concentrations.

Pesticide concentrations were generally higher in the wet season than the dry season at most inshore reef sampling sites, often increasing by 1 to 2 orders of magnitude. This was most likely due to the fact that pesticide application generally occurs during the wet season, with heavier rainfall then increasing the mobility of these chemicals and transport from catchments to the inshore reef sites.

Low concentrations of pesticides were detected at all inshore reef sites although there were some clear differences between regions. Overall, water concentrations of pesticides were lowest in both the Cape York and Fitzroy regions (typically below 2 ng/L). In the Wet Tropics region the maximum water concentrations of individual pesticides ranged from 2 to 15 ng/L). Maximum and median water concentrations in the Burdekin region were relatively similar. Monitoring in the Mackay Whitsunday region showed that water concentrations for individual pesticides were generally higher at the Inner Whitsundays including one very high diuron concentration in a sample collected in September 2008 (120 ng/L). Notwithstanding, this level is nonetheless well under the trigger value for diuron in the *Water Quality Guidelines for the Great Barrier Reef Marine Park 2009* (GBRMPA 2009).

Apart from the Inner Whitsunday site which was not given an overall rating, all inshore reef marine monitoring sites achieved overall pesticide ratings in the reporting period of either *low* or *very low* (North Keppel Island and Pixies Garden), and all had nil exceedances of the Water Quality Guidelines (WQG) trigger values for pesticides

Routine monitoring at the two river sites, Tully River and Pioneer River, revealed both a wider range of pesticides and elevated water concentrations compared to inshore reef sites, particularly in the Pioneer River. Water concentrations for dominant chemicals during flow events monitored at the Pioneer and Fitzroy Rivers in 2008/09 exceeded 500 ug/L, which is significantly less than last year's levels. However, the passive sampling flood monitoring for 2008/09 was limited due to some logistic problems with sampler deployment and retrieval. Flow events monitored were later in the wet season and less intense than in 2007/08 therefore lower concentrations of pesticides are to be expected. As with last year's results, atrazine was the most dominant chemical detected.

As pesticide concentrations in rivers are predictably substantially higher than marine sites, particularly in the wet season, suggested overall ratings for the 2 river sites based on routine monitoring are *moderate* (Tully River) and *high* (Pioneer River). The rating for the Pioneer River reflects that levels of both diuron and atrazine exceeded the WQG trigger values (for inshore reef waters), albeit only during one wet season sampling period. Diazinon levels also exceeded the WQG trigger values but there was no corresponding detection of this chemical at the inshore reef site within the region. High concentrations (above trigger values) of both diazinon and chlorpyrifos were detected in the Tully River, but again, there were no detections of these chemicals at inshore reef sites in the region.

Routine monitoring at inshore reef sites for pesticides using polydimethylsiloxane-based samplers (PDMS) and semipermeable membrane devices (SPMDs) showed that a wide range of chemicals could be detected including bifenthrin, chlorpyrifos, galaxolide, metolachlor, oxadiazon, pendimethalin, phosphate tri-n-butyl, propiconazole and TCPP. As indicated previously more chemicals of interest were detectable with PDMS compared to the SPMDs. All such detections were at very low concentrations.

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ASE	Accelerated Solvent Extraction
C_W	Estimated concentration in water (ng/L)
DCM	Dichloromethane
ED	Empore Disk™ polar passive sampler
Entox	National Research Centre for Environmental Toxicology
GC-MS	Gas Chromatography-Mass Spectroscopy
GPC	Gel Permeation Chromatography
HCl	Hydrochloric acid
HEq	Herbicide Equivalent Concentration
HPLC	High Performance Liquid Chromatography
LC-MS	Liquid Chromatography-Mass Spectroscopy
LDPE	Low Density Polyethylene
LOD	Limit of Detection
LOR	Limit Of Reporting
NATA	National Association of Testing Authorities
PAH	Polyaromatic hydrocarbons
PDMS	Polydimethylsiloxane passive sampler
PFM	Plaster Flow Monitor
PRC	Performance Reference Compound
PTFE	Polytetrafluoroethylene : Common brand name - Teflon
QHSS	Queensland Health Scientific Services
R_S	Sampling Rate
SDB-RPS	Poly(styrenedivinylbenzene) copolymer - sorbent phase
SOP	Standard Operating Procedure
SPE	Solid Phase Extraction
SPMD	Semi-permeable Membrane Devices
SPME	Solid Phase Micro Extraction

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Background

Anthropogenic pollutants such as pesticides and antifoulants have been detected in the Great Barrier Reef environment since the 1970s (Olafson, 1978). The effects from introducing land-based pollutants into the Great Barrier Reef are not well understood, however the potential for certain pollutants to impact on ecological processes and the health of reef ecosystems has been recognised (e.g. Brodie et al., 2001; Haynes, 2001; Bengtson-Nash et al., 2005).

Cattle grazing and cropping (in particular sugarcane) account for significant land use in the Wet Tropics region (Haynes, 2001). Pesticides commonly used in these industries include organophosphates (e.g. chlorpyrifos) and triazines (e.g. atrazine, simazine, ametryn, prometryn) as well as urea-based herbicides (e.g. diuron, tebuthiuron, flumeturon). Depending on the physical properties of these pesticides, their mobility varies, but those that are persistent have the potential to be transported from the sites of application in a catchment via rivers into the marine environment.

Monitoring the levels of organic pollutants in water bodies remains a challenge. Many pollutants occur at trace levels that are very difficult to detect and quantify, yet these low concentrations may potentially pose a risk to the environments in which they occur. In addition, standard sampling and analytical techniques often have limits of detections that are orders of magnitude above the relevant water quality guideline trigger levels.

In view of these limitations, time integrated passive sampling techniques have been developed for the monitoring of trace organic pollutants in water. These techniques are based on the diffusion of chemicals from the water into a sampling phase that has a relatively high capacity for the chemicals of interest. When deployed for an extended period of time the sequestration of chemicals in these passive samplers may further allow more sensitive detection of the chemicals of interest. Replicate samplers have consistently provided reproducible results. Initially, these methods were applicable only for non-polar chemicals such as organochlorine insecticides; however, more recently samplers have been developed for polar organic chemicals including herbicides such as atrazine.

Data on the concentrations of organic pollutants in rivers draining into the Great Barrier Reef have been gathered through a range of sampling efforts (e.g. Rohde et al 2008). In addition, analysis of biota or sediments have been used to assess exposure to contaminants in the ecosystem (e.g. von Westernhagen and Klumpp, 1995; Russell and Hales, 1993; Smith et al., 1985; Haynes et al., 2000; Müller et al., 2000; Bengtson-Nash et al., 2005). Overall, there is good evidence that land-sourced pollutants are entering waters of the Great Barrier Reef, but concentrations of pollutants are low, particularly in the offshore environment. Due to the sensitive nature and high conservation value of the Great Barrier Reef, concern remains for the potential consequences of continuous low exposure to these pollutants. This was highlighted with the development of the Reef Plan's Marine Monitoring Program, which aimed to evaluate and address long-term changes to pollutant concentrations and their effects on the Great Barrier Reef. Although now funded under the *Reef Rescue Program*, the goals of the monitoring program remain unchanged. To help achieve these objectives, it is necessary to closely monitor the concentrations of pollutants in Great Barrier Reef catchment waterways and in Great Barrier Reef inshore waters.

To assess whether environmental management practices are working, long term monitoring must be capable of detecting changes in water chemistry (Haynes, 2001) as well as monitoring pollutants at levels well below those which may have some immediate impact on ecosystem health but which through persistence and bio-accumulation, may pose a long-term threat. Therefore, monitoring tools which are reproducible and highly sensitive are essential. These tools should be simple to use and produce data easy to interpret, incorporating sampling methods that are both cost and time effective. In the last decade(s) time-integrated passive sampling tools have become a practical tool for cost-effective time-integrated monitoring of pollutants (Huckins et al., 1993). Samplers such as Semipermeable Membrane Devices (SPMDs) and Empore Disk based samplers (EDs) extract pollutants that are dissolved in water. Depending on the size and type of the samplers, the chemicals of interest, and certain environmental factors, these passive samplers can accumulate chemicals from several litres of water each day they are exposed. These techniques improve the feasibility of monitoring through increased sensitivity and reproducibility. Over the last decade, the University of Queensland's National Research Centre for Environmental Toxicology (Entox) has developed, calibrated and evaluated a range of passive samplers for both polar and non-polar organic contaminants. This expertise has been utilised in the monitoring component of the Reef Rescue. The Reef Rescue MMP River Mouth Monitoring task will provide the primary indicator of the delivery of pollutants to the Great Barrier Reef and will assess, over time, trends in concentrations and loads of nutrients, sediments and pollutants that have the potential to adversely affect Great Barrier Reef ecosystems.

The objectives of this task are to:

- Detect long-term trends in concentrations and loads of anthropogenic pollutants in river mouths and at inshore reef sites of the Great Barrier Reef and
- Assist with the assessment of the effectiveness of measures under the Reef Plan and Reef Rescue to reduce the delivery of these pollutants.

In addition, by involving and collaborating with community partners in the monitoring tasks, this work makes a significant contribution to education about, promotion of, and sense of ownership in the community of the Reef Rescue.

Methodology

The monitoring tasks in the Reef Rescue MMP have primarily focused on the evaluation of organic pollutants using time integrated passive sampling techniques including

- Empore^{TM} Disk (ED) based polar passive samplers for polar organic chemicals
- SPMD and PDMS passive samplers for non-polar organic chemicals
- A newly developed and calibrated passive flow monitor (PFM) to allow assessment of differences between deployment sites.

In addition grab or 'snap shot water' samples have also been collected to provide an additional validation tool for the comparability of passive sampling tools with traditional water sampling techniques and to undertake preliminary load calculations during flood events.

This program encourages community ownership of the Reef Rescue through direct participation of community groups, tourist operators and agencies. Volunteers contribute by receiving, deploying and returning the samplers. Most volunteers were trained by GBRMPA and/or Entox staff to follow Standard Operating Procedures utilising the correct techniques.

To further minimise variability, volunteers were also provided with an informative Handbook detailing handling, storing and deployment methods.

Passive samplers were constructed at Entox and dispatched to volunteers for deployment at sites. Sampling was performed routinely at 15 sites. Event sampling of flood and large rain events occurred during the wet season at two river sites including passive and snap shot collections at the Fitzroy and Pioneer Rivers. Samplers deployed at 12 inshore reef coral spawning sites were also tested using a bioassay for PSII herbicide toxicity using algae.

Samplers were sent by overnight courier on ice in eskies to sites. They were then deployed according to the SOP's. When retrieved, samplers were replaced by a new set of passive samplers and the old set was returned to Entox by overnight courier. Ideally samplers were kept refrigerated at all times while they were not deployed.

[Note: detailed documentation of methods was provided to GBRMPA in a separate reports previously: Water Quality and Ecosystem Monitoring Programs - Reef Water Quality Protection Plan: Methods and Quality Assurance/Quality Control Procedures.]

Types of sampling

Routine Monitoring

The devices were routinely deployed at 13 inshore reef sites in the Great Barrier Reef Marine Park, and in two river mouths entering the marine park (Figure 1). Routine sampling was for two 2 month and two 1 month periods during the dry season (May to October) and monthly during the wet season (November to April).

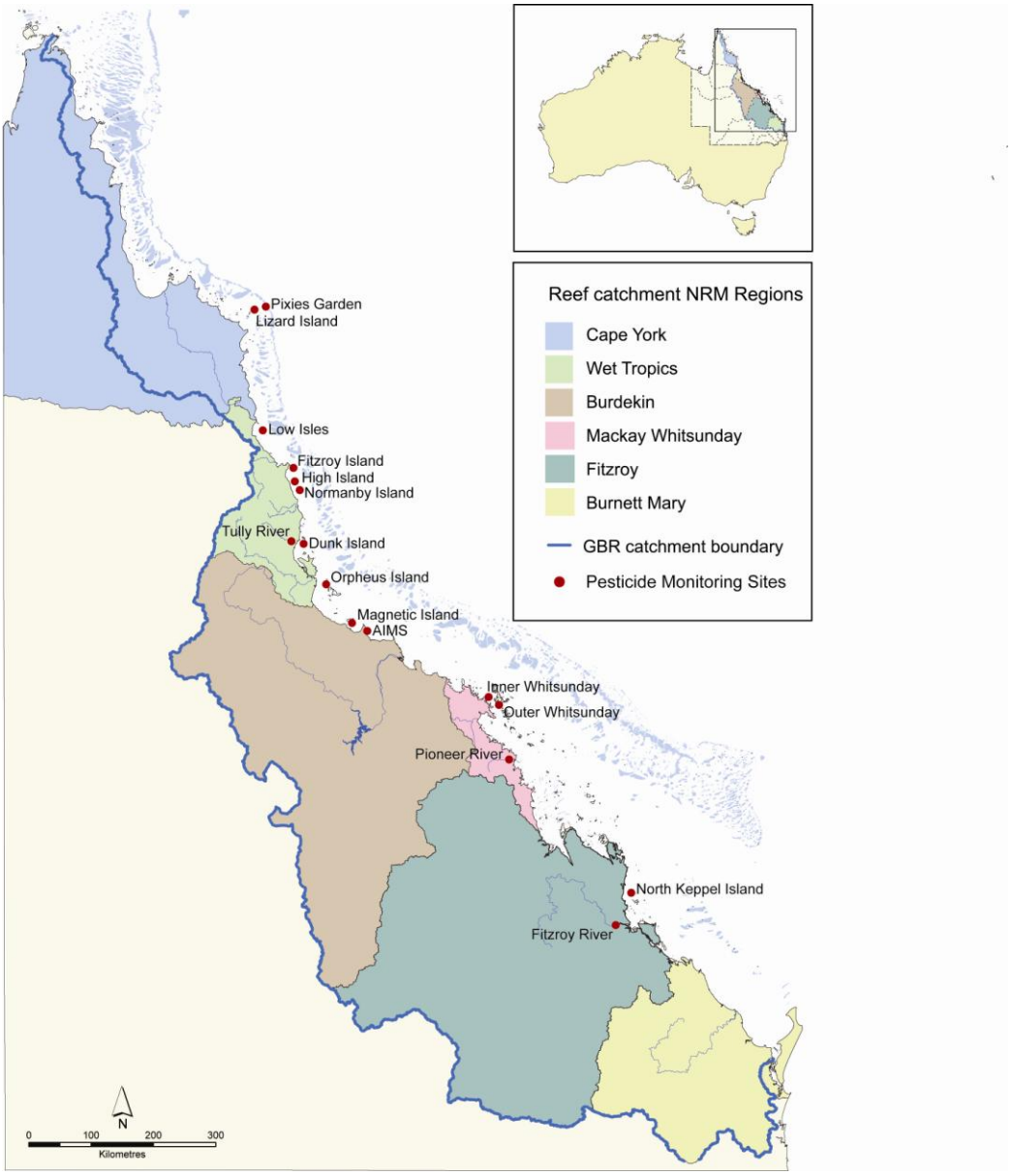

Figure 1. Locations of GBR lagoon sites monitored routinely using passive samplers during 2005 – 2009 (sourced from J.Prange 2008).

Table 1 provides details on the number of deployments at each site and the number of samplers for which results were successfully obtained.

Two EDs, 2 PFMs and for most sites 2 PDMS, (and for selected sites 2 SPMDs) were deployed per scheduled deployment in the wet season. In the dry season the SPMD/PDMS samplers were deployed only at the river sites and one reef site (Normanby Island). EDs were analysed individually though due to budget limitations only one replicate sample (ie one per site in each deployment period) was analysed. For the remaining replicates, the EDs were extracted and the extracts stored, while the SPMDs and PDMS were all analysed.

In 2008/09 a larger number of samplers were sent for deployment over 10 sampling periods, with around 90% returned for analysis. Overall this is an increase in the number of successful deployments compared with all previous years.

The number of successful deployments is dependent on a range of circumstances, such as weather conditions, availability of volunteers, sampler breakage, storm damage, and the number of samplers lost or damaged in transit. Ultimately, problems with the deployment and retrieval of samplers result in gaps in monitoring and excessively long deployment periods. The latter situation may cause samplers to go beyond their linear uptake phase making the calculation of time-averaged pesticide concentrations less reliable.

Figure 2 represents the times and duration of sampler deployment at each site during the dry and wet season for the current monitoring period, with explanations of sampling gaps.

Table 1. Details of routine passive sampler deployments over the 2008 – 09 wet and dry seasons (deployments for event sampling and bioanalytical testing not included).

