National Research Centre for ENVIRONMENTAL TOXICOLOGY

Queensland Government
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THE UNIVERSITY OF QUEENSLAND
AUSTRALIA

Monitoring of organic chemicals in the Great Barrier Reef Marine Park and selected tributaries using time integrated monitoring tools.

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National Research Centre for Environmental Toxicology (EnTox)

Great Barrier Reef Water Quality Protection Plan (RWQPP) Marine Monitoring Program (2005-2008)

SUPPORTING STATE, NATIONAL AND INTERNATIONAL HEALTH RISK ASSESSMENT

FROM A WORLD CLASS FOUNDATION IN ENVIRONMENTAL TOXICOLOGY

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Executive Summary

This monitoring program was designed to collect baseline monitoring data for pesticides in the Great Barrier Reef area. The objectives of the program are to detect long-term trends in concentrations of anthropogenic pollutants in river mouths and at inshore Reef sites of the Great Barrier Reef.

Routine monitoring was undertaken at 13 inshore reef sites and 2 river mouths. Routine sampling occurs monthly during the wet season (November to April) and for two month periods during the dry season (May to October). Of all samplers sent for deployment, 84% were returned for analysis. Overall this was an increase in the number of successful deployments compared with previous years. Additional event sampling was undertaken at 3 river mouth sites. Samplers were also deployed for toxicological testing at 12 sites.

This report details results from the current period of sampling (May 2007 to April 2008) with added comparison to results from routine monitoring conducted in the previous two monitoring periods (2005/6 and 2006/7). The temporal comparisons were made for sites monitored during the current period and do not include sites that were discontinued.

The pesticide profile at inshore reef sites was dominated by diuron, atrazine and hexazinone. For most sites diuron was detected at the highest concentrations, with the exception of AIMS and Magnetic Island where atrazine was highest. Higher proportions of simazine were observed at sites within the Wet Tropics region compared to other sites. A comparison between samplers deployed in the Tully and Pioneer Rivers showed that simazine was a dominant pesticide in the profile of the Tully River. The occurrence of these herbicides was not surprising as they are used extensively in the sugar cane industry.

Pesticide concentrations were generally higher in the wet season than the dry season at all 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. Within sites, there was general consistency between the wet and dry seasons in the percentage contribution of the major herbicides detected, although some herbicides were present at sites in the wet season that were not detectable in the dry season.

Low concentrations of pesticides were detected at all 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 the maximum water concentrations of individual pesticides were similar regardless of where samples were collected (e.g. maximum water concentration of diuron ranged from 12 to 15 ng/L). There was wider variation in maximum and median water concentrations in the Burdekin region, however sampling at AIMS only occurred during the 2007/8 wet season and hence could bias results. Monitoring in the Mackay Whitsundays region showed that water concentrations for individual pesticides were generally higher at the Outer Whitsundays. 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. Water concentrations for dominant chemicals often exceeded 1000 ng/L.

Further statistical analysis should determine whether significant differences occur between sites and seasons. Overall, the analysis should take into account when the wet season commenced based on rainfall or hydrographs. Appropriate time trend analysis should also be undertaken to determine whether the concentration of pesticides in water has changed over the duration of the monitoring program. However further baseline data may need to be collected to facilitate this process.

Routine monitoring at inshore reef sites for pesticides using SPMDs and PDMS showed that very few chemicals were detected using these samplers. During the most recent monitoring period, SPMDs detected only chlorpyrifos and HCB. In previous monitoring periods, SPMDs detected pesticides such as diazinon, chlorpyrifos and prothiophos at low concentrations only occasionally. PDMS samplers detected a wider range of pesticides when compared to co-deployed SPMDs, but only sporadically. For example diazinon (12-31 ng/L). was detected twice in the dry season and phosphate tri-n-butyl was detected several times during the wet season (1-16 ng/L). The ability of PDMS to detect a wider range of pesticides over the most recent monitoring period has shown that these samplers are an adequate replacement for SPMDs. However, the number of sites where these samplers are used could be reduced significantly due to the low number of detections. For example, monitoring using PDMS could be limited to the wet season and/or to representative sites in each region.

Event monitoring at Tully, Pioneer and Fitzroy Rivers showed that the pesticide profiles in the Tully and Pioneer were similar to previous results. In contrast, for the Fitzroy River, tebuthiuron dominated in 2007 flow events, whereas atrazine dominated in 2008 events. This was most likely due to the 2007 flow event being dominated by inflows from grazing areas only, where tebuthiuron usage predominates for woody weed control. Further work is required to determine the load of pesticides delivered by these systems during flow events.

Comparisons can be made between grab sample based water concentrations and passive sampler based water concentrations measured in the Fitzroy River. Overall, 80% of all passive sampler-based water concentrations were within a factor of 2 of corresponding grab sampler-based water concentrations. In many cases, analysis of grab samples produced non-detects whereas corresponding passive samplers detected a chemical. These results highlight the advantage of using passive samplers to detect chemicals that are present at water concentrations that are below detection limits in grab samples.

Phytotoxicity testing of samples collected at sites during coral spawning in 2007 and 2008 showed that extracts needed to be concentrated significantly to inhibit photosynthetic activity. In 2007 one sample from High Island exceeded detection limits. In 2008 only samples from 3 sites (Humpy & Halfway Is, Barron Is, Orpheus Is (Pelorus)) produced a response above detection limits. Results were converted to diuron equivalencies and did not exceed 3 ng/L at any site.

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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
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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Lizard Island Research Station, Undersea Explorer, Cardwell Shire Council, Low Isles Caretaker, Quicksilver Connections, Raging Thunder, Fitzroy Island Resort, Hunt Resort, Queensland Parks and Wildlife Service, Frankland Island Cruise & Dive, Voyages Dunk Island Resort, Orpheus Island Resort, Nautilus Aviation, Great Barrier Reef Marine Park Authority, Daydream Island resort, Hamilton Island Enterprises, Voyages Heron Island, North Keppel Island Environmental Education Centre, Department of Natural Resources and Water, and the Australian Centre for Tropical Freshwater Research.

Background

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 ultimately 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 makes for easier detection. Replicate samplers have consistently provided highly 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.

Passive sampling techniques provide a quantitative measure 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 a sampler. To date, limited calibration data is available for deployments under different temperature and flow conditions. Moreover, data that is available relates to a limited set of chemicals. Sampling of environments with stagnant or low flow conditions also remains a challenge. It should also be understood that the period of time that samplers provide 'integrative' or average water concentrations before acting as equilibrium samplers varies with the sampler type and the chemicals of interest. When applied and interpreted appropriately, passive sampling techniques provide a sensitive and reproducible tool for the assessment of water contaminant levels.

Introduction

Cattle grazing and cropping (in particular sugarcane) account for significant land use in the Wet Tropics (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.

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).

Data on the concentrations of organic pollutants in rivers draining into the Great Barrier Reef have been gathered through short-term sampling efforts employing a range of sampling strategies which are unsuitable for estimating input loads. In addition, analysis of biota or sediments have been used to assess exposure to contaminants in the ecosystem (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 has been highlighted with the development of the Reef Plan, which aims to address long-term changes to pollutant concentrations and their effects on the Great Barrier Reef. To help achieve this aim, 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 impact on ecosystem health. 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. Many of the traditional sampling methods for trace pollutants are not reliable for monitoring long term trends. Typically, individual "grab" or "snap shot" water samples are difficult to interpret if the variability of pollutants on a temporal scale is not known. Furthermore, the method is insensitive and careful handling is required to avoid degradation of chemicals between sampling and analysis. Analysis of biota or sediments has proved to be a more sensitive method for detecting persistent lipophilic pollutants, however interpretation of the results has remained a challenge. As a result, 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 Plan. The Reef Plan 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 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 Plan.

The monitoring tasks in the Reef Plan MMP have primarily focused on the evaluation of organic pollutants using time integrated passive sampling techniques. Empore Disk (ED) based polar passive samplers and SPMD passive samplers are the major monitoring tools utilised. Some 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. Efforts to continually improve detections of chemicals of interest and the reliability of their quantification include the deployment of an additional passive sampler and a flow monitoring device. These devices have been deployed alongside the EDs and SPMD samplers for part of the sampling period.

Polydimethylsiloxane (PDMS) is a widely used silicon-based organic polymer. It is a hydrophobic polymeric sorption material that has been used as a non-polar coating for gas chromatographic columns and SPME fibres (Heltsley, 2004). Use of this polymer in passive sampling has been relatively recent; PDMS strips as passive samplers were initially used by Smedes (2007). EnTox has adopted this method in recent years and continues to calibrate samplers for a broad range of chemicals (Bauer *et al.*, in preparation and Stephens *et al.,* in preparation). PDMS strips are an important contribution to passive sampling techniques since they are useful in detecting a wide range of pollutants including non-polar PAHs, organic insecticides and pesticides, and other more polar chemicals.

The uptake of chemicals into passive samplers is often governed by the resistance of chemical mass transfer through the boundary layer of water at the sampler-water interface. The thickness of that boundary layer is an important parameter that may affect sampling kinetics. In the last decade, methods such as the use of performance reference compounds (PRCs), have been used as an in-situ calibration for the effect of flow/turbulence on uptake in isokinetic samplers such as the SPMD. However research at EnTox and by others in this field (Huckins, personal communication), indicates the PRC technique to date is unreliable for in-situ calibration of polar samplers that use sorption phases such as the poly(styrenedivinylbenzene) co-polymer (SDB-RPS). The Plaster Flow Monitor (PFM) has recently been developed and introduced at EnTox to aid in the extrapolation of sampler kinetics from laboratory and semi-controlled field calibrations, towards use in routine field application of the devices. The devices aim to provide quantitative information on the effect of flow and turbulence on the kinetics of passive samplers (O'Brien and Mueller, accepted). The PFM's are constructed from dental plaster and cast into a polymer holder that is deployed alongside the passive samplers. Throughout the deployment period the plaster dissolves from the exposed surface at a rate determined by environmental factors such as flow/turbulence and also salinity and temperature. At present, the total loss of plaster from a PFM provides only an indication of the average flow during the deployment. Calibration studies are underway to allow a more accurate determination of passive sampling rates from total loss of plaster in the PFM's. Consequently, the PFM data are reported but not used at this time for recalibration of sampler uptake rate.

Methodology

[Note: detailed documentation of methods was provided to GBRMPA in a separate report in October 2005: Water Quality and Ecosystem Monitoring Programs - Reef Water Quality Protection Plan: Methods and Quality Assurance/Quality Control Procedures.]

This program encourages community ownership of the Reef Plan 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 three river sites including passive and snap shot collections at the Fitzroy River. Samplers deployed at 12 inshore reef sites were also tested using a bioassay for pollutant toxicity to coral zooxanthellae.

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.

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 month periods during the dry season (May to October) and monthly during the wet season (November to April).

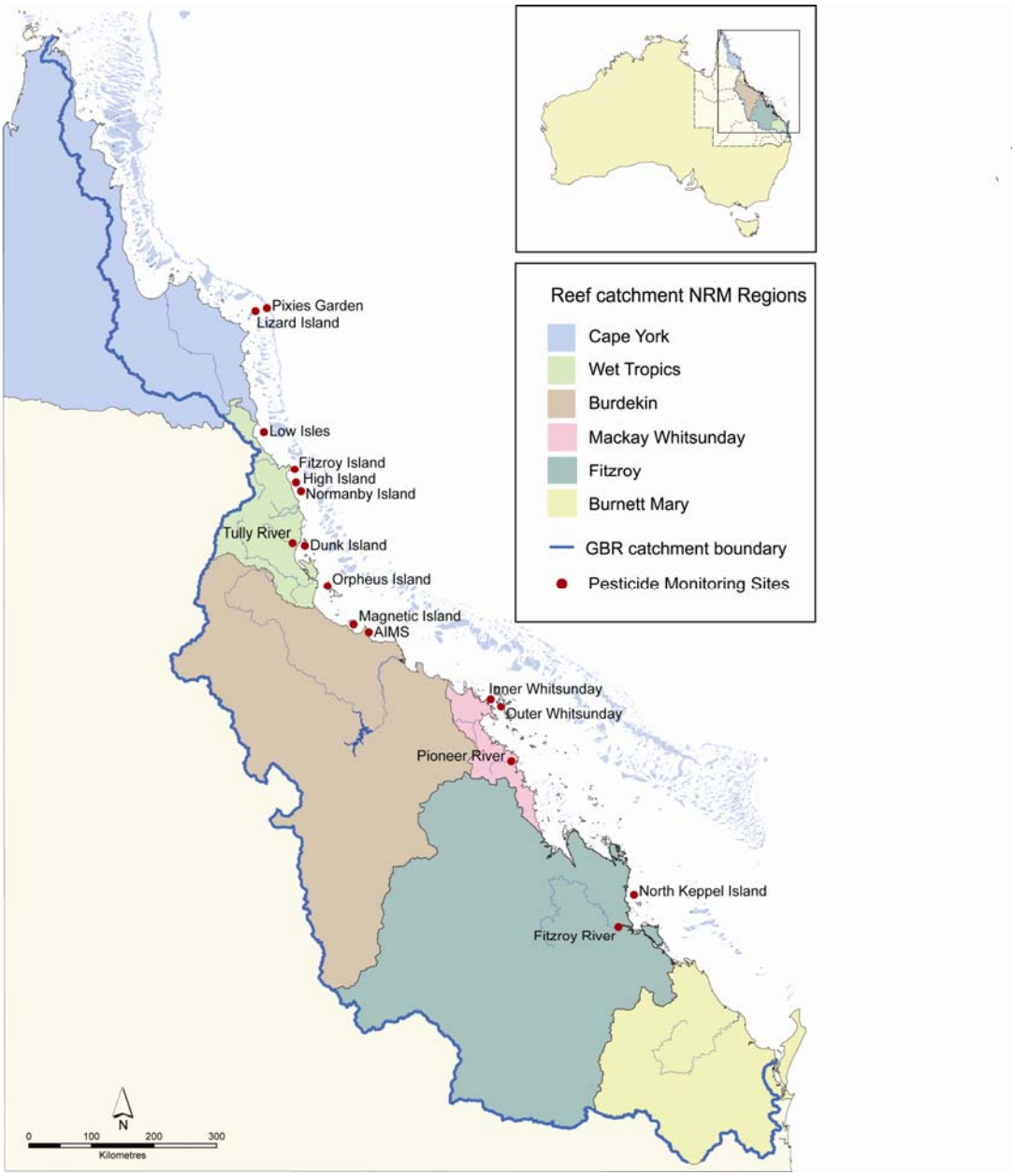

Figure 1.Locations of GBR lagoon sites monitored using passive samplers during 2006-2007 (sourced from J.Prange 2008).

Under ideal conditions 9 deployments were possible at each site during a monitoring cycle (May to April). However this did not always occur, either due to the later establishment of some sites or difficulties encountered at individual sites. *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 and two SPMDs and PDMS were deployed at each site per scheduled deployment. From early 2007, PFMs were also deployed. Of the replicate samples, for one site in each deployment period, both were extracted and analysed to test reproducibility. For the remaining replicates, the EDs were extracted and the extracts stored, while the SPMDs and PDMS were frozen for future use.

Of all samplers sent for deployment, 84% were returned for analysis. Overall this is an increase in the number of successful deployments compared with previous years.

The number of successful deployments is dependent on a range of conditions at the sites. Some deployments have been cancelled or delayed due to poor weather conditions. On occasion, volunteers have been absent, too busy or have been unable to access sampling sites due to boat breakdown. Samplers have also been lost in the field due to breakage, theft, or storm damage, or lost or damaged in transit. Ultimately problems with the deployment and retrieval of samplers can result in gaps in monitoring or excessively long deployment periods.

Figure 2 presents the times when samplers were deployed at each site during the dry and wet season for the current monitoring period. Explanations are provided where sampling at a particular site could not be undertaken.

At the majority of sites most samplers were deployed and returned with minimal problems. In some cases 1 set of samplers was either not deployed or lost at a site. Two sets of samplers were lost at Tully River and North Keppel Island due to bad weather conditions. Deployments at Orpheus Island were disrupted due to the unavailability of a boat.

Two sites experienced significant ongoing difficulties in managing the deployment and retrieval of samplers due to changes in staff, difficulties with boat access and breakdowns in communication (Dunk Island and Inner Whitsunday Islands). New personnel are now in charge of deploying samplers at both sites.

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. A specific staff member at EnTox is now in charge of contacting each site representative before and after samplers are sent for deployment. This increased level of communication between EnTox 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.

Table 1.Details of passive sampler deployments over the 2007-08 wet and dry seasons.

Site	Current Provider / Volunteer	Sent	Not deployed	Lost	Returned	Notes
Lizard Is	Lizard Is Research Station	6	0	1	5	Established 2007
Pixies Garden	Undersea Explorer	6	1	0	5	Established 2006, location changed Sept 2007 Deployed during multi-day cruise: some delays
Tully River	Cardwell Shire Council	6	0	2	4	Established 2007, also flood sampling
Low Isles	Quicksilver Connections	8	0	0	8	Established in 2005, problems with courier meeting boat, trialling use of local courier
Fitzroy Is	Raging Thunder Pty Ltd, Fitzroy Is Resort	8	0	0	8	Established 2005 Some changeover dates not recorded
High Is	Queensland Parks and Wildlife Service	5	0	0	5	Established 2006
Normanby Is	Frankland Island Cruise & Dive	8	1	0	7	Established 2005
Dunk Is	Dunk Island Resort	3	2	0	1 (late)	Major problem with deployments New deployer selected for future sampling
Orpheus Is	Orpheus Island Resort	3	0	1	2	Established in 2005, deployments halted in 2007 Site re-established Jan 08
Magnetic Is	GBRMPA	8	1	0	7	Established 2005
AIMS	GBRMPA	5	0	0	5	Established 2007
Pioneer River	NRM	8	0	0	8	Established 2005 Also used in flood sampling
Outer Whit. Is	Hamilton Island Resort	7	0	1	6	Established 2006
Inner Whit. Is	Daydream Is Resort	6	2	0	4	Established 2006, return rate low in wet season
North Keppel Is	North Keppel Is Education Centre	7	1	2	4	Established 2005
Total		**94**	**8**	**7**	**79**	

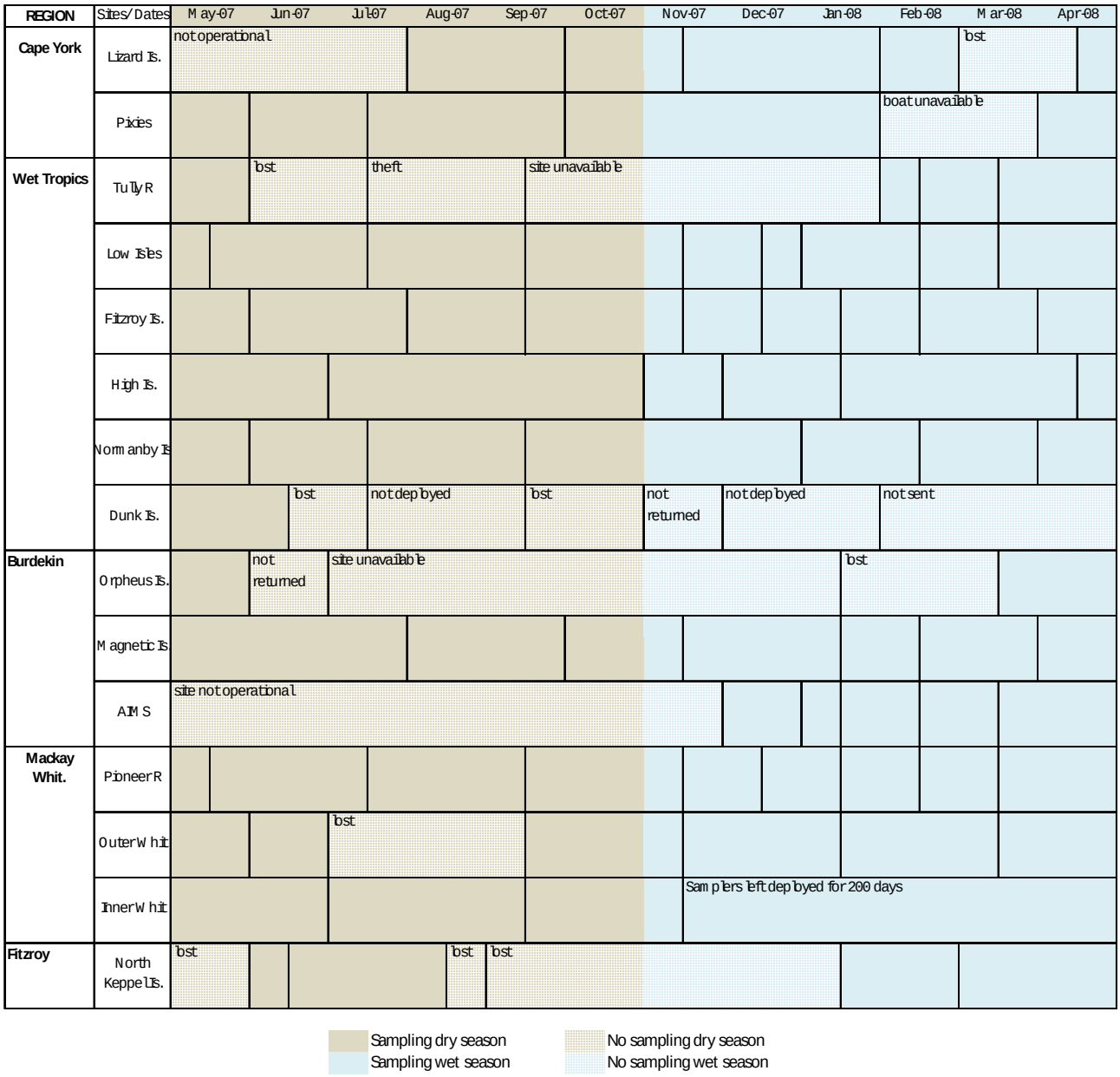

Figure 2. Passive Sampling Sites: Overview of Deployments, Deployment Lengths and Non-deployments During 07-08 Monitoring Period

Event Monitoring

Flow (sometimes referred to as 'flood') events were monitored using EDs and PDMS, in the Wet Tropics region (Tully River), Mackay Whitsunday region (Pioneer River) and Fitzroy regions (Fitzroy River between January and March 2008. 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 Fitzroy River to further assess the flood event. *Figure 3* shows the planned points during the flood event at which samples were to be deployed and collected at Fitzroy River.

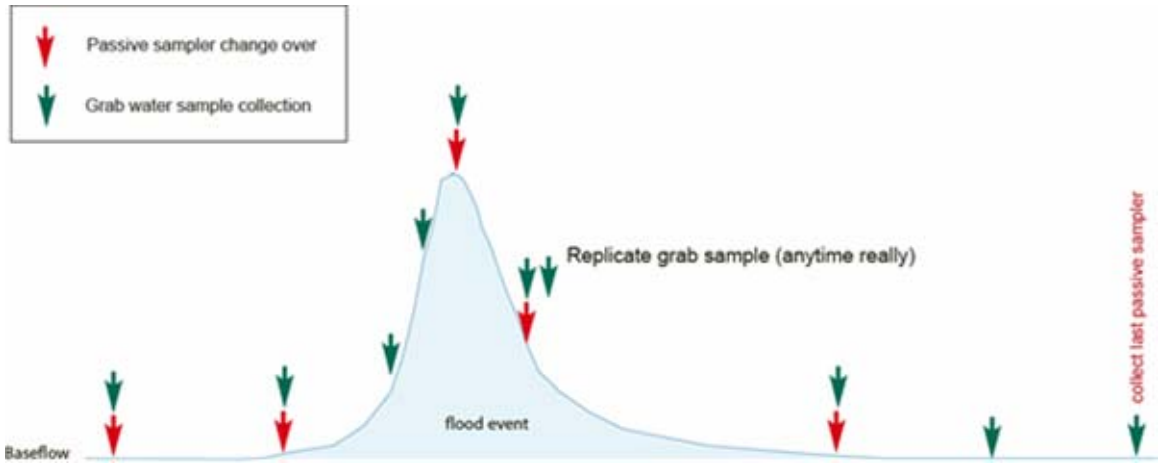

Figure 3. A diagram of a hydrograph showing the approximate points in time that snap shot samples and ED samplers were collected during a flood event at Fitzroy River(diagram provided by J. Prange, GBRMPA 2007).

