

Reef Rescue Research & Development

Technical Report

Pesticide exposure within the Barratta Creek Catchment RRRD037



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Rachael Smith, Ryan Turner, Michael Warne, Jochen Mueller and Jon Brodie**



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Project RRRD037 Pesticides in Sugar

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The Reef Rescue Research and Development Program (Reef Rescue R&D) was funded under the Australian Government's Caring for our Country program, and consisted of 18 projects. The Reef Rescue R&D is designed to improve our understanding of the link between land management practices and environmental impacts, and improve water quality across the Great Barrier Reef by informing on-ground projects to reduce the amounts of nutrients, pesticides and sediments reaching the Reef from agricultural lands.

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Cover photographs: Top Left - Jerona: Water sampling within the Bowling Green Bay wetland.

Top Right - Barratta estuary: Mangroves on the bank of Barratta Creek within the estuary; Bottom Left - Barratta Creek at Northcote in flood; Bottom Right - Passive samplers deployed from a tree within East Barratta Creek. Images supplied by James Cook University

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Executive Summary

Barratta Creek constitutes one of the major upstream catchments and drainage lines in the watershed of the Bowling Green Bay Ramsar wetland. The Barratta Creek catchment has been considerably altered following the development of the Burdekin-Haughton Water Supply Scheme (BHWSS) in the late 1980s largely for sugarcane cultivation, which led to the establishment of perennial flow within the creek after it became the main distributary channel for irrigation tailwater runoff. As such, pesticide concentrations within the creek prior to the undertaking of this project were elevated compared to most streams of the Great Barrier Reef catchment area. This study has utilised a combination of passive samplers deployed at monthly intervals and grab samples at four sites along the Barratta Creek Complex over two years to examine the persistence, concentration, pesticide use in the catchment area, seasonality and spatial variation of the multiple pesticide residues detected. In addition, this study further assesses the utility of passive sampling techniques vs grab sampling when undertaking water quality monitoring. This project initially proposed a 12 month monitoring program at four sites within the Barratta creek system. Additional resources were obtained and the project was continued for an additional twelve months so that at the conclusion of the monitoring program, 24 months of continuous monthly pesticide monitoring had been undertaken. During this study period, two changes in the regulated use of diuron by the sugarcane industry were introduced by the Australian Pesticides and Veterinary Medicines Authority (APVMA).

A total of 37 different pesticide residues (which does not include metabolites of some of these pesticides) were detected in the Barratta Creek Catchment during the two year research program, although a number of these residues were detected infrequently (< 5 occasions of the 27 deployments) and at low concentrations (i.e. below available ecological guidelines). Since pesticide usage data are unavailable in the upstream catchment area, this research program provides valuable insights on the pesticides in common use in this region. Moreover, long-term programs provide insights into changing patterns in pesticide usage. This study found increasing levels of metribuzin and metolachlor in Barratta Creek which likely reflects the wider adoption of these 'alternative' herbicides to diuron and atrazine in the lower Burdekin region. The herbicides diuron and atrazine regularly exceeded ANZECC and ARMCANZ (2000) ecological protection guidelines for several months (five to seven months of the year) at all four sites including in the Ramsar wetland in Bowling Green Bay. While concentrations of both atrazine and diuron progressively decrease towards the lower reaches of the Creek system (e.g. in the Ramsar wetland site concentrations were approximately a third to a half of the values measured at the upper site), they still exceeded the 99% species protection value for six months of the year.

The change in the types of pesticides and their concentrations detected throughout this monitoring program has provided a valuable record of the pesticides employed by the local industry and how the usage of pesticides by the industry has changed in response to regulatory action. As such it is advisable that the monitoring of pesticide residues within the Barratta Creek is continued. This monitoring program will ensure that any future changes in pesticide usage are captured so that pesticides used by local industries are not being

transported into the receiving environments at concentrations likely to put valuable species or ecosystems at risk.

Introduction

Background

As increased pressure is applied on the agricultural industry to produce higher yields from existing farmlands, farmers are relying more heavily on the use of fertilizer and pesticide control to maximize crop performance. Balancing this pressure is the increased focus being placed on ecological protection and the management of pesticide use within the environment (Hillocks 2012; King *et al.* 2013). Pesticide use within many countries is regulated to reduce the risk associated with exposure to both humans and the environment to any pesticide residues post application. A number of previously used agricultural pesticides, such as the organochlorine pesticides (OCPs), were found to impact on human and ecosystem health and have been widely banned in developed countries, where there has been a concerted effort to reduce the release of persistent organic pollutants (POPs) into the environment (Bilcke 2002). In 2000, the Australian and New Zealand Environmental Conservation Council (ANZECC and ARMCANZ 2000) established water quality (WQ) guidelines for a range of pollutants in order to protect and manage environmental values. Exceedance of the guideline values indicate that there is an environmental problem and management action is required to ensure the ongoing health of the ecosystem impacted. Where there were insufficient data to accurately calculate guideline values, trigger values were defined that if exceeded indicate a potential environmental problem and that a management response should investigate and refine the guidelines according to local conditions. The guideline and trigger values for pesticide concentrations in surface waters, where available, are listed in Table 5 of the appendix). Work undertaken as part of the Reef Plan Paddock to Reef Integrated Monitoring, Modelling and Reporting Program has since shown that there is a widespread pesticide contamination within rivers and streams draining into the Great Barrier Reef (GBR) (Brodie *et al.* 2012). The photosystem II (PSII) herbicides, atrazine, simazine, ametryn, prometryn, hexazinone, diuron and tebuthiuron, were found to be of particular concern as these herbicides are frequently detected in surface waters (Kennedy *et al.* 2012a; Kennedy *et al.* 2012b; Lewis *et al.* 2012; Smith *et al.* 2012; Turner *et al.* 2012) and have the potential to cause negative impacts on seagrass, mangroves, microalgae, coral-symbionts, and foraminifera-symbionts (Haynes *et al.* 2000; Jones and Kerswell 2003; Jones *et al.* 2003; Duke *et al.* 2005; Negri *et al.* 2005; Cantin *et al.* 2007; Magnusson *et al.* 2010; Magnusson *et al.* 2012; van Dam *et al.* 2012).

Barratta Creek Catchment

Barratta Creek drains a substantial area of the intensive cropping lands (predominately sugarcane) within the Dry Tropics Natural Resource Management (NRM) region. The construction of the Burdekin Falls Dam (completed 1987) and the development of the Burdekin-Haughton Water Supply Scheme (BHWSS) allowed for large tracts of land on the lower Burdekin floodplain to be exploited for irrigated cropping. In this regard, Barratta Creek formed the main distributary channel for irrigation tailwater runoff and as a result, this previously intermittent system became a perennially flowing creek containing elevated

levels of nutrients and pesticide residues (Lewis *et al.* 2007; Davis *et al.* 2008; Davis *et al.* 2012; Davis *et al.* 2013). Importantly, the creek's lower reaches are recognised as a wetland of international significance by the Ramsar convention (Davis *et al.* 2014), and also forms part of the Great Barrier Reef World Heritage Area. While water quality monitoring of the Barratta Creek system has sporadically been carried out since the development of the BHWSS, including monitoring for sediment, nutrient loads since 2004/05 and pesticide loads since 2005/06 (Bainbridge *et al.* 2007; Davis *et al.* 2008), no program has previously systematically examined the persistence, seasonal variability and pesticide dynamics throughout the Barratta Creek Complex that includes the Ramsar wetland. This study has utilised a combination of passive samplers deployed at monthly intervals and grab samples at four sites along the Barratta Creek Complex over two years to examine the persistence, concentration, pesticide use in the catchment area, seasonality and spatial variation of the multiple pesticide residues detected. In addition, this study will further assess the utility of passive sampling techniques vs grab sampling when undertaking water quality monitoring. Previous water quality monitoring programs undertaken within this region has only employed the use of grab sampling methods and the application of both grab and passive sampling techniques will provide a valuable comparison of the two methods.

Barratta Creek catchment has a total area of 1,167 sq km and covers 0.9% of the Dry Tropics NRM region (Dight 2009). The majority of land use within the Barratta Creek sub-catchment is grazing on native pastures (60%). Irrigated sugarcane production covers approximately 31% of the sub-catchment, while the remaining ~9% is wetland or conservation and minimal use area that includes other cropping. The four deployment sites monitored within the Barratta Creek Catchment as part of this study (Figure 1) included Upper Barratta Creek (19.70000°S; 147.16667°E), West Barratta Creek (19.53643°S; 147.21757 °E), East Barratta Creek (19.56180°S; 147.22098 °E) and Jerona – an estuarine site in the lower reaches of Barratta Creek (19.47815°S; 147.232366 °E). The Upper Barratta site has a catchment area of 695 sq km with land use including 84% grazing, 15% cropping (mainly irrigated sugar) and ~1% conservation. East/West Barratta Creeks have a combined catchment area of 912 sq km, of which ~72% is grazing and ~25% is irrigated cropping. There are mango orchards within this region that are expected to drain predominantly into the Haughton River catchment. Some runoff from mango land use may be draining into the West Barratta sub catchment; however the exact proportion of land use within the East and West Barratta sub catchments has not been quantified and probably varies according to flood water levels. The lower Barratta Creek site at Jerona has been included as an end of catchment site capturing the majority of runoff. The Jerona site is within the Ramsar wetland and is within the tidally mixed reaches of the estuary.