Site	Current Provider / Volunteer	Sent	Returned	Notes
Lizard Is	Site Closed in November08	3	3	Established 2007. Closed November 2008.
Pixies Garden	Mike Ball Dive Expeditions	8	6	Established 2006, location changed Sept 2007. Deployments taken over by Mike Ball Dive Expeditions early 09. Mike Ball personnel trained by GBRMPA regional co-ordinator. Deployed during multi-day cruises.
Tully River	Cardwell Shire Council	9	8	Established 2007, also flood sampling (not in 2009 due to bad weather).
Low Isles	Quicksilver Connections (transport logistics), Low Isles Caretakers (deployment)	9	9	Established in 2005. GBRMPA regional co-ordinator trained new caretakers in early 2009 and provided interim deployment resources.
Fitzroy Is	Raging Thunder Pty Ltd (transport logistics), Fitzroy Is Resort (deployment)	10	9	Established 2005.
High Is	Site Closed in November08	2	2	Established 2006. Closed November 2008.
Normanby Is	Frankland Island Cruise & Dive	10	10	Established 2005.
Dunk Is	Mission Beach/Dunk Island Water Taxi	9	6	Deployments carried out by Dunk Island Resort staff. MBDI Water Taxi staff trained by GBRMPA as new deployers early 2009. GBRMPA also provided interim sampling support.
Orpheus Is	Orpheus Island Research Station	9	7	Established in 2005, suspended in 2007, re-established Jan 08.. New deployers being established by GBRMPA.
Magnetic Is	GBRMPA	10	10	Established 2005.
AIMS	GBRMPA	10	10	Established 2007.
Pioneer River	NRM	10	10	Established 2005, also used in flood sampling.
Outer Whit. Is	Hamilton Island Resort	10	8	Established 2006. GBRMPA to retrain site personnel.
Inner Whit. Is	QPWS	6	4	Established 2006, GBRMPA currently training new deployer.
North Keppel Is	North Keppel Is Education Centre	9	6	Established 2005.
Total		**124**	**108**	

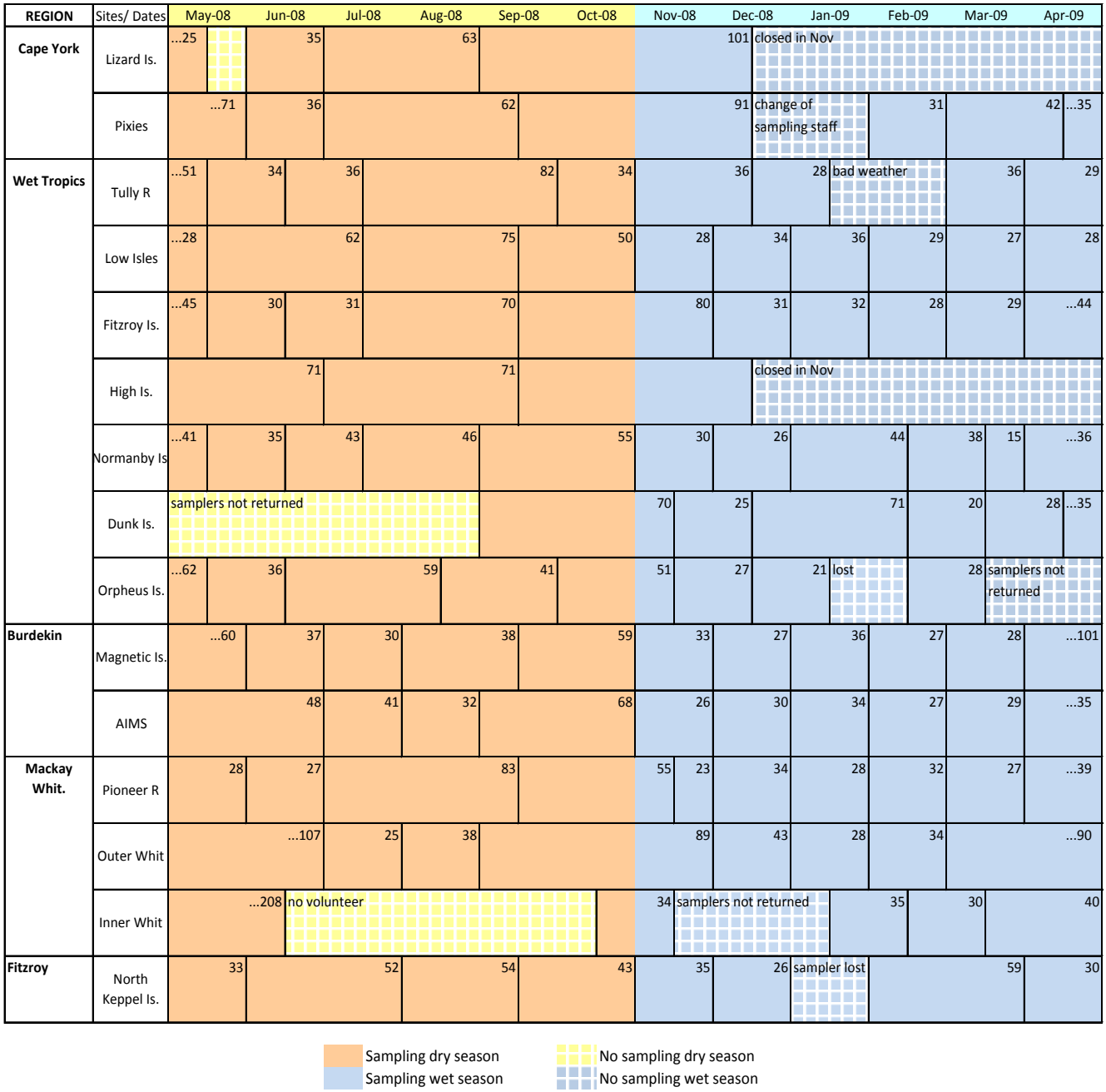

Figure 2. Passive Sampling Sites: Overview of Deployments, Deployment Lengths and Non-deployments During 2008/09 Monitoring Period

Event Monitoring

Monitoring pesticide concentrations in the water of rivers during floods is an additional component of the Marine Monitoring Program. Flood events were monitored using shorter exposure periods of membrane free polar samplers (ED-sampler) that have higher sampling rates compared to samplers that are typically deployed for monthly sample collection. Due to the faster kinetics these samplers approach equilibrium more rapidly, hence for herbicides sampling periods should be short (ie ideally 3 – 5 days for diuron). In addition PDMS samplers were deployed. Sampling was carried out in the Mackay Whitsunday (Pioneer River) and Fitzroy regions (Fitzroy River). Planned flood monitoring in the Wet Tropics region (Tully River) did not take place due to poor weather making the monitoring site inaccessible.

Flow (or flood) events were monitored using EDs and PDMS, in the Mackay Whitsunday (Pioneer River) and Fitzroy regions (Fitzroy River) during February 2009. Both EDs and PDMS were sent to each site for deployment at different intervals during the hydrograph of the event. Snap shot water samples were also collected at both sites to further assess the flood event. Table 2 details the sites and samples collected during the flood event for each site.

Table 2. Passive ED samplers and snap shot samples collected at Tully, Pioneer and Fitzroy Rivers during flood sampling.

Site	Snap shot samples collected	EDs/PDMS deployed
Tully R.	No sampling	No sampling
Pioneer R.	3 periods	1 period (x 2 replicates)
Fitzroy R.	14 periods	7 periods (x 2 replicates)

Toxicity Testing

For this specific study, 'double disk' polar passive samplers (two disks to increase the linear sampling period) were deployed in a standard housing, with replicates at 12 coral reef monitoring sites for periods ranging from 52 – 67 days between October and December 2008 (Table 3). To estimate the equivalent volume of the water from which the herbicides were extracted the average sampling rate 0.08 L/day was applied in this study.

The ED passive samplers were deployed at 12 sites across four NRM Regions between October and December 2008 (Table 3).

Table 3. Passive samplers and flow monitoring devices were deployed between October and December 2008 at the following sites.

NRM Region	Site	Sample code	Deployed	Retrieved
Wet Tropics	Fitzroy Is.	WFIT	10.10.08	02.12.08
	Frankland Is.	WFRA	10.10.08	01.12.08
	High Is.	WHIG	10.10.08	01.12.08
Burdekin	Geoffrey Bay	BGEO	08.10.08	04.12.08
	Pandora Reef	BPAN	08.10.08	03.12.08
	Orpheus Is (Pelorus)	BORP	09.10.08	03.12.08
Mackay Whitsunday	Daydream Is.	MDAY	01.10.08	06.12.08
	Doubles Cone Is.	MDCI	02.10.08	06.12.08
	Pine Is.	MPIN	01.10.08	07.12.08
Fitzroy (Keppel Island Group)	Barron Is.	FBAR	04.10.08	08.12.08
	Humpy & Halfway Is	FHUM	05.10.08	08.12.08
	Pelican Is.	FPEL	04.10.08	08.12.08

Sample procedures and calculations of concentrations

Passive sampling techniques provide an estimate of the concentration of analytes that are detected in the samplers. Average water concentrations in the environment during the time of deployment are derived from the concentrations sequestered in the sampler from a deployment using calibrations conducted in the laboratory. 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.

Polar Samplers - Empore Disks (EDs)

The polar samplers deployed were 3M™ Empore Extraction Disks (SDB-RPS) contained in teflon manifolds designed by Kingston *et al.,* (2000). The uptake was regulated using a diffusion-limiting membrane which allows rapid diffusion of polar chemicals and provides a longer period for time integration. Empore Disks were prepared by conditioning in methanol (HPLC grade) followed by ultra-pure water (18.2 M ohm conductivity). (It should be noted that we have abandoned the use of PRCs in EDs since the data could not be sufficiently interpreted. Hence the passive flow monitors were developed and included in the program.) The disks were then loaded into the teflon devices, with a diffusion limiting membrane secured on top of the disk. Note that in the case of flow event samplers, this limiting membrane was omitted to allow more rapid sampling. Ultra-pure water was sealed in the device.

To analyse for herbicides, the samplers were firstly spiked with a deuterated standard then extracted with 5 mL acetone followed by 5 mL methanol (HPLC grade) in an ultrasonic bath. The extracts were combined and reduced in volume before being filtered through a 0.45 µm PTFE syringe-driven filter unit. They were then reduced to 0.5 mL under nitrogen and made up to 1 mL with ultra-pure water. The extracts were spiked with another deuterated standard then transferred to QHSS for analysis by liquid chromatography-mass spectroscopy (LC-MS) (triple quadruple MS) for eight herbicides: diuron, atrazine, simazine, tebuthiuron, flumeturon, hexazinone, ametryn and prometryn. In addition to these, sampler extracts were analysed for two degradation products of atrazine; desethyl atrazine and desisopropyl atrazine.

Polar sampler concentrations were converted into estimates of water concentrations (C_W) using a sampling rate (L/day) calculated from laboratory studies (Booij et al., 2007; Stephens et al*.,* 2005):

$$C_W = \frac{C_{ED}}{R_S \times t} \qquad (1)$$

Where: C_W = aqueous concentration (ng/L)
C_{ED} = concentration of the compound in the ED (ng/ED)
R_S = sampling rate (L/day)
t = time deployed (days)

Polydimethylsiloxane samplers (PDMS)

The PDMS operating procedures utilised at Entox are based on those developed for SPMDs by Huckins *et al.,* (2000) with modifications appropriate to the PDMS medium. The PDMS strips (410 µm thick, 2.5 cm wide) were pre-extracted with acetone for two consecutive 24 hour periods followed by two consecutive 24 hour pre-extractions with redistilled hexane. The PDMS were then mounted into solvent washed stainless steel sampling devices and sealed in solvent washed metal cans prior to refrigerated shipment. Ordinarily, PDMS strips are co-deployed in cages with SPMD strips

After retrieval and prior to extraction, PDMS samplers were cleaned by scrubbing with water, dipping in 0.5 M HCL for 20 seconds and hexane for 30 seconds followed by rinsing with acetone and isopropanol. Each PDMS sampler was extracted in 200 mL of redistilled hexane at room temperature (21°C) for two consecutive 24 h periods. The combined extracts from each sampler was then reduced in volume, filtered using sodium sulphate columns then reduced to 0.5 ml before being filtered through 0.44 µm filters using 9.5 ml dichloromethane (DCM). The extracts were then subjected to size exclusion chromatography using a J2 Scientific Gel Permeation Chromatograph (GPC). Extracts were then concentrated, put in vials and made up to 1 ml before transferring to Queensland Health Forensic and Scientific Services (QHFSS) for analysis

Conversion of the final concentrations of compounds of interest in PDMS strips to C_W was calculated using a combination of the formulas used for SPMDs, and the results of laboratory and field calibration studies performed at Entox. However, if calibrations of the sampling rate (R_S) for a compound in PDMS were not available, the case R_S was extrapolated from other chemicals with similar physical chemical properties.

The calibration studies performed at Entox showed that the concentrations of diuron, atrazine and simazine (which are characterised by low K_{OW} values) reached their equilibrium values within 30 days of deployment. This allowed us to calculate their K_{SW} values. The K_{SW} values were further used for the estimation of the concentrations of these pesticides in water based on their amounts in PDMS (deployed for about 30 days).
To estimate the concentration of a pesticide in water based on its amount in PDMS it is necessary to know its sampling rate value. The sampling rate values for a number of pesticides were calculated from our laboratory calibration studies. If calibrations of the sampling rate (R_S) for a compound in PDMS were not available, the case R_S was extrapolated from other chemicals with similar physical chemical properties.

Semi-permeable membrane devices (SPMDs)

The methodology used at Entox for SPMD preparation, deployment and analysis was based on United States Geological Survey protocols (Huckins et al., 1993; 2000) with some modifications.

Standard SPMDs (surface area to volume ratio of ~460:1; 1 mL triolein) (Huckins et al., 2000) with slight modifications (mean low density polyethylene (LDPE) thickness 60 – 80 µm) were prepared in the laboratory from pre-extracted LDPE and 99% triolein. The LDPE was pre-extracted using a Dionex ASE 300 Accelerated Solvent Extractor.

Performance reference compounds (PRCs) were spiked into the triolein to provide a means for in-situ adjustment of the uptake of target chemicals into the samplers. The samplers were mounted into solvent washed stainless steel sampling devices and sealed in solvent washed metal cans prior to refrigerated shipment.

In the Entox laboratory, the surfaces of the SPMDs were cleaned with water and kimwipes, dipped in 0.1 M hydrochloric acid (HCl) then hexane, and rinsed briefly with acetone and isopropanol prior to extraction. Each SPMD strip was rolled and placed in cleaned stainless steel mesh and inserted into a 33 mL cell. They were then extracted using an Dionex ASE 300 Accelerated Solvent Extractor.

The extracts were reduced in volume, filtered using sodium sulphate columns, reduced to 0.5 ml before being filtered through 0.44 µm filters using 9.5 ml dichloromethane (DCM). The extracts were then subjected to size exclusion chromatography using a J2 Scientific Gel Permeation Chromatograph (GPC) The samples were collected between 1.5 – 9 minutes (first fraction) and 9 – 15.5 minutes (second fraction). The first fractions were stored for future use and the second fractions were reduced in volume to 200µL and transferred to Queensland Health Forensic and Scientific Services (QHFSS) for analysis. The separation and quantification of pesticides was performed using GC-MS. It should be noted that the uptake of chemicals into the sampler is expected to be primarily via the dissolved phase. Consequently water concentration (C_W) may be underestimated for extremely hydrophobic chemicals. Furthermore, an assumption is made that chemicals (including the PRCs) are not degraded in the passive samplers. However, for SPMDs deployed in shallow and very clean water, degradation may be an issue for compounds such as PAHs. Work is underway to address this issue. The use of photo-degradation PRCs spiked into the

samplers may allow corrections for losses caused by high light exposure, and modifications to the deployment apparatus will provide physical protection from sunlight.

A number of calibration studies have been carried out which indicate that a typical sampling rate of a standard SPMD, such as those used in the current study, is about 1 – 5 L/day.

Target chemicals and limits of reporting

The following table includes the range of pesticides specified under the MMP for analysis in passive sampler extracts plus other chemicals. Note that analyses were not limited to these compounds.

Table 4. Limits of reporting for pesticides specified under the MMP for analysis in passive sampler extracts.

Organic compounds		**LOR ng/L**	
	SPMD	**PDMS**	**ED**
Ametrin		<10	<0.3
Atrazine		<10	<0.3
Chlordane	<0.1	<0.5	
Chlorpyrifos	<0.03	<0.5	
DDT	<0.08	<0.5	
Diazinon	<5	<5	
Dieldrin	<0.2	<0.5	
Diuron		<25	<0.3
Endosulphan	<1.9	<5	
Fluometuron		<30	<0.3
HCB	<0.09	<0.5	
Heptachlor	<0.07	<0.5	
Hexazinone		<25	<0.3
Lindane	<0.5	<5	
Prometrin		<5	<0.3
Pendimethalin	<0.4	<0.5	
Prothiophos	<0.09	<0.5	
Simazine		<30	<0.3
Tebuthiuron		<25	<0.3
Metolachlor		<10	
Phosphate-tri-n-butil		<3	
Tebuconazole		<5	
Fenamiphos		<5	
Chlorfenvinphos		<2	
Fenvalerate		<0.5	
Trifluralin		<0.5	
Propiconazole		<2	
Bifenthrin		<1	
Propazine		<10	
Oxadiazon		<0.5	
Propoxur		<25	
Desisopropylatrazine		<25	

Flow Monitoring Devices

The Passive Flow Monitors (PFMs) are constructed from dental plaster which is cast into a plastic holder. The diameter of the exposed surface is 45 mm to reflect the same surface area of exposure as the EDs. Approximately 130 mL of liquid plaster (between 210 – 225 g dry weight) is cast into each holder. The plaster is allowed to set and then the lids are screwed onto the devices to prevent the plaster completely drying. The devices are weighed in the laboratory without caps prior to deployment. The devices are transported to and from the site with caps on. PFMs are normally deployed without caps, however during 2-month sampling periods, flow-limiting caps are used to slow the flow rate so that plaster does not completely dissolve.