Note that not all of the deployments were possible during all of the events due to safety and access issues. *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.	-	4
Pioneer R.	-	5
Fitzroy R.	15	10

Toxicity Testing

The ED passive samplers were deployed at 12 sites across four NRM Regions between October and December 2007 (*Table 3*).

Table 3. **Passive samplers and flow monitoring devices were deployed between October and December 2007 at the following sites.**

NRM Region	Site	Sample code	Deployed	Retrieved
Wet Tropics	Fitzroy Is.	WFIT	12.10.07	16.12.07
	Frankland Is.	WFRA	10.10.07	17.12.07
	High Is.	WHIG1, WHIG2	11.10.07	17.12.07
Burdekin	Geoffrey Bay	BGEO	07.10.07	14.12.07
	Pandora Reef	BPAN	09.10.07	15.12.07
	Orpheus Is (Pelorus)	BORP1, BORP2	09.10.07	15.12.07
Mackay Whitsunday	Daydream Is.	MDAY1, MDAY2	06.10.07	13.12.07
	Doubles Cone Is.	MDCI	06.10.07	12.12.07
	Pine Is.	MPIN	05.10.07	13.12.07
Fitzroy (Keppel)	Barron Is.	FBAR	03.10.07	11.12.07
	Humpy & Halfway Is	FHUM1, FHUM2	03.10.07	11.12.07
	Pelican Is.	FPEL	04.10.07	11.12.07

Sample procedures and calculations of concentrations

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). PRCs were then added to the disk by filtering ultra-pure water fortified with the PRCs through each disk. 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 5mL acetone followed by 5mL methanol (HPLC grade) in an ultrasonic bath. The extracts were combined and reduced in volume before being filtered through a 0.45µm PTFE syringe-driven filter unit. They were then reduced to 0.5mL under nitrogen and made up to 1mL 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 8 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. Samples deployed after and including September 2006 were also analysed for bromacil and metolachlor.

Polar sampler concentrations were converted into estimates of water concentrations (C_W) using a sampling rate (L d^{-1}) 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 (ngL^{-1})
- C_{ED} = concentration of the compound in the ED ($ngED^{-1}$)
- R_S = sampling rate ($Lday^{-1}$)
- t = time deployed (days)

For a complete list of the compounds analysed for on the LC-MS and their limits of detection see Table A2.3 in the appendix.

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; 1mL 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 with redistilled hexane for three consecutive 24 hour periods. 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 transported, refrigerated, in sealed solvent washed tin cans.

In the EnTox laboratory, the surfaces of the SPMDs were cleaned with water and kimwipes, dipped in hexane then 0.1M hydrochloric acid (HCl), 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 Accelerated Solvent Extractor (ASE) 300 under the following conditions:

- Pressure - 500 psi
- Temperature – 40^0 C
- Static time – 20 minutes
- Flush volume – 60%
- Cycles – 5
- Dialysis solvent mixture – *n*-hexane/acetone 90:10

The extracts were reduced in volume, transferred into dichloromethane (DCM) and subjected to size exclusion chromatography using an automated Gel Permeation Chromatograph (GPC) (19 mm by 150 mm guard column, followed by a 19 mm by 300 mm main column, packed with Envirogel [100 Å pore size, 15 µm particle size, Waters] as the stationary phase and with DCM as the mobile phase). The flow rate was 4.5 mL/min. The samples were collected between 13.30 – 16 minutes (first fraction) and 16 – 23 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 Scientific Services (QHSS) for analysis. The separation and quantification of pesticides was performed using GC-MS. Instrumental analysis was performed using a Shimadzu QP5050A GCMS splitless; injector temperature 250° C; GC columns: Phenomenex ZB5 and SGE HT5,30 m, 0.25 mm i.d., 0.25 µm film thickness.

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.

The change in concentration over time within the SPMD can be calculated using the following equation:

$$C_{SPMD} = K_{SW} \times C_W \left(1 - e^{-ket}\right) \qquad (2)$$

Where: C_{SPMD} = concentration of the compound in the SPMD ($ngSPMD^{-1}$)
K_{SW} = SPMD/water partition coefficient
C_W = aqueous concentration (ngL^{-1})
k_e = rate constant for the release process
t = deployment time (days)

Accumulation of compounds in passive samplers is initially a first order process. Therefore this equation can be simplified for the linear part of the equation to express the rate constant into a sampling rate (RS) which represents the estimated volume of water extracted per day for each compound. The resulting equation is widely used in the SPMD literature:

$$C_W = \frac{C_{SPMD} \times M_{SPMD}}{R_S \times t} \qquad (3)$$

Where: M_{SPMD} = the mass of the SPMD (g)

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 1-5L per day. For PAHs of a low molecular weight, such as those detected in this study, calibrations suggest that over a one month exposure the passive sampler may have moved out of a linear phase of uptake (Equation 3) into a curve-linear or equilibrium stage. Consequently Equation 3 would not apply and the sampler would no longer be time integrative. However, since we use Equation 2 for water concentration calculations, the result should reflect a good estimate of the water concentration over at least the second part of the deployment period.

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 redistilled hexane for three consecutive 24 hour periods before being 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 hexane for 30 seconds and 0.5 M HCL for 20 seconds following by rinsing with acetone and isopropanol. Each PDMS sampler was extracted in 180 mL of redistilled hexane at room temperature (21^0 C) for two 24 h periods. The combined extracts from each sampler were then reduced to about 1 mL under rotary evaporation. Each extract was passed through a column with sodium sulfate and blown down to 200 µl. The extracts were transferred to Queensland Health Scientific Services (QHSS) for analysis. The separation and quantification of pesticides was performed using GC-MS. Instrumental analysis was performed using a Shimadzu QP5050A GCMS splitless; injector temperature 250^o C; GC columns: Phenomenex ZB5 and SGE HT5,30 m, 0.25 mm i.d., 0.25 µm film thickness.

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 (Rs) for a compound in PDMS were not available, the case Rs 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) using the following equation:

$$C_W = \frac{C_{PDMS}}{K_{SW}} \qquad (4)$$

Where: C_{PDMS} = concentration of a compound in PDMS ($ngPDMS^{-1}$)
K_{SW} = PDMS/water partition coefficient.

Where K_{SW} values for pesticides were not available, for pesticides with similar physical properties to diuron, atrazine and simazine, the K_{SW} was extrapolated from the known values of listed chemicals.

The change in concentration over time within the PDMS can consequently be calculated using the following equation:

$$C_{PDMS} = K_{SW} \times C_W \left(1 - e^{-ket}\right) \quad (5)$$

Where: C_{PDMS} = concentration of the compound in the PDMS (ng/PDMS)
Ksw = PDMS/water partition coefficient
Cw = aqueous concentration (ngL^{-1})
k_e = rate constant for the release process
t = deployment time (days)

Accumulation of compounds in passive samplers is initially a first order process. Therefore this equation can be simplified for the linear part of the equation to express the rate constant into a sampling rate (Rs) which represents the estimated volume of water extracted per day for each compound. The resulting equation is:

$$C_W = \frac{C_{PDMS} \times M_{PDMS}}{R_S \times t} \quad (6)$$

Where: Cw = the aqueous concentration (ngL^{-1})
M_{PDMS} = the mass of the PDMS in grams

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 (Rs) for a compound in PDMS were not available, the case R_S was extrapolated from other chemicals with similar physical chemical properties.

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 flow monitors were constructed from dental plaster and cast into a plastic holder. The diameter of the exposed surface was 45mm to reflect the same surface area of exposure as the EDs. Approximately 130mL of liquid plaster (between 230-240g dry weight) was cast into each holder. The plaster was allowed to set and then the lids were screwed onto the devices to prevent the plaster completely drying. The devices were weighed in the laboratory without caps prior to deployment. Controls were created and weighed alongside the samples and kept capped during the deployment. The devices were transported to and from the site with caps on.

On return to EnTox, any bio-fouling was removed from the device cases and a final mass was obtained. Eventually the total mass of plaster lost from the PFM will be used to equate an average sampling rate over the deployment period. Until calibrations have been completed, PFM's will provide an indication only, of flow conditions and magnitude at the monitored sites.

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 EDs and 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. However, 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 is under review. 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 (i.e. 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 QHSS 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:

$$ND\% = \frac{\left|value\ a - value\ b\right|}{\left((value\ a + value\ b)/2\right)} \times 100 \qquad (7)$$

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.

For the purpose of this report, data are presented as follows:
For GC-MS data (SPMD data - pesticides)

- Bold values are detections greater or lower than the LOR and were confirmed on a full ion scan when GC-MS is used;
- Values not presented in bold and without a '<' symbol represent values greater or lower than the blanket LOR but were obtained during a SIM mode GC-MS scan i.e. they were not confirmed when a full ion scan was run; and
- Values marked with a '<' sign were either not detected and are based on the blanket LOR value or are a reported value which was obtained with low confidence.

For LC-MS data (ED and snap shot water data - herbicides)

- No values are reported using bold as a descriptor;
- Values presented without a '<' symbol, represent values detected in the LC-MS scan either greater or lower then the LOR; and
- Values marked with a '<' sign were either not detected in the LC-MS scan and are based on the blanket LOR value or are a value obtained with low confidence.

In the case of values detected but not confirmed on a full ion scan, the data is not as reliable as those in bold due to background interference within the individual samples. Although the compound was detected, the values could not be confirmed and as such should not be treated quantitatively.

While attempts were made to ensure recommended deployment lengths were not substantially exceeded, the degree of compliance varied, depending on site conditions and/or volunteer availability and commitment. Consequently, some samplers remained deployed substantially beyond our recommend 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.

Phytotoxicity – PSII inhibition I-PAM assay

A fluorescence based photosynthetic yield analysis technique was applied for phytotoxicity assessment. Pulse amplitude modulated (PAM) fluorometry was used to monitor PS II quantum yield (Y(II)), (equation 3), in algal suspensions via repetitive measurements of the chlorophyll fluorescence parameters (basal fluorescence (F) and maximal fluorescence (F'm)) following application of a saturation light pulse which transiently eliminates photochemistry (Schreiber et al, 2007).

$$Y(II) = \frac{F'm - F'}{F'm}$$

A new PAM, the Maxi-Imaging-PAM (Max-I-PAM, first prototype manufactured by J. Kolbowski and U. Schreiber, Würzburg, Germany; series production by Heinz Walz GmbH, Germany) is used, allowing chlorophyll fluorescence imaging of algae suspensions in multi-well plates.

Inhibition of PS II photosynthetic yield is calculated by comparison of Y(II) observed in samples with that of controls using the following equation:

$$Inhibition \quad [\%] = 1 - \left(\frac{sample}{control} \right) \times 100\%$$

The phytotoxic response of environmental samples is expressed as the diuron equivalent concentration against a standard curve.

Cultures of the freshwater chlorophyte Chlorella vulgaris obtained from the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Hobart, Australia, and grown in MBL (Stein and Phycological Society of America., 1973) media were routinely used. Such cultures are maintained in a custom built growth chamber (Axyos) at 23°C under a 12hr light/dark cycle at 50 µmol quanta/m²s. Young cells show maximal responses and are least affected by saturation pulse (SP) application (Schreiber et al., 2007), hence test cultures were maintained in the exponential growth phase. Consistent cell densities were maintained for all assays by ensuring basal fluorescence, F0, is within a the range of F0 = 0.080 to 0.120 and photosynthetic yield (Y(II)) within the range 0.500 to 0.550, as described by Muller et al (2007).

Bioassays are performed at laboratory ambient temperature (~23 °C) in black 96-well plates (Greiner). Each well contains 150 µL biomaterial and 150 uL of sample or reference compound serially diluted (1:2) in MBL media. Maximum permissible solvent concentrations are determined by dose response assessment of Ethanol. The highest solvent percentage exhibiting a response below 3x baseline standard deviation is considered non toxic. A maximum permissible solvent percentage of 3.5 % is thus derived. Dose-response assessment is undertaken using 8 concentrations of reference compounds and 8 concentrations of sample extracts in duplicates. Schreiber et al (2007) provide a detailed description of the instrument and the following recommended settings were applied in this study: measuring light intensity (ML) = 10 (producing a maximal response and optimal signal quality); measurement frequency (MF) = 8; Gain = 3; actinic light (AL) = 0 (recommended for diuron type inhibitors). These settings achieve an integrated quantum flux density of 3 µE/m²s (PAR). The saturation pulse (SP) is applied at 90 second intervals (minimizing photosystem damage due to saturation pulse application) with 5 readings averaged at each time point. Time points included: prior to sample dosing (t = 0), immediately following assay dosing (t = 0.1) and then at 30 minutes, 2hrs and 24hrs. Cultures are exposed to test light conditions for at least 20 minutes prior to assay commencement. Phytotoxic response is expressed as Diuron equivalent concentration (ng/L).

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^{o}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 in samples.

Reproducibility

Replicates were analysed for SPMD and PDMS for the following sites and deployment periods -

- Low Is – September 2006, November 2006 and November 2007
- Magnetic Is – July 2007
- Fitzroy Is – December 2006, March 2007
- Pioneer R – July 2006 and August 2006, November 2006 and February 2008

There were comparable detections of pesticides in replicates from Pioneer River and Magnetic Island only. The mean normalised difference was 9%.

At least one replicate ED sampler was analysed from a site during each deployment. Over 70 replicate samplers have been analysed since the monitoring program commenced in 2005. For approximately 13% of pesticides detected in replicates there was no corresponding detection in the second sampler. These detections were all very close to detection limits and excluded from reproducibility calculations.

Mean normalised differences for all replicate samplers where pesticides were detected in both replicates was 37%. Mean normalised differences in samplers deployed for routine sampling and flood event sampling was 36% and 40% respectively.

EDs

Spatial and temporal trends for ED-based water concentrations

Results from all monitoring periods are presented according to sites within each NRM region. No results were available from Dunk Island. Summary tables present the maximum, median and minimum water concentrations for each chemical detected at a site.

Box and whisker plots are presented for each site showing the distribution of water concentrations for each chemical. Only chemicals that were detected at a site are presented. The whiskers represent the highest and lowest values. The line within the box represents the median water concentration. Where replicates were deployed, these plots include the mean of these samplers. Pie charts are used to display the relative proportion of each pesticide during a wet or dry season (excluding degradation products).

Plots of water concentration versus flow from a local river are then presented for the dominant chemical at each site which was typically diuron. However for the Tully River, simazine, and for the Pioneer River, atrazine, are also presented. For both rivers, data collected during flow events are also included. These figures are included to give an indication of changes in water concentrations relative to when the wet season occurred. For this reason rivers are selected to provide a general indication of local rainfall conditions and may not be the river that most directly influences a site in terms of water quality impacts.

In the Cape York region no local river data was available. In the Wet Tropics region several rivers were likely to influence different sites, however most had similar flow patterns and hence the Barron River was used for Low Island and the North Johnstone for Fitzroy, High and Normanby Islands. In the Burdekin, Whitsundays and Fitzroy regions, flows from the Burdekin, Pioneer and Fitzroy Rivers were used. Where replicates were deployed, both values are shown.

Cape York (Lizard Is, Pixies Garden)

Lizard Island

Monitoring at Lizard Island commenced in August 2007 and a total of 5 sets of samples were analysed. Diuron, tebuthiuron and two breakdown products of atrazine were detected (Table 5). Only diuron was detected more than once, with a maximum water concentration of 1.8 ng/L. (Figure 4). Desisopropyl atrazine and tebuthiuron were present in the dry season, while desethyl atrazine was detected in the wet season (Figure 5).

Table 5 - ***Summary of maximum, median and minimum water concentrations (ng/L) for pesticides detected at Lizard Island using EDs.***

Pesticide	Max	Median	Min
Diuron	1.8	0.2	nd
Tebuthiuron	0.2	nd	nd
Desisopropyl atrazine	1.1	nd	nd
Desethyl atrazine	1.9	nd	nd

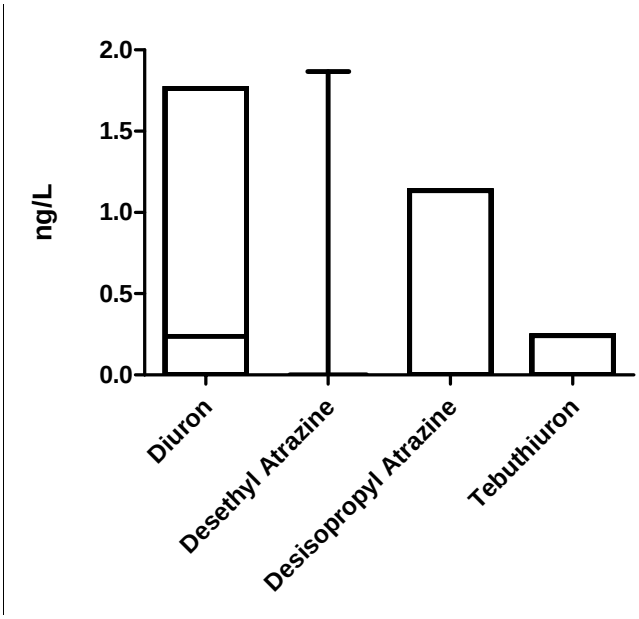

Figure 4- ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at Lizard Island using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

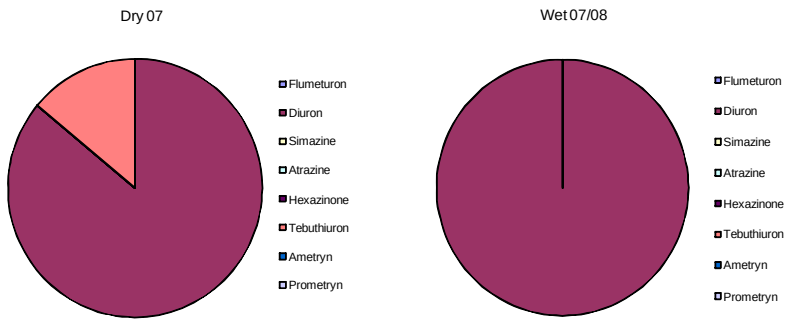

Figure 5 - ***Pie charts representing the relative proportion of pesticides detected at Lizard Island using EDs. Results presented according to wet and dry seasons for each monitoring year.***

Pixies Garden

Monitoring at Pixies Garden was relatively continuous from September 2006 although the samplers were deployed in a different area from September 2007. A total of 8 sets of samples were analysed. Diuron, atrazine, simazine and desethyl atrazine were detected (Table 6). Diuron was detected 3 times with a maximum water concentration of 1.4 ng/L. Atrazine, simazine and desethyl atrazine were only detected once each (Figure 6). Median values for all chemicals were at the detection limit. Atrazine and simazine were detected in the wet season and dry season respectively whereas diuron was only detected in the two wet seasons (Figure 7).

Table 6 - ***Summary of maximum, median and minimum water concentrations (ng/L) for pesticides detected at Pixies Garden using EDs.***

Pesticide	Max	Median	Min
Diuron	1.4	nd	nd
Atrazine	0.3	nd	nd
Simazine	0.6	nd	nd
Desethyl atrazine	0.05	nd	Nd

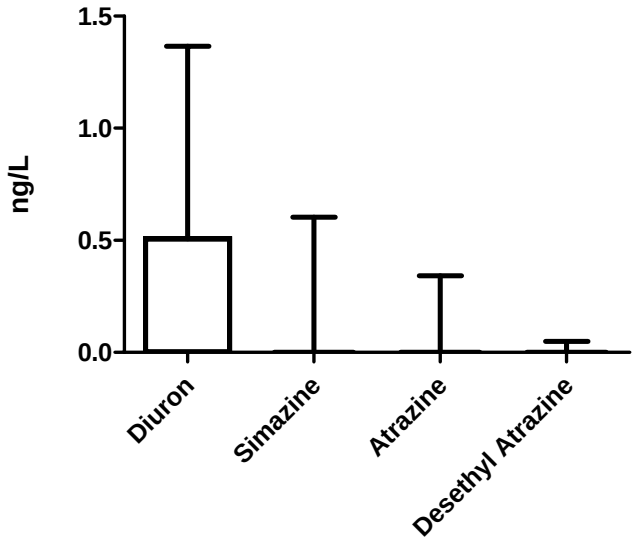

Figure 6 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at Pixies Garden using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

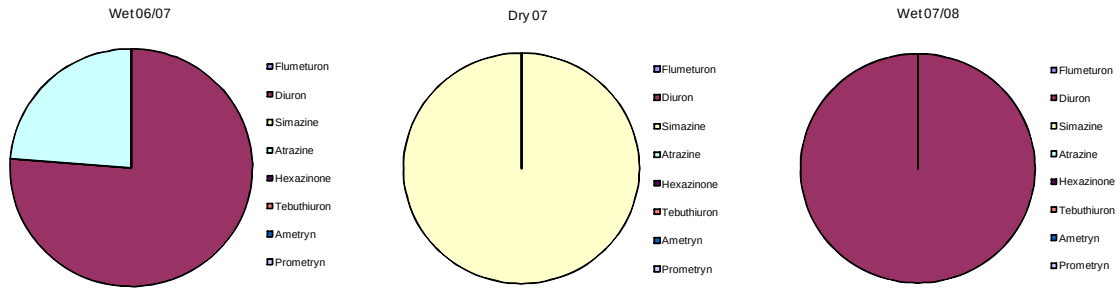

Figure 7 - ***Pie charts representing the relative proportion of pesticides detected at Pixies Garden using EDs. Results presented according to wet and dry seasons for each monitoring year.***

Wet Tropics (Tully R, Low Is, Fitzroy Is, High Is, Normanby Is, Dunk Is)

Tully River

Samplers were only deployed in the Tully River from February to March 2007 and from February to May 2008. Five sets of samples were analysed. The pesticide profile included diuron, simazine, atrazine and hexazinone with occasional detections of atrazine breakdown products and tebuthiuron (Table 7; Figure 8). Elevated median water concentrations for several pesticides and breakdown products indicates that the system is continuously exposed to pesticides, however more monitoring is required during the dry season to confirm this. Simazine dominated during the wet season of 06/07 and the dry season of 2007 whereas diuron dominated during the wet season of 07/08 (Figure 9). The Tully River was the only site that has shown elevated water concentrations of simazine (e.g. max: 120 ng/L; median 91 ng/L) although it is acknowledged that the sample number was low (n=5) with no monitoring during the dry season when pesticide water concentrations are typically lower.