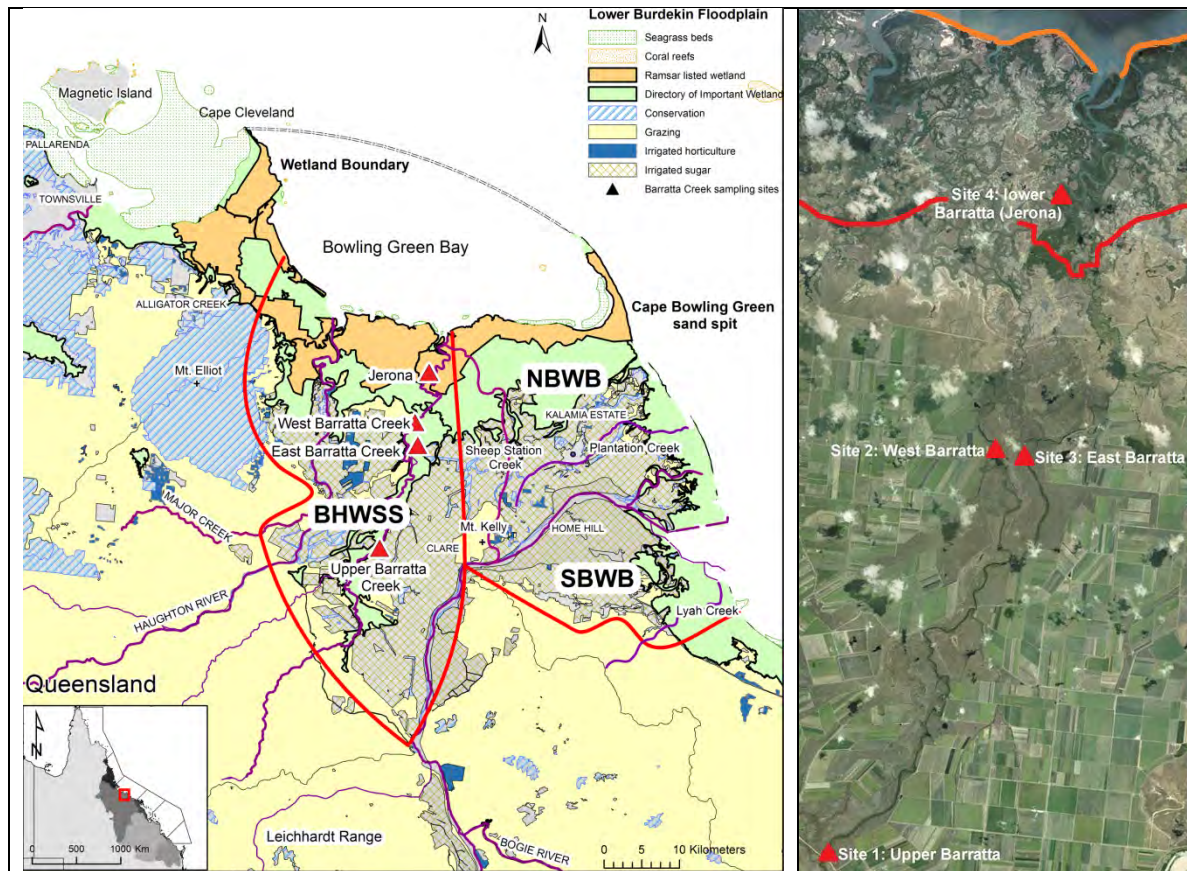


Figure 1 Sampling sites in the Barratta Creek Complex. The Left map (taken from Davis *et al.* (2014)) shows the location of the sampling sites (red triangles) in relation to the surrounding land use (classified based on the 2004 Queensland Land Use Mapping shape files obtained from the Queensland Department of Natural Resources and Water (DNRW). Boundaries of the major flood plain irrigation scheme areas are indicated by the red boundaries; BHWSS: Burdekin Haughton Water Supply Scheme; NBWB: North Burdekin Water Board; SBWB: South Burdekin Water Board. The right satellite image shows the locations of the four sampling sites in relation to the boundary of the Ramsar listed wetland (red line), the GBRMP boundary and the sugarcane croplands surrounding the wetlands supported by the Barratta Creek.

Study design

This study utilized a combination of passive samplers deployed at monthly intervals and grab samples at four sites along the Barratta Creek Complex over two years (July 2011 to July 2013). The combination of different passive samplers (PDMS and Empore Disks) with grab samples provided a wide screen of different pesticides and allowed their exposure and persistence to be determined over the two-year study period. The passive samplers were deployed at 4 sites in Barratta Creek (Figure 1) including the Upper Barratta Creek site and Lower Barratta Site (Jerona in the Ramsar site), where PDMS and Empore Disks were deployed and East and West Barratta Creeks, where Empore Disks only were deployed. The deployments typically occurred every ~ 28 days, unless large flow events occurred; in which case the samplers were generally collected earlier (~ 21 days). The passive and grab samples

were extracted at the Entox laboratory and analysed employing liquid and gas chromatography–mass spectrometry (LCMS and GCMS).

Table 1: Deployment details; date and times at which each site was visited per deployment and the length of each deployment period (Days deployed).

Deployment Name:	Deployment #		Date	1 - Upper Barratta		2 - West Barratta		3 - East Barratta		4 - Lower Barratta (Jerona)	
	IN	OUT		Time	Days deployed	Time	Days deployed	Time	Days deployed	Time	Days deployed
Jul	1		4/07/2011	10:00		14:30		15:45		12:20	
Aug	2	1	2/08/2011	11:00	29	14:10	29	15:15	29	12:20	29
Sep	3	2	8/09/2011	11:00	37	14:10	37	13:00	37	12:00	29
Oct	4	3	4/10/2011	10:15	26	12:15	26	13:00	26	12:15	37
Nov	5	4	2/11/2011	9:45	29	11:00	29	12:00	29	13:20	26
Dec (1)	6	5	30/11/2011	9:00	28	12:15	28	14:00	28	10:30	29
Dec (2)	7	6	22/12/2011	10:00	22	12:50	22	13:30	22	14:30	28
Jan	8	7	4/01/2012	10:15	13	12:50	13	11:10	13	14:00	22
Jan/Feb	9	8	25/01/2012	11:30	21	13:00	21	15:30	21	14:00	13
Feb/Mar	10	9	15/02/2012	10:30	21	12:00	21	14:05	21	13:00	21
Mar	11	10	13/03/2012	9:45	27	13:30	27	14:45	27	11:15	21
Mar/Apr	12	11	30/03/2012	10:20	17	13:50	17	14:50	17	11:40	27
Apr/May	13	12	23/04/2012	9:50	24	12:15	24	13:00	24	11:00	17
May/Jun	14	13	22/05/2012	9:55	29	12:30	29	13:00	29	11:15	24
Jun/Jul	15	14	22/06/2012	9:45	31	11:45	31	11:00	31	12:25	29
Jul/Aug	16	15	20/07/2012	9:30	28	13:00	28	13:50	28	12:10	31
Aug/Sep	17	16	23/08/2012	12:20	34	10:45	34	11:20	34	10:00	28
Sep/Oct	18	17	21/09/2012	14:00	29	11:05	29	11:47	29	9:54	34
Oct/Nov	19	18	18/10/2012	12:55	27	10:00	27	11:50	27	11:00	29
Nov/Dec	20	19	14/11/2012	9:30	27	11:30	27	10:45	27	12:15	27
Dec/Jan	21	20	14/12/2012	12:00	30	9:55	30	10:40	30	8:40	27
Jan/Feb	22	21	14/01/2013	14:00	31	15:15	31	14:45	31	16:20	30
Feb/Mar	23	22	7/02/2013	9:30	24	11:40	24	10:45	24	12:40	31
Mar	24	23	7/03/2013	10:05	28	12:15	28	11:15	28	13:15	24
Apr	25	24	5/04/2013	9:30	29	11:45	29	11:15	29	11:00	28
May	26	25	9/05/2013	10:30	34	12:20	34	13:00	34	11:40	29
Jun	27	26	5/06/2013	10:40	27	12:40	27	11:40	27	13:30	34
		27	4/07/2013	10:15	29	11:55	29	11:10	29	12:40	27

Methods

Deployment sites

Deployment sites were selected within areas of low or restricted accessibility to the general public to prevent interference with the samplers. The Passive Sampler Devices (PSDs) installed at the Upper, East and West Barratta sites were deployed ~ 50cm below the water surface, secured to chain attached to the trunk of trees overhanging the stream bank in sections of defined flow. The Upper Barratta deployment site was located within the riparian zone adjacent to the Queensland Government stream flow gauging station at Northcote (119101A), while deployments at the East and West Barratta sites were located on private grazing land. The PSDs installed at the Jerona estuarine site were secured attached to a mangrove within the Bowling Green Bay Wetland that was away from easily accessible pathways.

The water chemistry (pH, temperature, conductivity and dissolved O₂) was recorded during most site visits using a Hydrolab Quanta (ECO Environmental).

Grab sampling

Grab water samples (2 × 1L) were collected at each time point when PSDs were deployed and retrieved from each sampling site. Grab water samples were collected from approximately 20cm below the water surface within amber glass bottles using an extendable sampling pole. All water samples were kept on ice when returning from the field and were stored at 4°C prior to analysis. Analysis of all grab water samples was undertaken by the Queensland Health Forensic and Scientific Services (QHFSS).

Passive sampling devices (PSDs)

The “chemcatcher” passive sampler (referred to as ED passive samplers in this report) selectively accumulates polar chemicals and has been extensively employed in the assessment of the concentrations of hydrophilic organic compounds in environmental waters (Vrana *et al.* 2006; Shaw *et al.* 2009; O’Brien *et al.* 2011a). The ED passive sampler employs the use of a high surface area adsorptive sequestering phase, the styrenedivinylbenzene-reverse phase sulfonated (SDB-RPS) Empore disk (ED) (Phenomenex; 0.45 mm). The ED is then secured within a Teflon housing for exposure to environmental waters behind a diffusion limiting membrane (Sartorius, 0.45 µm; 47 mm polyethersulfone PES).

The semipermeable membrane device (SPMD) and polydimethylsiloxane (PDMS) passive samplers selectively accumulate non-polar chemicals and have been employed in the assessment of the concentrations of hydrophobic organic compounds in environmental waters (Esteve-Turrillas *et al.* 2007; Shaw *et al.* 2010; O’Brien *et al.* 2012). The SPMD is constructed from lay-flat low density polyethylene (LDPE) tubing (60 µm thickness, 2.5 cm wide, 92 cm length) with 1 mL of 99% pure triolein (Sigma–Aldrich) injected into the interior with the end of the tubing heat sealed. The PDMS strips (410 µm thick, 2.5 cm wide, 92 cm length) with a hole punched at each end are cut from larger PDMS sheets (Purple Pig, Australia). The SPMD and PDMS are deployed inside stainless steel cages within which the strips are supported by stainless steel rods (see Figure 2). Both the SPMD and PDMS have an overall surface area of approx. 460 cm² and an absorbent volume of approx. 1ml.

The PFM, or passive flow monitor, is a device developed for use in the calibration of passive sampling uptake rate when PSDs are exposed to unknown flow conditions. The PFM devices are prepared by casting dental plaster (BORAL) into a 120ml specimen container that has been altered to facilitate the attachment of the PFM to a mooring when deployed in the field. The rate at which plaster mass is lost from the device during deployment is then used to correct chemical specific uptake rates for changes in ambient flow and facilitates greater accuracy in the quantification of chemical concentrations in environmental waters from the mass of an analyte accumulated within the employed PSDs.

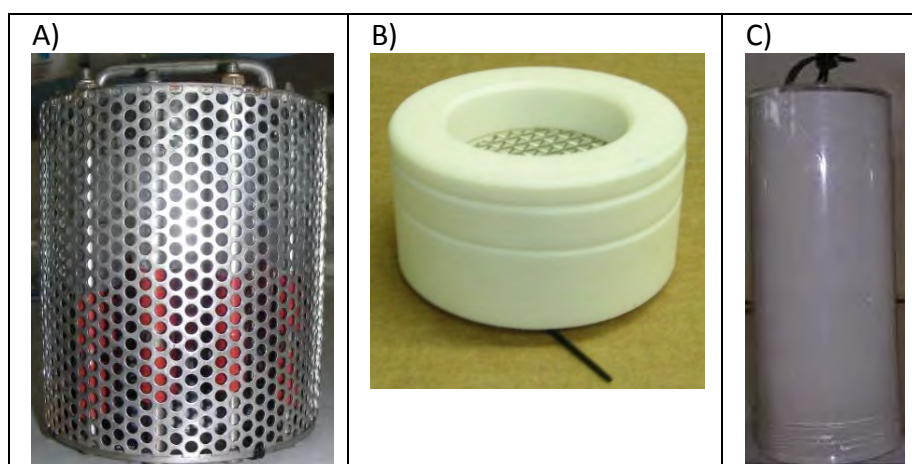


Figure 2 Passive sampling devices employed in this study: A) The SPMD and PDMS supported within a stainless steel cage; B) the ED passive sampler; and C) the PFM.