On return to Entox, any bio-fouling is removed from the device cases and a final mass is obtained. The total mass of plaster lost from the PFM is used to equate an average flow rate over the deployment period based on rates determined in flow tank experiments. Further calibration against the uptake rate of known chemicals into ED samplers means that PFMs can be used to provide an indication of sampling rates of certain chemicals at the monitored sites. However, for consistency, in this document, for both the inshore reef monitoring data and the river monitoring data we appliedsampling rates consistent with the 2007/08 period with a blanket sampling rate for all chemicals of interest of 0.08 L/day. We propose to revisit this value with three new studies being published where we found that diuron sampling rates may be lower than those of the other herbicides found (Shaw et al. 2009 a,b). It is noteworthy that this was not confirmed by the work of Stephens et al. 2009) who found similar sampling rates for diuron, atrazine and simazine in a field calibration study in the Brisbane River. PFMs have been used only to determine relative flow rates at the monitoring sites. Table 5 shows the average loss of plaster from PFMs deployed at routine monitoring sites during 2008 – 09 while Table 6 shows the plaster lost expressed as an average flow in cm/s at each sampling site.

Studies have shown (O'Brien et al. *Accepted*) that the sampling rate methods used to calculate water concentrations are most accurate where flow averages over 15 cm/s. Accordingly, the flow data based on PFMs at routine monitoring sites would suggest that the water concentrations for AIMS, Magnetic Island, Fitzroy Island, and Pixies Garden sites may be slightly under-estimated for some sampling periods. No correction has been made related to PFM data.

Table 5. Average loss of plaster in grams/day from Passive Flow Monitors (PFMs) at sampling sites during 2008 – 09 sampling periods

Site\Month	May-08	Jun-08	Jul-08	Sep-08	Nov-08	Dec-08	Jan-09	Feb-09	Mar-09	Apr-09
AIMS	2.0	1.6	2.2	2.3	1.8	2.0	2.1	3.4	2.3	2.1
DUNK				3.1	>2.1	>3.1	>7.0	6.1	5.5	5.2
FITZROY IS	2.0	3.3	3.1	2.5		2.0	3.1	3.1	3.1	2.6
INNER WHIT				6.1				>7.2	>5.5	
LOW IS	3.1		>3.6	5.4	5.7	6.2	>6.0	7.1	6.1	6.4
MAGNETIC IS	2.8	3.2	3.3	3.9	3.3	3.2	3.9	>7.1	4.0	
NORMANBY IS	6.2	>5.0	>5.8	>4.9	5.9	>8.3	>5.0	>5.8	7.6	5.8
NORTH KEPPEL IS	5.3	>4.2	4.1	3.6	5.1	>8.4				
ORPHEUS IS		4.2			3.7	4.8		3.2		
OUTER WHIT		6.6	4.7	>3.2	5.9		3.6	>2.4		
PIONEER RIVER	4.7	5.1	2.7	3.9	6.4	5.2	4.8	4.3	4.2	4.1
TULLY RIVER	2.8	3.5	2.8	4.9	4.7	5.3			4.9	
PIXIES GARDEN	2.6		2.5	2.0			3.8		2.3	2.5
HIGH IS			>3.8	>3.0						
LIZARD IS		3.2	>4.2	>2.7						

Table 6. Average flow in cm/s calculated from plaster lost from PFMs at sampling sites during 2008 – 09 sampling periods

Site	May-08	Jun-08	Jul-08	Sep-08	Nov-08	Dec-08	Jan-09	Feb-09	Mar-09	Apr-09
AIMS	9	7	10	11	8	9	10	17	11	10
DUNK				16	>10	>16	>	39	30	28
FITZROY IS	9	17	12	12		9	15	16	16	13
INNER WHIT				33				>40	>30	
LOW IS	15		>19	29	31	34	>33	39	34	35
MAGNETIC IS	14	16	17	20	17	16	20	>39	21	
NORMANBY IS	34	>27	>32	>26	32	>47	>27	>32	42	32
NORTH KEPPEL IS	29	>22	21	19	28	>47				
ORPHEUS IS		22			20	26		17		
OUTER WHIT		37	25	>16	32		18	>12		
PIONEER RIVER	29	31	15	23	40	32	30	26	25	25
TULLY RIVER	16	21	16	30	29	33			30	
PIXIES GARDEN	13		12	9			20		11	12
HIGH IS			>20	>15						
LIZARD IS		16	>22	>13						

Standard Operating Procedures

All Entox laboratory procedures are performed by fully trained staff according to internally developed Standard Operation Procedures (SOPs). For this project, Entox used the following internal SOPs for the preparation and extraction of the samplers:

- SWPE 01 - Preparation of EDs for herbicide passive sampling
- SWPE 04 - Extraction clean-up and analysis of EDs for herbicides
- SWPP 01 - Precleaning PDMS
- SWPP 04 - Extraction of PDMS from water

- SWPP 05 - Evaporation of PDMS extracts
- SWPP 06 - Calculation of C_W from GC-MS in PDMS
- SWPS 01 - Precleaning LDPE for SPMDs
- SWPS 02 - Preparation of SPMDs
- SWPS 04 - Extraction of SPMDs deployed in Water for PAHs and Pesticides
- SWPS 05 - ASE-Extraction of SPMDs in Water
- SWPF 01 - Preparation of flow monitoring devices for water passive sampling
- SWAS 02 - Extraction using the Visiprep Vacuum Manifold
- SWAS 05 - Elution of the SPE cartridge for LC-MS analysis of herbicides

These procedures include the use of procedural, fabrication and or field blanks that are analysed with the field samples to determine background levels of contamination associated with preparation, storage and transport of the samplers to and from the field. Additionally, the use of deuterated standards added to the samplers prior to deployment and during their extraction provides information regarding sample recoveries.

Detailed guidelines on handling, storage and use of passive samplers were provided to volunteer staff to maximize the quality and consistency of sample treatment.

Blanks

Laboratory blanks of each passive sampler type were created and extracted simultaneously with each set of deployed samplers. These blanks were refrigerated and stored at Entox during the deployment.

Performance and Recovery Standards

Entox used deuterated Performance Reference Compounds (PRCs) that were loaded into the SPMDs prior to exposure. The rationale for using PRCs is that, based on the assumption of isotropic kinetic sampling, the uptake of chemicals sampled can be related to the clearance of the PRCs from the sampler into the water. Recent work at Entox supported by evidence from other researchers indicates that the loss of chemicals from EDs is deviating from isotropic kinetics and hence the use of PRCs in ED samplers has been discontinued. Therefore, at present Entox does not use a PRC based correction of the kinetics for the ED samplers. To allow a field based correction, work is underway on a novel technique for estimating the effect of flow and turbulence on the kinetics (ie the sampling rate) using PFM's.

Note that there are currently no PRCs routinely loaded into PDMS before deployment. A variety of compounds and techniques are currently being trialed to determine a suitable methodology to load PDMS samplers with the standards.

Surrogate standards were added to samples prior to extraction to monitor any loss during procedures. Recovery standards were also added to extracts immediately prior to analysis. The surrogate and recovery standards allowed calibration of the analyte mass measured in the sample which corrects for any sample loss or volume variability during extraction and analysis.

Data analysis

Data received from QHFSS in ng/sampler for ED, SPMD and PDMS samples were used for the calculation of C_W (concentrations in water). Minimum, maximum and median values were for each site were calculated and tabulated. Data was also graphed to facilitate comparison within and between NRM Regions.

Normalised Differences

The reproducibility of replicate samples was determined using normalised difference (ND) (replicates =2). The normalised difference between two samples A and B was calculated according to:

$$ND\% = \frac{|valuea - valueb|}{((valuea + valueb)/2)} \times 100 \quad (7)$$

Limits of Reporting

The analytical limits of reporting (LOR) used in this report have been defined by the Queensland Health Scientific Services laboratory. They are based on 10 x the mean standard deviation of the minimum amount of analyte added to a matrix and repeatedly (6 – 7 times) injected into the analysis instrument. The LOR are used as blanket values; depending on the individual sample it is possible that lower concentrations of analytes can be quantified and confirmed. A further criterion for the LOR is that the analyte value should exceed 3 times the mass detected in the blank.

While attempts were made to ensure recommended deployment lengths were not substantially exceeded, the degree of compliance varied, depending on various conditions. In addition samplers are routinely deployed for 60 days during the wet season. Consequently, some samplers remained deployed substantially beyond our recommended maximum deployment period (4 – 5 weeks). Entox has previously undertaken calibration experiments in the Brisbane River (which has a relatively high flow and high turbidity) for deployment lengths of up to 50 days, where linear uptake of herbicides was observed in samplers for the entire 50 days (Stephens *et al*, unpublished data). Accordingly, no corrections were made to data. For chemicals that have exceeded the linear kinetic phase this may result in an underestimation of the time averaged concentration. However, as most long deployments were in the dry season when contaminant concentrations were typically low any such underestimations were unlikely to be significant.

Phytotoxicity – PSII inhibition I-PAM assay

Samplers were extracted for toxicity testing and analysed using the Imaging PAM (Max-I-PAM, first prototype manufactured by J. Kolbowski and U. Schreiber, Würzburg, Germany; series production by Heinz Walz GmbH, Germany) assay using *Chlorella vulgaris* obtained from the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Hobart, Australia as described by Schreiber et al, 2007; Muller et al, 2007.

Based on the average sampling rate of 0.08 L/day that was applied in this study we estimate that the samplers have extracted herbicides from the equivalent of between 4.2 and 5.4 litre of water The final volume of each extract was 0.5 mL therefore the sample extracts were enriched from 8,300 to 10,700-times compared to the source water. Proportion of the enriched sample extracts were then added to the microtiter plate of the I-PAM assay and serially diluted by a test medium to obtain a concentration-effect curve. Sample extracts are composed of a mixture of unknown substances at unknown concentrations, so the concentration-effect curves were obtained based on the relative enrichment factor (REF), which is equivalent to the concentration (Figure 18B). The final REF is the combination of the enrichment of the extraction and the dilution in the bioassay (Escher et al., 2006; Muller et al., 2007; Macova et al., in press).

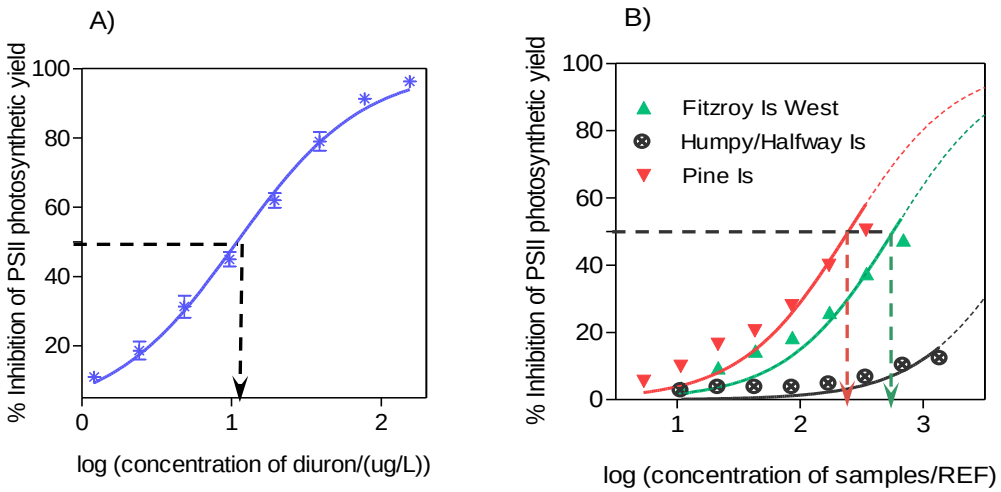

Figure 3. Concentration-effect assessment of diuron (A) and selected samples (B).

Dose-response curves of diuron and the samples followed a sigmoidal log concentration-effect curve and were fitted using Prism 5.0 software (GraphPad, San Diego, Ca, USA.) to obtain EC_{50} values, the x-value that provokes a 50 % effect (Figure 18). The EC_{50} of the sample represents the enrichment/dilution (REF) of the sample required to elicit 50% response in the assay.

Passive sampling blank: For the bioanalytical evaluation we initially used passive samplers that were prepared and extracted using the same methods as those that were deployed in the field. However – this resulted in blank interference, (ie an unexpected high response from the blank sample). We have previously reported such interference (Muller et al. 2007) and have found a simple technique to overcome this problem through a 'pseudo-deployment' of samplers in MilliQ water for the storage period. Unfortunately in this study this method was not included in the QAQC and we found a high response in the blank that was not kept in MilliQ compared to both a second blank that was subsequently (after obtaining the results) stored in MilliQ for a comparative period and a solvent blank (Figure 19). Although this problem should not occur with samples that are deployed, it means that an important QAQC condition, (ie a low blank value) is not met. Hence we conclude that in future a 'pseudo-deployment' is essential to achieve sufficiently low blank levels for interpretation of the data (Figure 19).

The response of the new blank submerged in MilliQ water for a period of deployment was below detection limit, < 8 % inhibition of the PSII photosynthetic yield (Figure 19), which corresponds to about 0.002 ug/L. The detection limit of the I-PAM assay was defined as three times the standard deviation of the response using the lowest concentration of the diuron that induced an effect above the baseline.

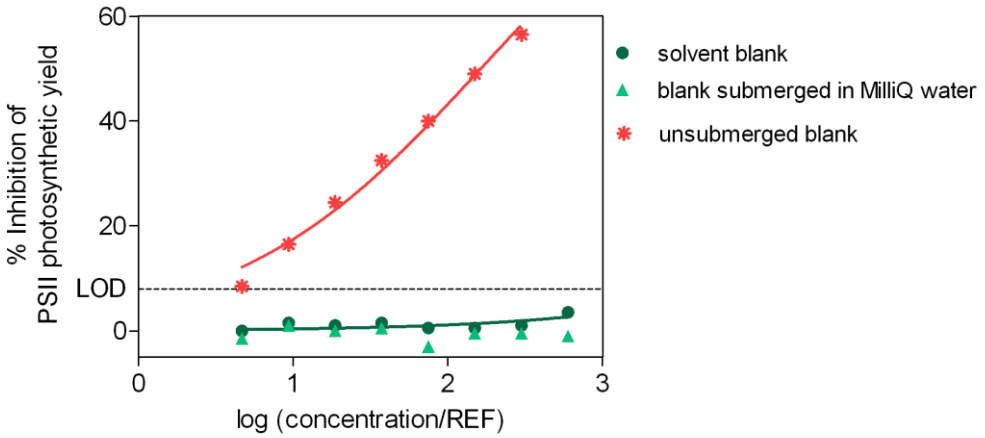

Figure 4. Concentration-effect assessment of blanks. To obtain the REF of the blanks, the arbitrary equivalent volume of 4.8 L of water, calculated as the average equivalent volume of the samples, has been applied in this study.

Calculation of Herbicide Equivalent Concentrations (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. Specifically we assume that herbicides act additively and the HEq concentration can be predicted from:

$$HEq = \sum C_i \times REP_i$$

Where Ci is the concentration of the chemical i in the water and REPi is the relative potency of chemical i. REP values for the chemicals of interest were collated from relevant laboratory studies and are provided in Table 7. For this initial determination of consensus values we did not weigh different organisms but obtained average values from studies obtained using corals, phaeodactylum and chlorella. The HEq concentrations in this report were then predicted using REP average values giving equal weight to EC50 and EC20 values. Due to time constraints we developed these initial consensus values and used them throughout this report without further consultations. However subsequent review found that more data are available and these consensus values should be revisited and updated following a more thorough review.

Table 7. Herbicide potency factors for different herbicides and selected degradation products. Preliminary summary of available data that are used for calculating HEq concentrations from data obtained in passive samplers.

	Relative potency (range)			Relative potency (mean based on various EC)			
Herbicides	Zooxanthellae (Corals) [a]	*P. tricornutum*[bcd]	*C. vulgaris*[bde]	Zooxanthellae (Corals) [a]	*P. tricornutum*[bcd]	*C. vulgaris*[bde]	Mean/ Preliminary consensus value
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
promertyn			1-1.1			1.05	1.05
terbuthylazine			0.3			0.3	0.3
desethylatrazine			0.01-0.2			0.105	0.11
desisopropylatrazine			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., 2005

[d] Schmidt, 2005

[e] Macova et al., unpublished data (Entox)

Preliminary Pesticide Index

For the interpretation of the herbicide data in this report we applied a draft framework for the herbicide index that is currently being considered as a metric to report across the Reef Rescue Marine Monitoring Program.