Table 7- ***Summary of maximum, median and minimum water concentrations (ng/L) for pesticides detected at Tully River using EDs.***

Pesticide	Max	Median	Min
Diuron	1100	31	1.0
Atrazine	72	39	nd
Simazine	120	91	nd
Hexazinone	200	13	nd
Tebuthiuron	0.8	nd	nd
Desisopropyl atrazine	14	2.1	nd
Desethyl atrazine	24	6.0	nd

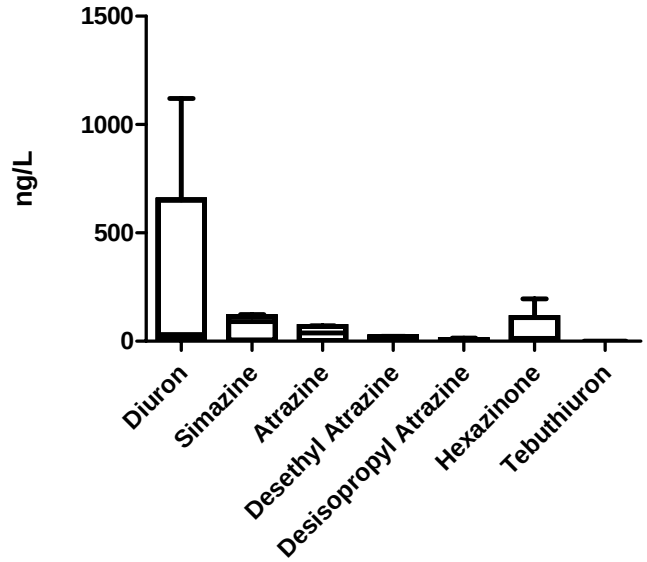

Figure 8- ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at Tully River using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

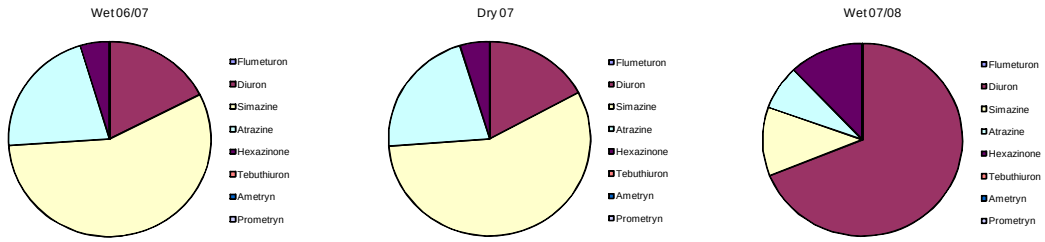

Figure 9 - ***Pie charts representing the relative proportion of pesticides detected at Tully River using EDs. Results presented according to wet and dry seasons for each monitoring year.***

Due to the limited number of sampling events on the Tully River it is difficult to assess trends. Diuron and hexazinone showed relatively low concentrations late in the 06/07 wet season (e.g. Figure 10). In the 07/08 wet season an initial peak water concentration during high flow events was followed immediately by a significant decrease during the highest flow events for this period. In contrast, atrazine and simazine showed an increase during the 06/07 wet season (e.g. *Figure 11*). In the 07/08 wet season water concentrations remained elevated during the highest flow events before decreasing with decreasing flows.

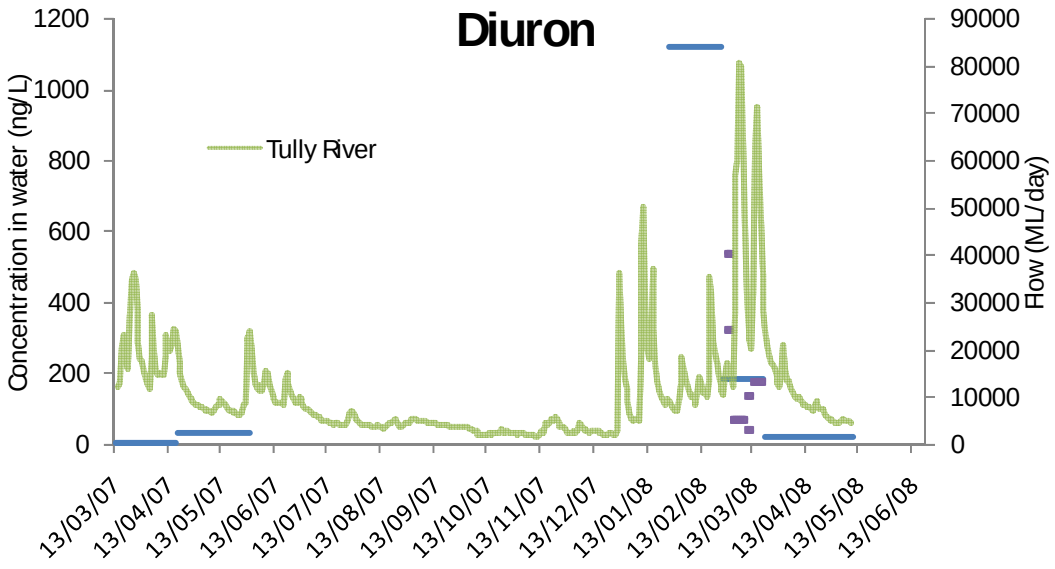

Figure 10 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Tully River. Water concentrations presented as time integrated water concentration over period of sampler deployment. Water concentrations measured during flow events by passive samplers also included. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

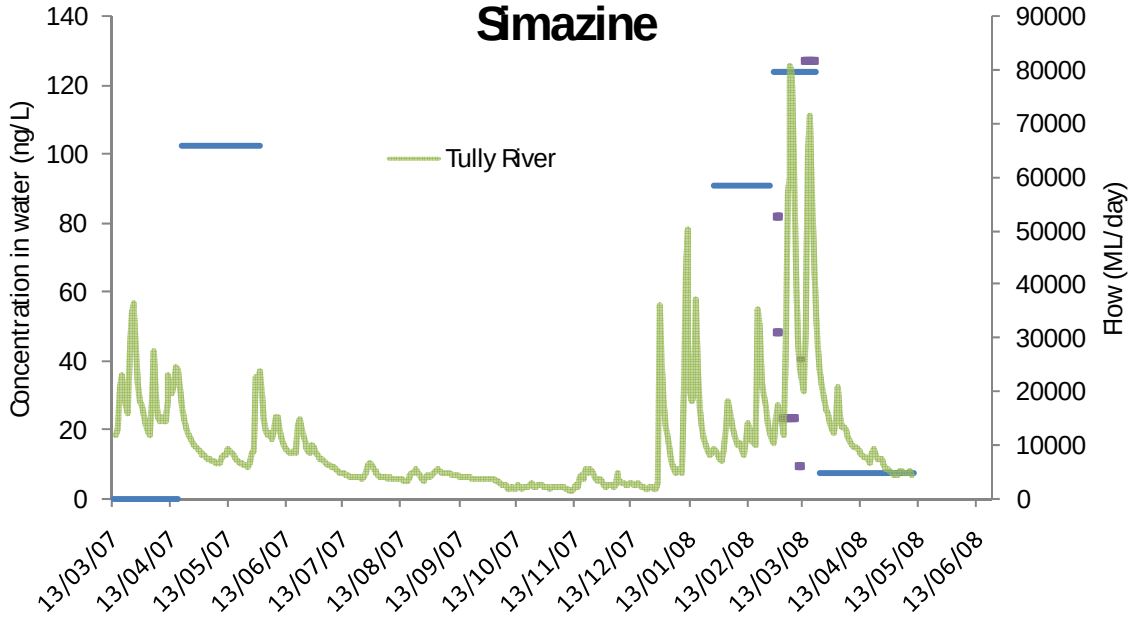

Figure 11- Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Tully River. Water concentrations presented as time integrated water concentration over period of sampler deployment. Water concentrations measured during flow events by passive samplers also included. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.

Low Island

Monitoring at Low Island has been ongoing since 2005 with 21 samples analysed. Overall the chemical profile was dominated by diuron, followed by atrazine and hexazinone. Median water concentrations for all chemicals except diuron were at the detection limit (Table 8). Where pesticides were detected, maximum water concentrations did not exceed 4 ng/L for any pesticide except diuron (Figure 12).

Table 8 - ***Summary of maximum, median and minimum water concentrations (ng/L) for pesticides detected at Low Island using EDs.***

Pesticide	Max	Median	Min
Diuron	12	1.0	nd
Atrazine	4.0	nd	nd
Simazine	1.1	nd	nd
Hexazinone	3.8	nd	nd
Tebuthiuron	1.5	nd	nd
Desethyl atrazine	1.8	nd	nd

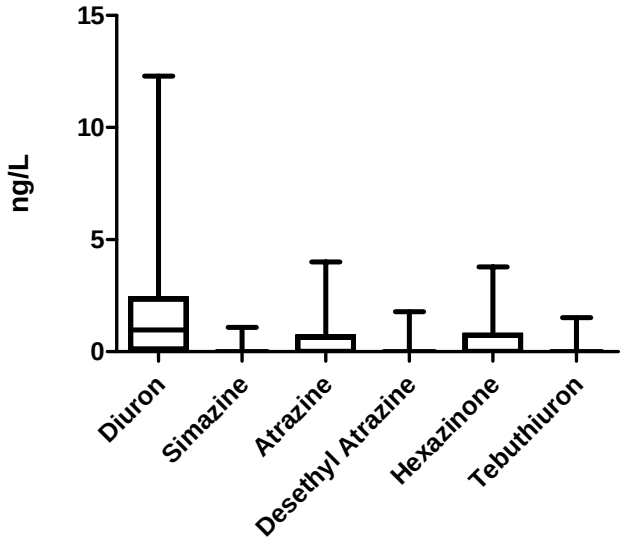

Figure 12 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at Low Island using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

Figure 13 shows that diuron dominated the pesticide profile during all seasons. Temporal trends in water concentrations relative to flow show that the highest water concentrations were associated with flow events (**Figure 14**). In contrast to Normanby and Fitzroy Islands, the highest concentration was measured during the 2005/06 wet season.

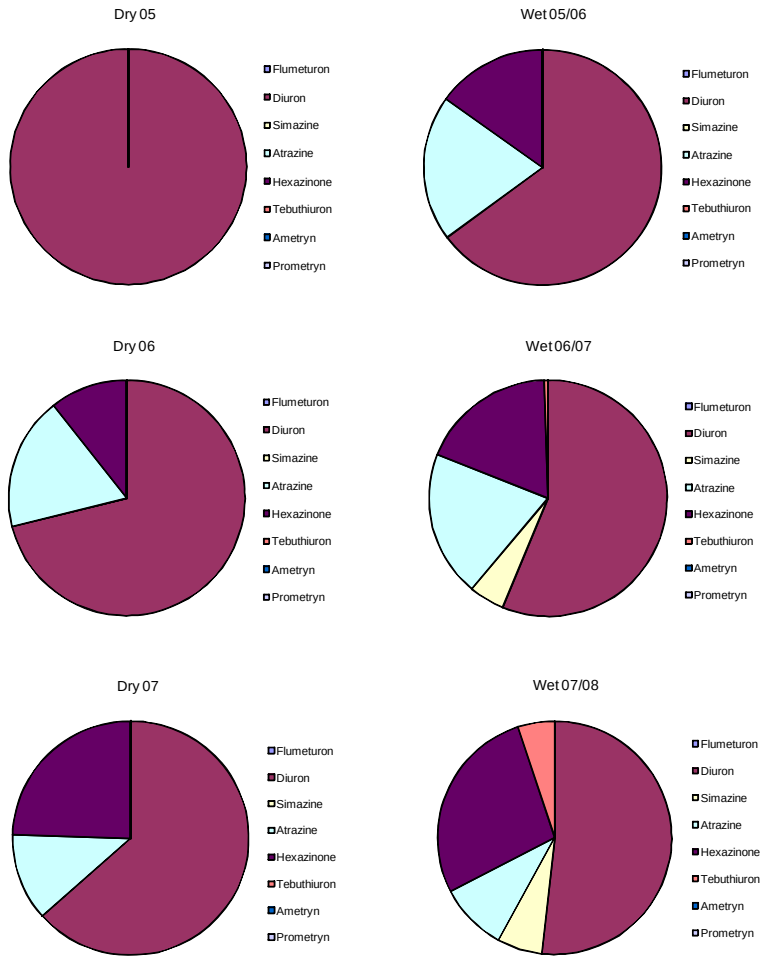

Figure 13 - ***Pie charts representing the relative proportion of pesticides detected at Low Island using EDs. Results presented according to wet and dry seasons for each monitoring year.***

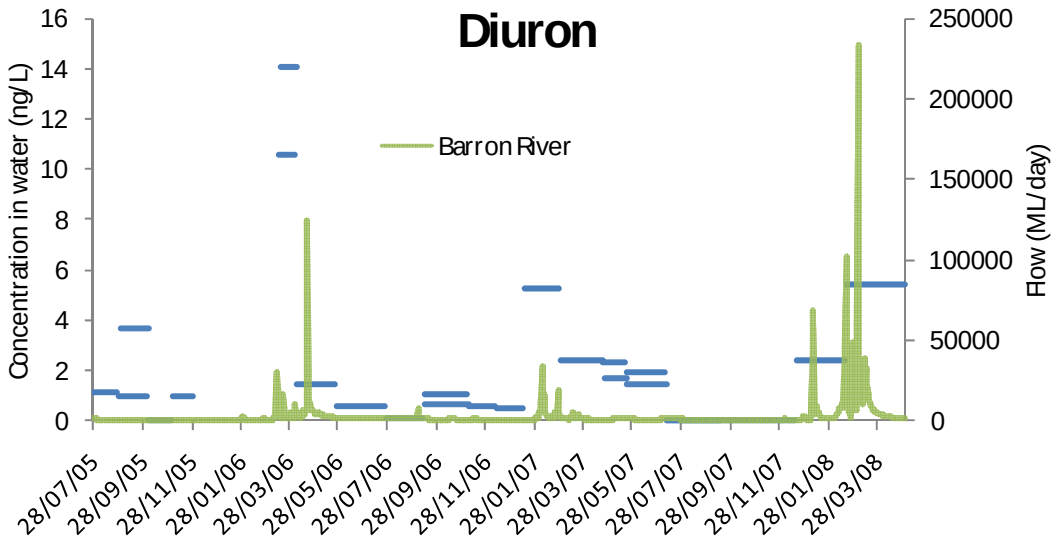

Figure 14 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Low Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right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

Fitzroy Island

Monitoring at Fitzroy Island commenced in 2005 and included 25 samples for analysis. Results revealed a similar chemical profile to other islands in this region with diuron, atrazine, hexazinone, simazine, tebuthiuron and desethyl atrazine detected (Table 9). For all pesticides except diuron, median water concentrations were at the detection limit. Maximum water concentrations only exceeded 3.7 ng/L for diuron (Figure 15).

Table 9 - *Summary of maximum, median and minimum water concentrations (ng/L) for pesticides detected at Fitzroy Island using EDs.*

Pesticide	Max	Median	Min
Diuron	13	2.0	nd
Atrazine	3.7	nd	nd
Simazine	1.5	nd	nd
Hexazinone	3.1	nd	nd
Tebuthiuron	1.8	nd	nd
Desethyl atrazine	1.1	nd	nd

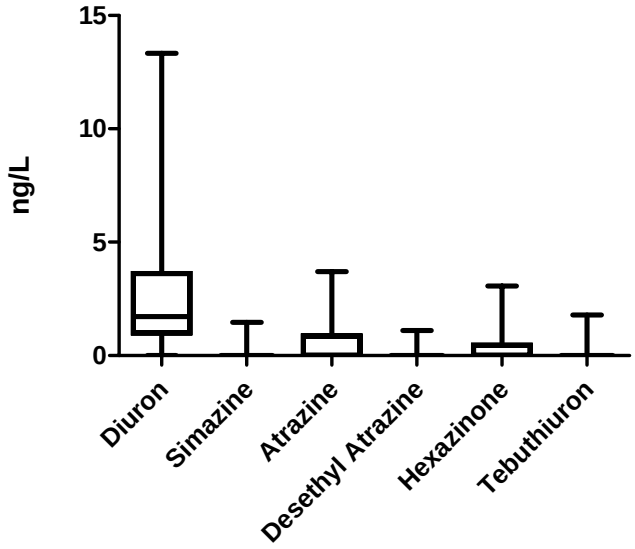

Figure 15 - *Box plots showing the range of water concentrations (ng/L) for pesticides detected at Fitzroy Island using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.*

Diuron was the dominant pesticide during all seasons, followed by atrazine and hexazinone (Figure 16). In general, elevated water concentrations of pesticides were associated with the wet season flow events (e.g. Figure 17). The highest water concentration for diuron was measured from April to June 2007 after the traditional 'wet season'. However the hydrographs show that rivers in the area were still experiencing significant flow events during that period.

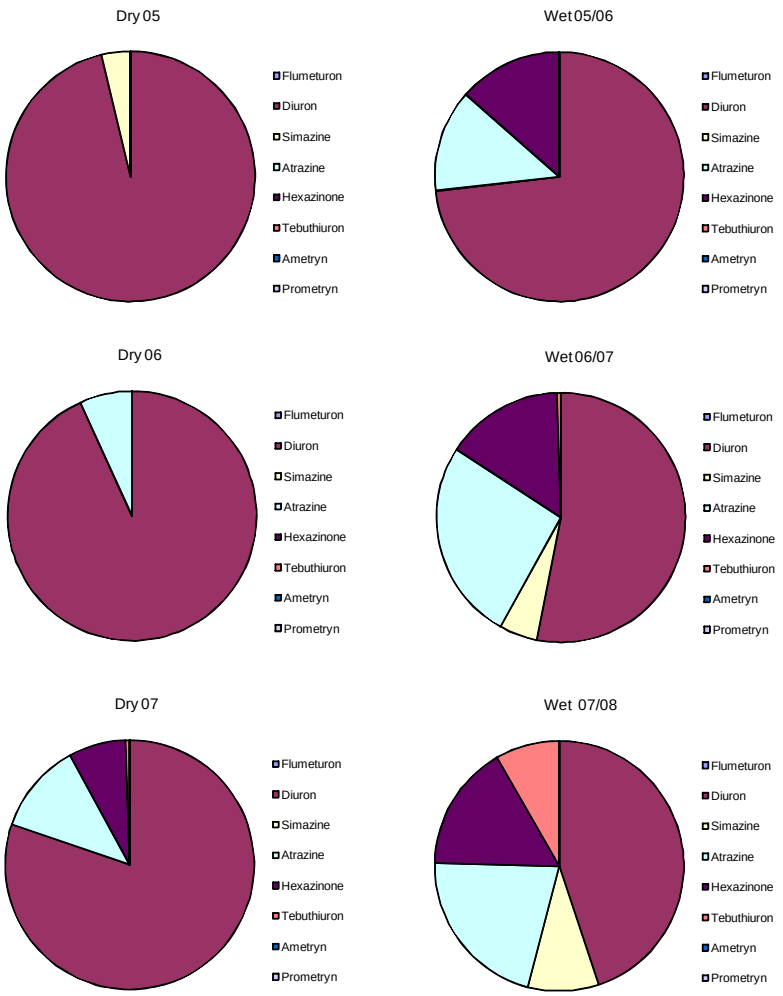

Figure 16 - ***Pie charts representing the relative proportion of pesticides detected at Fitzroy Island using EDs. Results presented according to wet and dry seasons for each monitoring year.***

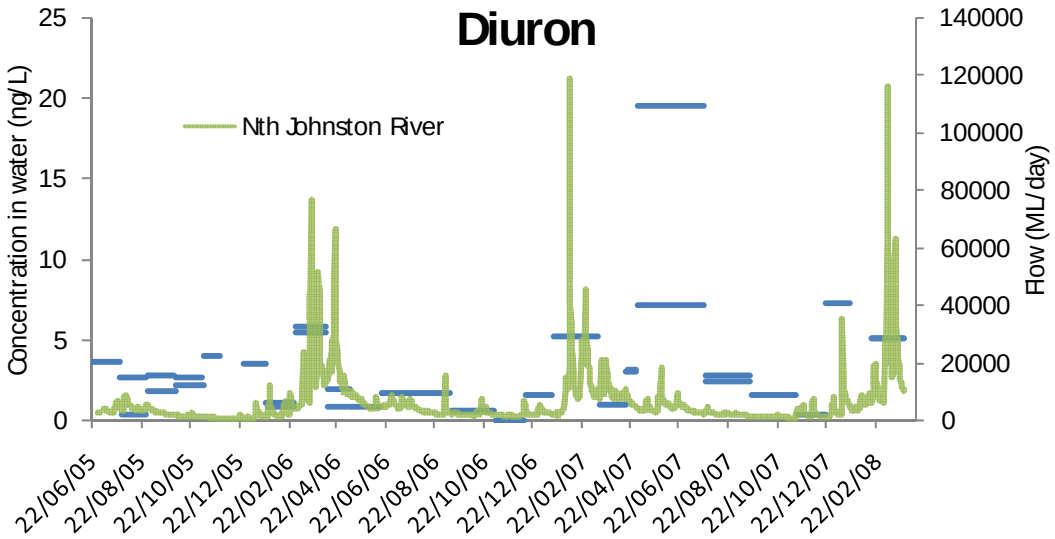

Figure 17 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Fitzroy Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water***

concentrations and the right axis shows flow rates. Non detects are presented as zero.

High Island

Monitoring at High Island commenced in July 2006 and 10 samples have been analysed. The chemical profile included diuron, hexazinone, atrazine simazine, tebuthiuron and ametryn (Table 10; Figure 18). Maximum and median water concentrations for diuron, hexazinone and atrazine were the highest in the region. Monitoring at this site has covered both the wet and dry season and the results indicate that this site was more impacted than other sites monitored in the region. The median water concentration for diuron was the highest measured for all inshore reef sites. However comparisons between sites must always be considered with respect to the number of samples collected and the seasons during which they were collected. In addition to the occasional detection of simazine and tebuthiuron, ametryn was measured twice, but at very low concentrations.

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

Pesticide	Max	Median	Min
Diuron	14	5.1	nd
Atrazine	6.8	1.2	nd
Simazine	1.1	nd	nd
Hexazinone	6.0	1.5	nd
Tebuthiuron	1.3	nd	nd
Ametryn	0.3	nd	nd

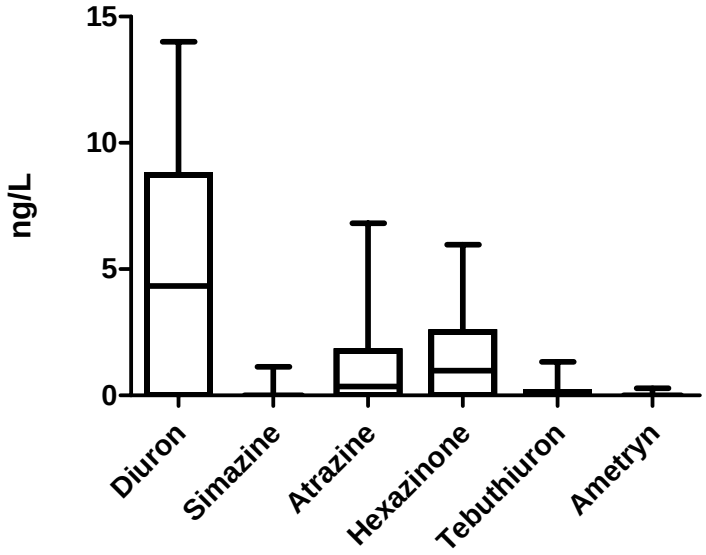

Figure 18 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at High Island using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

The pesticide profile was dominated by diuron, hexazinone and atrazine (Figure 19). Profiles were similar between seasons. Elevated water concentrations of pesticides were associated with flow events as seen at the other sites (e.g. Figure 20).