Passive sampler deployment and retrieval

The sampling devices described above were obtained from The National Research Centre for Environmental Toxicology (Entox). All deployment devices were rinsed with acetone prior to assembly. The ED passive samplers were transported sealed with a Teflon cap to prevent light exposure to the ED prior to deployment and within a clip sealed plastic bag to prevent desiccation during transport. The SPMD and PDMS secured within the stainless steel cages were enclosed in metal cans (pre-cleaned with acetone) for transportation between laboratories and to field sites. After deployment the EDs were again sealed behind the Teflon cap and the PDMS cages returned to the same cans they were received in. All PSDs were stored at 4°C when not deployed and were returned to Entox for extraction and analysis.

Greater detail on the preparation of these devices and the extraction and analysis of the chemicals accumulated by each device has been described elsewhere (O'Brien *et al.* 2009; O'Brien *et al.* 2011b; O'Brien *et al.* 2012).

Results

Water chemistry

The monitoring of water chemistry showed that there were relatively stable and consistent conditions across the investigated sites with respect to temperature and pH. Temperatures ranged between 16 and 32 °C across all sites with averages falling between 24 and 26 °C (Table 2).

The measurement of conductivity revealed that while the conductivity at Site 1 and 3 remained below 1 ms/cm, Site 2 (West Barratta) is occasionally influenced by tidal flows and the estuarine Site 4 is exposed to conductivity values between 3.3 and 51.5 ms/cm.

Generally, attempts were made to ensure that each sampling trip was undertaken so that Site 4 was accessed as close to low tide as possible to minimise the risk associated with approaching waterways from a mangrove bank in areas inhabited by crocodiles. Despite our best efforts timing restrictions on some sampling visits led to water quality measurement being made at or approaching the high tide and resulted in the higher conductivity and dissolved oxygen. This sampling approach, however, would have led to the introduction of some sampling bias in the range of conductivity recorded at both Site 4 and Site 2 (which was generally sampled directly prior to or after sampling at Site 4). At Site 2, four of the recorded conductivity measurements were above 1 ms/cm (3.1, 9, 15.9 and 18 ms/cm). The highest recorded conductivity (18 ms/cm) was recorded when our visit to the site coincided with the local high tide. The remaining “high” conductivity measurements concurred with a rising tide (around the ‘mid tide’ point).

Table 2: Water chemistry profile for each site over the 24 month study period. Temperature, pH, dissolved O₂ and conductivity were recorded on 17 of the 28 visits to each site using a Hydrolab Quanta (ECO Environmental).

		Site 1 Upper Barratta	Site 2 West Barratta	Site 3 East Barratta	Site 4 Lower Barratta (Jerona)
Temp. (°C)	min	16.03	19.50	18.44	20.51
	max	30.00	30.30	30.60	31.30
	median	25.30	23.98	24.83	24.95
	mean	24.29	25.06	24.99	25.41
pH	min	6.50	6.60	7.03	6.30
	max	8.39	8.20	8.20	7.58
	median	7.50	7.23	7.50	7.12
	mean	7.45	7.27	7.55	7.10
DO (mg/L)	min	4.51	1.23	4.44	1.40
	max	7.90	7.36	8.04	8.15
	median	6.75	4.86	6.64	4.91
	mean	6.53	4.71	6.57	4.74
Cond. (ms/cm)	min	0.12	0.17	0.17	3.30
	max	0.59	18.00	0.66	51.50
	median	0.37	0.45	0.49	16.61
	mean	0.36	2.86	0.47	20.38

Herbicide Persistence and Exposure

A total of 37 different pesticide residues (does not include metabolites of some of these pesticides) were detected in the Barratta Creek Complex during the two-year research program (Table 3), although a number of these residues were detected infrequently (< 5 occasions of the 27 deployments) and at low concentrations (i.e. below available ecological guidelines). Of the 37 different pesticide residues detected, 13 were detected in the grab water samples, 30 detected when employing the ED passive sampler (18 exclusively) and 15 detected when employing the PDMS passive sampler (8 exclusively). Fourteen pesticide residues were detected by more than one sampling method.

Tables 4 and 5 list the pesticide residues detected when employing both passive (ED and PDMS) and grab sampling methods, respectively. Listed within both tables is the number and frequency with which the individual residues have been detected and exceeded existing ecological protection guideline and trigger values (ANZECC and ARMCANZ, 2000) (Appendix 1). Eight residues (ametryn, atrazine + breakdown products, diuron, hexazinone, metolachlor, tebuthiuron, simazine, and imadicloprid) were detected in greater than 90% of the extracts obtained from all sites during the study period when employing the ED passive samplers. These same residues were detected less frequently (7 - 82%) within the grab samples collected across all sites at the start and end of each passive sampler deployment period. PDMS PSDs were deployed only at sites 1 and 4 and selectively accumulate more hydrophobic chemical residue. Of the above eight residues; atrazine, metolachlor and ametryn were detected in 100, 96 and 50 % of all PDMS extracts, respectively. Propazine and pendimethalin were detected in 50 and 30 % of PDMS extracts respectively compared to a detection rate of 9% for both pesticides in the grab samples collected. A further eleven residues (galaxolide, chlorpyrifos, fipronil, terbuthylazine, DEET, diazinon, methamidophos, tonalid, permethrin isomers, phosphamidon, 2,6-di-t-butyl-p-cresol (bht)) were detected in the PDMS extracts that were not identified in either the ED or grab samples collected. Residues detected within PDMS extracts have been presented in Figures 9 to 12.

Pesticides found at concentrations equal to or greater than 1 µg/L were, in descending order of concentration, diuron, atrazine, metribuzin, metolachlor and ametryn. Diuron, atrazine and ametryn are three of the five priority photosystem II (PSII) herbicides targeted in Reef Plan (2013). The herbicides, diuron and atrazine regularly exceeded ANZECC and ARMCANZ (2000) ecological protection guidelines for several months (5-7 months of the year) at all four sites including in the Ramsar wetland. Despite concentrations of both atrazine and diuron progressively decreasing towards the lower reaches of the Creek system (e.g. in the Ramsar wetland site, concentrations were ~ ⅓ to ½ of the values measured at the upper site), they still exceeded the 99% species protection value for 6 months of the year. Maximum concentrations recorded for both atrazine and diuron were 9.2 and 12.8 µg/L, respectively when employing grab sampling and 11.5 and 12.3 µg/L, respectively when employing passive sampling techniques (Table 2). The highest measurements of diuron and atrazine within the freshwater reaches of the Barratta Creek occurred at the Upper Barratta Creek site and were an order of magnitude greater than the established water quality guideline/trigger values.

Total concentrations of ametryn, atrazine, diuron, hexazinone, metolachlor, metribuzin and imidacloprid were plotted for each site over time in Figure 3 and 4. These seven pesticide

residues were found at the highest concentrations over the study period and are of particular concern with regard to ecological protection due to their frequent detection, relative abundance and potency. Diuron and atrazine concentrations dominated the detection profile across all sites monitored with highest concentrations observed between August and February. Metolachlor (detected in both grab and passive samples) and metribuzin (detected only in grab samples) are being marketed as suggested replacement products for PSII herbicides, in particular atrazine and diuron (Fillols and Callow 2010; Seeruttun *et al.* 2010). Metribuzin was detected at between at concentrations of between 0.15 and 4.83 µg/L in grab samples collected during the months of October 2011 and March 2012, September 2012 and March 2013 and in July of 2013 and across the whole sampling period; concentrations in samples collected at all other time points were below the detection limit of 0.2 µg/L. Method development during the sampling period led to the introduction of metribuzin in the analytical suite undertaken on the passive sampler extracts for deployments that occurred during April and July of 2013 (deployments 24 – 27). While grab sampling recorded only one detection of metribuzin above the detection limit at Site 1 in July of 2013 (0.3 µg/L) the passive samplers exposed during April, May and June of 2013 recorded metribuzin concentrations of between 0.0016 and 0.069 µg/L. The concentrations detected using the PSDs are all below the detection limit for quantification of metribuzin in grab water samples and thus these results demonstrate the ability of PSDs to detect trace concentrations of chemical residues within the environment.

Imidacloprid was detected in 8% of grab and 93% of passive samples collected. Concentrations of imidacloprid measured in grab samples ranged between 0.02 and 0.5 µg/L (with a detection limit of 0.02 µg/L). Imidacloprid concentrations measured through the use of the PSDs ranged between 0.0004 and 0.041 µg/L. Five passive sampler deployments recorded an average concentration of greater than grab water analytical detection limit of 0.02 µg/L. For each of these five PSD deployments imidacloprid was detected in the grab water sample collected at the time of deployment and/or at the time of retrieval. The highest imidacloprid concentrations detected by both grab and PSD methods were recorded in July 2011, December 2011 – February 2012, September – December 2012 and June 2013; dates which correspond both with wet season event runoff and dry season irrigation.

Sample extracts from the PSDs have been stored following analysis and there is the potential for retrospective analysis in the future for those time points where concentrations within the grab samples were below the detection limit of the analytical methods employed. During the monitoring undertaken APVMA introduced a suspension on diuron use in November of 2011 that was amended in November of 2012 when the registration of three products was cancelled and the registration of all remaining diuron products was affirmed however with significant restriction on use. The concentrations of diuron observed during the course of this monitoring appears to reflect these changes in regulation as the observed decrease in diuron corresponded with an increase in the frequency of detections and concentrations of metolachlor and metribuzin. However without access to definitive sales and usage data within the catchment this apparent trend in response to changing regulation is purely speculative.

Pesticide residues detected at low concentrations relative to guideline values or detection limits and low frequency when employing both grab (two pesticides) and passive sampling (twelve pesticides) methods are presented in Figure 7 – 8. As with the pesticides presented in Figure 3 and 3, the highest concentrations were again observed between the months of

August and February. Simazine, a PSII inhibitor, was frequently detected by 16% of grab and 100% of passive samples collected at concentrations of 0.01-0.1 µg/L and 0.0001- 0.55 µg/L respectively. Isoxaflutole, a pigment synthesis inhibitor used in the control of broad leaf weeds and grasses in sugarcane, was detected by passive sampling only (in 50% of exposed PSDs) at concentrations of up to 0.4 µg/L. 2,4-D, a synthetic plant hormone used in the control of broadleaf weeds in sugarcane cultivation, was detected only by passive sampling (in 67% of exposed PSDs) at concentrations between 0.0003 and 0.22 µg/L and one detection of 2.2 µg/L at Site 2 in December of 2011. Passive sampling detected a further ten pesticides which have not been included in the Figure 7 – 8. Those pesticides were detected at concentrations of between 0.0001 – 0.025 µg/L; may not all be sourced from application within sugarcane cultivation and include (in order of lowest concentration to highest) flusilazole, clomazone, imidacloprid urea, terbuthylazine desethyl, bromacil, flumeturon, imazethapyr, terbuthylazine, imazapic, and acifluorfen.