The criteria for herbicide for the herbicide index are suggested to be:

Category 5 – *Very High:* HEq > 900 ng/L: based on a concentration higher than observed effect levels in algae using growth as an endpoint based on just diuron which is the most commonly detected herbicide.

Category 4 – *High:* HEq 100 – 900 ng/L: Concentration sufficiently high for measurable PSII response of diuron.

Category 3 – *Moderate:* HEq 10 – 100 ng/L: Lower end of potential measurable PSII inhibition in sensitive species using PSII inhibition (noted in GBR water quality guidelines).

Category 2 – *Low:* HEq 1 – 10 ng/L: PSII herbicides clearly detectable using modern sampling tools but time averaged concentrations are below those that can be expected to cause measurable inhibition of PSII.

Category 1 – *Very Low:* HEq < 1 ng/L: Concentrations are below those that can be expected to cause measurable inhibition of PSII and are near or below the limit of detection.

The application of the criteria catalogue to flood plume monitoring will require further discussion.

Results

QA/QC

Blanks

The following procedure was used for SPMDs, PDMS and EDs. Samplers for all sites in a deployment were prepared at the same time. Procedural blanks were also prepared at this time and stored at < 4°C in the laboratory while the samplers were in the field. The blanks were extracted and analysed simultaneously with the exposed samplers. In all cases no pesticides exceeded the detection limit for samples.

Reproducibility

Replicates were routinely analysed for SPMD and PDMS for both Pioneer and Tully Rivers during the 2008/09 period. The mean normalised difference was 30%.

14 ED replicate samplers were selected for analysis. Pesticides were detected in 7% of replicates where there was no corresponding detection in the second sampler. These detections were very close to detection limits and were excluded from reproducibility calculations.

Mean normalised differences for all samplers deployed for routine sampling, where pesticides were detected in both replicates, was 21%. Mean normalised differences in samplers deployed for flood event sampling was 20%.

Passive sampling at inshore reef sites

Cape York (Lizard Is, Pixies Garden)

Lizard Island

Monitoring at Lizard Island was successful in three consecutive periods in the dry season of 2008. The site was subsequently discontinued as a pesticide monitoring site.
Diuron was detectable in the ED samplers deployed at Lizard Island with predicted concentration of diuron in the three deployments in the range of 1.1 – 2.6 ng/L.

Table 8. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at Lizard Island using EDs. Only chemicals detected are shown.

Pesticide	Samples/detects	Max (Dry)	Median	Mean	Min
Diuron	3/3	2.5	2.1	1.9	1.1
Herbicide EQ		2.5	2.1	1.9	1.1

No chemicals of interest (those being monitored) were detected in PDMS deployed at Lizard Island.

The herbicide equivalent concentration (HEq) in the three samples collected from Lizard Island suggests that the herbicide index for this site is *low*.

Pixies Garden

Empore™ disks were successfully deployed during 6 sampling periods (3 each in the dry and wet season) in the 2008/09 reporting period. Only diuron (3 of the 6 periods) and hexazinone (once) were detected in any of the samples.

Table 9. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at Pixies Garden using EDs. Only chemicals detected are shown.

Pesticide	Sampling Periods/Detects	Max/(Max Dry Season)	Median	Mean	Min
Diuron	6/3	1.7/0.43	0.22	0.47	nd
Hexazinone	6/1	0.34/nd	nd	0.06	nd
Herbicide EQ		1.8/0.4	nd	0.5	nd

DEET, galaxolide, pendimethalin and TCPP were detected in PDMS samplers, during the wet season. Galaxolide was detected multiple times with concentration estimates ranging from 0.3 – 0.5 ng/L. It should be noted that no calibration data are available for the uptake of galaxolide into PDMS and hence these estimates are preliminary.

For Pixies Pinnacles, one result exceeded 1 ng/L HEq and suggests a herbicide index of *very low*.

Cape York – Regional Summary

Based on herbicide indices of *low* and *very low*, and no exceedances of the GBRMPA WQG, the Cape York region could be considered relatively pristine in terms of herbicide contamination.

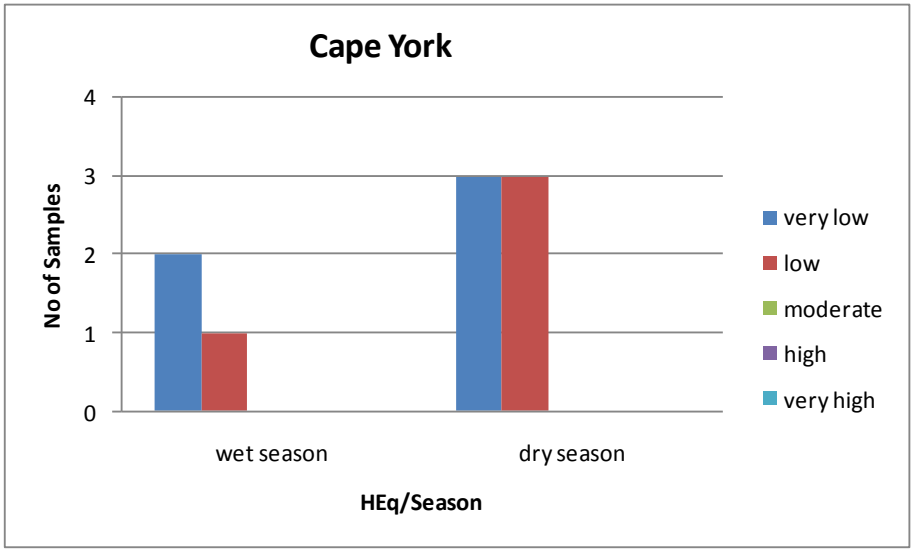

Figure 5. HEq index of all samples collected in Cape York region in wet and dry seasons 2008/2009

Wet Tropics (Low Isles, Fitzroy Is, High Is, Normanby Is, Dunk Is)

Low Isles

Herbicides were detected consistently through the wet and dry season at the Low Island site. Diuron was most consistently detected with a mean concentration of 1.8 ng/L and a maximum concentration of about 5 ng/L. A series of other herbicides were detected in the polar passive samplers with hexazinone and atrazine dominating. Average concentrations of these chemicals over the deployment periods exceeded 1 ng/L.

Table 10. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at Low Island using EDs.

Pesticide	Samples/detects	Max/max dry	Median	Mean	Min
Diuron	9/8	5/3.5	0.56	1.8	nd
Simazine	9/1	0.8/nd	nd	0.09	nd
Atrazine	9/3	2/1.5	nd	0.43	nd
Hexazinone	9/4	1.8/0.89	nd	0.41	nd
Tebuthiuron	9/2	0.61/0.61	nd	0.08	nd
Herbicide Eq		5.7/4.1	0.9	1.9	nd

No chemicals of interest were detected in PDMS samplers deployed at Low Island.

The herbicide equivalent concentration in the nine samples collected from Low Island suggests that the herbicide index for this site is *low*.

An evaluation of the data from the last four years shows that consistent with expectation concentrations of herbicides increase during the wet season and can be somewhat related to river flows (see Figure 3). The data do not indicate any significant long term decrease of the concentration of herbicides in the water at Low Island.

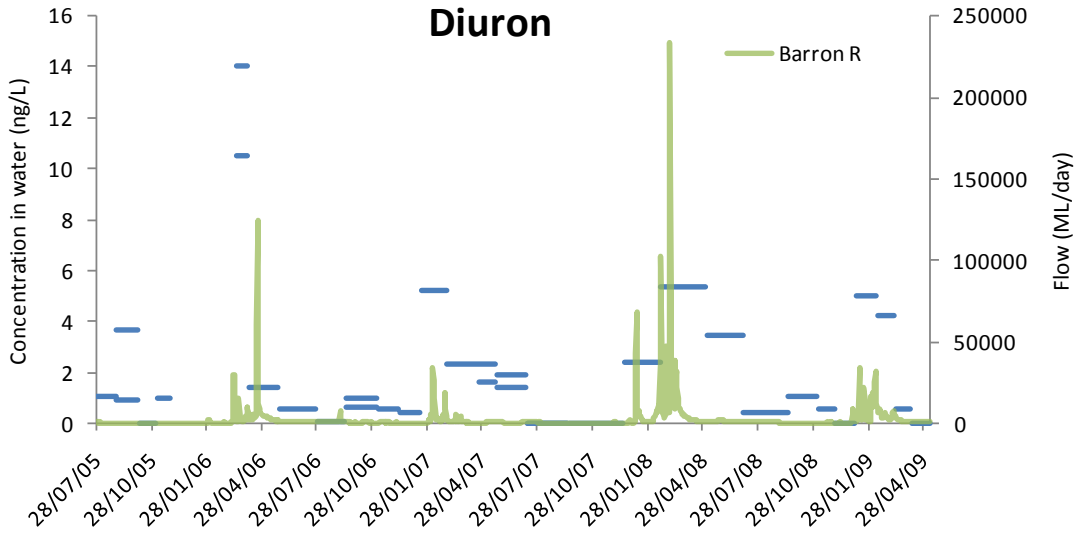

Figure 6. Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Low Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero

Fitzroy Island

Diuron was detected in all polar passive samplers deployed at Fitzroy Island with a mean concentration of 3.8 ng/L and a maximum concentration of about 15 ng/L. Atrazine and hexazinone were detected in 4 of the 8 sampling periods, typically at concentrations lower than those of diuron. The data are in the same range as data obtained by Shaw et al. (2005; 2009) from inshore reefs including Fitzroy Island using the same sampling tools.

Table 11. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at Fitzroy Island using EDs.

Pesticide	Samples/detects	Max/max dry	Median	Mean	Min
Diuron	8/8	15/3	1.8	3.8	0.88
Simazine	8/2	1.3/nd	nd	0.25	nd
Atrazine	8/4	3.7/1.8	0.6	1.3	nd
Hexazinone	8/4	3/0.29	0.14	0.64	nd
Tebuthiuron	8/3	0.32/0.3	0.0	0.11	nd
Herbicide EQ		17/3	2.0	4.0	0.9

Galaxolide was detected in PDMS samplers on 3 occasions, each at 0.4 ng/L. Pendimethalin was detected once in March measuring 0.9 ng/L, while TCPP was detected twice, with an estimated 30 ng/L in April 2009 and 13 ng/L in the July/August 2008 period.

The HEq concentration in the eight samples collected from Fitzroy Island suggests that the herbicide index for this site is *low* with only one monthly sample in the *moderate* category and the remainder of the samples in the category *low*.

The four year data shows again that concentrations of herbicides are typically increased during the wet seasons and appears to be associated with river flows (see Figure 4). The data do not indicate any significant long term decrease of the concentration of herbicides in the water at Fitzroy Island.

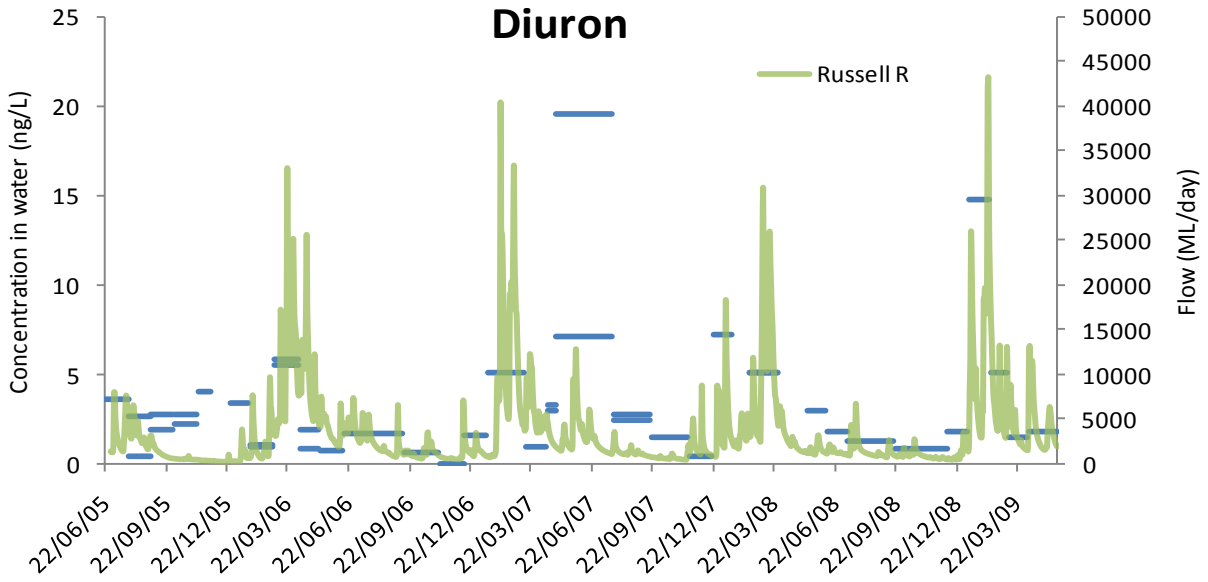

Figure 7. Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Fitzroy Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.

<u>High Island</u>

High Island was only covered during 2 sampling periods in the 08/09 period (both in the dry season) as it was discontinued as a herbicide monitoring site in late 2008. Diuron was detected during both sampling periods with a mean concentration of 1.8 ng/L.

Table 12. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at High Island using EDs.

Pesticide	Samples/detects	Max/max dry	Median	Mean	Min
Diuron	2/2	2.3/2.3	1.8	1.8	1.2
Hexazinone	2/1	0.26/0.26	0.13	0.13	nd
Tebuthiuron	2/1	0.29/0.29	0.15	0.15	nd
Herbicide EQ		2.3/2.3	1.8	1.8	1.3

No chemicals of interest were detected in PDMS deployed at High Island.

With only two sampling periods no estimation of overall herbicide index was made although the HEq concentrations for the two sampling periods were both in the *low* category.

Normanby Island

Herbicides were detected in 9 out of the 10 sampling periods at Normanby Island. Typically diuron was most consistently detected and at the highest concentrations (in 8 of the 10 sampling periods with a mean concentration of 2.2 ng/L). Atrazine, hexazinone and tebuthiuron were also all detected in at least 5 of the 10 sampling periods but usually at lower concentrations than diuron.

Table 13. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at Normanby Island using EDs.

Pesticide	Samples/detects	Max/max dry	Median	Mean	Min
Diuron	10/8	7.8/3	1.7	2.2	nd
Simazine	10/1	0.74/nd	nd	0.07	nd
Atrazine	10/6	3.5/3.5	0.76	1	nd
Desethyl atrazine	10/1	2.6/nd	nd	0.26	nd
Hexazinone	10/5	1.5/1.1	0.13	0.46	nd
Tebuthiuron	10/5	1.5/1.5	nd	0.26	nd
Herbicide EQ		9.3/3.9	1.8	2.9	nd

No chemicals of interest were detected in PDMS during the dry season at Normanby Island, galaxolide was detected 4 times during the wet season ranging from an estimated 0.2 – 4 ng/L. TCPP was also detected twice in the dry season at concentrations between 13 – 18 ng/L. Furthermore phosphate tri-n-butyl and chlorpyrifos were detected in January with an estimated 1.2 ng/L and 0.3 ng/L respectively. DEET was detected during March with a predicted concentration of about 31 ng/L.

The HEq concentration in the 10 samples collected from Normanby Island suggests that the herbicide index for this site is in the *low* category.

The Normanby Island site is again one with relatively good data for the last four years. This data clearly demonstrate a high variability and show that while concentrations are often higher in the wet season there is no consistent long term trend discernable at this stage (Figure 5).

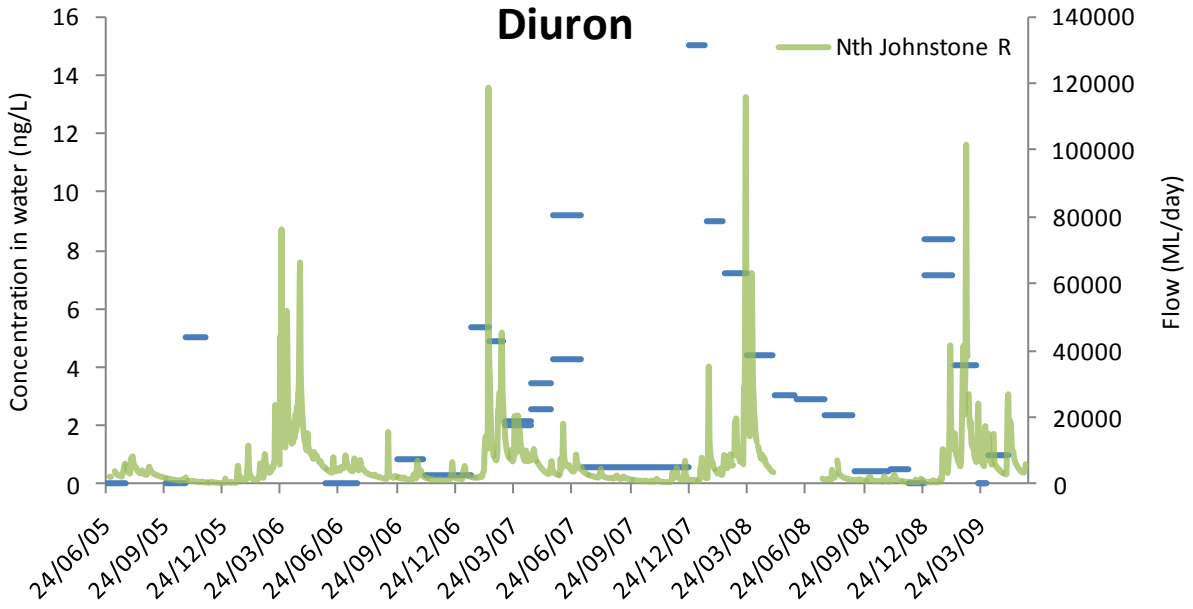

Figure 8. Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Normanby Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.