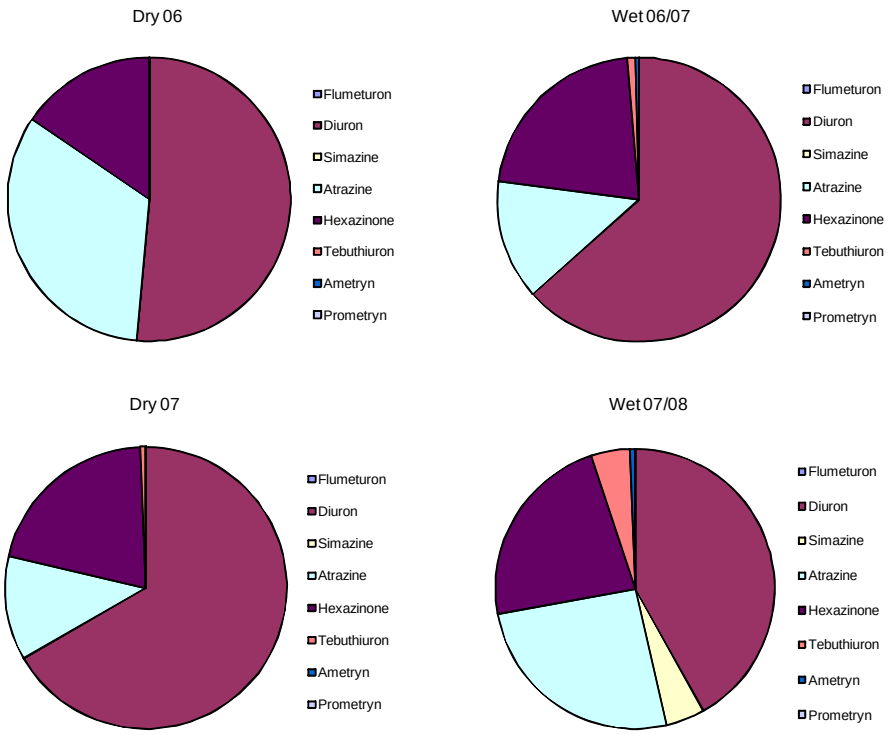

Figure 19 - ***Pie charts representing the relative proportion of pesticides detected at High Island using EDs. Results presented according to wet and dry seasons for each monitoring year.***

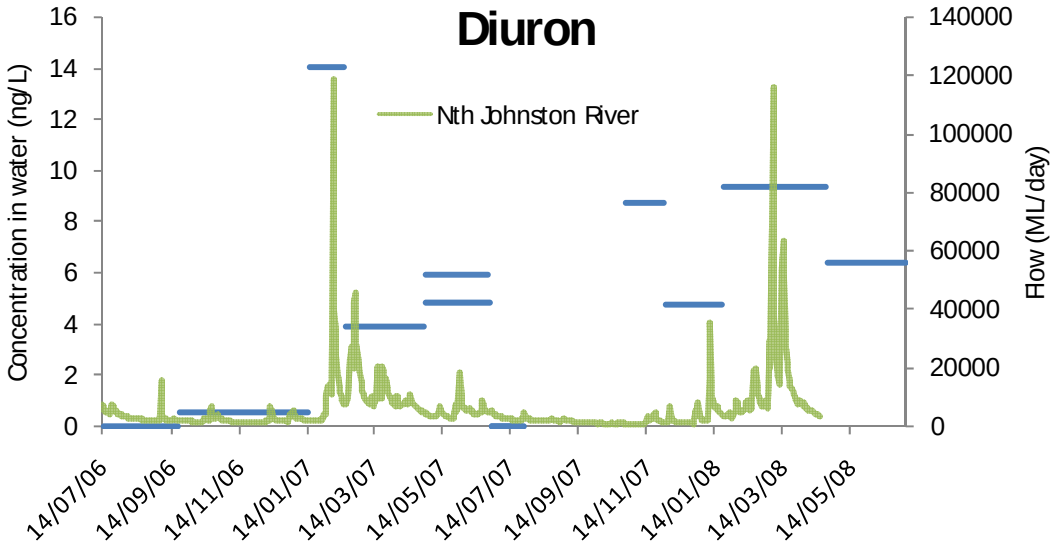

Figure 20 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at High Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

Normanby Island

Monitoring at Normanby Island commenced in 2005 and 22 samples have been analysed. Diuron, hexazinone, atrazine, simazine, tebuthiuron and desethyl atrazine were detected (Table 11). Water concentrations for diuron only, exceeded 4 ng/L. Simazine, tebuthiuron and desethyl atrazine were also occasionally detected.

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

Pesticide	Max	Median	Min
Diuron	15	1.5	nd
Atrazine	3.9	0.5	nd
Simazine	1.9	nd	nd
Hexazinone	3.1	0.2	nd
Tebuthiuron	1.9	nd	nd
Desethyl atrazine	5.1	nd	nd

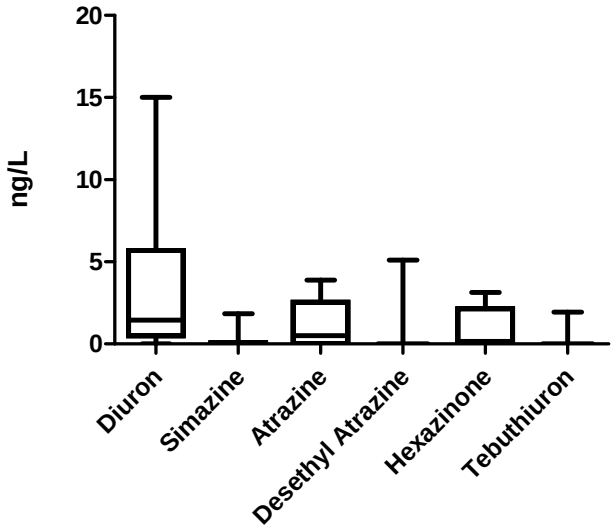

Figure 21 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at Normanby Island using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

Monitoring during 05/06 did not detect many chemicals, although samplers were not deployed during most of the wet season (Figure 22). During the subsequent monitoring periods, most detections were associated with the wet seasons of 06/07 and 07/08 with both diuron and atrazine dominating. Temporal trends at the site relative to flow shows the typical relationship between flow events and diuron (Figure 23). The highest water concentrations for diuron, atrazine and hexazinone were typically measured after flow events.

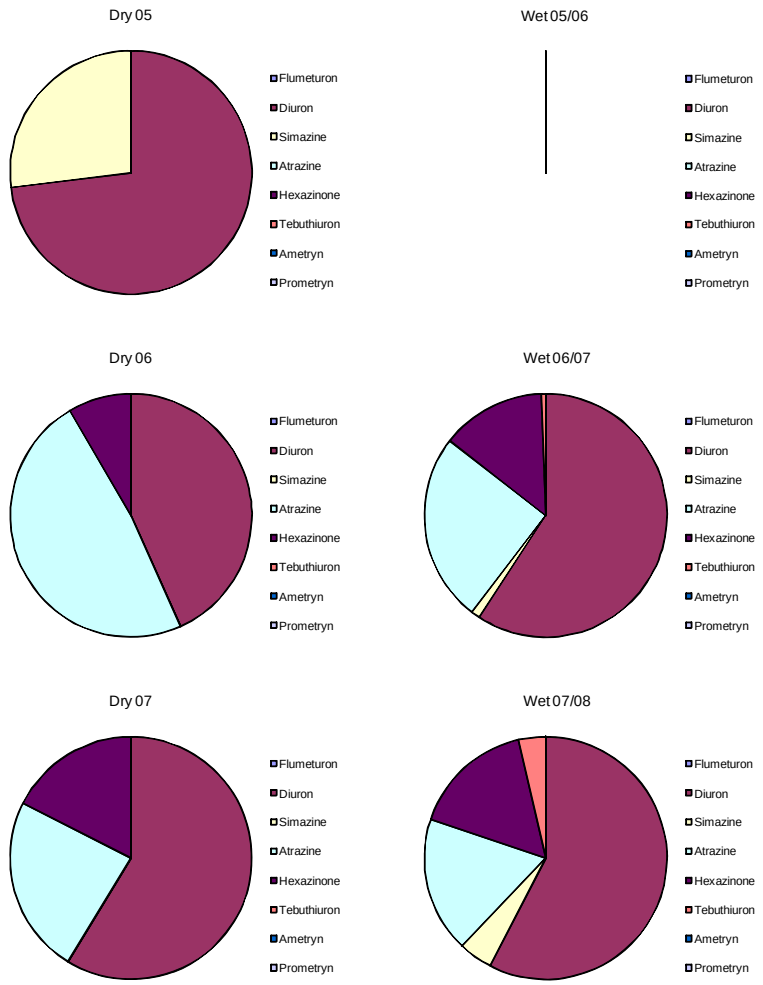

Figure 22 - ***Pie charts representing the relative proportion of pesticides detected at Normanby Island using EDs. Results presented according to wet and dry seasons for each monitoring year.***

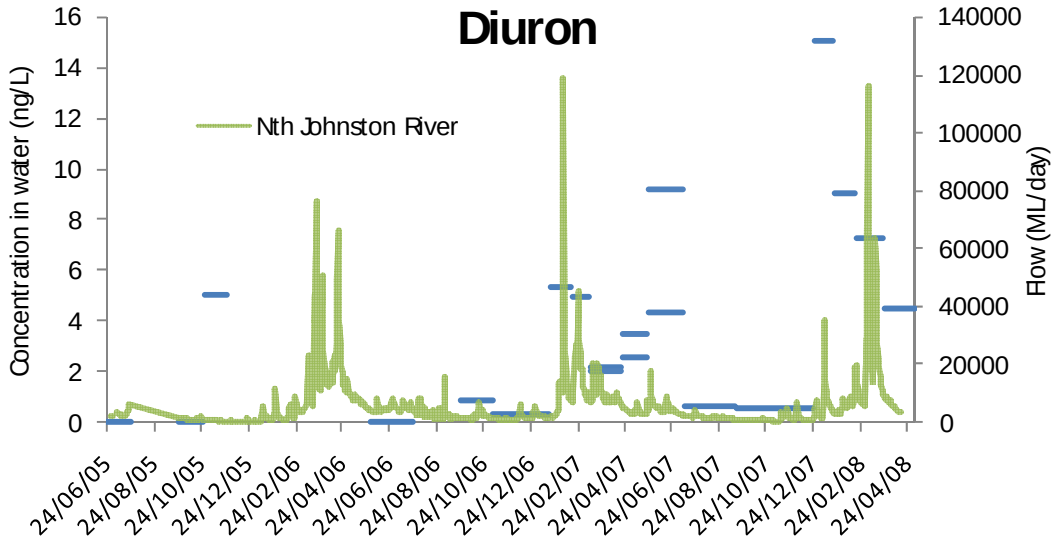

Figure 23 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Normanby Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

Burdekin (Orpheus Is, Magnetic Is, AIMS)

Orpheus Island

Monitoring at Orpheus Island commenced in July 2005 but stopped temporarily during the latter half of 2007. A total of 15 samples have been analysed. Diuron, atrazine, hexazinone, tebuthiuron and desethyl atrazine have been detected (Table 12). Overall, water concentrations are low with median values at the detection limit (Figure 24). In general, only diuron has been regularly detected and only in the most recent monitoring period. Tebuthiuron, hexazinone and atrazine were also detected but at levels below 3 ng/L (Figure 25). Although the detection of these pesticides occurred after the highest recorded flow events in the Burdekin River during the monitoring program, it is unclear whether flow from the Burdekin or the Herbert River most influenced the site.

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

Pesticide	Max	Median	Min
Diuron	4.5	0.1	nd
Atrazine	2.7	nd	nd
Hexazinone	1.9	nd	nd
Tebuthiuron	0.7	nd	nd
Desethyl atrazine	0.9	nd	nd

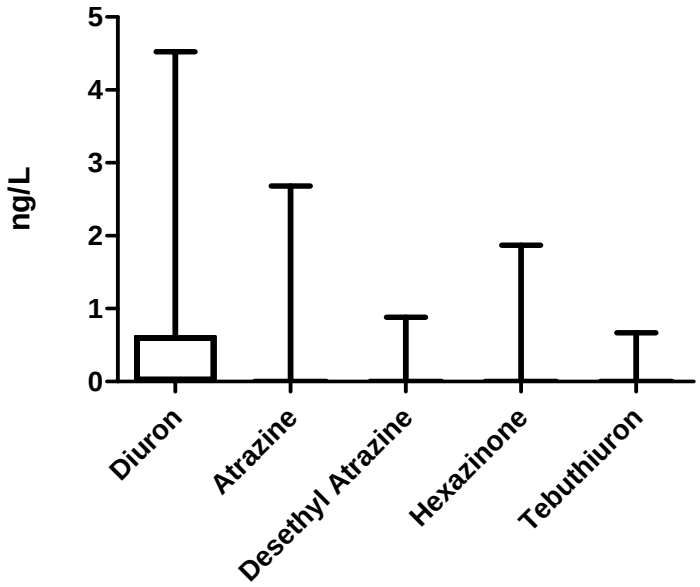

Figure 24 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at Orpheus Island using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

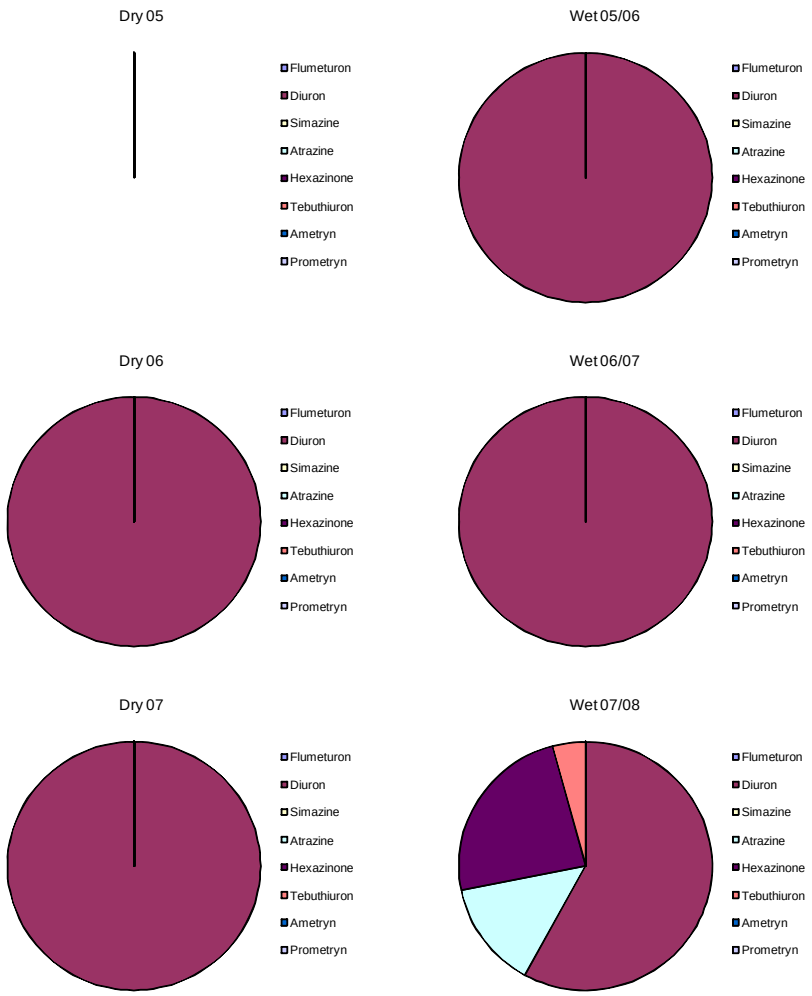

Figure 25 - ***Pie charts representing the relative proportion of pesticides detected at Orpheus Island using EDs. Results presented according to wet and dry seasons for each monitoring year.***

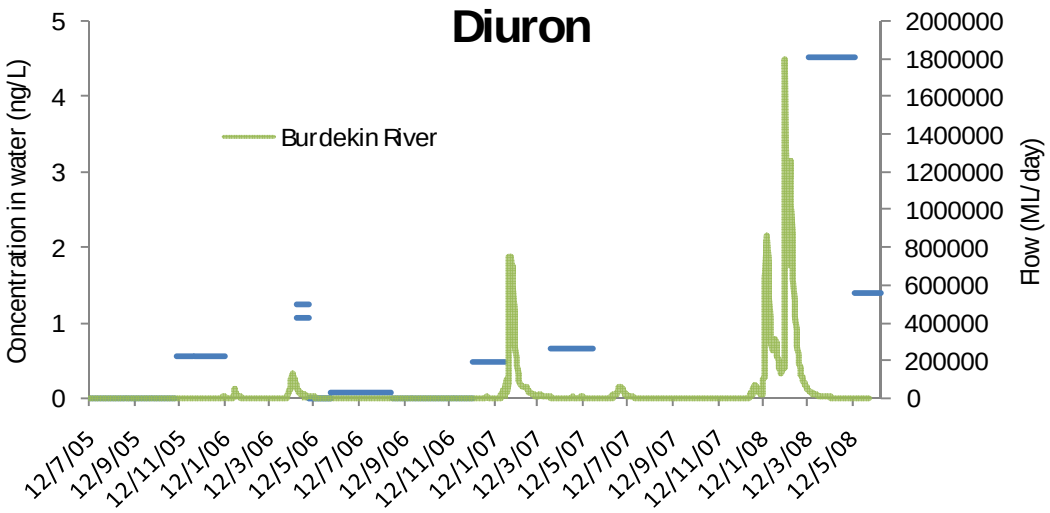

Figure 26- Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Orpheus Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.

Magnetic Island

Sampling commenced at Magnetic Island in July 2005 and 13 samples have been analysed. Monitoring detected diuron, atrazine, hexazinone, tebuthiuron and desethyl atrazine (Table 13). Results showed that diuron and atrazine were present at the highest concentrations (Figure 27). The pesticide profile shows that in the wet seasons, atrazine sometimes dominated (Figure 28). These results differ from other sites where diuron consistently dominated.

Comparisons between flow rates and water concentrations showed that increases in water concentrations of diuron and atrazine were associated with significant flow events in 06/07 and 07/08 (Figure 29). Increases in the water concentration of diuron and atrazine were also measured during the 05/06 wet season. These increases also appear to be related to flow events, but of much lower intensity relative to flow events in subsequent wet seasons (Figure 30). The high flow events in early 2008 appear to have not only increased the water concentration of the commonly detected diuron, but also increased levels of other pesticides such as tebuthiuron (e.g. Figure 31).

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

Pesticide	Max	Median	Min
Diuron	6.1	1.5	nd
Atrazine	8.0	0.8	nd
Hexazinone	1.5	nd	nd
Tebuthiuron	2.8	nd	nd
Desethyl atrazine	0.2	nd	nd

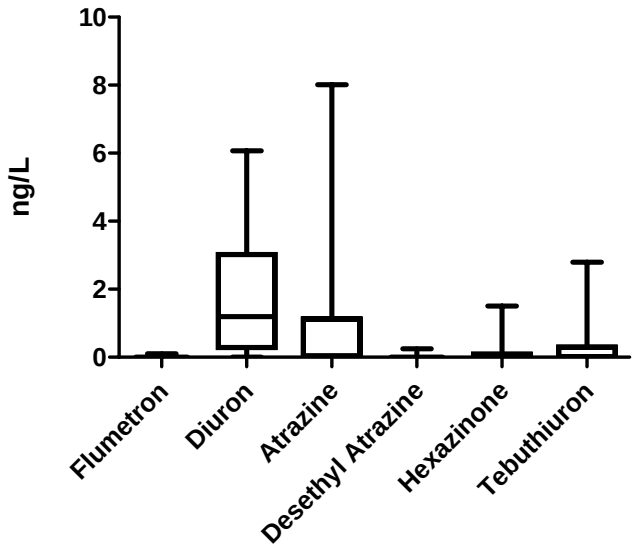

Figure 27 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at Magnetic Island using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

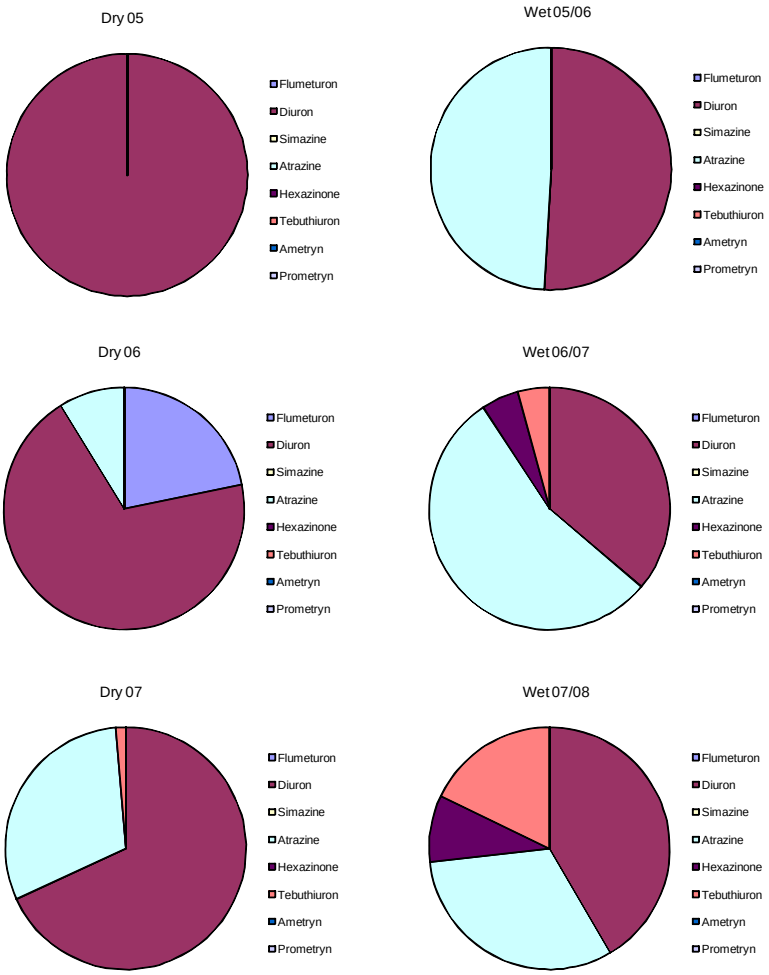

Figure 28 - ***Pie charts representing the relative proportion of pesticides detected at Magnetic Island using EDs. Results presented according to wet and dry seasons for each monitoring year.***

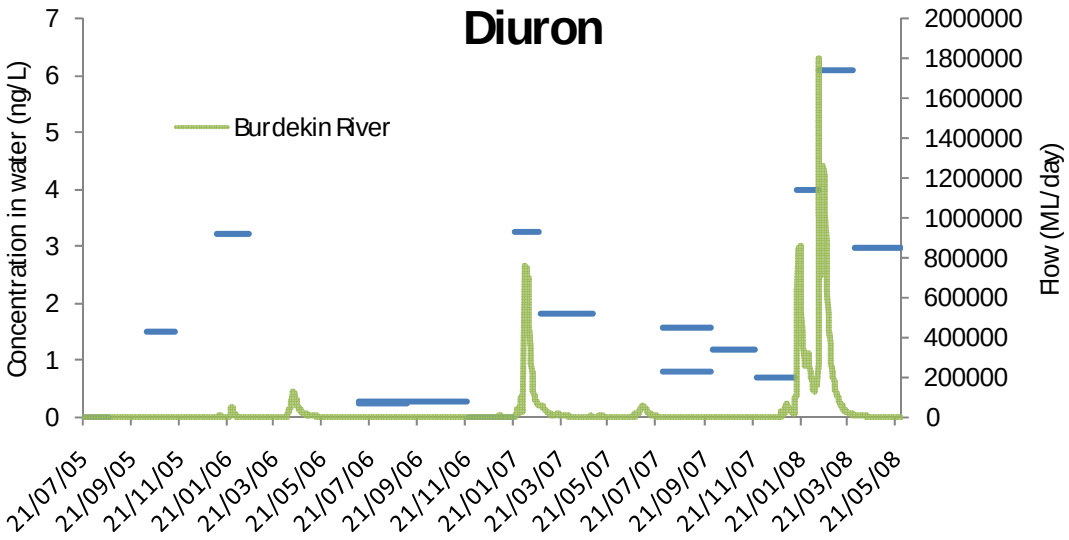

Figure 29 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Magnetic Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