Hexazinone and tebuthiuron, the two remaining priority PSII herbicides were also detected during this study but at comparatively lower concentrations (maximum concentrations of 327 and 7 ng/L, respectively). Hexazinone was detected when employing both grab (26% of samples) and PSDs (99% of samples) across all sampling sites. Tebuthiuron was detected across all sites in PSDs (99% of samples) however was only detected in 8 grab water samples collected at the Upper Barratta site (7% of all samples, 30% of samples collected from Site 1).

Pesticide exposure within Barratta Creek Catchment

Table 3: Pesticide concentrations (µg/L) detected when employing conventional grab sampling methods and passive sampling techniques.

	Grab Sampling					Empore Disk passive sampling				PDMS passive sampling			
	LOD	Min	Max	Median	Mean	Min	Max	Median	Mean	Min	Max	Median	Mean
Ametryn	0.01	BDL	2	0.04	0.1008	0.00115	0.5047	0.0135	0.0461	0.022	1.996	0.0799	0.1563048
Atrazine	0.01	0.0235	9.165	0.6801	1.5625	0.03377	11.5011	0.7023	1.8245	0.0755	10.989	0.80345	1.8442746
Desethyl Atrazine	0.01	BDL	2.2042	0.1639	0.3965	0.01896	1.7463	0.1456	0.3947	NR	NR	NR	NR
Desisopropyl Atrazine	0.02	BDL	0.5552	0.141	0.1716	0.00304	0.4074	0.0299	0.0792	NR	NR	NR	NR
Diuron	0.01	BDL	12.807	0.186	0.8633	0.01823	12.3386	0.2803	1.2588	NR	NR	NR	NR
Hexazinone	0.01	BDL	0.259	0.03	0.0465	0.00069	0.327	0.0044	0.0202	NR	NR	NR	NR
Metolachlor	0.01	BDL	2.8	0.0882	0.2562	0.00046	0.9637	0.0212	0.0868	0.0034	5.313	0.062	0.2758226
Tebuthiuron	0.01	BDL	BDL	BDL	BDL	0.00045	0.007	0.0021	0.0024	NR	NR	NR	NR
Simazine	0.01	BDL	0.1	0.0165	0.0215	0.00014	0.5429	0.0018	0.0094	NR	NR	NR	NR
Imadicloprid	0.01	BDL	0.504	0.035	0.0943	0.00039	0.0407	0.0035	0.0064	NR	NR	NR	NR
Prometryn	0.01	BDL	0.03	0.0251	0.0251	0.00004	0.0029	0.0003	0.0005	0.0065	0.0065	0.0065	0.0065
Propazine	0.1	BDL	4	1	1.6101	0.00015	0.0113	0.0014	0.0024	0.0027	0.07	0.012	0.0199926
2,4-D	0.01	NR	NR	NR	NR	0.00034	2.2335	0.0067	0.0507	NR	NR	NR	NR
MCPA	0.01	NR	NR	NR	NR	0.00009	0.0892	0.004	0.0093	NR	NR	NR	NR
Metsulfuron methyl		NR	NR	NR	NR	0.00041	0.0145	0.0022	0.0031	NR	NR	NR	NR
Triclopyr	0.01	NR	NR	NR	NR	0.00018	0.302	0.001	0.0087	NR	NR	NR	NR
Metribuzin	0.1	BDL	4.83	0.4	0.7997	0.00162	0.0699	0.006	0.0179	0.399	0.399	0.399	0.399
3,4 Di Cl Analine		NR	NR	NR	NR	0.0028	0.0201	0.0095	0.0094	NR	NR	NR	NR
Isoxaflutole		NR	NR	NR	NR	0.00008	0.4024	0.0247	0.073	NR	NR	NR	NR
Imazapic		NR	NR	NR	NR	0.00004	0.0086	0.0002	0.0005	NR	NR	NR	NR
Haloxypop	0.1	BDL	BDL	BDL	BDL	0.00008	0.0149	0.0009	0.0018	NR	NR	NR	NR
Imazethapyr		NR	NR	NR	NR	0.00002	0.0026	0.0001	0.0004	NR	NR	NR	NR
Terbutryn	0.01	BDL				0.00001	0.0196	0.0012	0.0039	NR	NR	NR	NR
Terbutylazine	0.1	BDL	BDL	BDL	BDL	0.00003	0.0024	0.0002	0.0004	NR	NR	NR	NR
Fluroxypyr	700	NR	NR	NR	NR	0.00033	0.035	0.0011	0.0032	NR	NR	NR	NR
Imidacloprid urea		NR	NR	NR	NR	0.0002	0.0019	0.0004	0.0007	NR	NR	NR	NR

Table3: Pesticide concentrations (µg/L) detected when employing conventional grab sampling methods and passive sampling techniques (CONT.)

	Grab Sampling					Empore Disk passive sampling				PDMS passive sampling			
	LOD	Min	Max	Median	Mean	Min	Max	Median	Mean	Min	Max	Median	Mean
Acifluorfen		NR	NR	NR	NR	0.00016	0.0134	0.0011	0.0034	NR	NR	NR	NR
Bromacil	0.01	BDL	BDL	BDL	BDL	0.00019	0.0018	0.0004	0.0006	NR	NR	NR	NR
Flusilazole		BDL	BDL	BDL	BDL	0	0	0	0	NR	NR	NR	NR
Terbuthylazine desethyl		NR	NR	NR	NR	0.00013	0.0014	0.0004	0.0006	NR	NR	NR	NR
Flumeturon		NR	NR	NR	NR	0.00016	0.0038	0.0004	0.0009	NR	NR	NR	NR
Clomazone		NR	NR	NR	NR	0.00005	0.0001	0.0001	0.0001	NR	NR	NR	NR
Mecoprop	0.01	NR	NR	NR	NR	0.00003	0	0	0	NR	NR	NR	NR
Pendimethalin	0.1	BDL	4	1	1.6184	NR	NR	NR	NR	0.00027	0.0668	0.000735	0.0090181
Tris(dichloropropyl) phosphate	0.2	BDL	7	3	3.8429	NR	NR	NR	NR	NR	NR	NR	NR
Bisphenol A	0.1	BDL	0.33	0.1885	0.2025	NR	NR	NR	NR	NR	NR	NR	NR
Bifenthrin	0.1	BDL	4	1	1.66	NR	NR	NR	NR	NR	NR	NR	NR
2,6-DI-t-BUTYL-p-CRESOL (bht)		NR	NR	NR	NR	NR	NR	NR	NR	0.00039	0.00039	0.00039	0.00039
Chlorpyrifos		NR	NR	NR	NR	NR	NR	NR	NR	0.00004	0.0011	0.0003	0.0003529
DEET		NR	NR	NR	NR	NR	NR	NR	NR	0.0067	0.014	0.00795	0.00915
Diazinon		NR	NR	NR	NR	NR	NR	NR	NR	0.00036	0.00091	0.000635	0.000635
Fipronil		NR	NR	NR	NR	NR	NR	NR	NR	0.00006	0.0041	0.00128	0.001635
Galaxolide		NR	NR	NR	NR	NR	NR	NR	NR	0.00005	0.0002	0.000095	0.000094
Methamidophos		NR	NR	NR	NR	NR	NR	NR	NR	0.973	0.973	0.973	0.973
Permethrin Isomers		NR	NR	NR	NR	NR	NR	NR	NR	0.0004	0.0004	0.0004	0.0004
Phosphamidon		NR	NR	NR	NR	NR	NR	NR	NR	0.108	0.108	0.108	0.108
Terbuthylazine		NR	NR	NR	NR	NR	NR	NR	NR	0.0041	0.0076	0.006	0.005925
Tonalid		NR	NR	NR	NR	NR	NR	NR	NR	0.00003	0.00003	0.00003	0.00003

NR: not reported, BDL: below detection limit

Pesticide exposure within Barratta Creek Catchment

Table 4: Pesticide residues detected by the ED passive samplers: including number of samples collected per site, number of detections per chemical and frequency of detected at each site.