Dunk Island

Diuron and hexazinone were detected in three of the four samples collected at Dunk Island with a predicted mean diuron concentration of about 1.9 ng/L.

Table 14. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at Dunk Island using EDs.

Pesticide	Samples/detects	Max/max dry	Median	Mean	Min
Diuron	4/3	3.2/nd	2.2	1.9	nd
Atrazine	4/1	1.1/nd	nd	0.26	nd
Hexazinone	4/3	2.3/nd	0.56	0.85	nd
Tebuthiuron	4/2	0.46/nd	0.16	0.19	nd
Herbicide EQ		4.1/nd	2.5	2.3	nd

PDMS samplers were only deployed at Dunk Island during the wet season and enabled the detection of galaxolide in three samples with estimated concentrations in the water ranging between 0.4 – 0.5 ng/L. TCPP and chlorpyrifos were both detected twice at predicted concentrations of 11 – 20 ng/L and 0.3 – 0.7 ng/L respectively. Fipronil was detected in January 09 with predicted concentrations of 0.3 ng/L and pendimethalin in March 09 at approximately 1.2 ng/L.

The HEq concentration in the four samples collected from Dunk Island suggests that the herbicide index for this site is *low*.

Wet Tropics- Regional Summary

All 5 inshore reef sites sampled in the Wet Tropics region had herbicide indices of *low*, and there were no exceedances of the GBRMPA WQG.

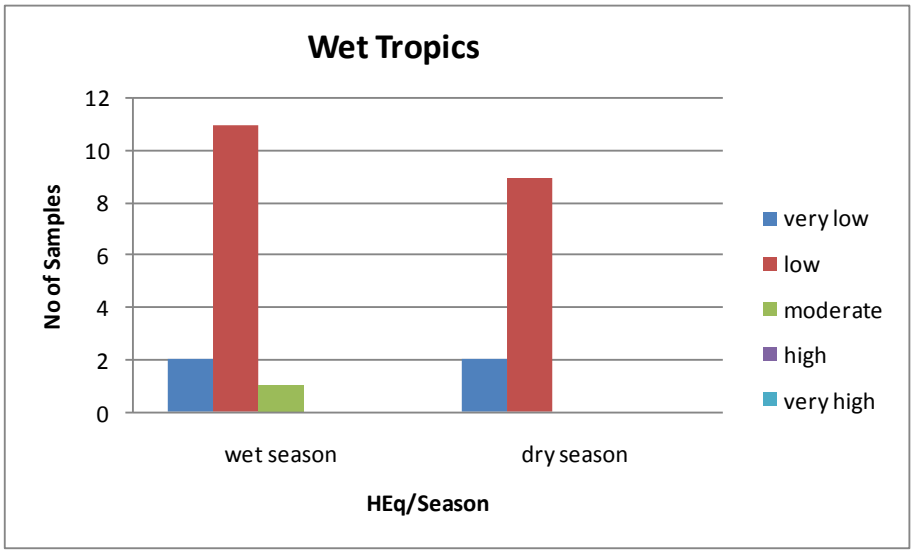

Figure 9. HEq index of all samples collected in Wet Tropics region in wet and dry seasons 2008/2009

Burdekin (Orpheus Is, Magnetic Is, Cape Cleveland/AIMS)

Orpheus Island

Herbicides were detected in 5 out of the 7 sampling periods at Orpheus Island, typically with diuron detected most commonly and at the highest concentrations. Atrazine, hexazinone and tebuthiuron were also all detected in selected samples.

Table 15. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at Orpheus Island using EDs.

Pesticide	Samples/detects	Max/max dry	Median	Mean	Min
Diuron	7/5	1.7/1.7	0.95	0.94	nd
Atrazine	7/1	1.4/1.4	nd	0.2	nd
Desethyl atrazine	7/1	0.74/0.74	nd	0.11	nd
Hexazinone	7/2	0.26/0.26	nd	0.07	nd
Tebuthiuron	7/4	0.8/0.8	0.07	0.25	nd
Herbicide EQ		1.9/1.9	1.2	1.0	nd

May was the only sampling period where compounds of interest were detected in PDMS at Orpheus Island. These include phosphate tri-n-butyl, oxadiazon, propiconazole and bifenthrin but all were at low concentrations. The highest concentration is estimated for propiconazole at 5 ng/L.

The HEq concentration in the seven samples collected from Orpheus Island suggests that the herbicide index for this site is *low*.

Magnetic Island

Diuron was detected in all 9 sampling periods at Magnetic Island with consistent concentrations ranging from 1 – 4.4 ng/L. Atrazine and tebuthiuron were also all detected in at least 5 of the 9 sampling periods. Interestingly, the highest concentrations of both atrazine and diuron were detected in the dry season (August/September 08).

Table 16. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at Magnetic Island using EDs.

Pesticide	Samples/detects	Max/ max dry	Median	Mean	Min
Diuron	9/9	4.4/4.4	1.8	2.1	1
Simazine	9/1	0.36/0.36	nd	nd	nd
Atrazine	9/5	6.3/6.3	1.7	1.9	nd
Desethyl atrazine	9/1	0.63/0.63	nd	0.07	nd
Hexazinone	9/1	0.25/0.25	nd	nd	nd
Tebuthiuron	9/7	1.2/0.82	0.58	0.51	nd
Herbicide EQ		5.6/5.6	2.0	2.5	1.2

PDMS deployed at Magnetic Island detected a few compounds of interest at low concentrations. These include phosphate tri-n-butyl (12 ng/L), galaxolide (0.1 – 0.9 ng/L), metolachlor (4 – 6 ng/L), pendimethalin (1 ng/L), TCPP (12 – 24 ng/L) and DEET (34 ng/L).

The HEq concentration in the nine samples collected from Magnetic Island suggests that the herbicide index for this site is *low*.

The four year data from Magnetic Island show that concentrations of herbicides may substantially vary between sampling periods and while the data indicate some seasonal trends these cannot easily be related to the flow of, for example, the Burdekin River (Figure 6). The data do not indicate any significant long term decrease in the concentration of herbicides in the water at Magnetic Island.

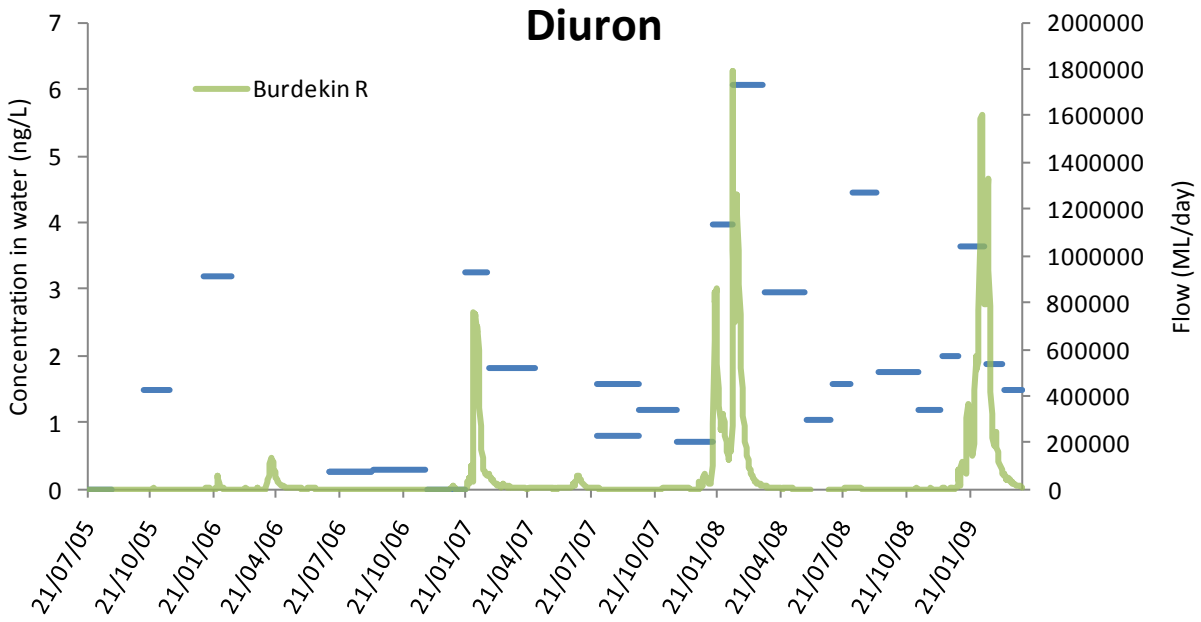

Figure 10. Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Magnetic Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.

Cape Cleveland (AIMS)

Herbicides were detected in all but two of the 10 sampling periods at the Cape Cleveland site. Although diuron was detected most often the concentrations of atrazine were typically higher than that of diuron, which is somewhat different to most other sites. Predictably, the highest concentrations of both atrazine and diuron were detected in the January/February period in 2009.

Table 17. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at Cape Cleveland using EDs.

Pesticide	Samples/detects	Max/max dry	Median	Mean	Min
Diuron	10/8	4.5/0.92	0.85	1.2	nd
Atrazine	10/7	10/5.4	2.7	3	nd
Desethyl atrazine	10/2	1.2/nd	nd	0.23	nd
Hexazinone	10/3	0.59/0.4	nd	0.12	nd
Tebuthiuron	10/7	1.3/0.78	0.49	0.45	nd
Ametryn	10/1	0.49/nd	nd	nd	nd
Herbicide EQ		6.2/1.8	1.6	2.1	nd

PDMS deployed at Cape Cleveland detected chemicals of interest in all but 2 deployments. The chemicals included TCPP, galaxolide, metolachlor, pendimethalin, phosphate tri-n-butyl and chlorpyrifos. The highest concentration was TCPP at 19 ng/L during November 2008.

The HEq concentration in the eight samples collected from Cape Cleveland suggests that the overall herbicide index for this site is *low*. November 08 was in the *very low* category.

Burdekin - Regional Summary

All 3 inshore reef sites sampled in the Burdekin region had herbicide indices of *low*, and there were no exceedances of the GBRMPA WQG.

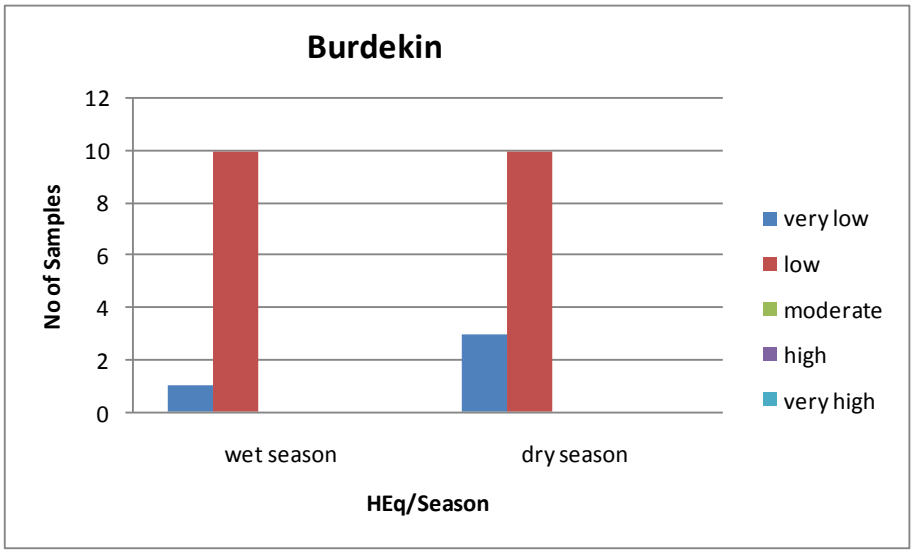

Figure 11. HEq index of all samples collected in Burdekin region in wet and dry seasons 2008/2009

Mackay Whitsunday (Inner Whitsunday, Outer Whitsunday)

Inner Whitsunday (Daydream Island)

Diuron was detected in all three successful sampling periods. There is a notable outlier in the data with a mean predicted diuron concentration of 120 ng/L during the August/September 09 deployment. Unfortunately we have no data for the months before or after this sampling period and hence it is unclear whether this result stems from a contamination of samplers during preparation, deployment or in the laboratory. As the blank for this period showed no contamination and no other herbicides except atrazine were also detected in this sample, it is suggested that some form of contamination of the sample or the site through a point source (potentially antifoulant) has occurred. We recommend that this data point not be considered in any trend analysis.

Table 18. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at Inner Whitsunday using EDs.

Pesticide	Samples/detects	Max/max dry	Median	Mean	Min
Diuron	3/3	(120/120)	8.5	44.7	4.4
Atrazine	3/2	1.2/nd	0.79	0.7	nd
Desethyl atrazine	3/2	2.6/2.6	0.77	1.1	nd
Hexazinone	3/2	2.8/nd	1.4	1.4	nd
Tebuthiuron	3/1	0.15/nd	nd	nd	nd
Herbicide EQ		120/120	9.8	45	3.7

No chemicals of interest were detected in PDMS deployed at this site in the 2008/09 period.

In light of the limited number of samples and the potential contamination of one of the samples (see above) we suggest that the site should not receive an overall herbicide index for the 2008/09 period.

Outer Whitsunday (Hamilton Island)

Herbicides were detected in two of the 3 sampling periods at the Outer Whitsunday site. Although diuron was detected most often, the concentrations of atrazine were typically higher than those of diuron, which is not the norm at most other sites.

Table 19. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at Outer Whitsunday using EDs.

Pesticide	Samples/detects	Max/max dry	Median	Mean	Min
Diuron	3/2	3.9/3.9	0.8	1.6	nd
Atrazine	3/2	2.7/2.7	2.2	1.6	nd
Tebuthiuron	3/2	4.1/4.1	0.57	1.6	nd
Herbicide EQ		4.7/4.7	1.2	1.9	nd

Galaxolide and TCPP were detected in PDMS deployed at this site during the wet season. Galaxolide was estimated at an average concentration of 0.6 ng/L in November while the concentration of TCPP was estimated at 11 ng/L during January. It should be noted that no calibration data are available for the uptake of galaxolide into PDMS and hence these estimates are preliminary.

The HEq concentration in the three samples collected from Outer Whitsunday suggests that the herbicide index for this site is *low*. Three years of data from monitoring at this site show relatively variable data with a potential indication of a decrease in the concentration over this period (Figure 7).

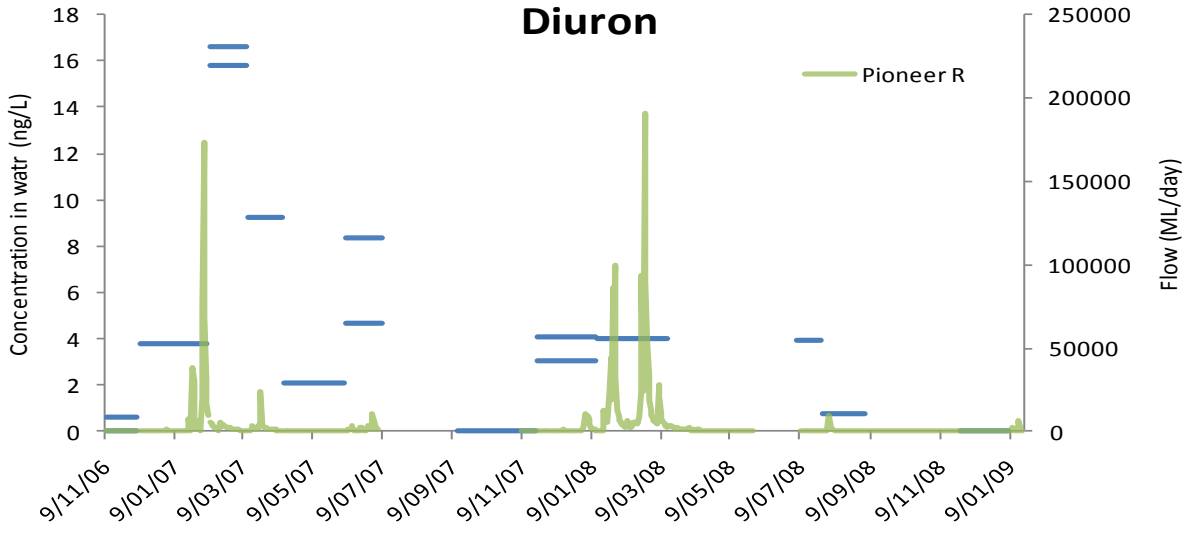

Figure 12. Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Outer Whitsunday. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.