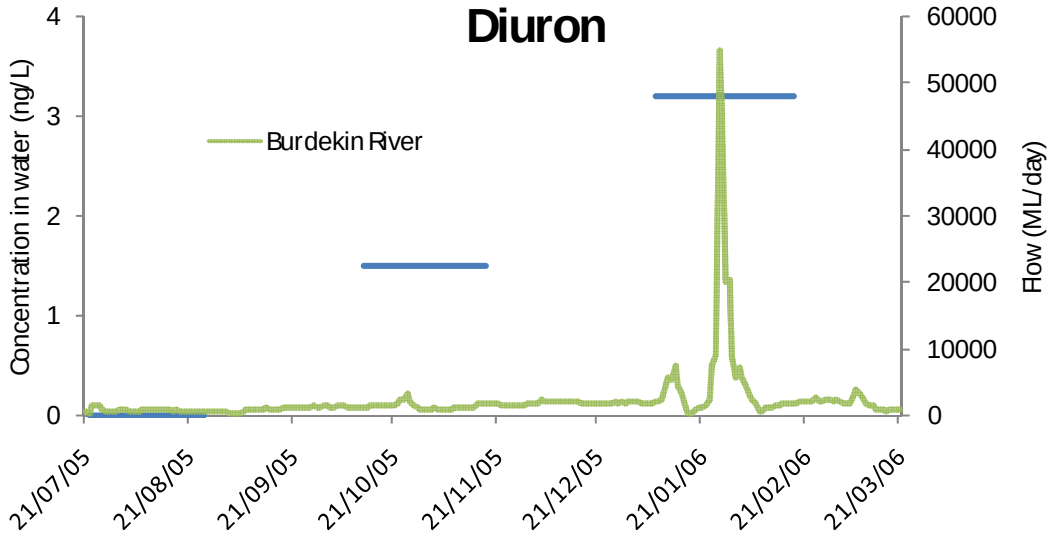

Figure 30 - ***Extra flow chart comparing water concentration (ng/L) to flow rate (ML/day) over first several months of monitoring at Magnetic Island to show relationship between water concentration and lower flow rates. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

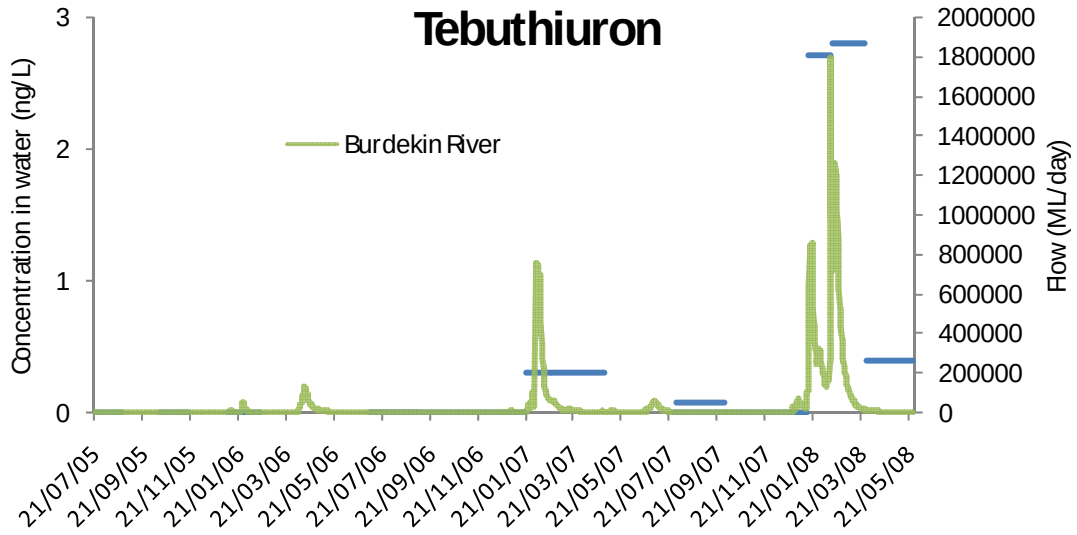

Figure 31 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Magnetic Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

AIMS

This site was only established during the 07/08 monitoring period and only four sets of samples from December 2007 to April 2008, have been analysed. The pesticide profile included atrazine, diuron, hexazinone and tebuthiuron (Table 14). In contrast to sites in other regions, atrazine was often present at higher concentrations than diuron and tebuthiuron was dominant in the profile (Figure 32 and Figure 33). The highest water concentrations occurred during the flow events from the Burdekin River (Figure 34). Water concentrations appear elevated at this site, however 2 of the 4 samples were collected during uncharacteristically high flow events from the Burdekin River. Further monitoring is required during the dry season to characterise seasonal changes.

Table 14 - ***Summary of maximum, median and minimum water concentrations (ng/L) for pesticides detected at AIMS using EDs.***

Pesticide	Max	Median	Min
Diuron	8.4	4.4	1.1
Atrazine	20	3.5	0.5
Hexazinone	1.4	1.0	nd
Tebuthiuron	6.3	1.2	nd

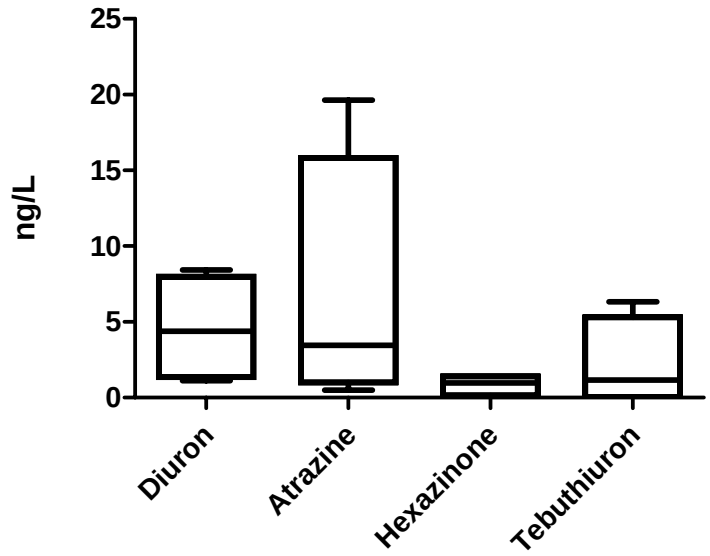

Figure 32 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at AIMS using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

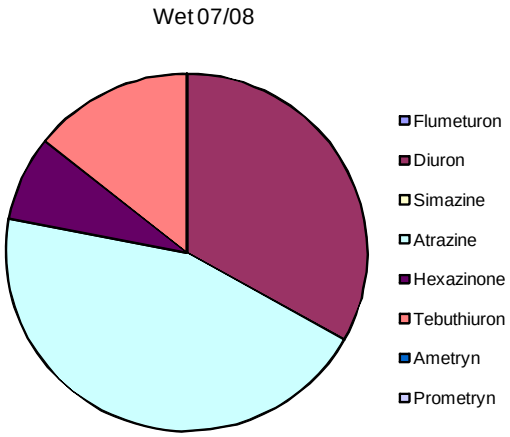

Figure 33 - ***Pie chart representing the relative proportion of pesticides detected at AIMS using EDs. Results presented according to wet and dry seasons for each monitoring year.***

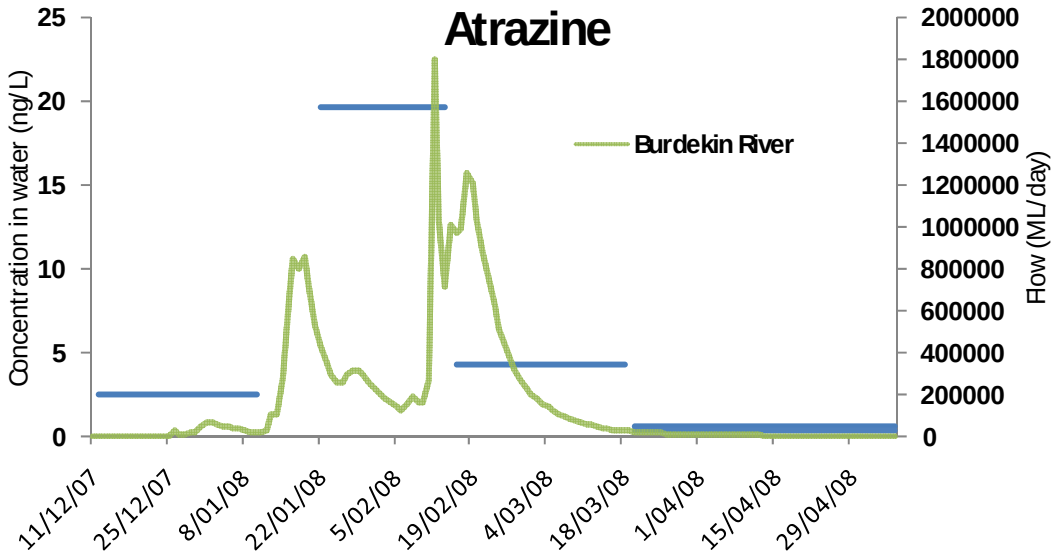

Figure 34 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at AIMS. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

Mackay Whitsunday (Pioneer River, Inner Whitsunday, Outer Whitsunday)

Pioneer River

At Pioneer River samplers were deployed continuously over most of the monitoring program since October 2005 and 23 sets of sampler have been analysed. A range of pesticides were detected with atrazine and diuron present at the highest concentrations followed by hexazinone, ametryn, flumeturon, tebuthiuron, simazine and prometryn(Table 15). The water concentrations of atrazine, diuron and hexazinone varied over a large range (Figure 35) and was on several occasions close to or in excess of 1000 ng/L.

Table 15 - ***Summary of maximum, median and minimum water concentrations (ng/L) for pesticides detected at Pioneer River using EDs.***

Pesticide	Max	Median	Min
Diuron	1700	130	Nd
Atrazine	1500	61	1.6
Simazine	7.0	nd	Nd
Hexazinone	730	45	Nd
Tebuthiuron	11	nd	Nd
Ametryn	72	5.0	Nd
Flumetron	90	nd	Nd
Prometryn	0.8	nd	Nd
Desisopropyl atrazine	31	0.7	Nd
Desethyl atrazine	110	7.2	Nd

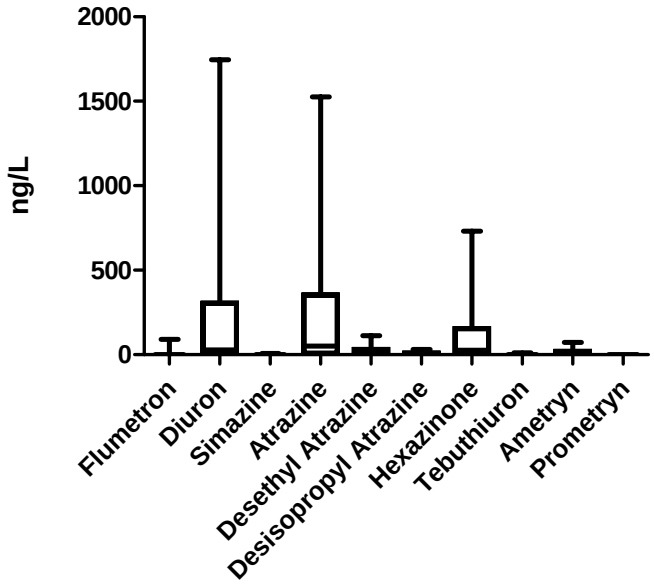

Figure 35 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at Pioneer River using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

The pesticide profile at the Pioneer River did not vary significantly between seasons or over time (Figure 36). Both atrazine and diuron dominated followed by hexazinone and ametryn. In contrast to sites in the Cape York and Wet Tropics regions, ametryn was commonly detected and at relatively elevated water concentrations. There were also occasional detections of both prometryn and flumeturon.

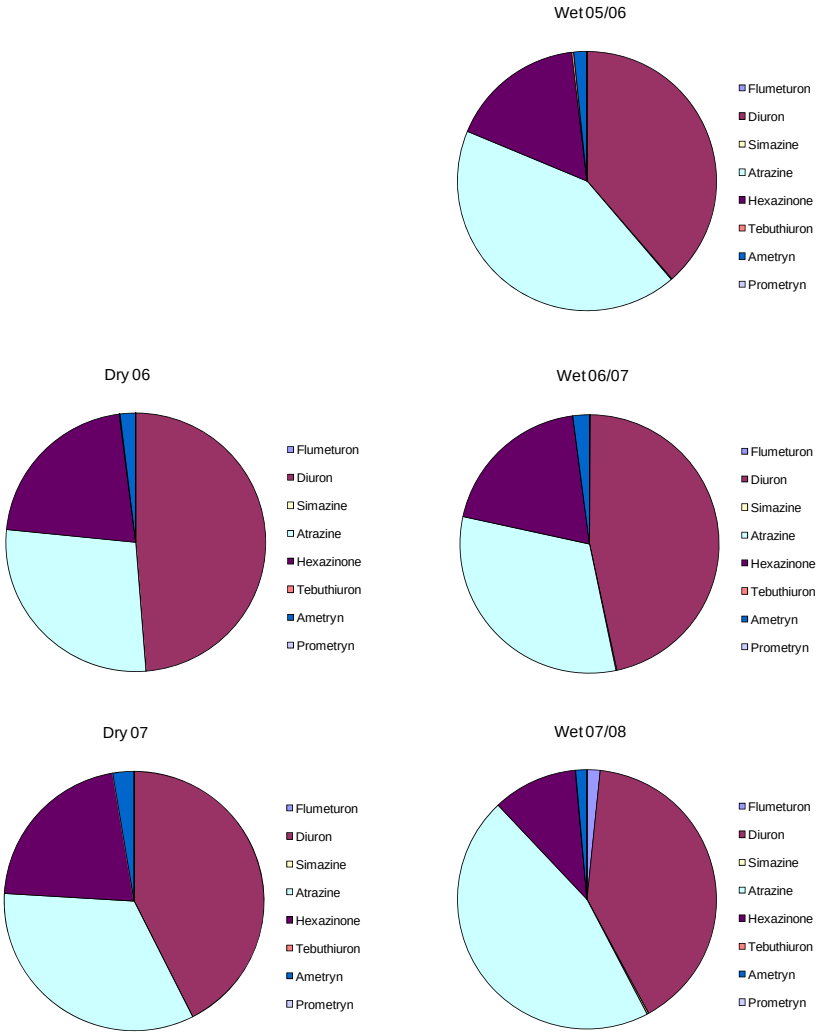

Figure 36 - ***Pie charts representing the relative proportion of pesticides detected at Pioneer River using EDs. Results presented according to wet and dry seasons for each monitoring year.***

Elevated concentrations of most chemicals measured in 06/07 and 07/08 coincided with high flow events (Figure 37). However, equally high water concentrations measured during the summer of 05/06 were associated with much lower increases in flow rates. For example, the increase in atrazine concentrations from between 200-400 ng/L to almost 1600 ng/L occurred when flow rates increased from <100 ML/day to a peak of 1700 ML/day (Figure 38).

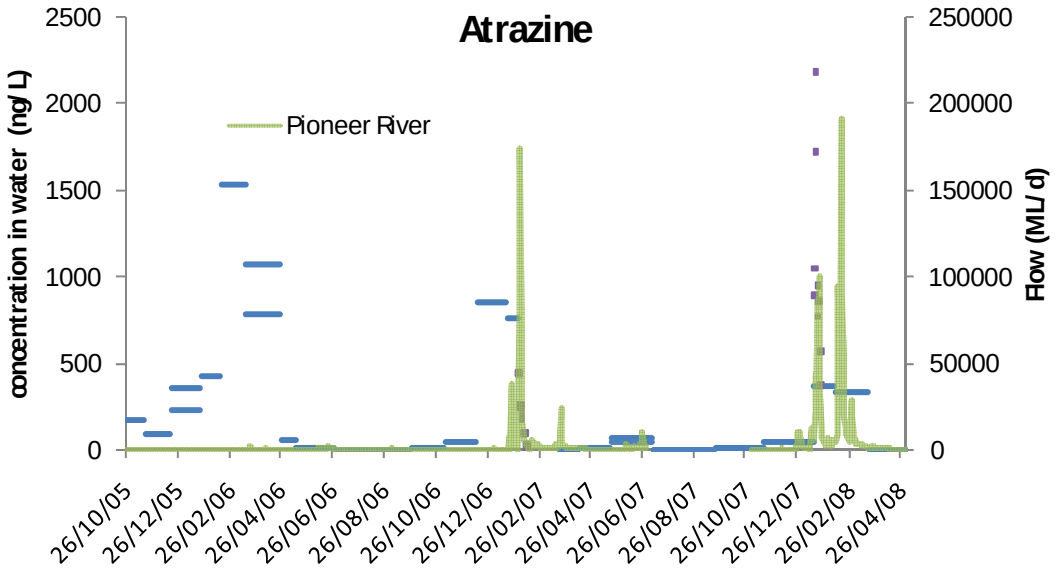

Figure 37 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Pioneer River. Water concentrations presented as time integrated water concentration over period of sampler deployment. Water concentrations measured during flow events by passive samplers also included. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

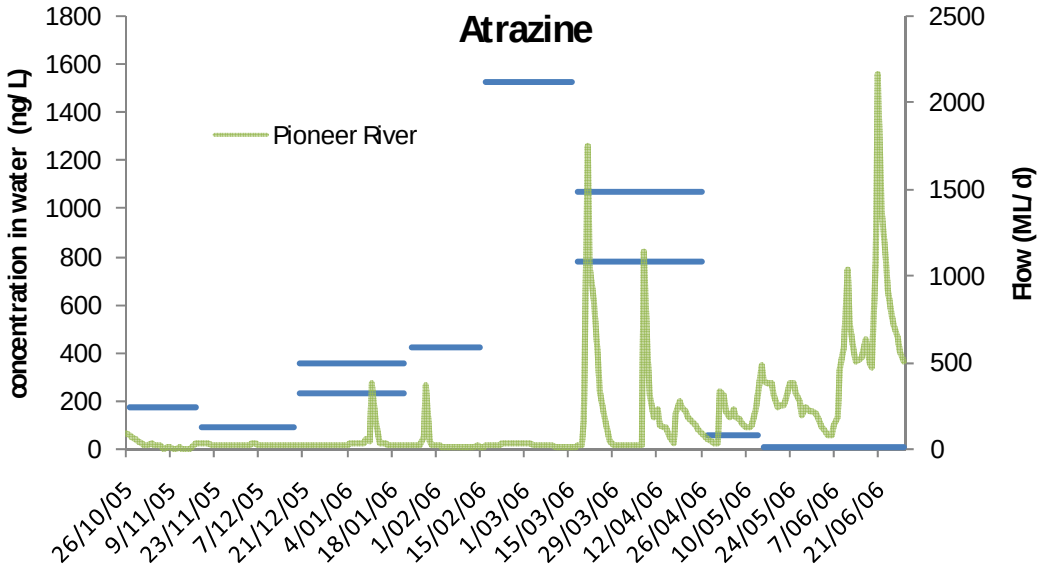

Figure 38 - ***Extra flow chart comparing water concentration (ng/L) to flow rate (ML/day) over first period of monitoring at Pioneer River to show relationship between water concentration and lower flow rates. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

Inner Whitsunday (Daydream Island)

Monitoring at the Inner Whitsunday Islands commenced in November 2006 and 7 samples have been analysed. Diuron, hexazinone, atrazine, tebuthiuron and ametryn were detected (Table 16). Diuron dominated the chemical profile with median water concentrations of all other pesticides at the detection limit (Figure 39). Across seasons, diuron dominated followed by hexazinone and atrazine (Figure 40). Overall, peak water concentrations for diuron were 1-2 magnitudes lower than levels measured during similar periods in the Pioneer River. Interestingly the position of atrazine in the pesticide profile for Pioneer River (second to diuron) was replaced by hexazinone at the Inner Whitsundays site.

Table 16 - ***Summary of maximum, median and minimum water concentrations (ng/L) for pesticides detected at Inner Whitsunday using EDs.***

Pesticide	Max	Median	Min
Diuron	9.4	1.1	nd
Atrazine	1.9	nd	nd
Hexazinone	4.4	nd	nd
Tebuthiuron	0.7	nd	nd
Ametryn	0.2	nd	nd

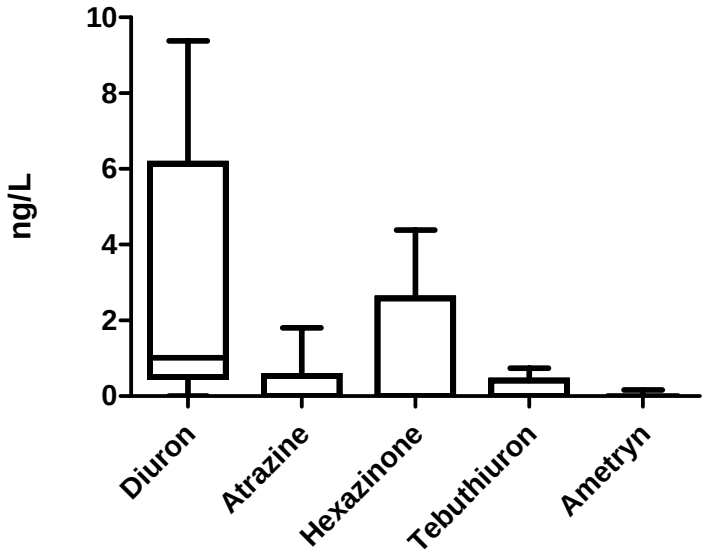

Figure 39 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at Inner Whitsunday using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

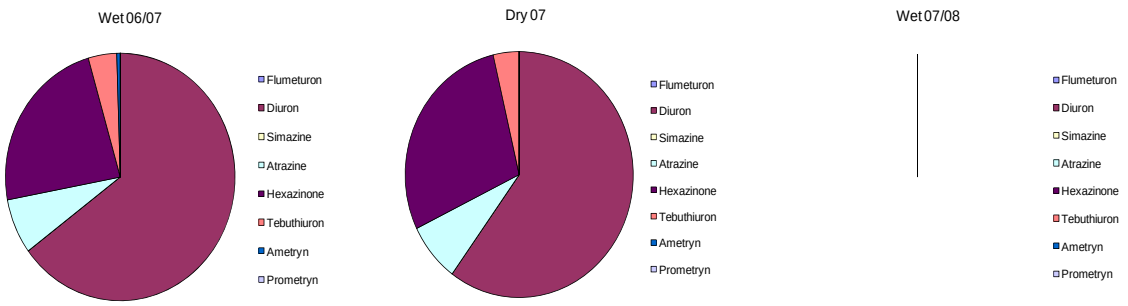

Figure 40 - ***Pie charts representing the relative proportion of pesticides detected at Inner Whitsunday using EDs. Results presented according to wet and dry seasons for each monitoring year.***

Elevated water concentrations at the Inner Whitsundays coincided with the highest flow event in the Pioneer River during the period samplers were deployed. For example, the water concentration of diuron increased from approximately 1 ng/L to almost 10 ng/L (Figure 41).

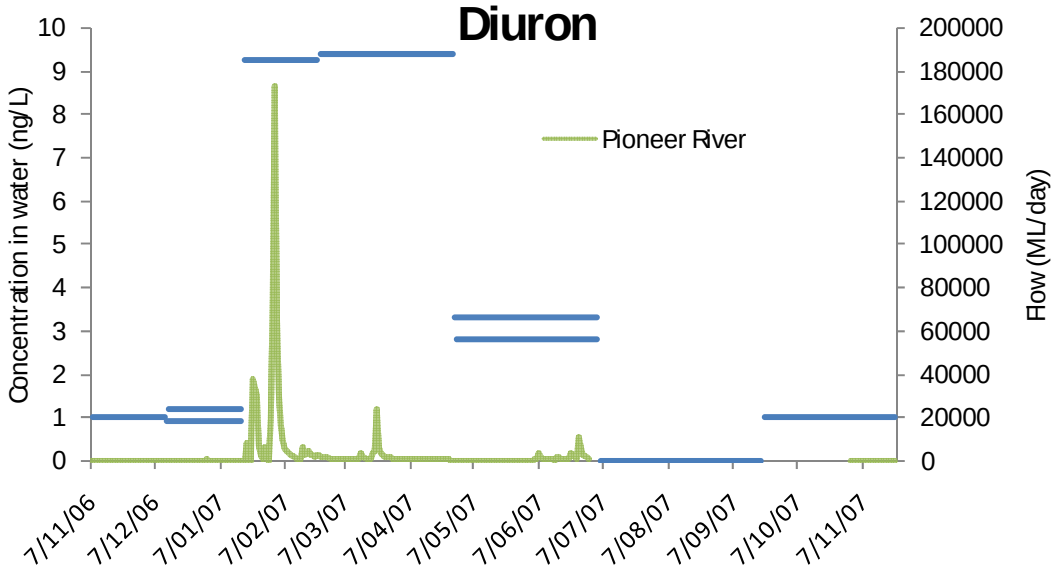

Figure 41 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Inner Whitsunday. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

Outer Whitsunday (Hamilton Island)

Monitoring at the Outer Whitsunday Islands commenced in November 2006 and 9 sets of samplers have been analysed. Diuron, hexazinone, atrazine, tebuthiuron, ametryn and desethyl atrazine were detected (Table 17). Diuron dominated the chemical profile followed by hexazinone and atrazine (Figure 42). The range of water concentrations measured for each chemical was higher at the Outer Whitsundays compared to the Inner Whitsundays. As with the Inner Whitsundays site, the position of atrazine in the pesticide profile for Pioneer River (second to diuron) was replaced by hexazinone at the Outer Whitsundays site (Figure 43).