	Number of samples collected:					Number of detection per chemical:					Frequency of detections per chemical (%):					Guideline/Trigger value (µg/L)	Number of samples exceeding guideline/trigger:					Frequency of detections exceeding guideline (%):				
	Total	Site 1	Site 2	Site 3	Site 4	Total	Site 1	Site 2	Site 3	Site 4	Total	Site 1	Site 2	Site 3	Site 4		Total	Site 1	Site 2	Site 3	Site 4	Total	Site 1	Site 2	Site 3	Site 4
Ametryn	107	27	26	27	27	107	27	26	27	27	99	100	100	100	100	0.5	1	0	1	0	0	1	0	4	0	0
Atrazine	107	27	26	27	27	107	27	26	27	27	99	100	100	100	100	0.7	54	14	15	14	10	50	52	56	52	37
Atrazine desethyl	107	27	26	27	27	107	27	26	27	27	99	100	100	100	100	NA						NA	NA	NA	NA	NA
Atrazine	107	27	26	27	27	107	27	26	27	27	99	100	100	100	100	NA						NA	NA	NA	NA	NA
Diuron	107	27	26	27	27	107	27	26	27	27	99	100	100	100	100	0.2	60	15	17	16	11	56	56	63	59	41
Hexazinone	107	27	26	27	27	107	27	26	27	27	99	100	100	100	100	NA						NA	NA	NA	NA	NA
Metolachlor	107	27	26	27	27	107	27	26	27	27	99	100	100	100	100	0.02	54	13	19	14	10	50	48	70	52	37
Tebuthiuron	107	27	26	27	27	107	27	26	27	27	99	100	100	100	100	0.02	0	0	0	0	0	NA	NA	NA	NA	NA
Simazine	107	27	26	27	27	105	27	24	27	27	97	100	89	100	100	0.2	1	0	1	0	0	1	NA	4	NA	NA
Imadicloprid	107	27	26	27	27	100	27	21	27	25	93	100	78	100	93	0.23*	0	0	0	0	0	NA	NA	NA	NA	NA
Prometryn	107	27	26	27	27	90	23	18	25	24	83	85	67	93	89	NA						NA	NA	NA	NA	NA
Propazin-2-hydroxy	101	20	26	27	27	79	20	19	20	20	78	100	70	74	74	NA						NA	NA	NA	NA	NA
2,4-D	107	26	26	27	27	73	18	19	18	18	68	69	70	67	67	NA						NA	NA	NA	NA	NA
MCPA	107	26	26	27	27	69	18	17	18	16	64	69	63	67	59	NA						NA	NA	NA	NA	NA
Metsulfuron methyl	94	13	26	27	27	50	13	13	13	11	53	100	48	48	41	NA						NA	NA	NA	NA	NA
Triclopyr	107	26	26	27	27	56	15	12	17	12	52	58	44	63	44	NA						NA	NA	NA	NA	NA
Metribuzin	23	7	5	4	7	12	3	3	3	3	52	43	60	75	43	NA						NA	NA	NA	NA	NA
3,4 Di Cl Analine	23	7	5	4	7	12	3	3	3	3	52	43	60	75	43	NA						NA	NA	NA	NA	NA
Isoxaflutole	101	20	27	27	27	49	12	13	12	12	49	60	48	44	44	NA						NA	NA	NA	NA	NA
Imazapic	101	20	27	27	27	43	2	16	10	15	43	10	59	37	56	NA						NA	NA	NA	NA	NA
Haloxypop	106	25	27	27	27	41	13	9	12	7	39	52	33	44	26	NA						NA	NA	NA	NA	NA
Imazethapyr	101	20	27	27	27	36	4	16	9	7	36	20	59	33	26	NA						NA	NA	NA	NA	NA
Terbutryn	108	27	27	27	27	38	10	9	12	7	35	37	33	44	26	NA						NA	NA	NA	NA	NA
Terbutylazine	108	27	27	27	27	31	10	6	9	6	29	37	22	33	22	NA						NA	NA	NA	NA	NA
Fluroxypyr	106	25	27	27	27	24	7	7	7	3	23	28	26	26	11	NA						NA	NA	NA	NA	NA
Imidacloprid urea	23	7	5	4	7	4	2	0	2	0	17	29	0	50	0	NA						NA	NA	NA	NA	NA
Acifluorfen	101	20	27	27	27	10	1	4	4	1	10	5	15	15	4	NA						NA	NA	NA	NA	NA
Bromacil	94	13	27	27	27	9	3	5	0	1	10	23	19	0	4	NA						NA	NA	NA	NA	NA
Flusilazole	94	13	27	27	27	9	4	3	1	1	10	31	11	4	4	NA						NA	NA	NA	NA	NA
Terbutylazine	101	20	27	27	27	7	2	1	3	1	7	10	4	11	4	NA						NA	NA	NA	NA	NA
Flumeturon	94	13	27	27	27	6	1	5	0	0	6	8	19	0	0	NA						NA	NA	NA	NA	NA
Clomazone	94	13	27	27	27	2	0	2	0	0	2	0	7	0	0	NA						NA	NA	NA	NA	NA
Mecoprop	108	27	27	27	27	1	1	0	0	0	1	4	0	0	0	NA						NA	NA	NA	NA	NA

Table 5: Pesticide residues detected by grab sampling: including number of samples collected per site, number of detections per chemical and frequency of detected at each site.

	Number of samples collected:					Number of detection per chemical:					Frequency of detections per chemical:					Guideline/Trigger value (ng/L)	Number of samples exceeding guideline/trigger:					Frequency of detections exceeding guideline (%):				
	Total	Site 1	Site 2	Site 3	Site 4	Total	Site 1	Site 2	Site 3	Site 4	Total	Site 1	Site 2	Site 3	Site 4		Total	Site 1	Site 2	Site 3	Site 4	Total	Site 1	Site 2	Site 3	Site 4
Atrazine	106	26	26	27	27	106	26	26	27	27	100	100	100	100	100	0.7	52	15	13	17	7	49	58	50	63	26
Desethyl Atrazine	106	26	26	27	27	106	26	26	27	27	100	100	100	100	100	NA						NA	NA	NA	NA	NA
Desisopropyl Atrazine	106	26	26	27	27	57	18	12	16	11	54	69	46	59	41	NA						NA	NA	NA	NA	NA
Diuron	106	26	26	27	27	97	24	25	27	21	92	92	96	100	78	0.2	48	14	12	14	8	45	54	46	52	30
Ametryn	106	26	26	27	27	71	20	13	17	21	67	77	50	63	78	0.02	49	10	11	16	12	46	38	42	59	44
Metolachlor	106	26	26	27	27	61	17	15	16	13	58	65	58	59	48	NA						NA	NA	NA	NA	NA
Metribuzin	106	26	26	27	27	37	13	11	9	4	35	50	42	33	15	0.5	2	1	0	1	0	2	4	NA	4	NA
Hexazinone	106	26	26	27	27	29	11	7	5	6	27	42	27	19	22	NA						NA	NA	NA	NA	NA
Simazine	106	26	26	27	27	23	10	2	8	3	22	38	8	30	11	NA						NA	NA	NA	NA	NA
Bifenthrin	106	26	26	27	27	10	0	3	4	3	9	0	12	15	11	NA						NA	NA	NA	NA	NA
Pendimethalin	106	26	26	27	27	10	0	2	5	3	9	0	8	19	11	0.23	1	1	0	0	0	1	4	NA	NA	NA
Propazine	106	26	26	27	27	10	0	2	5	3	9	0	8	19	11	NA						NA	NA	NA	NA	NA
Imidacloprid	106	26	26	27	27	8	3	2	2	1	8	12	8	7	4	0.2	0	0	0	0	0	NA	NA	NA	NA	NA
Tris(dichloropropyl) phosphate	106	26	26	27	27	7	0	1	3	3	7	0	4	11	11	NA						NA	NA	NA	NA	NA
Bisphenol A	106	26	26	27	27	4	0	2	1	1	4	0	8	4	4	NA						NA	NA	NA	NA	NA
Prometryn	106	26	26	27	27	2	1	0	1	0	2	4	0	4	0	NA						NA	NA	NA	NA	NA
Terbutryn	106	26	26	27	27	1	0	0	1	0	1	0	0	4	0	NA						NA	NA	NA	NA	NA

Pesticide exposure within Barratta Creek Catchment

Table 6: Pesticide residues detected by PDMS passive sampling: including number of samples collected per site, number of detections per chemical and frequency of detected at each site.

	Number of detection per chemical:			Frequency of detections per chemical:			Guideline/Trigger value (ng/L)	Number of samples exceeding guideline/trigger:			Frequency of detections exceeding guideline (%):		
	Total	Site 1	Site 4	Total	Site 1	Site 4		Total	Site 1	Site 4	Total	Site 1	Site 4
Atrazine	54	27	27	100	100	100	0.7	32	18	14	59	67	52
Metolachlor	52	25	27	96	93	100	NA	NA	NA	NA	NA	NA	NA
Propazine	27	17	10	50	63	37	NA	NA	NA	NA	NA	NA	NA
Ametryn	27	13	14	50	48	52	0.02	27	13	14	50	48	52
Pendimethalin	16	12	4	30	44	15	0.23	0	0	0	0	0	0
Galaxolide	10	6	4	19	22	15	NA	NA	NA	NA	NA	NA	NA
Chlorpyrifos	7	6	1	13	22	4	NA	NA	NA	NA	NA	NA	NA
Fipronil	6	5	1	11	19	4	NA	NA	NA	NA	NA	NA	NA
Terbutylazine	4	4	0	7	15	0	NA	NA	NA	NA	NA	NA	NA
DEETe	4	0	4	7	0	15	NA	NA	NA	NA	NA	NA	NA
Diazinone	2	0	2	4	0	7	NA	NA	NA	NA	NA	NA	NA
Methamidiphos	1	1	0	2	4	0	NA	NA	NA	NA	NA	NA	NA
Metribuzin	1	1	0	2	4	0	0.5	0	0	0	0	0	0
Tonalid	1	1	0	2	4	0	NA	NA	NA	NA	NA	NA	NA
Permethrin Isomers	1	1	0	2	4	0	NA	NA	NA	NA	NA	NA	NA
Prometryn	1	1	0	2	4	0	NA	NA	NA	NA	NA	NA	NA
Phosphamidon	1	0	1	2	0	4	NA	NA	NA	NA	NA	NA	NA
2,6-DI-t-BUTYL-p-CRESOL (bht)e	1	0	1	2	0	4	NA	NA	NA	NA	NA	NA	NA

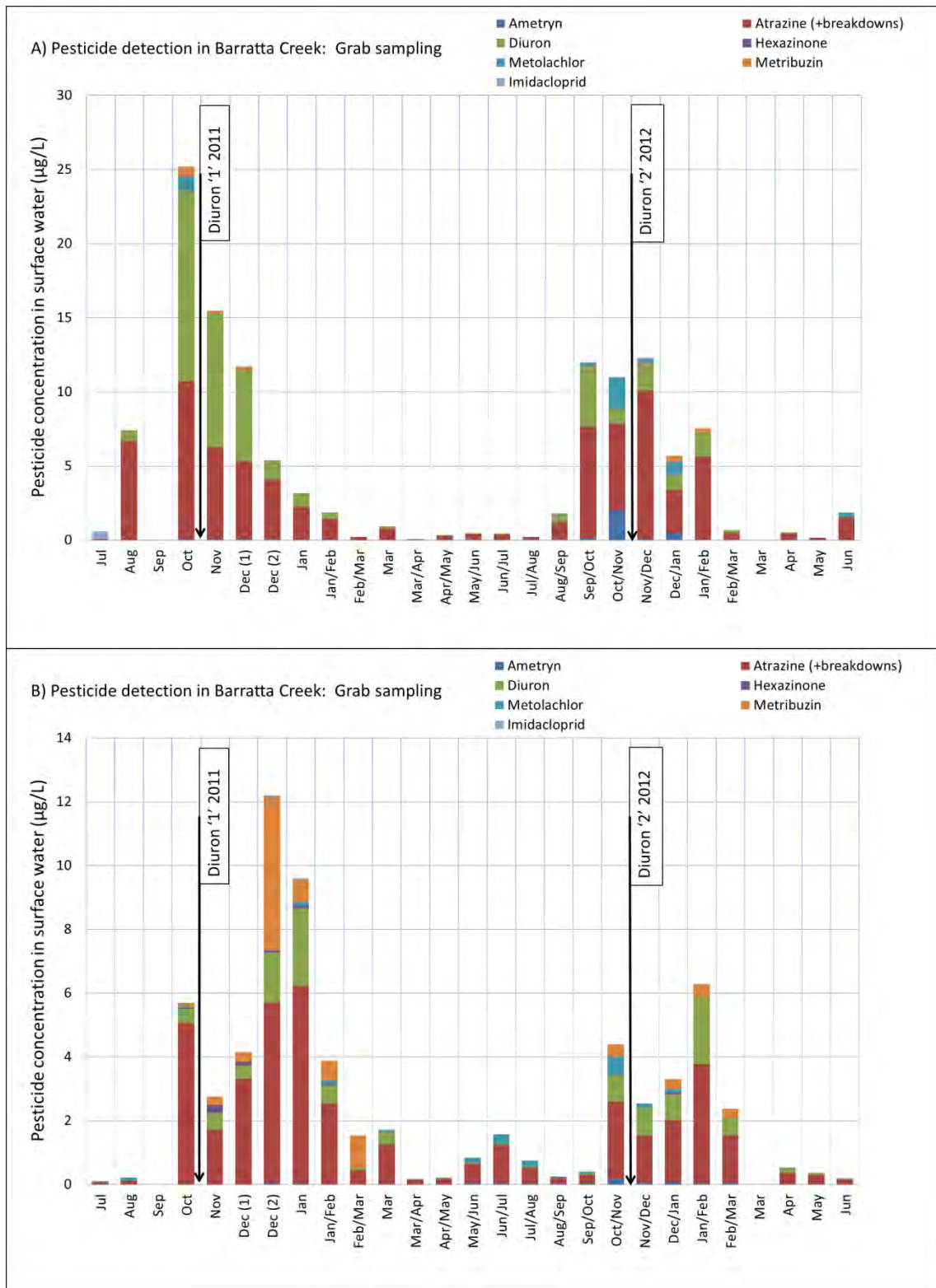


Figure 3 Prominent pesticide concentrations detected across the four monitoring sites within Barratta Creek when employing grab sampling techniques.