Mackay Whitsunday - Regional Summary

Two of the 3 inshore reef sites sampled in the Mackay Whitsunday region had herbicide indices of *low*, and despite there being an uncharacteristically high diuron concentration at the Inner Whitsunday site there were no exceedances of the GBRMPA WQG.

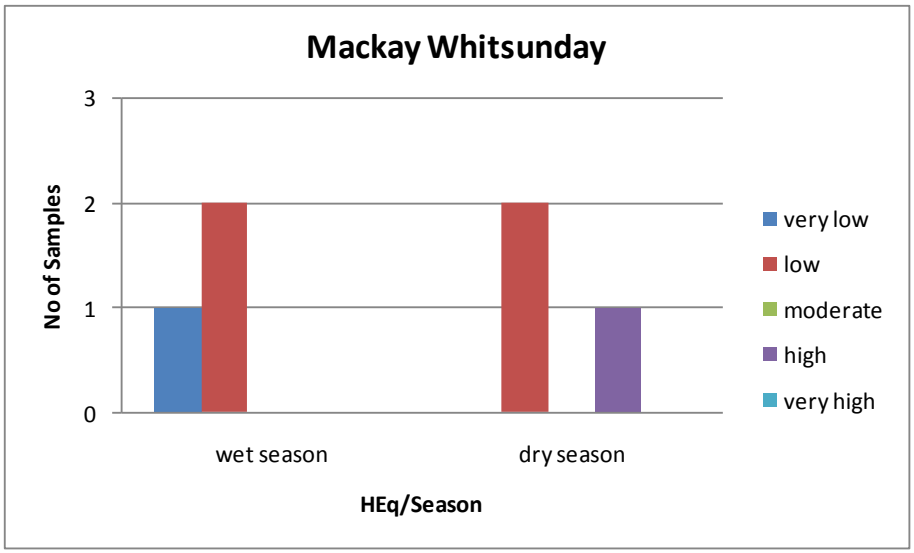

Figure 13. HEq index of all samples collected in Mackay Whitsunday region in wet and dry seasons 2008/2009

Fitzroy (North Keppel Is)

North Keppel Island

Diuron was detected in all 6 sampling periods at North Keppel Island at consistently very low detectable concentrations. Tebuthiuron was the only other herbicide that was detected.

Table 20. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at North Keppel Island using EDs.

Pesticide	Samples/detects	Max/max dry	Median	Mean	Min
Diuron	6/6	1.1/1.1	0.91	0.82	0.46
Tebuthiuron	6/1	0.18/0.18	nd	nd	nd
Herbicide EQ		1.1/1.1	0.9	0.8	0.5

TCPP was the only chemical of interest that was detectable in PDMS deployed at North Keppel Island in a sampler deployed in the July-August 2008 deployment. We estimate a time averaged concentration of TCPP of about 11 ng/L for that period.

The HEq concentration in the six samples collected from North Keppel Island suggests that the herbicide index for this site is *very low*. Only the September 2008 sample was in the *low* category, with the five other periods in the *very low* category.

Four years of data at Keppel Island show consistently low concentrations at this site with a potential indication of a decrease in the concentration over this period (Figure 8)

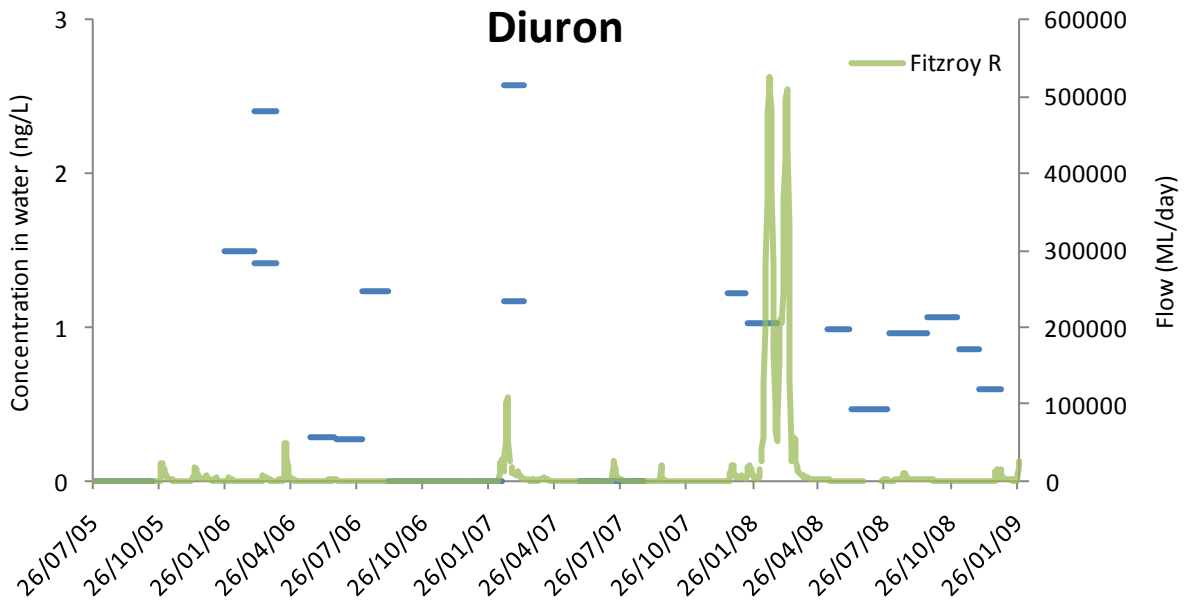

Figure 14. Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at North Keppel Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.

Fitzroy Region - Regional Summary

With 5 out of 6 sampling periods at the only inshore reef site in this region receiving a herbicide index of very low and no exceedances of the WQG, there is no evidence to suggest this region has any major herbicide contamination issues.

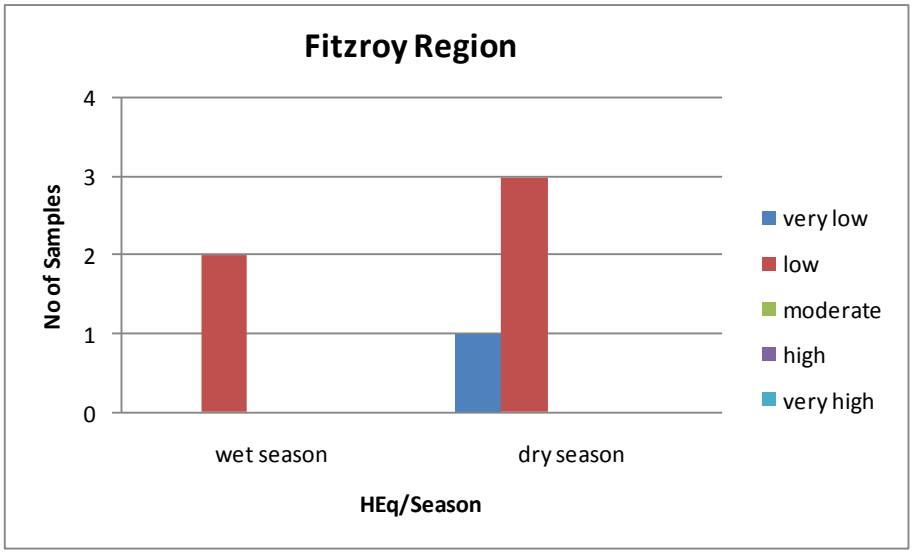

Figure 15. HEq index of all samples collected in Fitzroy region in wet and dry seasons 2008/2009

Passive sampling at river mouth sites

Wet Tropics (Tully River)

Tully River

Due to sampler losses, only five sampling periods were covered using polar samplers in the Tully River. Four herbicides (diuron, simazine, atrazine and hexazinone) as well as degradation products of atrazine and simazine were detected consistently for all 5 sampling periods. Concentrations were highest for diuron and atrazine with peak time-averaged concentrations in the December/January deployment of 120 ng/L (for both chemicals). Concentrations of hexazinone and simazine were lower with concentrations of 29 and 16 ng/L respectively during this sampling period (Table 21).

Table 21. Summary of maximum, median, mean and minimum water concentrations (ng/L) for pesticides detected at Tully River using EDs.

Pesticide	Samples/detects	Max/max dry	Median	Mean	Min
Diuron	5/5	120/18	7.6	32	6.2
Simazine	5/5	16/8.7	2.5	6.1	1.3
Atrazine	5/5	120/9.8	9.7	31	8.9
Desethyl Atrazine	5/5	8/3.4	2.6	3.5	1.8
Desisopropyl Atrazine	5/3	2.8/0.5	0.39	0.74	nd
Hexazinone	5/5	29/10	7.5	12	4.8
Herbicide EQ		150/28	16	39	9.7

At Tully River both PDMS and SPMD samplers were continuously deployed from May to December 2008, and from March to April 2009. Fifteen compounds of interest were detected in PDMS including bifenthrin (0.4 – 2 ng/L), chlordane trans (1.2 ng/L), chlorothalonil (93 – 137 ng/L), chlorpyrifos (0.3 – 28 ng/L), diazinon (7 – 92 ng/L), dieldrin (0.4 – 1 ng/L), galaxolide (1 – 3 ng/L), parathion ethyl (4 ng/L), pendimethalin (0.6 – 12 ng/L), phosphate tri-n-butyl (1 – 1.2 ng/L), piperonyl butoxide (0.4 ng/L), propiconazole (3 – 17 ng/L), prothiophos (1.1 – 4 ng/L), tebuconazole (1.3 – 8 ng/L) and tonalide (0.4 ng/L). Concentrations for many of the chemicals are estimates due to a lack of calibration data. It is noteworthy that the levels of both chlorpyrifos and

diazinon are generally well above the trigger values for marine waters of the GBR as set out in the GBRMPA WQG, however these chemicals were not detected at any inshore reef sites within the region.

The herbicide equivalent concentrations in the samples collected from Tully River suggest that the herbicide index for this site is *moderate*. (July 2008 was in the *low* category while December 2008 was in the *high* category.)

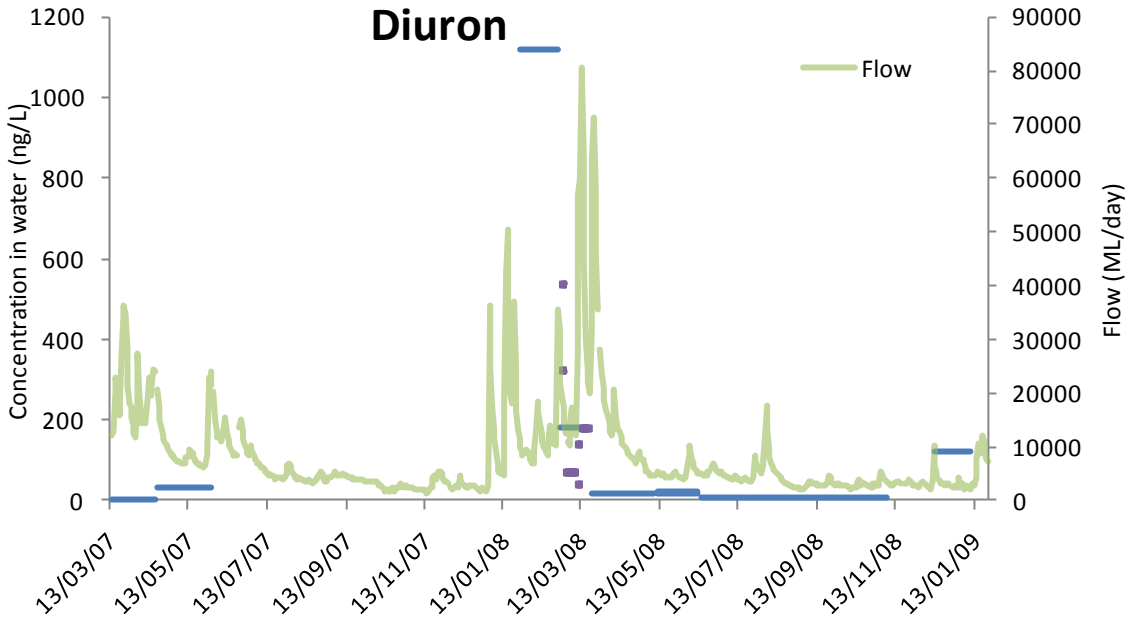

Figure 16. Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time integrated monitoring was conducted at Tully River. Water concentrations presented as time integrated water concentration over period of sampler deployment. Water concentrations measured during flow events by rapid (membrane free) passive samplers (short lines) and grab sampling (dots during high flow) are also included. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.

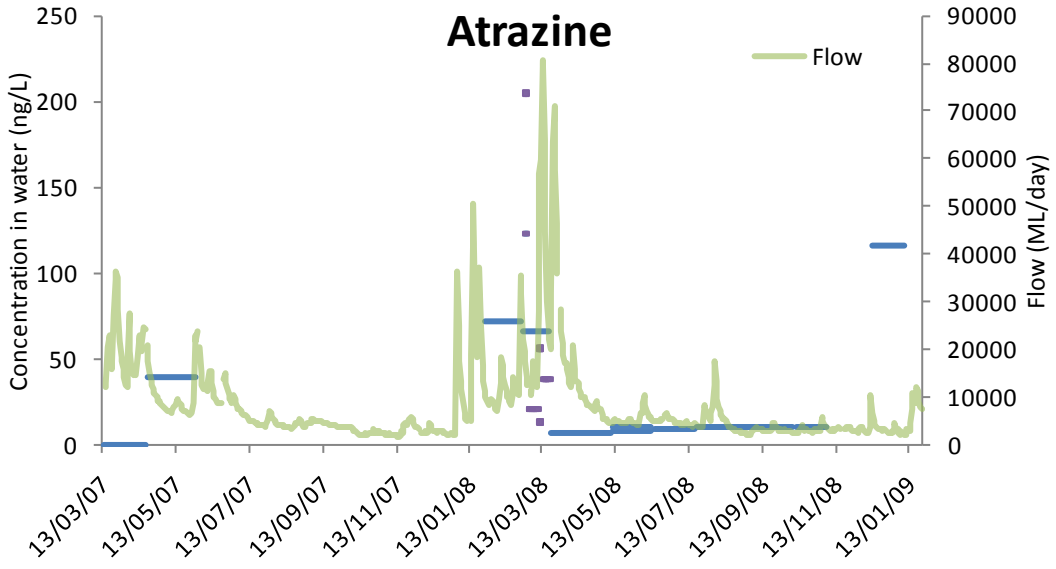

Figure 17. Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Tully River. Water concentrations presented as time integrated water concentration over period of sampler deployment. Water concentrations measured during flow events by rapid (membrane free) passive samplers (short lines) and grab sampling (dots during high flow) are also included. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.

Mackay Whitsunday (Pioneer River)

Pioneer River

For the routine pesticide monitoring in the Pioneer River polar samplers with membranes were successfully deployed and retrieved for 9 monitoring periods. For the 2008/09 sampling period a broad range of pesticides were detected using the ED sampler for polar chemicals with atrazine and diuron continuously detected at the highest concentrations followed by hexazinone, ametryn, flumeturon, tebuthiuron, simazine and prometryn. The concentrations of atrazine, diuron and hexazinone varied over a large range (Table 17) and were on several occasions close to, or in excess, of 1000 ng/L. The maximum monthly concentrations (time averaged and based on passive sampler data) were similar to the 'event mean concentrations' calculated by Lewis et al. (2009) for the Pioneer River for diuron and hexazinone for the 04/05 and 05/06 wet seasons. Our estimates are higher for atrazine. Our use of a blanket estimated sampling rate for all chemicals detected may have contributed to the difference.

Table 22. Summary of maximum, median and minimum water concentrations (ng/L) for pesticides detected at Pioneer River using EDs.

Pesticide	Samples/detects	Max/max dry	Median	Mean	Min
Diuron	9/9	1600/34	34	230	12
Simazine	9/1	3.7/nd	nd	0.41	nd
Atrazine	9/9	1400/33	28	180	4.1
Desethyl Atrazine	9/9	82/7.7	6.4	14	1.3

Desisopropyl Atrazine	9/2	33/nd	nd	3.8	nd
Hexazinone	9/9	320/19	11	51	5.9
Tebuthiuron	9/3	1.8/nd	nd	0.29	nd
Ametryn	9/8	46/3	3	8.2	nd
Prometryn	9/1	0.59/nd	nd	0.07	nd
Herbicide EQ		2000/47	41	260	18

At Pioneer River PDMS and SPMD samplers were continuously deployed for the whole monitoring period. Thirteen compounds of interest were detected in PDMS including chlorpyrifos (0.4 – 2 ng/L), chlorfenvinphos (6 – 8 ng/L), diazinon (6 ng/L), dieldrin (0.9 – 4 ng/L), galaxolide (0.2 – 0.8 ng/L), metolachlor (5 – 43 ng/L), pendimethalin (0.5 – 1.3 ng/L), phosphate tri-n-butyl (1 – 1.2 ng/L), propazine (23 – 24 ng/L), propiconazole (7 ng/L), TCPP (23 ng/L), terbutryn (3 – 4 ng/L) and trifluralin (0.1 – 0.5 ng/L). All concentrations are estimates and it should be noted that as no calibration data are available for the uptake of galaxolide into PDMS, estimates for galaxolide are preliminary. It should be noted that the concentration of diazinon exceeds the trigger value for this chemical in the GBRMPA WQG, which apply to marine waters, by two orders of magnitude. However, there was no detection of this chemical at the inshore reef site at Great Keppel Island.