Table 17 - ***Summary of maximum, median and minimum water concentrations (ng/L) for pesticides detected at Outer Whitsunday using EDs.***

Pesticide	Max	Median	Min
Diuron	16	3.8	1.0
Atrazine	3.6	nd	nd
Hexazinone	6.8	0.8	nd
Tebuthiuron	1.1	nd	nd
Ametryn	0.1	nd	nd
Desethyl atrazine	0.7	nd	nd

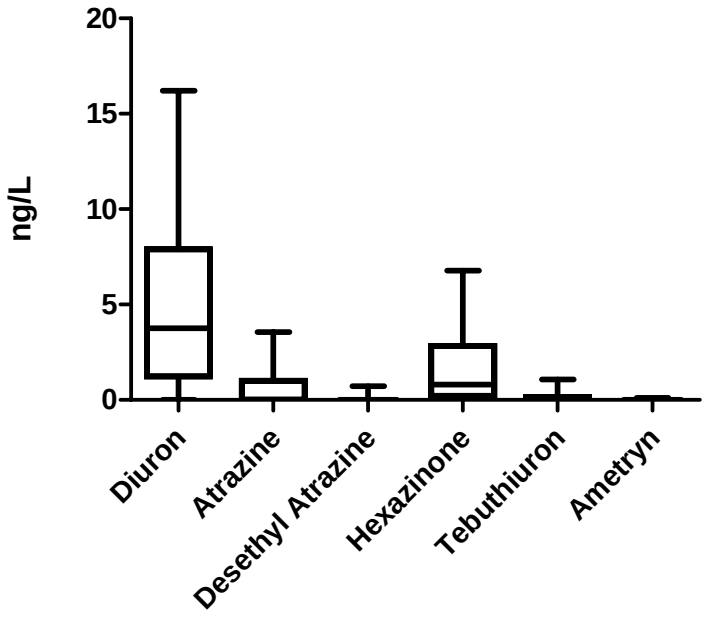

Figure 42 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at Outer Whitsunday using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

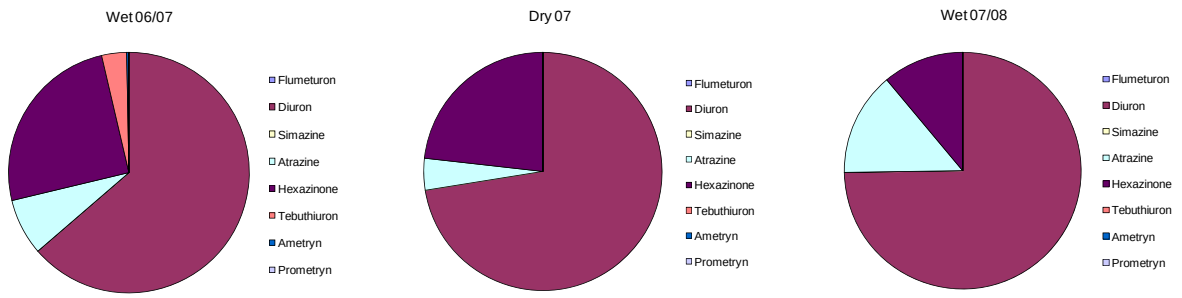

Figure 43 - ***Pie charts representing the relative proportion of pesticides detected at Outer Whitsunday using EDs. Results presented according to wet and dry seasons for each monitoring year.***

Monitoring showed the water concentrations of diuron, atrazine, hexazinone and tebuthiuron peaked after the highest flow event in the Pioneer. However, water concentrations measured during the next highest flow event in January and February of 2008 did not show a similar increase in magnitude. For example, the water concentration of diuron peaked at 16 ng/L after the largest flow event in the Pioneer River but only increased to approximately 4 ng/L in January and February of 2008. Water concentrations of comparable levels were measured during the year between these two flow events.

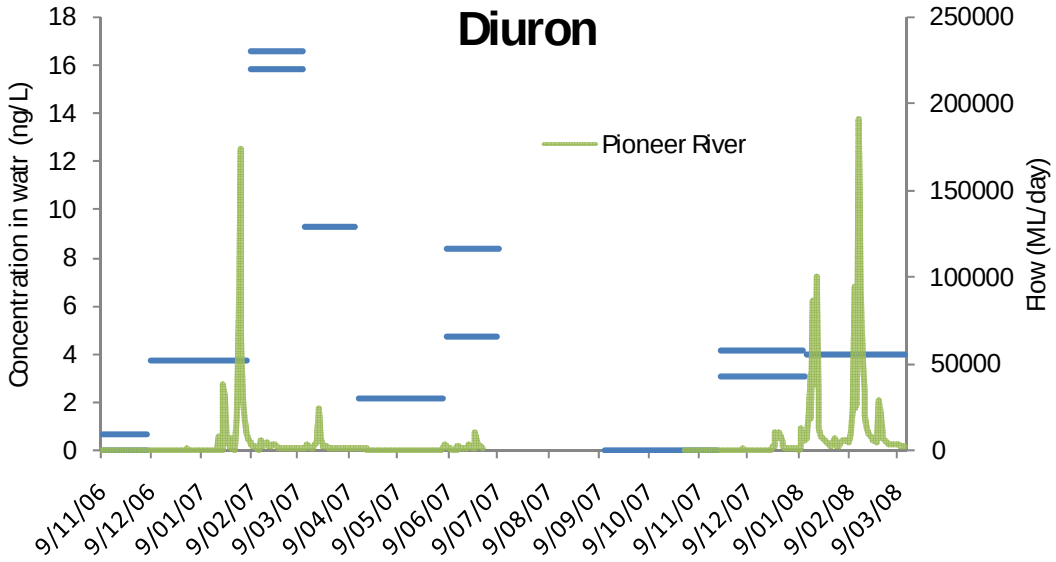

Figure 44 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at Outer Whitsunday. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

Fitzroy (North Keppel Is)

North Keppel Island

Sampling at North Keppel Island commenced in July 2005 and 15 sets of samples have been analysed. Diuron, atrazine, tebuthiuron, simazine, desisopropyl atrazine and desethyl atrazine were detected (Table 18 and Figure 45). Only diuron was detected more than once during the entire period and the water concentrations were low. Atrazine, tebuthiuron and simazine were detected in samplers deployed at this site for the first time only during Jan/Feb 2008 (Figure 46). The change in chemical profile at the site could be due to a high flow event in the Fitzroy River during that deployment. Plume mapping has shown that the flow events from the Fitzroy during that period reached North Keppel Island. Figure 47 shows that the appearance of atrazine coincided with the Fitzroy flow event (Figure 47) even though there would have been a lag time between the occurrence of the flow event and its impact at the island. Interestingly, the water concentrations of diuron did not increase during the same event (Figure 48). The diuron levels at this site were possibly influenced by the Keppel Bay Marina, located approximately 7 nautical miles (13km) from the island which contains 290 marina berths as well as a boat yard. Results are pending for samplers deployed after January 2008.

Table 18 - ***Summary of maximum, median and minimum water concentrations (ng/L) for pesticides detected at North Keppel Island using EDs.***

Pesticide	Max	Median	Min
Diuron	1.9	0.3	nd
Atrazine	7.2	nd	nd
Simazine	0.5	nd	nd
Tebuthiuron	4.8	nd	nd
Desisopropyl atrazine	0.3	nd	nd
Desethyl atrazine	0.8	nd	nd

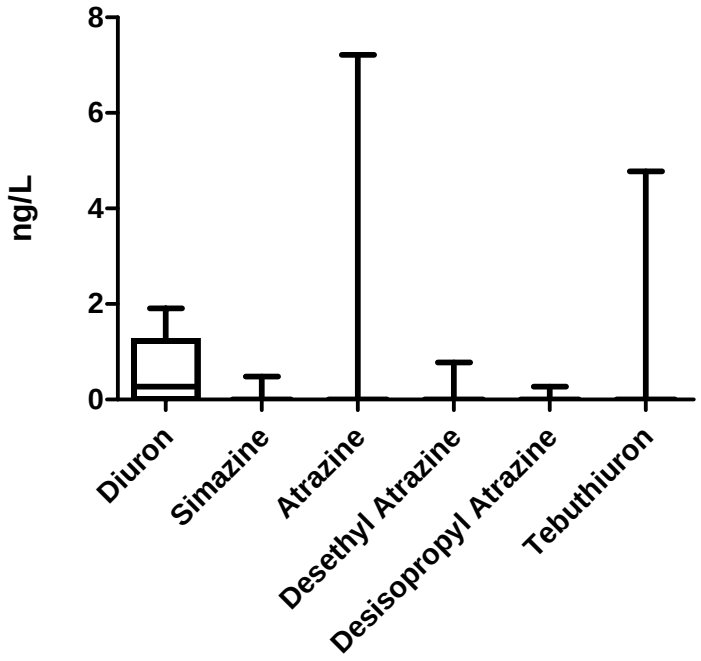

Figure 45 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected at North Keppel Island using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

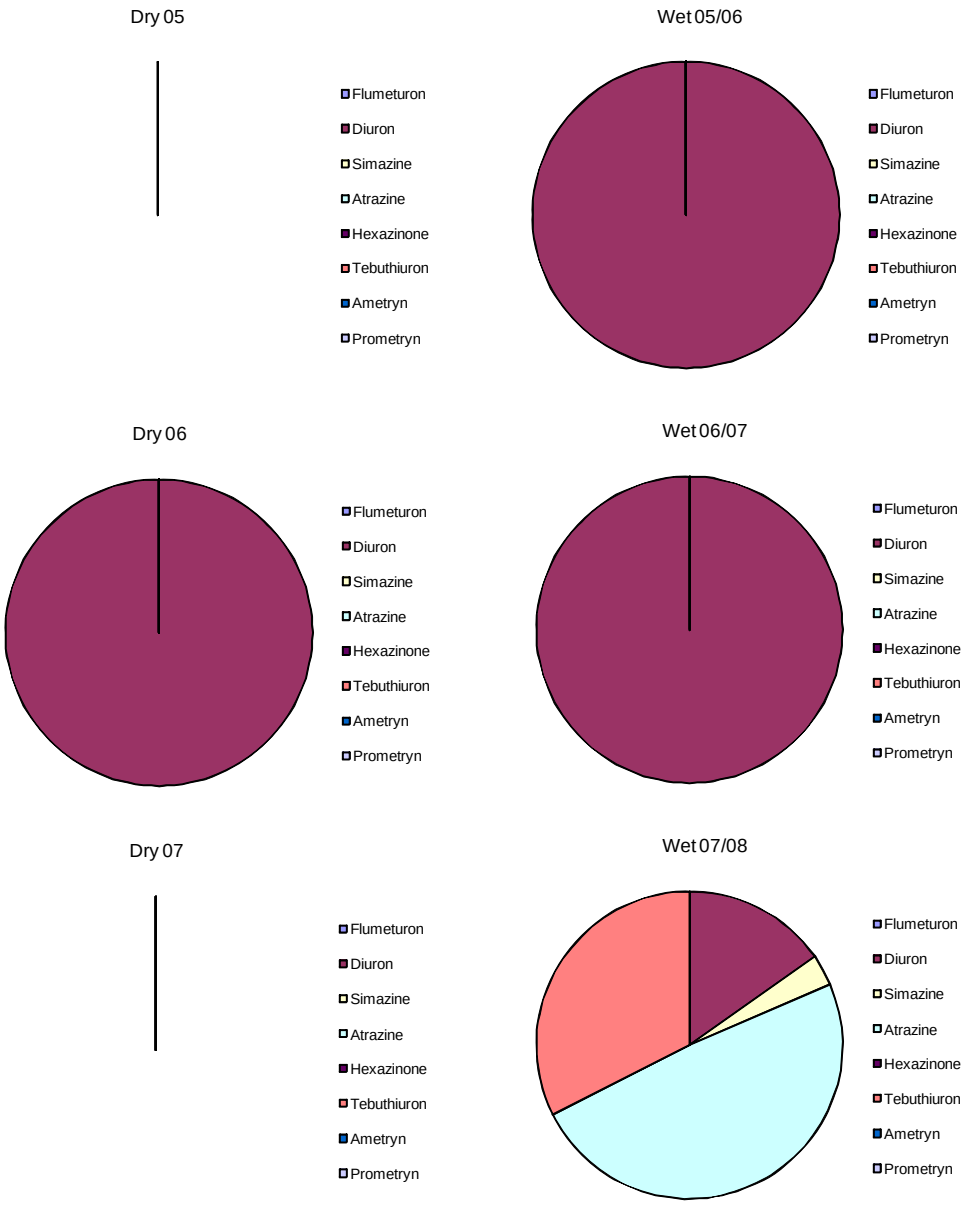

Figure 46 - ***Pie charts representing the relative proportion of pesticides detected at North Keppel Island using EDs. Results presented according to wet and dry seasons for each monitoring year.***

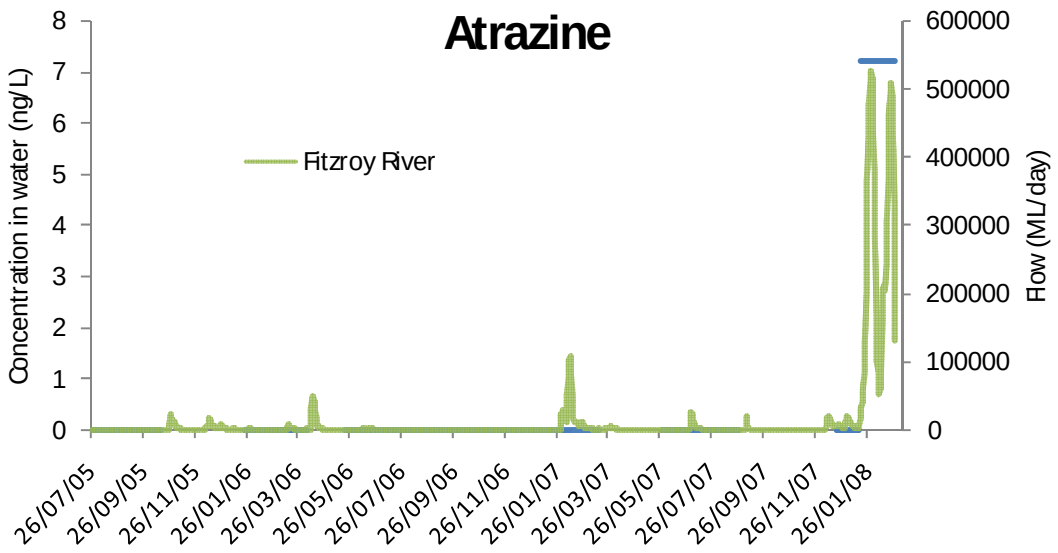

Figure 47 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at North Keppel Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

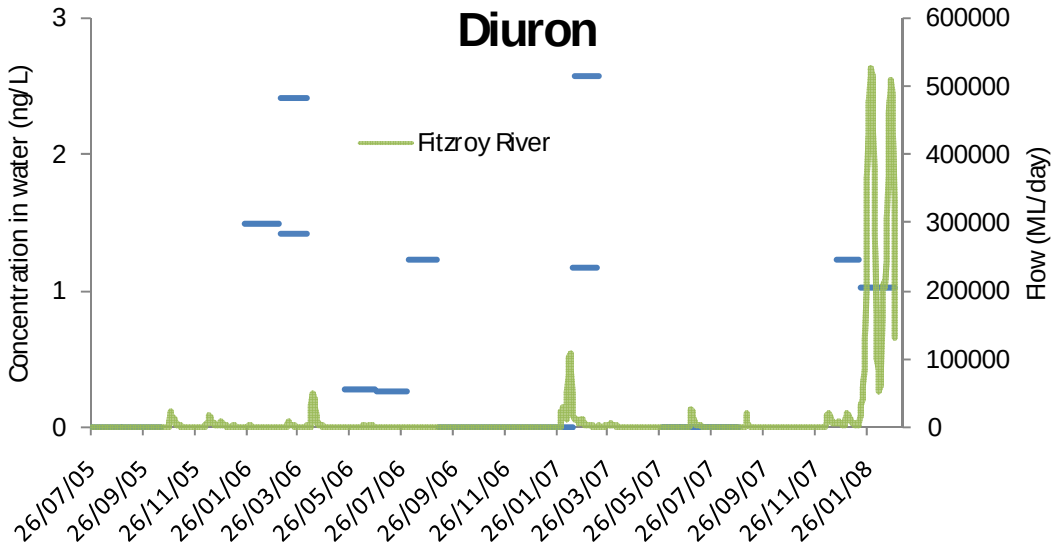

Figure 48 - ***Flow chart comparing water concentration (ng/L) to flow rate (ML/day) over period of time monitoring was conducted at North Keppel Island. Water concentrations presented as time integrated water concentration over period of sampler deployment. Left axis shows water concentrations and the right axis shows flow rates. Non detects are presented as zero.***

SPMDs and PDMS

Spatial and temporal trends for SPMD-based water concentration

Only chlorpyrifos and HCB were detected using SPMDs during 2007/08. Chlorpyrifos was detected at Magnetic Island (0.09 ng/L), Inner Whitsundays (0.04 ng/L) and Pioneer River (0.04 ng/L) once during the dry season and once during the wet season at Tully River (1.4 ng/L). HCB was detected at Magnetic Island (0.05 ng/L) once during the dry season.

The data from the two previous monitoring reports (2005/06 and 2006/07) indicate that non-polar organic pesticides were detected in SPMDs at only a few sites. For example during 2005/6 pesticides such as chlorpyrifos, diazinon, dieldrin and DDE were detected at some river mouth sites. Only low concentrations of diazinon and chlorpyrifos were occasionally detected at inshore reef sites. In 2006/7 the non-polar pesticides, chlorpyrifos and prothiophos were detected at Tully River and Outer Whitsundays in the wet season. At Pioneer River, chlorpyrifos and dieldrin were detected in the wet season.

Spatial and temporal trends for PDMS-based water concentration

The PDMS detected a wider range of chemicals at most sites when compared to SPMDs. Results from samplers deployed at the two river sites are discussed below according to NRM regions. Due to the relatively sporadic occurrence of non-polar pesticides at inshore reef sites, these results are summarised in Table 1. Phosphate tri-n-butyl was the most commonly detected chemical, sampled at least once at 8 inshore reef sites during the wet season. Chlorpyrifos, metalochlor, propiconazole, oxadiazon and bifenthrin were occasionally detected in the wet season. Diazinon and trifluralin were only detected in the dry season. Overall there were no consistent trends in pesticides detected using PDMS at any inshore reef site.

Cape York (Pixies Garden, Lizard Is)

Monitoring at these sites was relatively continuous and only occasionally detected phosphate tri-n-butyl between 2 and 4 ng/L.

Wet Tropics (Tully R, Low Is, Fitzroy Is, High Is, Normanby Is, Dunk Is)

At Tully River, results are only available for 3 deployment periods: April/May 2007, January/February 2008 and May/June 2008, hence it is difficult to examine temporal trends in terms of wet and dry seasons (4 other deployments of SPMD/PDMS at Tully were lost in the field). Diazinon (20-71 ng/L), propiconazole (7-43 ng/L), chlorpyrifos (9-23 ng/L), pendimethalin (4-15 ng/L),) and prothiophos (2-11 ng/L) were reliably detected in samplers for each deployment period. Tebuconazole (10-23 ng/L) was also detected in all periods, but only confirmed via a full scan in samplers from two periods. Other pesticides included bifenthrin (0.4-1.4 ng/L), dieldrin (1 ng/L). Overall there was a general trend of increasing water concentrations in the samples collected during the wet season. The water concentrations of diazinon, chlorpyrifos and propiconazole measured at this site were some of the highest recorded during this monitoring period.

Monitoring at the inshore reef sites was near continuous for most sites (excluding Dunk Is for which there is no data). Results show that Low Is was relatively uncontaminated by the non-polar pesticides sampled by PDMS. Only phosphate tri-n-butyl was detected at this site (0.7 ng/L) in Jan/Feb 2008. Sampling at High Is only detected chlorpyrifos (0.2 ng/L) and phosphate tri-n-butyl (2 ng/L) during an extended sampling event from April to July 2008. Relatively elevated

concentrations of diazinon, propoxur and desisopropylatrazine were each measured during separate sampling events at Normanby Is. A higher water concentration of propoxur was also detected at Fitzroy Is, along with tebuthiuron and phosphate tri-n-butyl. Water concentrations for propoxur and desisopropylatrazine are considered preliminary until more calibration data is available. Although several sets of samplers were sent to Dunk Is, only one set was deployed and none returned for analysis. Future monitoring with PDMS should still incorporate Dunk Island if possible because such elevated water concentrations in the Tully River were measured.

Burdekin (Orpheus Is, Magnetic Is, AIMS)

The limited sampling at Orpheus Is during the end of the wet season detected propiconazole, oxadiazinon and bifenthrin. Near continuous sampling at Magnetic Island detected phosphate tri-n-butyl during most of the wet season, diazinon once in the dry season (Aug/Sept 2007) and bifenthrin once during the wet season (Nov 2007 to Jan 2008). Sampling at AIMS was established late in 2007. Monitoring during this period detected phosphate tri-n-butyl in Jan/Feb 2008 and metalochlor from March to May 2008.

Mackay Whitsunday (Pioneer River, Inner and Outer Whitsunday)

At Pioneer River samplers were deployed continuously over the monitoring period. Seven non-polar pesticides including metolachlor (3-14 ng/L), phosphat tri n butil (1-13 ng/L), pendimethalin (1-11 ng/L), dieldrin (0.6-5 ng/L), chlorpyrifos (1-3 ng/L), chlorfenvinphos (3 ng/L) and trifluralin (1-2 ng/L) were detected. Heptachlor (0.6-1 ng/L), fenamiphos (8-11 ng/L) and propiconazole (9.5 ng/L) were also detected but not confirmed using full scan. Chlorpyrifos, dieldrin and phosphate tri-n-butyl were detected several times but mostly during the wet season. The highest water concentrations were generally measured during the wet season, except for propiconazole.

In the previous wet season (2006/07) PDMS were also trialled at Pioneer River. During this sampling period, a wider range of pesticides were detected, including, metalochlor, heptachlor, pendimethalin, phosphate tri-n-butil, fenamiphos, chlorfenvinphos, trifluralin as well as chlorpyrifos and dieldrin.

Sampling at the Whitsunday Islands was sporadic but occurred during both the dry and wet season. Phosphate tri-n-butyl was the only chemical detected at the Outer Whitsundays. No chemicals were detected at the Inner Whitsundays, however the samplers used for the wet season were deployed for over 200 days. Due to this long deployment period it is likely that chemical uptake into the sampler was approaching equilibrium for many chemicals and therefore the results from this period of sampling are more representative of the later part of the period.

Fitzroy (North Keppel Is)
Sampling at North Keppel Is was relatively constant with some gaps during the dry season. No chemicals were detected in samplers.

Overall the PDMS data indicates that there are a range of pesticides present at both inshore reef sites and river mouth sites. The presence of these chemicals at inshore reef sites appears to be sporadic and predominantly during the wet season. However at the river mouth sites the presence of these chemicals was more constant. Potentially, monitoring using SPMDs or PDMS could be restricted to the wet season and/or to representative sites in each region. Considering the relatively elevated water concentrations measured in the Tully River, continued use of PDMS at Dunk Island is recommended.