Pesticide exposure within Barratta Creek Catchment

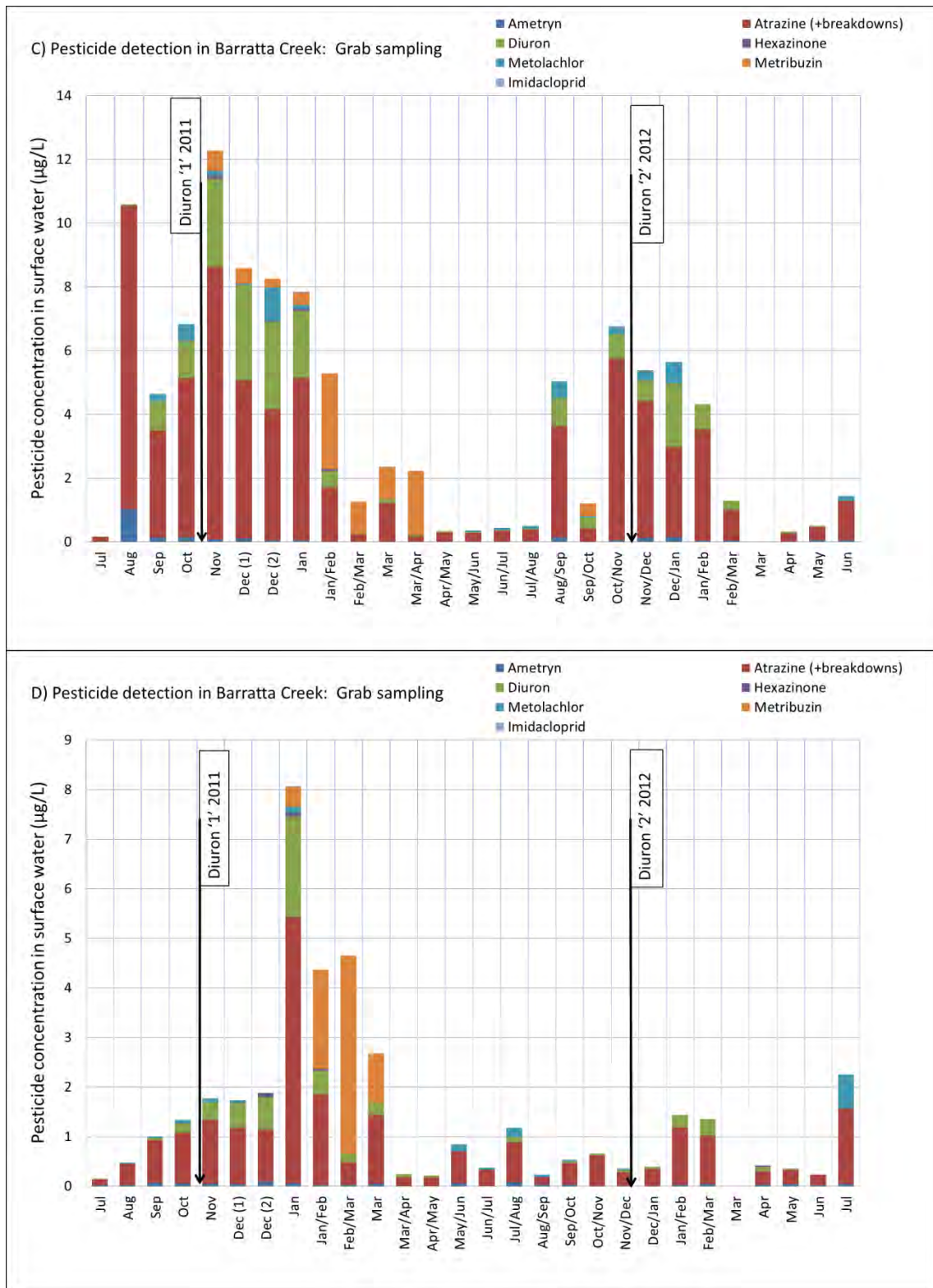


Figure 3 (cont.) Prominent pesticide concentrations detected across the four monitoring sites within Barratta Creek when employing grab sampling techniques.

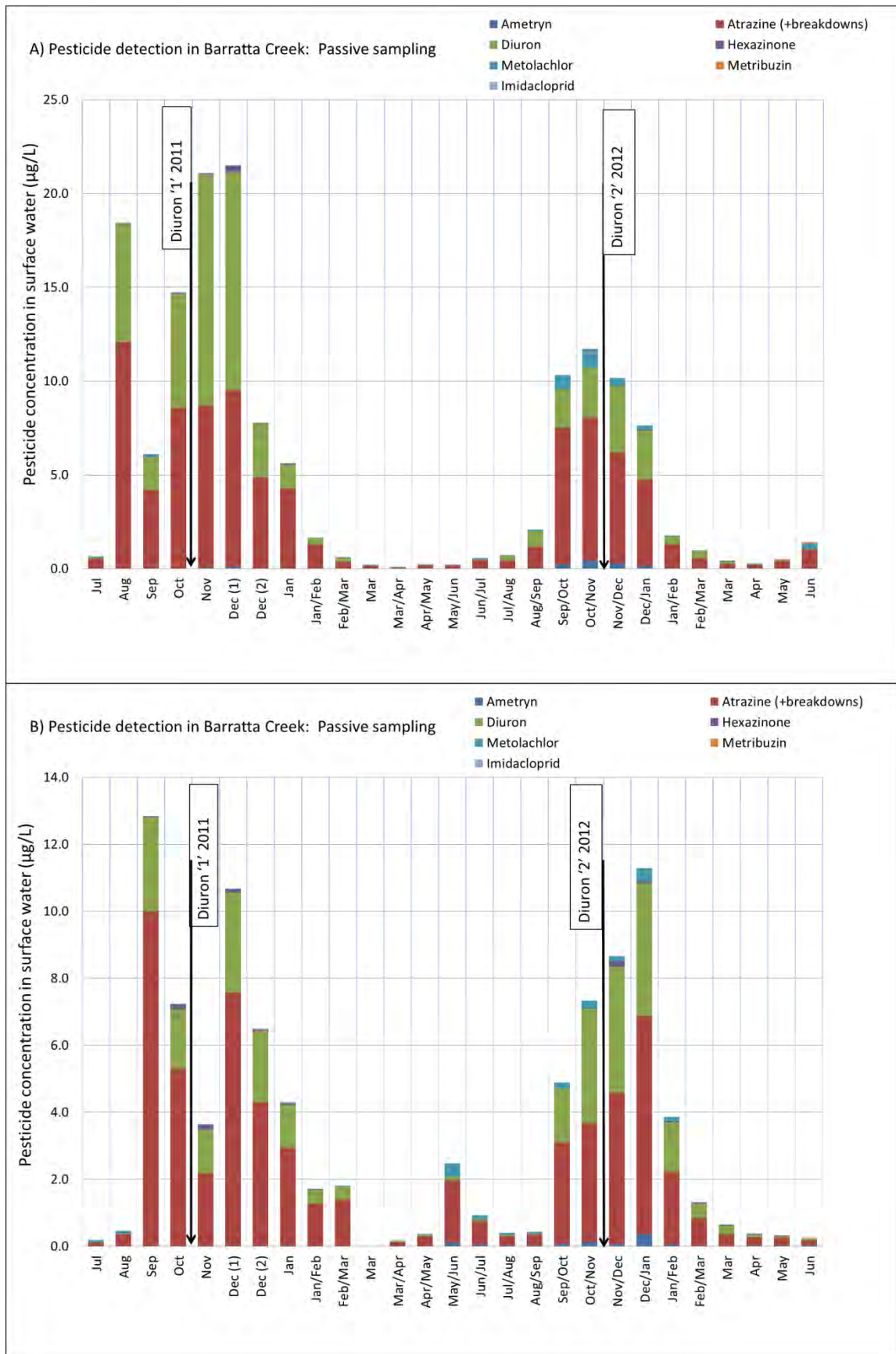


Figure 4 Prominent pesticide concentrations detected across the four monitoring sites within Barratta Creek when employing passive sampling techniques.