The HEq concentration in the samples collected from Pioneer River in the 2008/09 reporting period span over 3 categories from *moderate* in 2008 through to *very high* in January 2009 and *high* in February and March 2009. A suggested overall index is *high*.

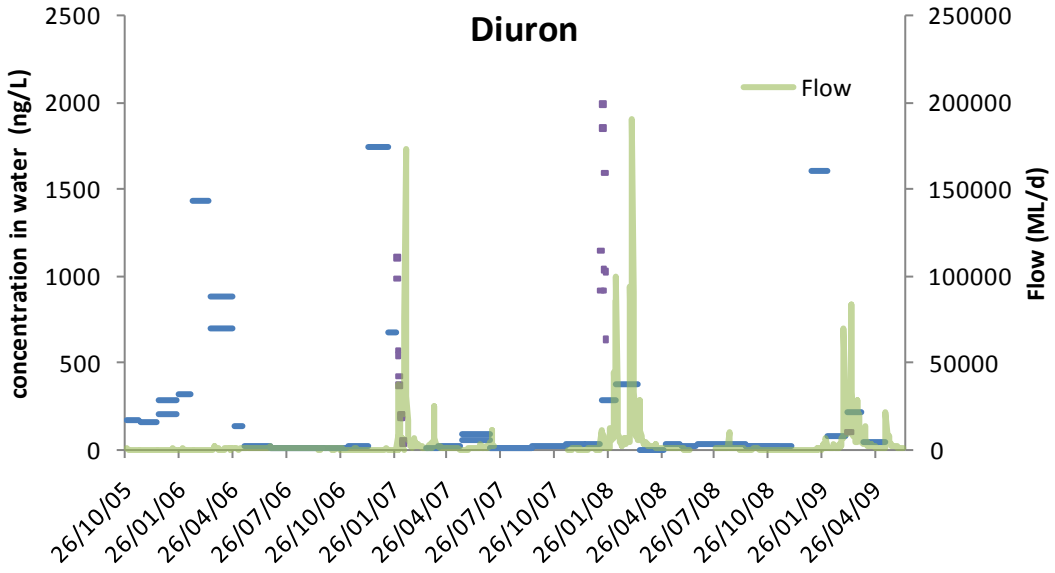

Figure 18. Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Pioneer River. Water concentrations presented as time integrated water concentration over period of sampler deployment. Water concentrations measured during flow events by passive samplers also included. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.

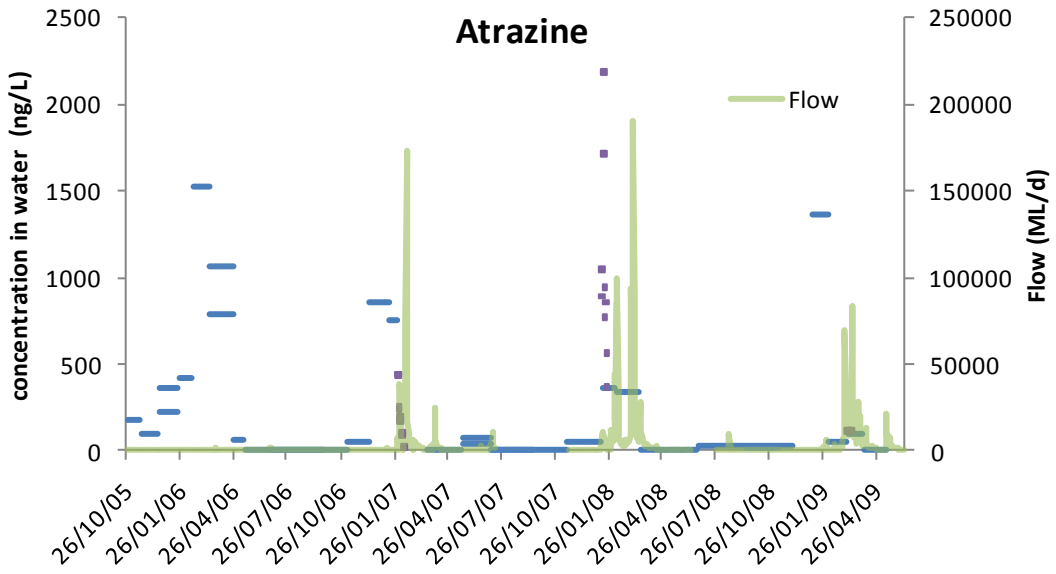

Figure 19. Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Pioneer River. Water concentrations presented as time integrated water concentration over period of sampler deployment. Water concentrations measured during flow events by passive samplers also included. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.

Routine River Mouth Sampling - Summary

As expected, pesticide levels were markedly higher in river mouths than in inshore reef sites but these levels are not reflected in the results from adjacent inshore reef sites. Pesticide levels were generally higher in the Pioneer River which is consistent with previous years, although wet season monitoring in the Tully River was truncated.

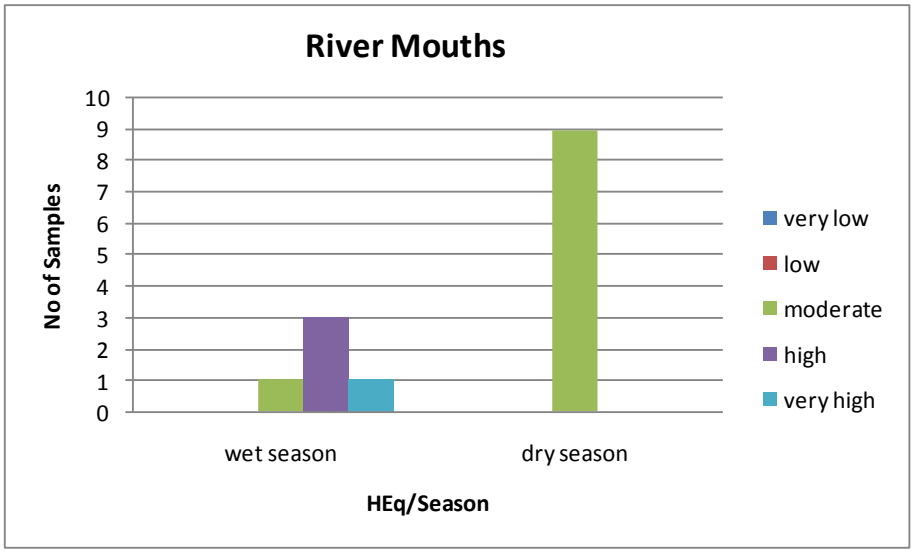

Figure 20. HEq index of all samples collected in River Mouths (Pioneer and Tully Rivers) in wet and dry seasons 2008/2009

Region	Sites/Dates	May-08	Jun-08	Jul-08	Aug-08	Sep-08	Oct-08
Cape York	Lizard Island						
	Pixies Garden						
Wet Tropics	Low Isles						
	Fitzroy Island			TCPP 13 ng/L		galaxolide 0.1 ng/L	
	High Island						
	Normanby Island						
	Dunk Island						
Burdekin	Orpheus Island	phosphate tri-n-butyl 0.5 ng/L oxadiazon 3 ng/L propiconazole 5 ng/L bifenthrin 1 ng/L	(atrazine 5 ng/L)				
	Magnetic Island	phosphate tri-n-butyl 11 ng/L (atrazine 10 ng/L)	(atrazine 6 ng/L)	(atrazine 7 ng/L) galaxolide 0.1 ng/L			
	Cape Cleveland		phosphate tri-n-butyl 1.2 ng/L (atrazine 11 ng/L) chlorpyrifos 0.4 ng/L metolachlor 5 ng/L pendimethalin 0.6 ng/L	(atrazine 15 ng/L) TCPP 12 ng/L metolachlor 8 ng/L			
Mackay-Whitsundays	Outer Whitsunday - Hamilton						
	Inner Whitsunday - Daydream					(diuron 31 ng/L)	
Fitzroy	North Keppel Island			TCPP 11 ng/L			

Sampling No sampling

Figure 21. Passive sampling sites: Overview of PDMS sampling periods and major chemicals detected during Dry Season – May 08 to Oct 08

Region	Sites/Dates	Nov-08	Dec-08	Jan-09	Feb-09	Mar-09	Apr-09
Cape York	Lizard Island						
	Pixies Garden			galaxolide 0.3 ng/L	TCPP 16 ng/L galaxolide 0.5 ng/L		DEET 28 ng/L galaxolide 0.4 ng/L pendimethalin 0.6 ng/L
Wet Tropics	Low Isles						
	Fitzroy Island			(atrazine 4 ng/L)		galaxolide 0.4 ng/L pendimethalin 0.9 ng/L	galaxolide 0.4 ng/L TCPP 30 ng/L
	High Island						
	Normanby Island	TCPP 13 ng/L galaxolide 0.9 ng/L		phosphate tri-n-butyl 1.2 ng/L TCPP 18 ng/L galaxolide 0.2 ng/L chlorpyrifos 0.3 ng/L		DEET 31 ng/L galaxolide 4 ng/L	galaxolide 0.5 ng/L
	Dunk Island	(diuron 8 ng/L) TCPP 20 ng/L galaxolide 0.4 ng/L		chlorpyrifos 0.3 ng/L fipronil 0.3 ng/L	TCPP 12 ng/L galaxolide 0.4 ng/L chlorpyrifos 0.7 ng/L	pendimethalin 1.2 ng/L	galaxolide 0.5 ng/L
Burdekin	Orpheus Island						
	Magnetic Island	TCPP 17 ng/L galaxolide 0.4 ng/L		DEET 34 ng/L (atrazine 6 ng/L) TCPP 12 ng/L galaxolide 0.5 ng/L metolachlor 4 ng/L	TCPP 24 ng/L galaxolide 0.9 ng/L metolachlor 6 ng/L	pendimethalin 1 ng/L	
	Cape Cleveland	TCPP 19 ng/L galaxolide 0.4 ng/L		(atrazine 11 ng/L) galaxolide 0.2 ng/L metolachlor 8 ng/L	metolachlor 13 ng/L	TCPP 17 ng/L galaxolide 0.3 ng/L	TCPP 12 ng/L galaxolide 0.3 ng/L pendimethalin 0.9 ng/L
Mackay-Whitsundays	Outer Whitsunday - Hamilton	galaxolide 0.6 ng/L		TCPP 11 ng/L			
	Inner Whitsunday - Daydream						
Fitzroy	North Keppel Island						

Sampling No sampling

Figure 22. Passive sampling sites: Overview of PDMS sampling periods and major chemicals detected during Wet Season – Nov 08 to Apr 09

Event Sampling (Project 3.7.2)

Mackay-Whitsunday Region: Pioneer River

Only one set of samplers was deployed in the Pioneer River from the 7-13 March 2009. Grab samples were taken on the 7th and 13th of March. A range of polar pesticides were quantified in the ED samplers with diuron and atrazine dominating the chemical profile, followed by hexazinone, and ametryn.

Overall the water concentration of pesticides in EDs tended to decrease during the monitoring period, although the concentration of diuron in the water fluctuated significantly (Figure 15). Decreasing levels of phosphate tri-n-butyl were detected in co-deployed PDMS throughout the flow events.

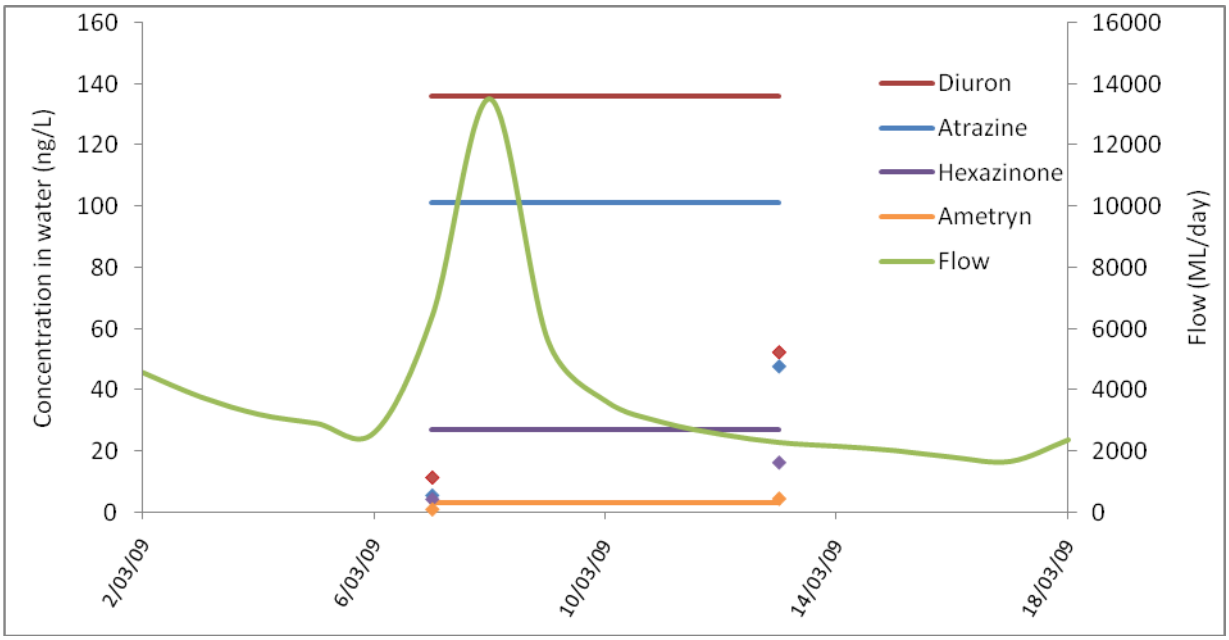

Figure 23. Flow rates (ML/day) and water concentrations (ng/L) of pesticides measured during Pioneer River flow events. Left axis shows water concentrations and the right axis shows flow rates.

Fitzroy Region: Fitzroy River

Six sets of passive samplers were deployed in the Fitzroy River during and after the flow event. Results from ED samplers showed that atrazine dominated the polar pesticides with a maximum water concentration of 1700 ng/L. Tebuthiuron was the second highest polar pesticide, with a maximum of 430 ng/L. These results are in contrast to event monitoring in the previous year which showed that tebuthiuron dominated followed by atrazine. Land use appears to have a substantial effect on the type of pesticides in flood waters from the Fitzroy River Basin. Tebuthiuron was the dominant chemical detected during 2007 seasonal floods which originated from lands used for grazing. The 2008 seasonal flood waters were dominated by atrazine which originated from lands used for cropping and grazing. The data are consistent with findings by Packett et al. (2009) who also found similar event mean concentrations (EMCs) during 2007 and 2008 events in the Fitzroy including tebuthiuron being the dominant herbicide in the 2007 event and atrazine in the 2008 event. Other polar pesticides and degradation products that were detected included desethly

atrazine, simazine, desisopropyl atrazine, diuron, and hexazinone. Prometryn, flumeturon and ametryn were also present, mostly below 1 – 2 ng/L.

In terms of comparison of the monthly samplers (with membrane) versus the samplers that were deployed for relatively short periods (event samplers without membrane), the February/March result from the Fitzroy River indicate good agreement between the two sets of results with a mean concentration of about 100 ng/L for atrazine in the monthly sample compared to a mean concentration of atrazine in the four weekly samples of about 90 ng/L. Similarly the average concentrations for tebuthiuron in the monthly and weekly samples were in overall good agreement. Due to the difficulties with the deployment of samplers during floods it is suggested that the benefit from deploying event samplers may be relatively small compared to the associated additional costs and potential risks. Naturally, in terms of load calculations the uncertainty is increased when the sampling period covers periods of fluctuating concentrations and flow.