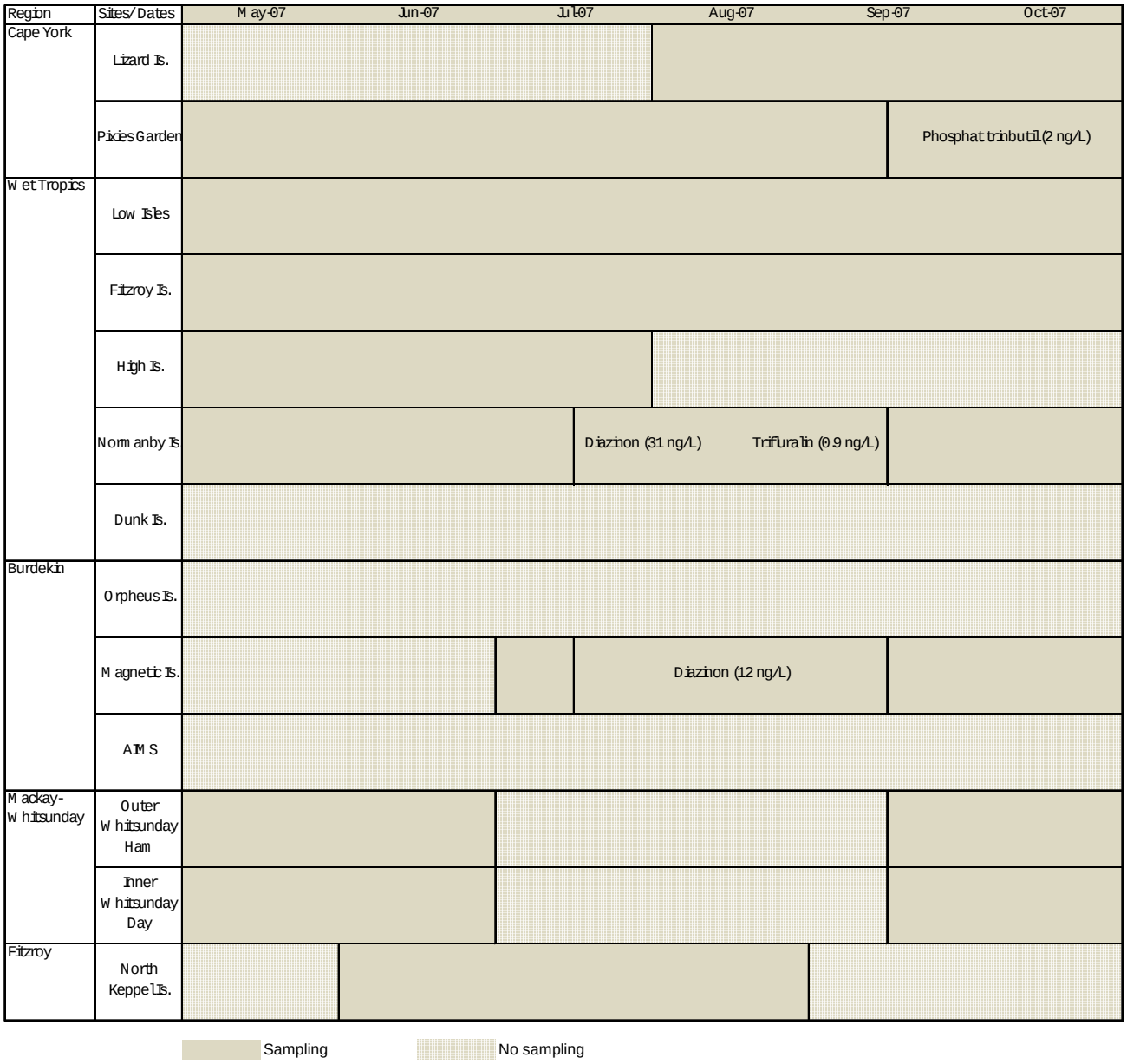

Figure 49 – *Passive Sampling Sites: Overview of PDMS Sampling Periods and Major Chemicals Detected During Dry Season – May 07 to Oct 07*

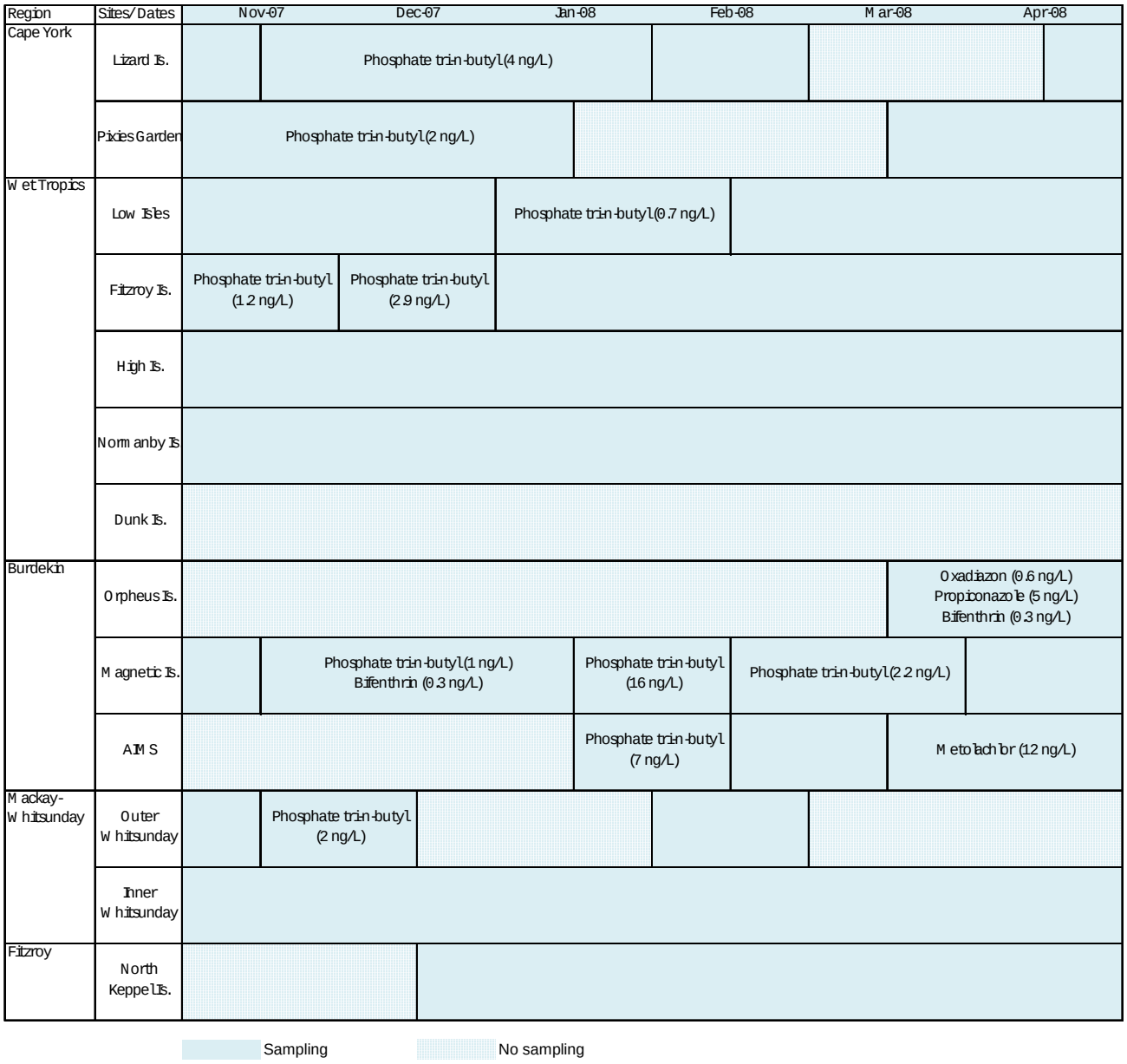

Figure 50 – *Passive Sampling Sites: Overview of PDMS Sampling Periods and Major Chemicals Detected During Wet Season – Nov 07 to Apr 08*

SPMDs vs PDMS

SPMDs and PDMS were co-deployed for the entire monitoring season. The inclusion of PDMS (financed by EnTox) was undertaken to allow a comparison between the performance of the two samplers. In general the PDMS samplers detected a wider range of chemicals when compared with codeployed SPMDs. Results show that the PDMS detected several chemicals at Pioneer River and Tully River and more sporadically at inshore reef sites. Many of these chemicals could not be quantified in co-deployed SPMDs. The only exceptions were for chlorpyrifos and HCB. At two sites, the detection limit for chlorpyrifos and HCB in PDMS (0.5 ng/L) exceeded the SPMD-based water concentrations. At one other site (Tully River) both SPMDs and PDMS detected chlorpyrifos however the PDMS-based water concentration (16 ng/L) was much higher than the SPMD-based water concentration (1.4 ng/L).

One reason there is a difference between the performance of the samplers relates to the extra clean up step required to analyse SPMDs. All SPMD extracts require GPC to remove triolein from samples to ensure that there is no contamination of the GCMS. Unfortunately this results in the partial removal of certain target chemicals such as the organophosphates.

Overall the results indicate that the PDMS may be a more suitable sampler. Further work is required to accurately determine sampling rates for PDMS samplers. However this work is currently underway and is expected to be available for future monitoring activities. Work will also be undertaken to improve detection limits using these samplers because in general, detection limits in PDMS are higher compared with SPMDs. Overall, we recommend that PDMS replace the use of SPMDs as a monitoring tool on the GBR. Ongoing developmental work on the PDMS sampler will be incorporated into the GBR program when available.

Flood data

Flow (sometimes referred to as 'flood') events were monitored using EDs and PDMS, in the Wet Tropics region (Tully River), Mackay Whitsunday region (Pioneer River) and Fitzroy regions (Fitzroy River).

Wet Tropics: Tully River

Samplers were deployed to monitor 2 flow events which occurred over several days in late February and early March 2008. Samplers were deployed for consecutive periods but different lengths of time. Samplers were deployed for 2 days, followed by an 11 day, 2 day and 7 day deployment. PDMS samplers were lost during the 11 day deployment.

Diuron, simazine, atrazine and hexazinone dominated the profile followed by flumeturon and atrazine breakdown products (Figure 51). This profile was similar to that detected using samplers deployed routinely during 2007/08 and during flow events in 2007.

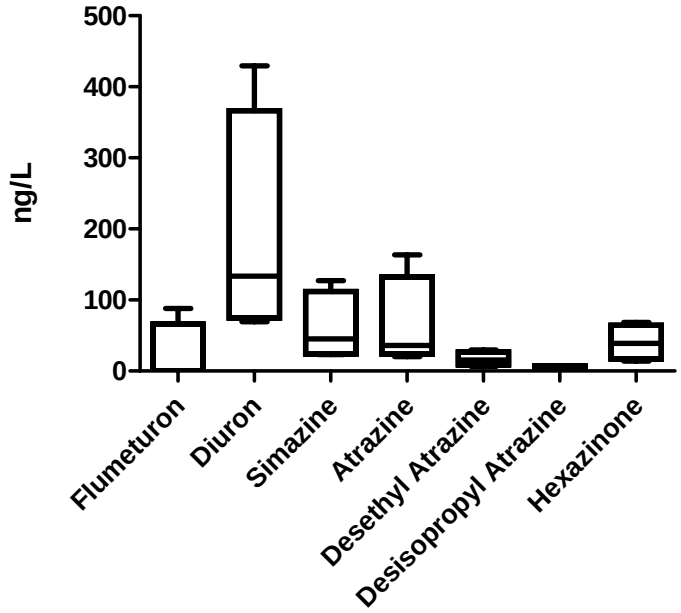

Figure 51 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected during Tully River flow events using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

In general, a decrease in water concentrations was measured for all chemicals during the first peak flow event, followed by an increase in water concentrations for diuron and atrazine during the second flow event. In contrast, simazine and hexazinone decreased again during the second flow event. This decrease in water concentrations was also detected in samplers deployed for routine monitoring. For example, diuron decreased from 1120 ng/L before the flow events to 180 ng/L during the events (sampling actually covered 3 peak flow events, including the 2 largest events). Interestingly, the mean of all water concentrations measured during the flow events (n=4, 200 ng/L) was very close to the time integrated water concentration measured using the passive samplers deployed during the whole period (13/2 to 19/3).

PDMS deployed before the first peak flow event showed that only phosphate tri-n-butyl was detectable. Samplers deployed during the flow event were lost. Following this event, chlorpyrifos, diazinon, propiconazole, prothiophos and tebuconazole were detectable, whereas phosphate tri-n-

butyl was not detectable. The water concentration for some chemicals (diazinon, propiconazole, pendimethalin and tebuconazole) increased during the second peak flow event.

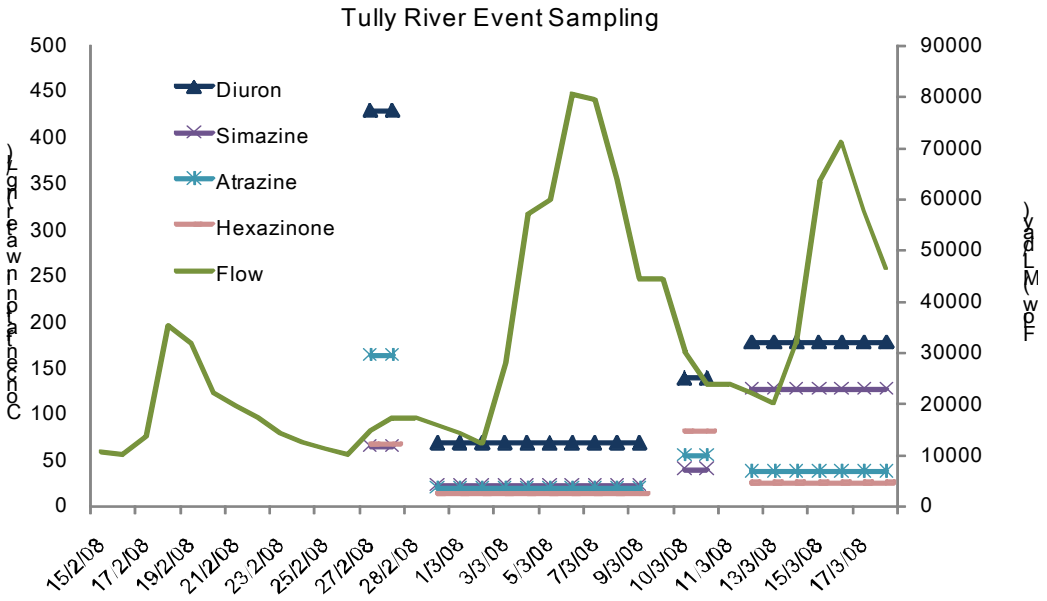

Figure 52 – ***Flow rates (ML/day) and water concentrations (ng/L) of pesticides measured during Tully River flow events. Left axis shows water concentrations and the right axis shows flow rates.***

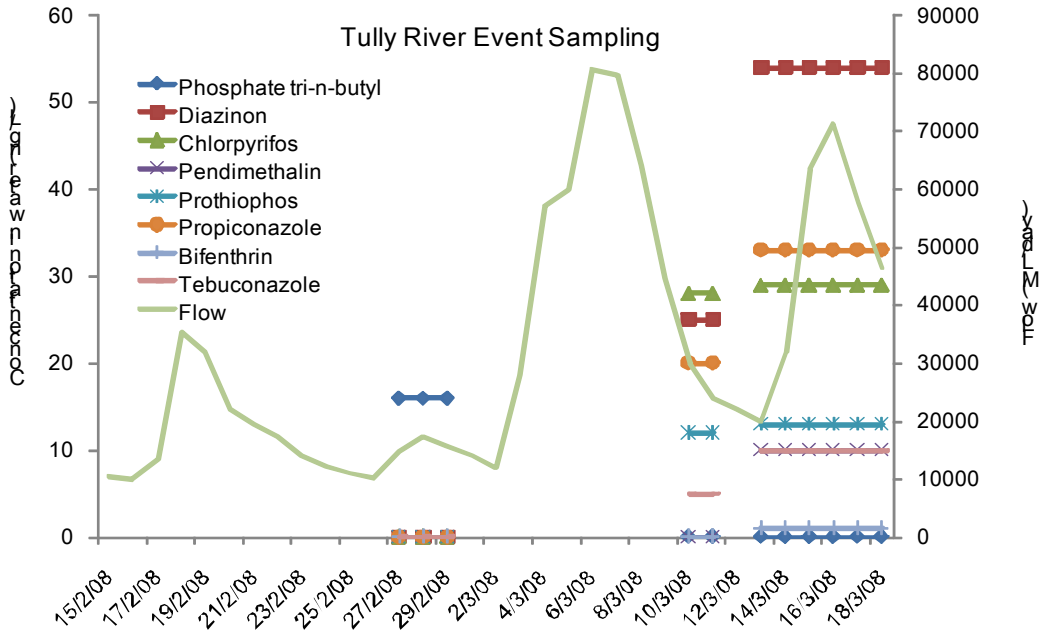

Figure 53 - ***Flow rates (ML/day) and water concentrations (ng/L) of pesticides measured during Tully River flow events. Left axis shows water concentrations and the right axis shows flow rates.***

Mackay-Whitsunday Region: Pioneer River

Samplers were deployed each day in the Pioneer River from the 14th to the 18th of January 2008. These dates coincided with flow events of fluctuating volume. A range of polar pesticides were quantified in the ED samplers with diuron and atrazine dominating the chemical profile, followed by hexazinone, desethyl atrazine, ametryn and desethyl atrazine (Figure 54). Tebuthiuron, prometryn and simazine were in most cases < 1ng/L. A similar profile was detected using samplers during event monitoring in 2007.

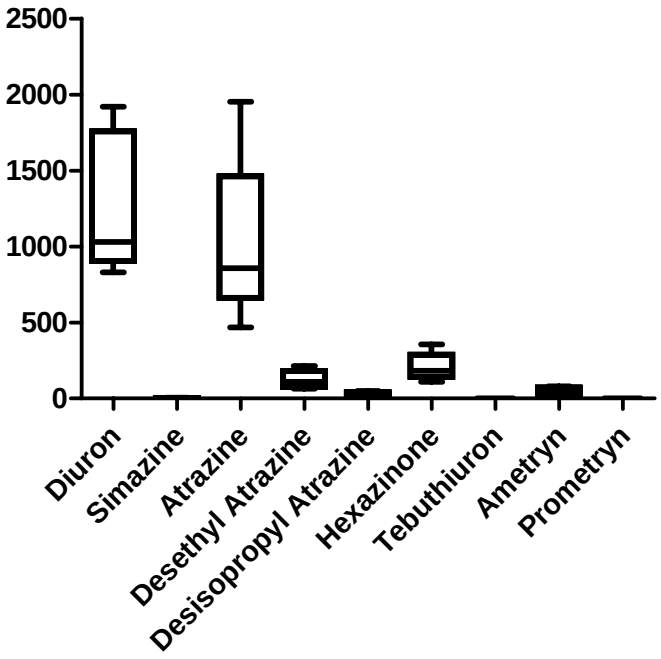

Figure 54 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected during Pioneer River flow events using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

The water concentration of diuron appeared to increase with flow volume (Figure 55). In contrast, the water concentrations of atrazine and other chemicals tended to decrease through the flow events (Figure 56). Decreasing levels of phosphate tri-n-butyl were detected in co-deployed PDMS throughout the flow events.

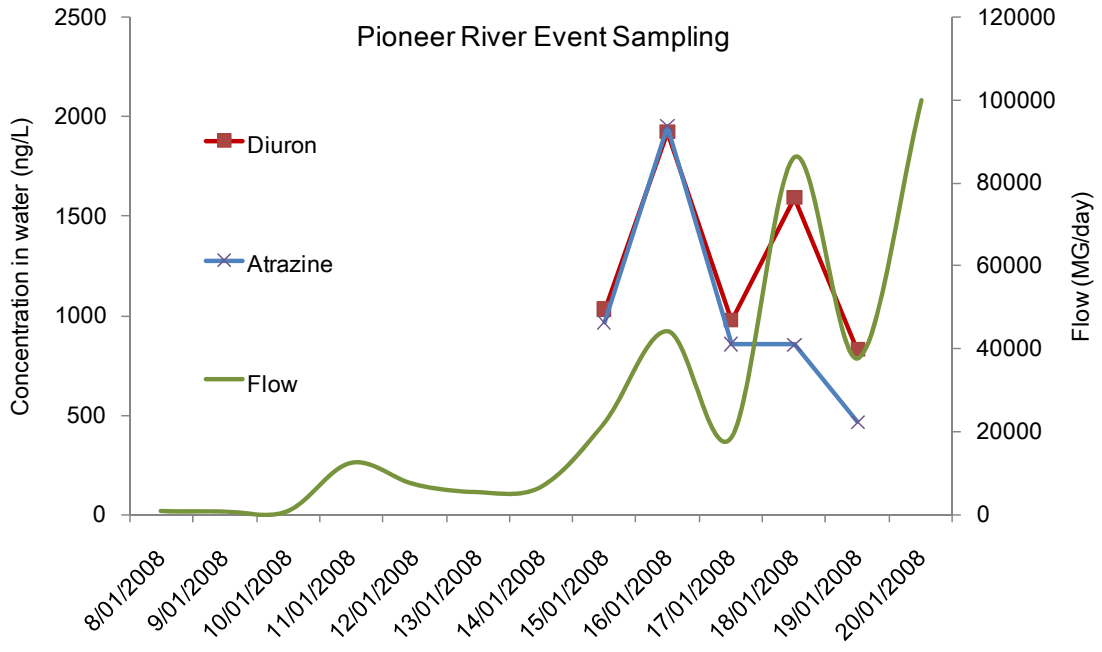

Figure 55 - ***Flow rates (ML/day) and water concentrations (ng/L) of pesticides measured during Pioneer River flow events. Left axis shows water concentrations and the right axis shows flow rates.***

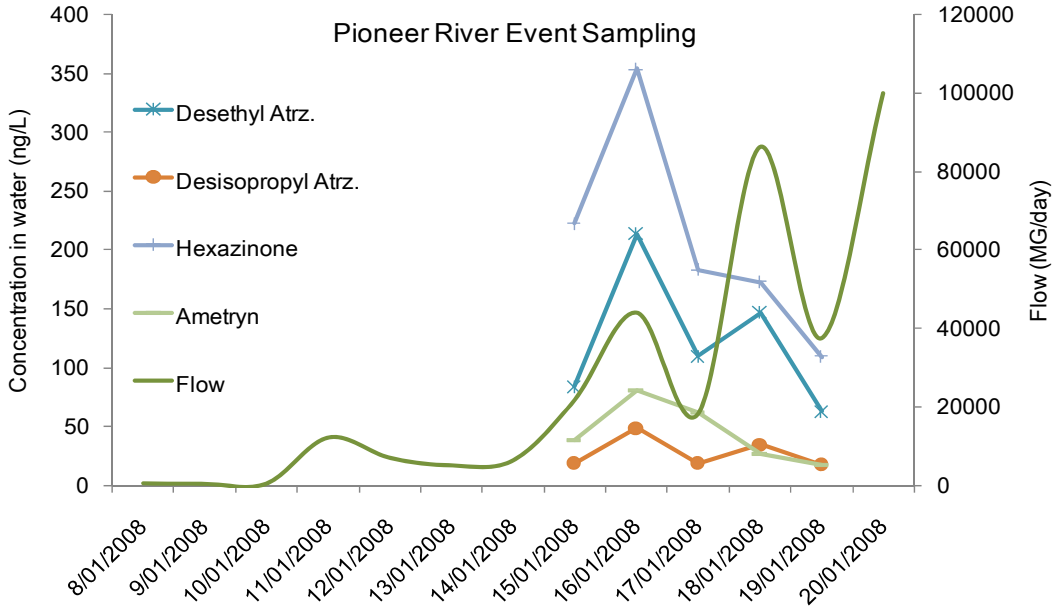

Figure 56 - ***Flow rates (ML/day) and water concentrations (ng/L) of pesticides measured during Pioneer River flow events. Left axis shows water concentrations and the right axis shows flow rates.***

Fitzroy Region: Fitzroy River

Ten sets of samplers were deployed in the Fitzroy River during two peak flow events. These flow event included inflows from both cropping and grazing areas. Results from ED samplers showed that atrazine dominated the polar pesticides with a maximum water concentration of 1663 ng/L. Tebuthiuron was the second highest polar pesticide, with a maximum of 431 ng/L. These results are in contrast to event monitoring in the previous year which showed that tebuthiuron dominated followed by atrazine. However that flow event was dominated by inflows from grazing areas only, where tebuthiuron usage predominates for woody weed control. Other polar pesticides and degradation products present at relatively significant concentrations included desethly atrazine, simazine, desisopropyl atrazine, diuron, and hexazinone. Prometryn, flumeturon and ametryn were also present, mostly below 1-2 ng/L.