Pesticide exposure within Barratta Creek Catchment

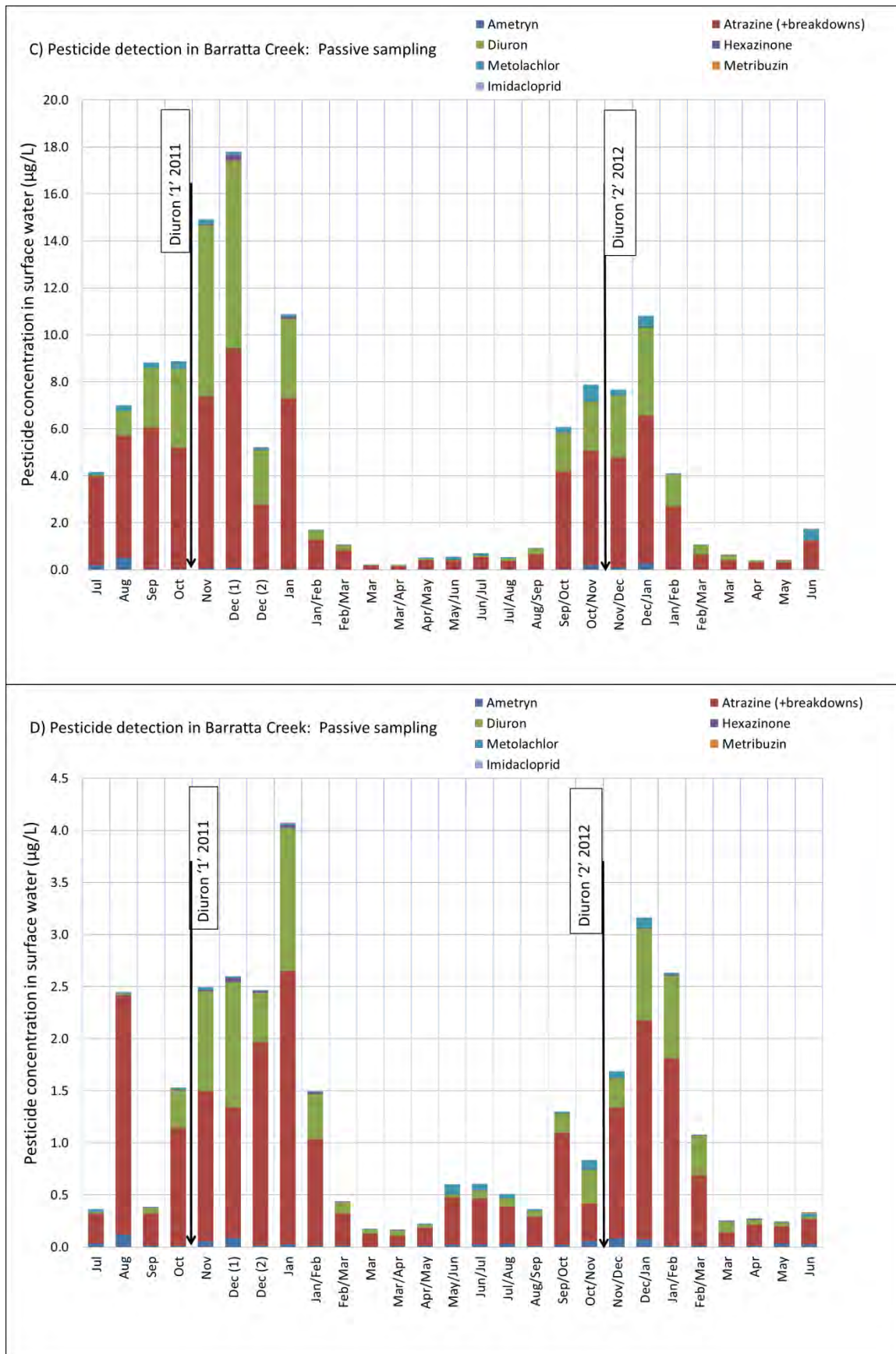


Figure 3 (cont.) Prominent pesticide concentrations detected across the four monitoring sites within Barratta Creek when employing passive sampling techniques.

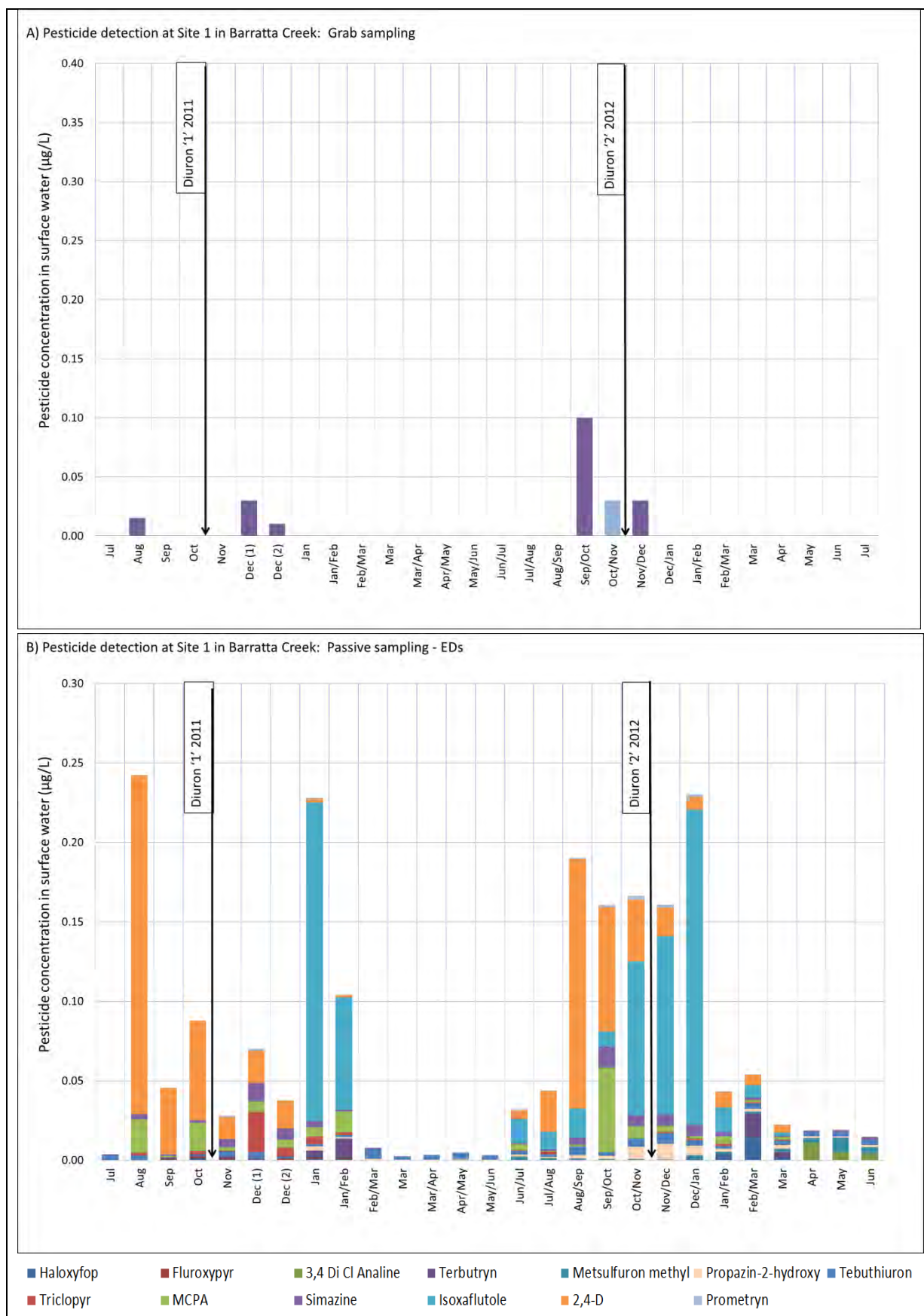


Figure 5 Pesticide concentrations detected at low concentrations at Site 1: Upper Barratta when employing a) grab sampling and b) passive sampling methods.

Pesticide exposure within Barratta Creek Catchment

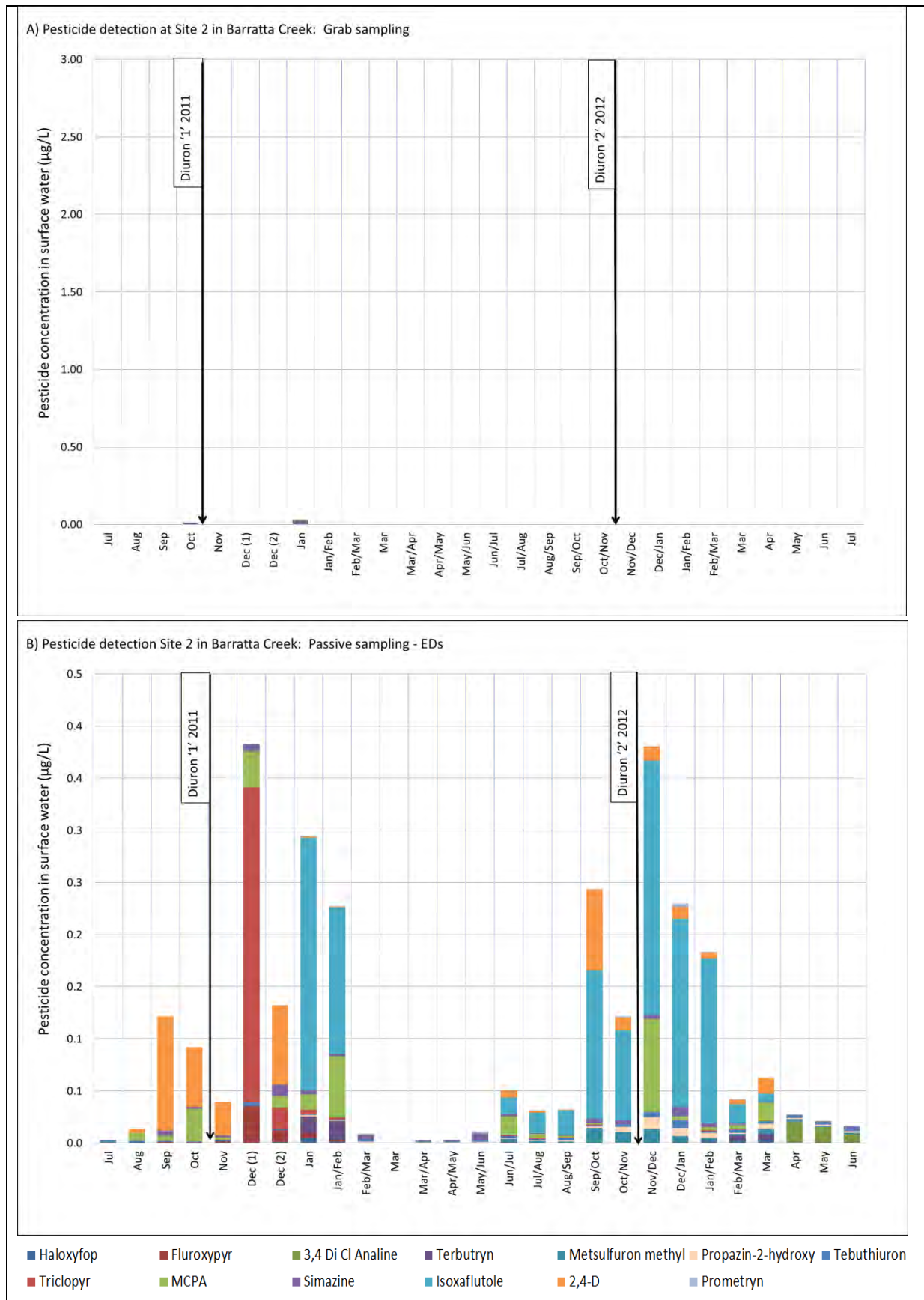


Figure 6 Pesticide concentrations detected at low concentrations at Site 2: West Barratta when employing a) grab sampling and b) passive sampling methods.