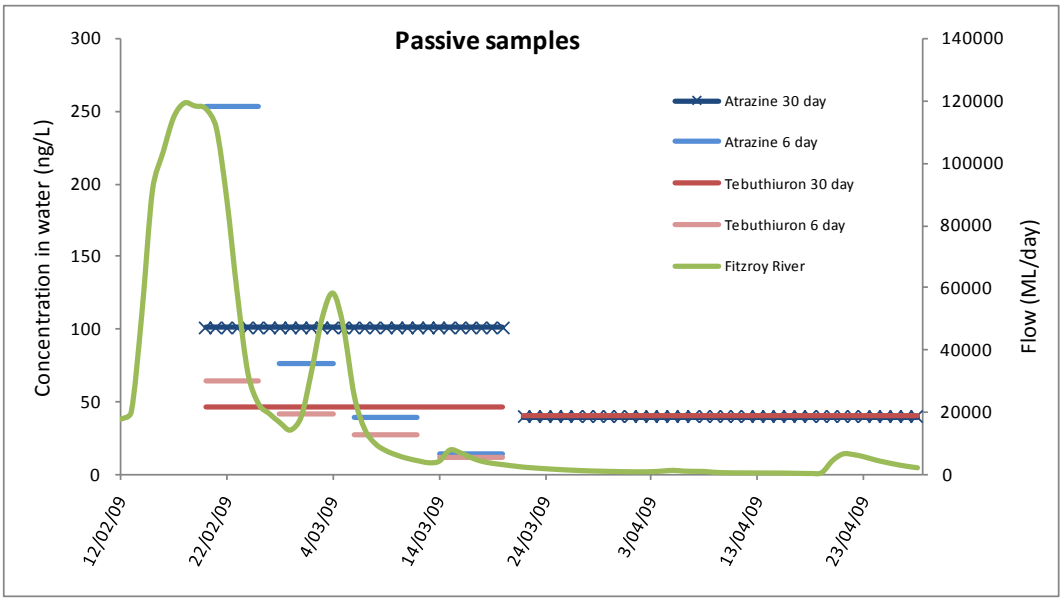

Figure 24. Flow rates (ML/day) and water concentrations (ng/L) of pesticides measured during Fitzroy River flow events. Left axis shows water concentrations and the right axis shows flow rates.

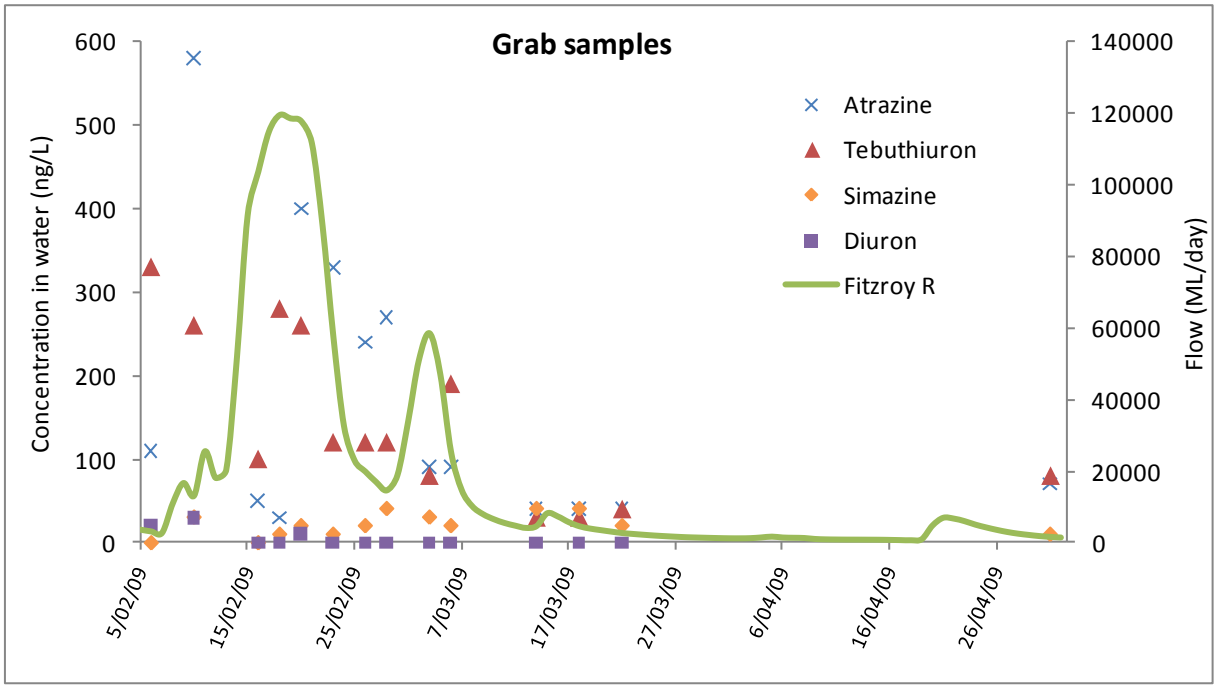

Figure 25. Flow rates (ML/day) and water concentrations (ng/L) of pesticides measured during Fitzroy River flow events. Left axis shows water concentrations and the right axis shows flow rates.

Analysis of passive samplers deployed at inshore coral reef sites using the I-PAM phytotoxicity assay. (Project 3.7.1- b)

Toxicological assessment of chemical pollutants present at coral reef monitoring sites

The third component of this project stems from a need to improve our understanding of the environmental relevance of the presence of herbicides at inshore reefs but also to better integrate the herbicide data with biological monitoring data. Hence this component is based on the use of passive sampling techniques co-located at coral recruitment sites during the spawning season. For this component samplers are analysed by assessing the inhibition of photosynthesis in algae (ideally isolated zooxanthellae) that are dosed with concentrated extracts from passive samplers that were exposed at selected sites over the coral spawning season. Details of the deployment are summarised in Table 23.

Table 23. Details of the deployment of the samplers, PFM based sampling rates and 'equivalent volume' sampled assuming linear uptake over the entire sampling period.

	Deployment Details			Rs (diuron)	Equivalent Volume
Deployment Location	Deployed	Retrieved	Days	(L/day)	(L)
High Is West	10/10/2008	1/12/2008	52	0.08	4.2
Frankland Is West	10/10/2008	1/12/2008	52	0.08	4.2
Fitzroy Is West	10/10/2008	2/12/2008	52	0.08	4.2
Pine Is	1/10/2008	7/12/2008	67	0.08	5.4
Double Cone Is	2/10/2008	6/12/2008	65	0.08	5.2

Daydream Is	1/10/2008	6/12/2008	66	0.08	5.3
Pelican Is	4/10/2008	8/12/2008	65	0.08	5.2
Humpy/Halfway Is	5/10/2008	8/12/2008	64	0.08	5.1
Barren Is	4/10/2008	8/12/2008	65	0.08	5.2
Pandora Reef	8/10/2008	3/12/2008	56	0.08	4.5
Pelorus/Orpheus Is	9/10/2008	3/12/2008	55	0.08	4.4
Geoffrey bay	8/10/2008	4/12/2008	57	0.08	4.6

Results

Results are reported as herbicide equivalent concentrations (ie. ng HEq/L). Equivalent concentration represents the concentration of the reference compound that would be required to produce the same effect as the mixture of different compounds in the sample and was calculated using the EC_{50} of the reference compound diuron and the samples:

HEq = EC_{50} (diuron) / EC_{50} (sample)

Since the EC_{50} (diuron) is expressed in ug/L and the EC_{50} (sample) in dimensionless REF, the herbicide equivalent concentration is also expressed in ug/L and can be viewed as the concentration of diuron that would be required in a sample to express the observed inhibition.

Dose response assessments were carried out in replicates in samplers from all sites. Second replicates were tested on a different day than the first replicate to evaluate repeatability of the assay and the results were expressed as an average ± sd of two replicates (Figure 20). Diuron as a reference compound and also as a positive control of the assay was included on each microplate. The herbicide equivalent concentrations of the samples were calculated based on the average EC_{50} (diuron) of the day (n = 4 – 5).

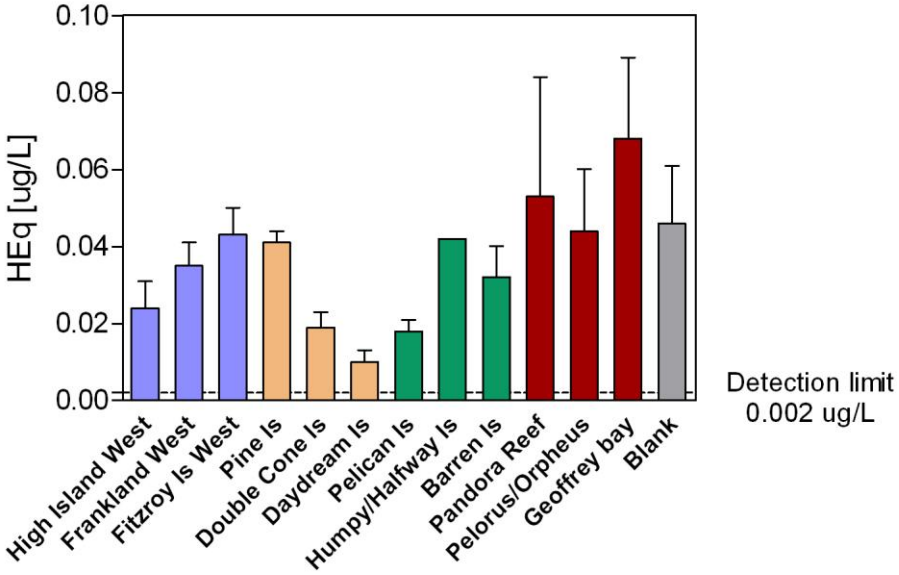

Figure 26. Phytotoxic response of the samples in the I-PAM assay expressed as herbicide equivalent concentrations (HEq). Data represent the average ± sd of two replicates. HEq of the blank was calculated based on the average equivalent volume of the samples (4.8 L of water).

Due to the high blank values obtained using unsubmerged blank samplers the results of this study are inconclusive. The treatment of blanks in MilliQ water is now included as a standard operating procedure.

Discussion

Communication difficulties are continuing with some sites and there are still some issues with volunteers returning Deployment Changeover forms containing dates and any details of sampler losses. Improvement in the communication between Entox/GBRMPA and volunteers has enabled a number of deployment issues to be dealt with as they arise and appears to be contributing toward an improving sampler return rate.

GBRMPA regional co-ordinators have provided interim sampling support and training for staff at sites where difficulties have occurred. This has contributed to improved sampler return rates.

Regional trends in water concentrations and pesticide profiles

Pesticides, and specifically herbicides were detectable at all sampling sites where passive samplers were deployed. Mean concentrations (expressed as HEq concentrations in ng/L) were typically in the 1 – 4 ng/L range with a mean concentration in the subnanogram per litre range at Pixies Garden and an elevated mean concentration at the Inner Whitsundays that was based on a very high result (120 ng/L) during the September 2008 deployment.

While the data shows differences between sites related to the absolute concentrations and the specific chemicals that are detectable, the overall pesticide index is relatively consistently *low* across sites and regions with a trend towards slightly lower concentrations/higher rating (*very low*) in the most northern and southern regions that were monitored.

At most sites diuron was the chemical that was found most frequently and at the highest mean concentrations (A notable exception is the Cape Cleveland site where the mean and median concentration of atrazine was higher than that of diuron). In combination with its high relative potency thus diuron is the key contributor to the overall HEq in water on the GBR, contributing typically to more than 90% of the HEq concentration.

Herbicide concentrations observed are in good agreement with the few other studies on herbicide concentrations at inshore reefs (Shaw et al. 2005, 2009a). With regards to seasonal differences our data indicate a trend of higher concentrations during early in the wet season. There may be a relationship between river flow and increased concentrations, however the association has not been quantified to date. For sites such as Fitzroy and Normanby Islands, located in the wet tropic region an evaluation of the last two years data suggest that time averaged concentrations vary by a factor of 10 – 20 for diuron.

The data obtained to date have not been analysed statistically for time trends.

Table 24. Herbicide equivalent toxicity categories based on regions.

Region	Site (sampling periods)	Maximum (HEq)	Mean HEq	HEq category
Cape York	Lizard Island (3)	2.5	1.9	Low (Cat. 2)
	Pixies Garden (6)	1.8	0.5	Very Low (Cat. 1)
Wet Tropics	Low Isle (9)	5.7	1.9	Low (Cat. 2)

	Fitzroy Isl. (8)	17	4.0	Low (Cat. 2)
	High Isl. (2)	2.3	1.8	Low (Cat. 2)
	Normanby Isl. (10)	9.3	2.9	Low (Cat. 2)
	Dunk Isl. (4)	4.1	2.3	Low (Cat. 2)
Burdekin	Orpheus Isl. (7)	1.9	1.0	Low (Cat. 2)
	Magnetic Isl. (9)	5.6	2.5	Low (Cat. 2)
	Cape Cleveland (10)	6.2	2.1	Low (Cat. 2)
MacKay/Whitsunday	Inner Whitsunday (3)	120	45	No rating due to a yet to be explained outlier
	Outer Whitsunday (3)	4.7	1.9	Low (Cat. 2)
Fitzroy	North Keppel (6)	1.1	0.8	Very Low (Cat. 1)

Routine monitoring at the two river sites, Tully River and Pioneer River, revealed both a wider range of pesticides and elevated water concentrations compared to inshore reef sites. Diuron and atrazine were the dominant herbicides detected in the Tully River during both the dry and wet season with estimated concentrations of up to approximately 120 ng/L for both these chemicals in the period leading to a flood event in January 2009. No event samplers were deployed in the Tully River at this time and the baseline sampler was lost during the event, hence no data are available for this period.

For the Pioneer River both baseline (monthly) and event sampling data are available demonstrating that monthly mean concentrations up to 1600 ng/L were estimated from samplers deployed prior to the first main wet season event. Interestingly the concentrations during the event obtained using both event passive samplers, baseline passive samplers and limited grab samples were substantially lower (max. 100 – 200 ng/L). For the Fitzroy River event, passive samplers and monthly samplers showed that atrazine was the dominant herbicide in the water during the February 2009 flow event. Good agreement was observed between mean concentrations predicted from event (weekly) and baseline (monthly) samplers. Furthermore the concentrations obtained with passive samplers in the river mouths of the Tully and Fitzroy Rivers over the flood periods were in good agreement with grab sample data obtained in the near shore area in flood waters (low salinity) by Devlin et al. (unpublished data).

The analysis of passive sampling extracts using bioanalytical methods (I-PAM assay on *Chlorella*) unfortunately failed to provide conclusive results due to interferences in the blank sample. Work is underway to assess whether this is due to real contamination of the blank with a common herbicide or as previously observed due to unrelated chemicals that may be associated with the unexposed solid phases used in the passive samplers.

Further work

In terms of quality assurance and long term comparability of data there are a number of specific tasks that are required before we tackle the summary report in 2010. In brief we need to

- Revisit sampling rates and apply compound specific sampling rates for ED samplers.
- Consider incorporation of the flow data although it appears that most samples are obtained under flow conditions which indicate a maximum sampling rate
- A more thorough evaluation of the herbicide potency factors for calculation of HEq concentrations is required.

- Samplers analysed for biological effect using I-PAM assays require a blank that is stored in MilliQ water.

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Appendix A: DERM acknowledgement for use of flow data

'Based on or contains data provided by the State of Queensland (Department of Environment and Resource Management) [2008,2009]. 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

Disclaimer and indemnity: You agree to accept all responsibility and risks associated with the use of the data. DERM makes 'no representations or warranties in relation to the data, and, you agree that, to the extent permitted by law, all warranties relating to accuracy, reliability, completeness, currency or suitability for any particular purpose and all liability for any loss, damage or costs (including consequential damage) incurred in any way (including but not limited to that arising from negligence) in connection with any use of or reliance on the data are excluded or limited. You agree to continually indemnify the State of Queensland and DERM (and their officers and employees) against any loss, cost, expense, damage and liability of any kind (including consequential damage and liability in negligence) arising directly or indirectly from or related to any claim relating to your use of the data or any product made from the data.

Appendix B: Herbicide Potency Factors (Summary of Available Data)

Table 25. Herbicide potency factors for different herbicides and selected degradation products. Preliminary summary of available data that are used for calculating HEq concentrations from data obtained in passive samplers.

	Relative potency (range)			Relative potency (mean based on various EC)				Relative potency (mean based on IC10 and IC50)[f]			
Herbicides	Zooxanthellae (Corals) [a]	*P. tricornutum*[bcd]	*C. vulgaris*[bde]	Zooxanthellae (Corals) [a]	*P. tricornutum*[bcd]	*C. vulgaris*[bde]	Mean	*Navicula* sp.	*Nephroselmis pyriformis*	*Phaeodactylum tricornutum*	*Cylindrotheca Closterium sp.*
diuron	1	1	1	1	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	0.51	0.89	0.32	0.44
atrazine	0.05-0.06	0.1-0.4	0.15 -0.3	0.05	0.22	0.21	0.16	0.11	0.15	0.09	0.06
simazine	0.02	0.03-0.05	0.02-0.26	0.02	0.04	0.14	0.07	0.02	0.09	0.03	0.02
tebuthiuron	0.01	0.07	0.11-0.2	0.01	0.07	0.15	0.08	0.04	0.16	0.05	0.06
promertyn			1-1.1			1.05	1.05				
terbuthylazine			0.3			0.3	0.3				
desethylatrazine			0.01-0.2			0.105	0.11				
desisopropylatrazine			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., 2005

[d] Schmidt, 2005

[e] Macova et al., unpublished data (Entox)

[f] Magnusson, 2009