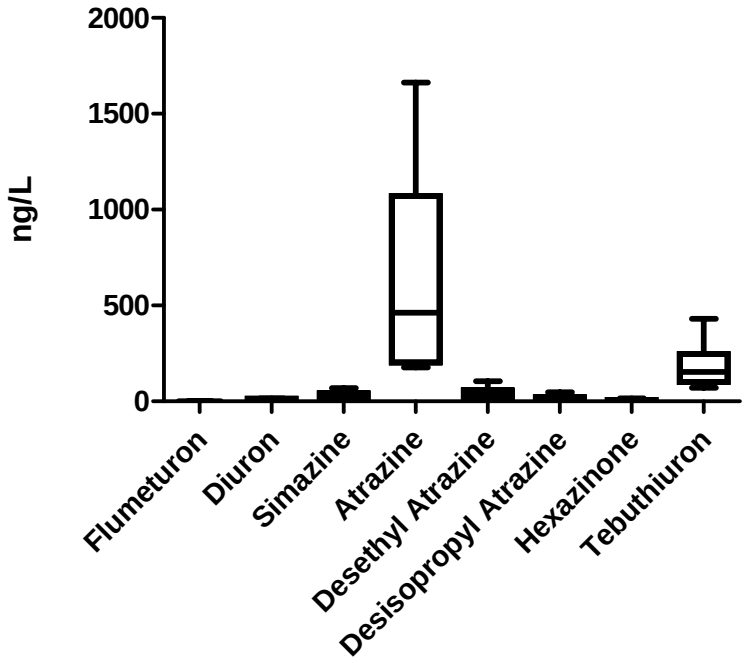

Figure 57 - ***Box plots showing the range of water concentrations (ng/L) for pesticides detected during Fitzroy River flow events using EDs. Maximum and minimum values represented by whiskers and the median represented by horizontal line within box.***

The water concentration of atrazine and tebuthiuron tended to increase prior to the peak of the flow event and decrease as the flow event passed (Figure 58). A similar trend was also evident for the other chemicals detected using EDs.

Eight sets of PDMS samplers were retrieved during this event monitoring period. Results showed that metalochlor was present at the highest concentrations with a maximum water concentration of 98 ng/L followed by phosphate tri-n-butyl with a maximum concentration of 32 ng/L. Other non-polar pesticides present at low concentration were diazinon, chlorpyrifos, prometryn, fenitrothion, fipronil, dieldrin and piperonyl butoxide.

Metalochlor and phosphate tri-n-butyl followed a similar trend to the polar pesticides with peak water concentrations occurring prior to the peak of each flow event (Figure 59). In comparison, the trend in water concentrations for the other chemicals was less clear, typically peaking during or between the two peak flow events.

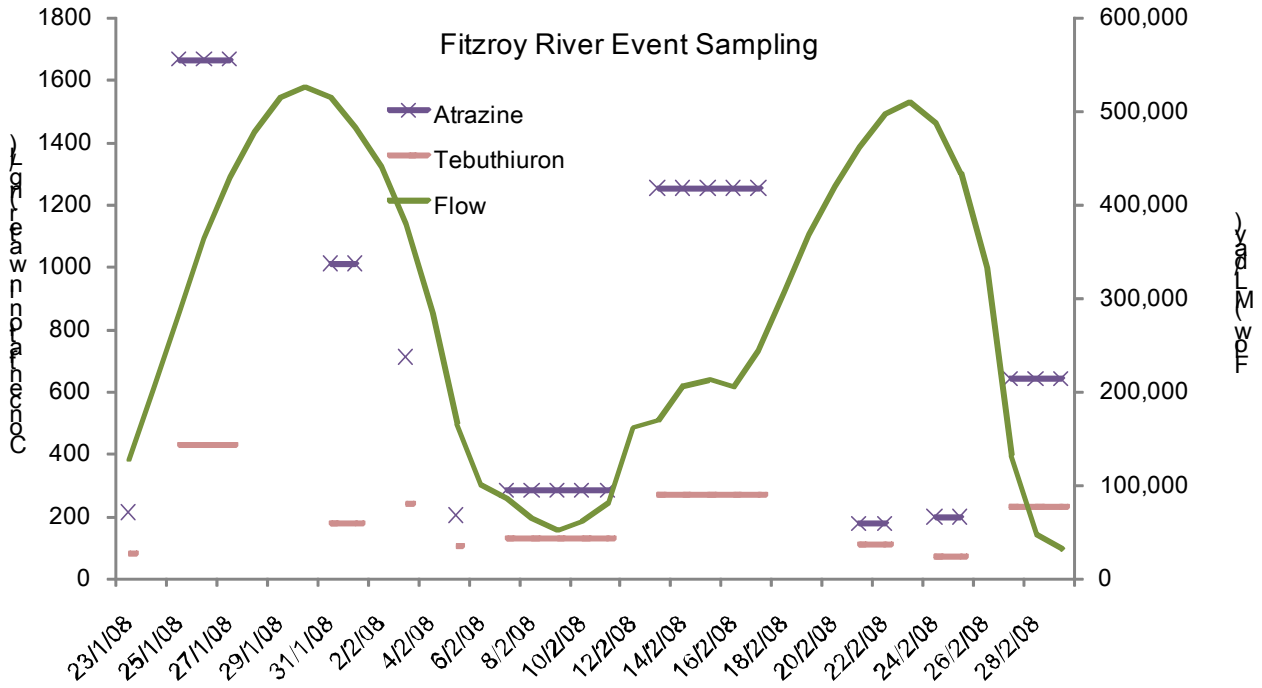

Figure 58 - ***Flow rates (ML/day) and water concentrations (ng/L) of pesticides measured during Fitzroy River flow events. Left axis shows water concentrations and the right axis shows flow rates.***

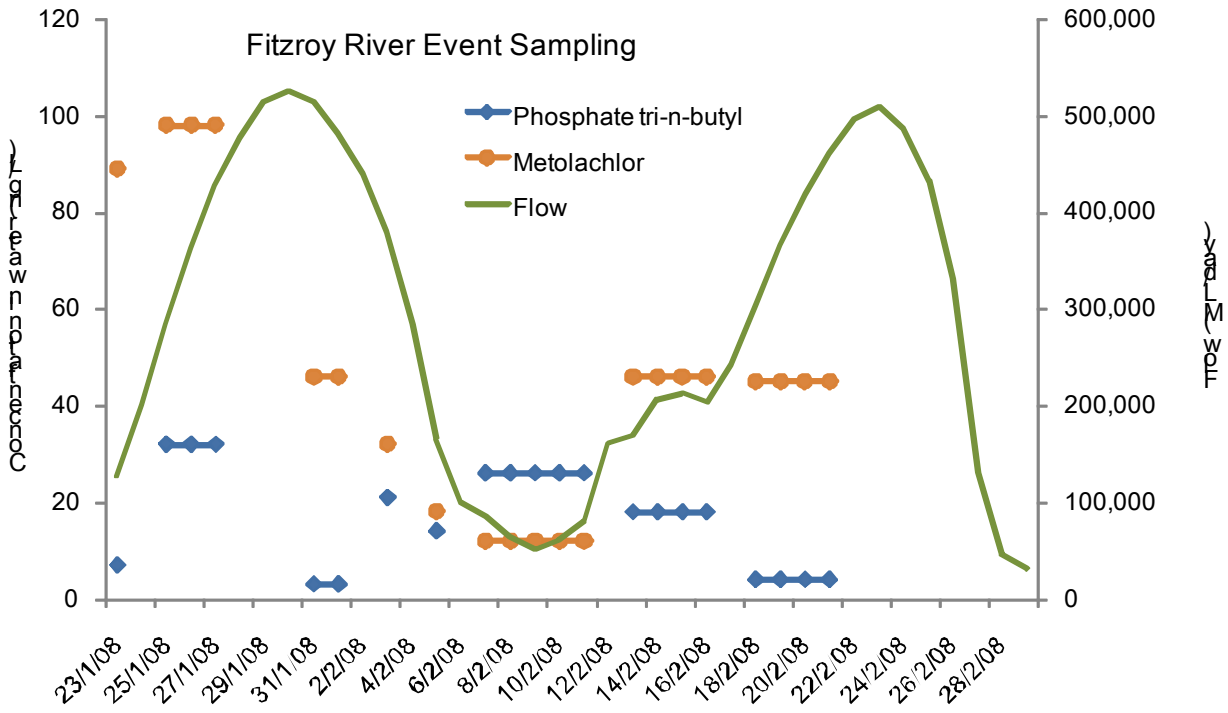

Figure 59 - ***Flow rates (ML/day) and water concentrations (ng/L) of pesticides measured during Fitzroy River flow events. Left axis shows water concentrations and the right axis shows flow rates.***

Comparison between passive sampler and grab sampler water concentrations

Multiple grab samples were collected from the Fitzroy River during the period when passive samplers were deployed to monitor peak flow events (data provided courtesy of Bob Packet, NRW). Grab sample based water concentrations were averaged where more than one grab sample was collected during a corresponding passive sampler deployment. A comparison between grab sample based and passive sampler based water concentrations show that in general passive samplers overestimated the water concentration of chemicals (Figure 60). Overall, 80% of all passive sampler-based water concentrations were within a factor 2 of corresponding grab sampler-based water concentrations.

In many cases analysis of grab samples produced non-detects where corresponding passive samplers detected a chemical. This was particularly evident for diuron, atrazine and hexazinone where approximately half of the grab samples did not detect the chemical when it was detected using the passive samplers. These results highlight the advantage of using passive samples to detect chemicals that are present at water concentrations that are below detection limits in grab samples.

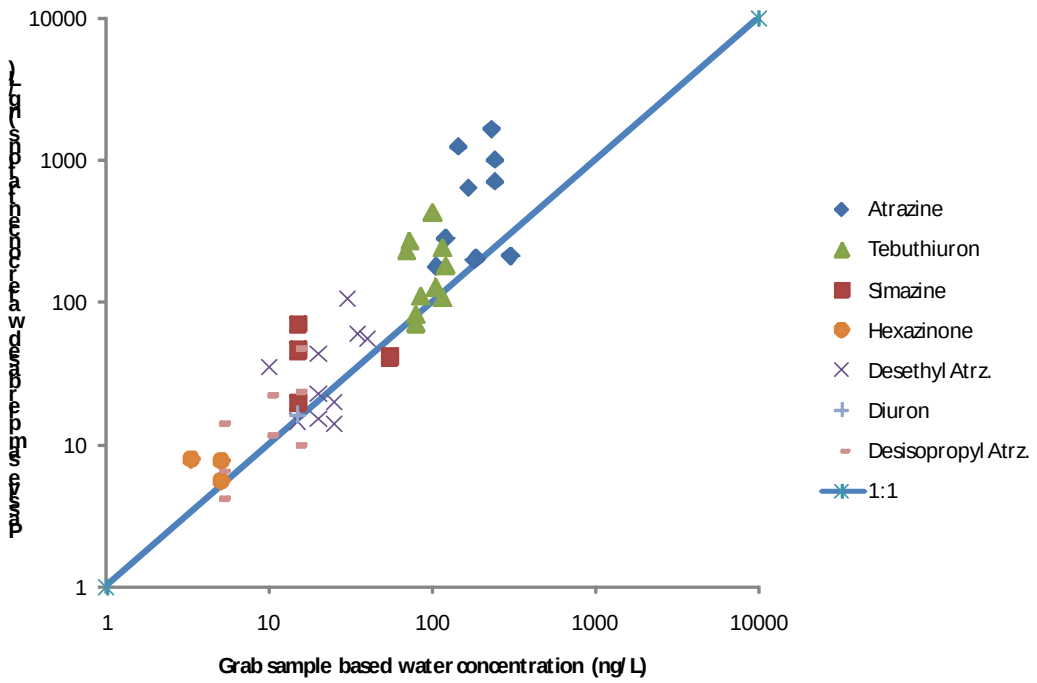

Figure 60 – ***Graph showing comparison between passive sampler and grab sampler water concentrations of chemicals detected during flow events at Fitzroy River during Jan/Feb 08***

Toxicity Testing

Phytotoxic response in ED samples

A fluorescence based photosynthetic yield analysis technique, the Maxi-Imaging-PAM chlorophyll fluorometer (IPAM), was used to assess phytotoxicity (Schreiber et al 2007). The IPAM bioassay allowed for sensitive assessment of phytotoxicity of PS II impacting herbicides, which bind to the quinine binding site of PSII in photosynthesis and inhibit energy conversion, and has been applied for detection of herbicide pollutants in aquatic environments (Escher et al 2006; Muller et al 2007). Samples and blanks were tested at 8 concentrations in duplicates along with a positive control (diuron). The response of the procedural blank was below the detection limit (7% inhibition; ~1.5 ng/L diuron equivalency).

Extracts from all samples inhibited photosynthesis in the test, indicating that herbicides were probably present at all sites. The concentrations required to illicit the inhibition of photosynthesis were approximately X times higher than actual levels at the sites (i.e. samples were concentrated up to X times before an effect could be measured). Similar results were seen in samples collected at the same sites in 2007 (note: samples from 2007 were tested on zooxanthellae). Therefore, according to these results, the water concentration of herbicides at these sites would have to increase significantly to inhibit photosynthetic activity. It is unlikely that the water concentration of herbicides at these sites could increase by 3 orders of magnitude. For example, monitoring to date has shown that water concentrations typically only increase by 1 or 2 magnitudes during the wet season.

Only samples from 3 sites produced a response that exceeded the detection limit (Figure 61). The percent inhibition of photosynthetic yield above detection limits was converted to diuron equivalent concentrations from dose-response curves and did not exceed 3 ng/L (Humpy & Halfway Is: 1.9 – 2.9 ng/L; Barron Is: 2.3 ng/L; and Orpheus Is: 1.3 – 1.7 ng/L). In 2007 only the sample collected from High Island exceeded the detection limit.

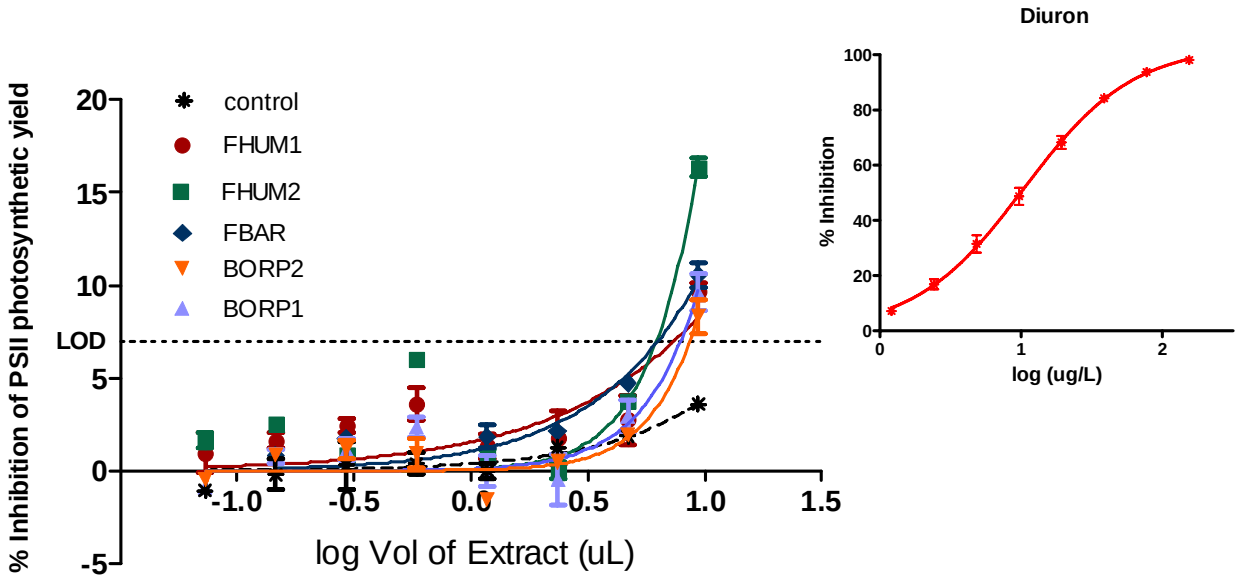

Figure 61 – . ***Phytotoxic response on*** **Chlorella** ***spp. Insert: positive control diuron.***

Discussion

Regional trends in water concentrations and pesticide profiles

There are some clear differences between regions. Monitoring at sites in both the Cape York and Fitzroy regions show that the water concentration of pesticides is typically below 2 ng/L with median values at the detection limit. The only exception was after high flow events in the Fitzroy River which appear to have affected the pesticide profile at North Keppel Island significantly. Forthcoming data will show how long the change in water quality persisted. The relatively low concentrations detected in the Cape York region may be explained by the pristine catchment in the area. Potentially, monitoring at one of the sites in Cape York could be discontinued.

In the Wet Tropics the maximum water concentrations of individual pesticides were similar regardless of where samples were collected. For example, the maximum water concentration of diuron ranged from 12 to 15 ng/L. The maximum water concentrations of atrazine (4 to 7 ng/L) and hexazinone (3 to 6 ng/L) were also similar. At Low and Fitzroy Islands median values were at the detection limit except for diuron (1 to 2 ng/L). At Normanby and High there were more detections of atrazine and hexazinone, although sampling at High Island only commenced in mid 2006. The median water concentration for diuron at High Island (5 ng/L) was the highest in the study but only based on 10 samples. One or two of these sites could be removed from the monitoring program due to the similarities in water concentrations and proximity to the coast.

There was wider variation in maximum and median water concentrations in the Burdekin region, however sampling at AIMS only occurred during the 2007/8 wet season and hence could bias results. Overall AIMS had the highest maximum and median water concentrations followed by Magnetic Island. Higher variation was detected for atrazine and tebuthiuron due to relatively high concentrations measured in early 2008 at AIMS.

Monitoring in the Mackay Whitsundays region showed that water concentrations for individual pesticides were generally higher at the Outer Whitsundays. The median diuron water concentration at Outer Whitsundays (n=9) was the second highest in the study (excluding AIMS). Considering the difficulties in managing deployments at the Inner Whitsundays site, it could be removed from the program if sampling was maintained at the Outer Whitsundays site.

The pesticide profile at inshore reef sites was dominated by diuron, atrazine and hexazinone. For most sites diuron was detected at the highest concentrations, with the exception of AIMS and Magnetic Island where atrazine was highest. Higher proportions of simazine were observed at sites within the Wet Tropics region compared to other sites. A comparison between samplers deployed in the Tully and Pioneer Rivers showed that simazine was dominant in the pesticide profile of the Tully River. All these chemicals are used extensively in the sugar cane industry which is a significant land use in the GBR catchments.

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. Monitoring was only recently established at the Tully River site but showed that the pesticide profile was dominated by diuron and simazine, followed by atrazine, hexazinone and occasional detections of atrazine breakdown products and tebuthiuron. The limited sampling events indicated that water concentrations for diuron could exceed 1000 ng/L. Eight pesticides were detected at different times using PDMS samplers, with diazinon, propiconazole and chlorpyrifos present at the highest concentrations.

Sampling at the Pioneer River, established in late 2005, showed a pesticide profile dominated by atrazine and diuron, followed by hexazinone, atrazine breakdown products, ametryn, tebuthiuron and simazine. In contrast to other sites, ametryn was commonly detected and at relatively elevated water concentrations. There were also occasional detections of both prometryn and flumeturon. During high flow events, the water concentrations of diuron and atrazine exceeded 1500 ng/L. Interestingly some of the higher water concentrations measured in the 2005/6 monitoring period occurred after relatively low increases in flow rates. These results suggest that very high flow rates are not necessarily required to increase water concentrations in these river systems. A range of pesticides were also detected using PDMS samplers, including phosphate tri-n-butyl and pendimethalin, although concentrations for individual pesticides did not exceed 15 ng/L.

Seasonal Trends

Pesticide concentrations were generally higher in the wet season than the dry season at all sampling sites. This is likely related to not only the fact that pesticide application occurs during the wet season, but also that rainfall increases the mobility of these chemicals. Within sites, there was general consistency between the wet and dry seasons in the percentage contribution of the major herbicides detected. Some herbicides were present at sites in the wet season that were not detectable in the dry season. This may reflect changes in land based usage patterns between seasons, but could also be attributed to improved transportation of these compounds due to rainfall mobilisation.

Comparison with other studies

The herbicide concentrations detected in this sampling program compare closely with the results of Rohde et al. (2006) who studied flow events in January 2005. Rohde et al. (2006) found median diuron concentrations in the Pioneer River of 1190 ngL^{-1} in flow events in January 2005. This study found diuron concentrations of approximately 1000 ngL^{-1} at the same location in flow events in early February 2007.

Rhode et al. (2006) also examined herbicide concentrations at inshore reef sites in the Mackay Whitsunday region during a flood in late January 2005. The concentrations detected in that study (diuron concentrations of 50 to 440 ngL^{-1}) were notably higher than those detected in inshore reefs in the Mackay Whitsunday region in this study (diuron concentrations of up to 16 ngL^{-1}). This difference could be explained by the fact that the sites in their study were closer to major river mouths (O'Connell and Pioneer Rivers) than the reef sites in this study. The study of Rhode et al. 2006 also followed a flood plume, so it could be expected to be higher than the concentrations detected in this study which were sampled only routinely at inshore sites, not in response to flood events.

Further work

Further statistical analysis should determine whether significant differences occur between sites and seasons. Overall the analysis should take into account when the wet season commenced based on rainfall or hydrographs. Appropriate time trend analysis should also be undertaken to determine whether the concentration of pesticides in water has changed over the duration of the monitoring program. However further baseline data may need to be collected to facilitate this process.

Due to the prevalence of diuron at sites, chemical analysis could be expanded to include diuron breakdown products. Further research could also be directed into the development of passive samplers for glyphosate and 24-D.

Certain chemicals that are relatively polar were detected in PDMS but not analysed for in ED samplers. These included propoxur and propazine. Propoxur was detected once in PDMS deployed at Fitzroy Island and Normanby Island. Propazine was detected once in PDMS deployed in the Pioneer River. In other cases, chemicals that are analysed for in EDs were only detected in co-deployed PDMS. Desisopropylatrazine was detected once in PDMS at Normanby Island and tebuthiuron was detected once in PDMS at Fitzroy Island. During the same deployment neither of these chemicals were detected in co-deployed EDs. Due to the unreliability of the extraction and quantification process for these chemicals using PDMS and GCMS, these results are not reported. However the occurrence of propoxur and propazine indicates that these chemicals could be present and potentially should be analysed for in ED samplers. The difference between PDMS and EDs for tebuthiuron and desisopropylatrazine could be due to analytical inconsistencies or lower uptake rates in EDs.

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Appendix: DNRW acknowledgement for use of flow data

'Based on or contains data provided by the State of Queensland (Department of Natural Resources and Mines) [2008]. 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.'

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