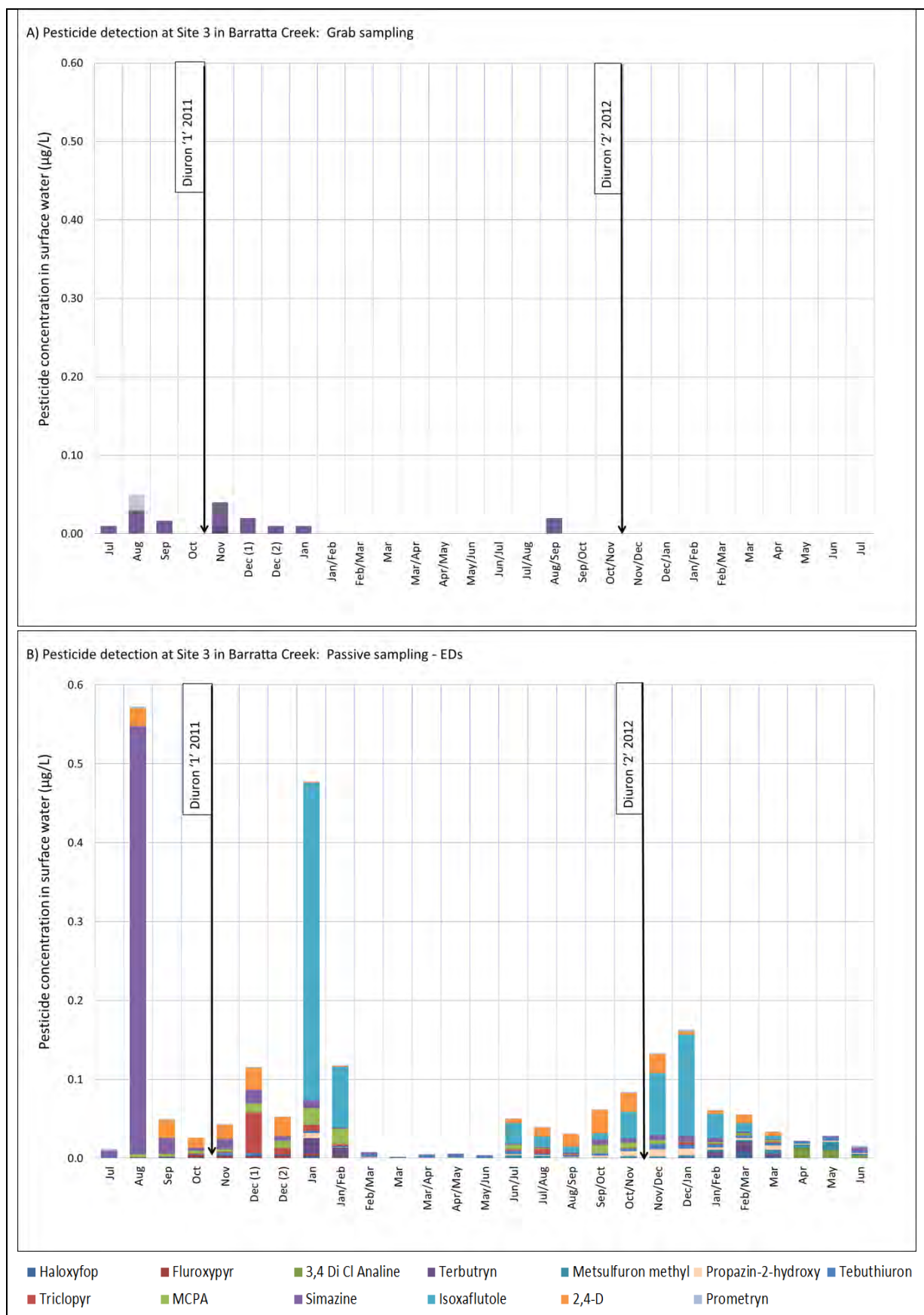


Figure 7 Pesticide concentrations detected at low concentrations at Site 3: East Barratta when employing a) grab sampling and b) passive sampling methods.

Pesticide exposure within Barratta Creek Catchment

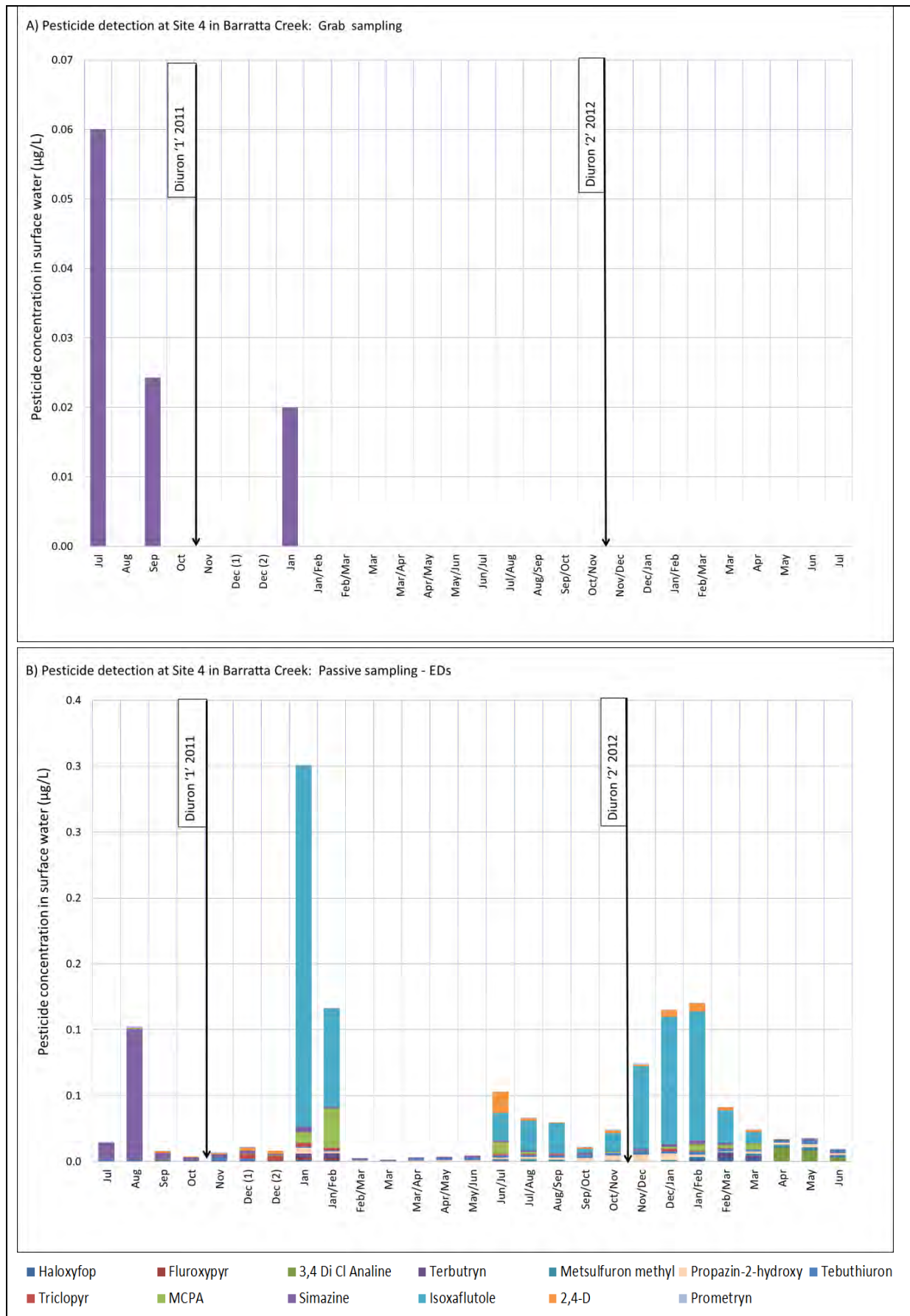


Figure 8 Pesticide concentrations detected at low concentrations at Site 4: Lower Barratta when employing a) grab sampling and b) passive sampling methods.

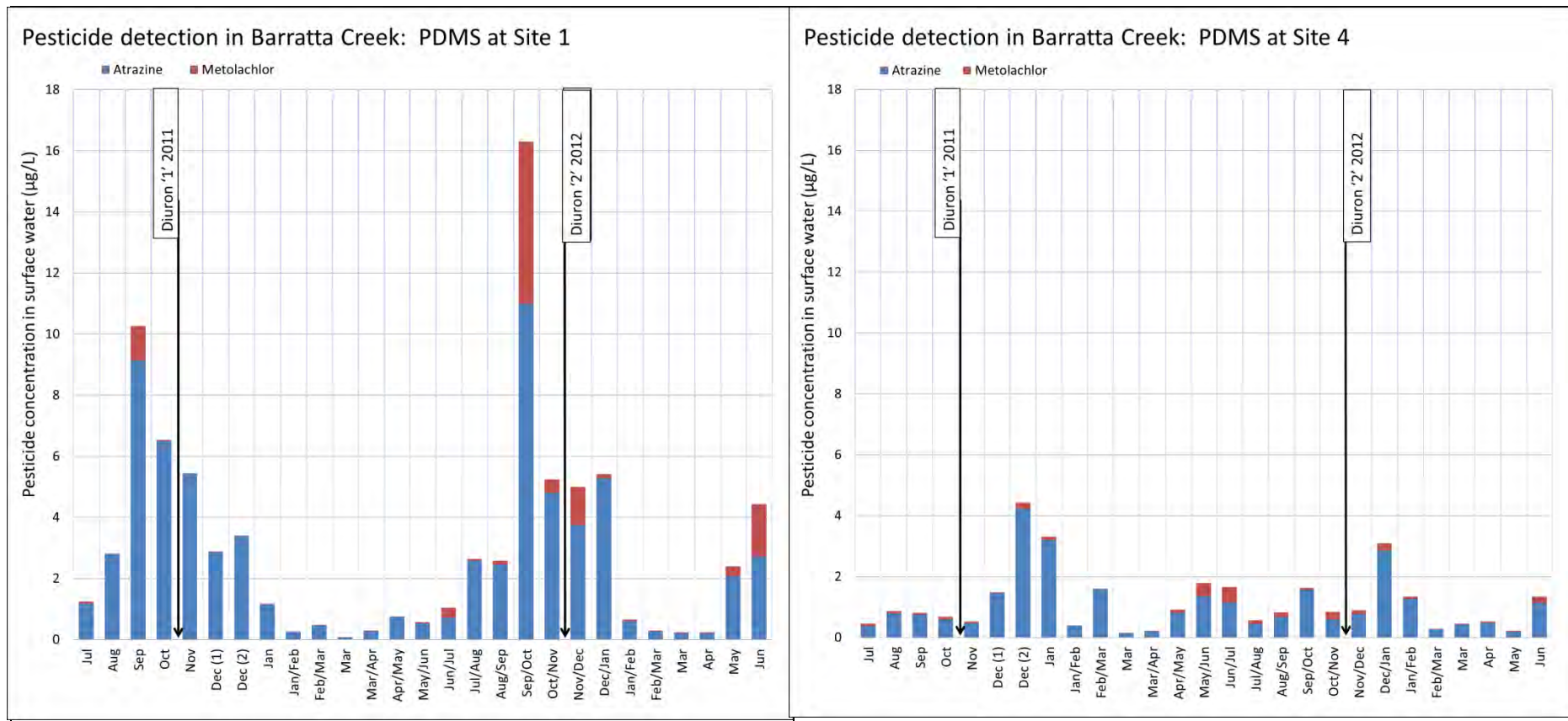


Figure 9 Pesticide concentrations detected using PDMS passive samplers: Atrazine and metolachlor.

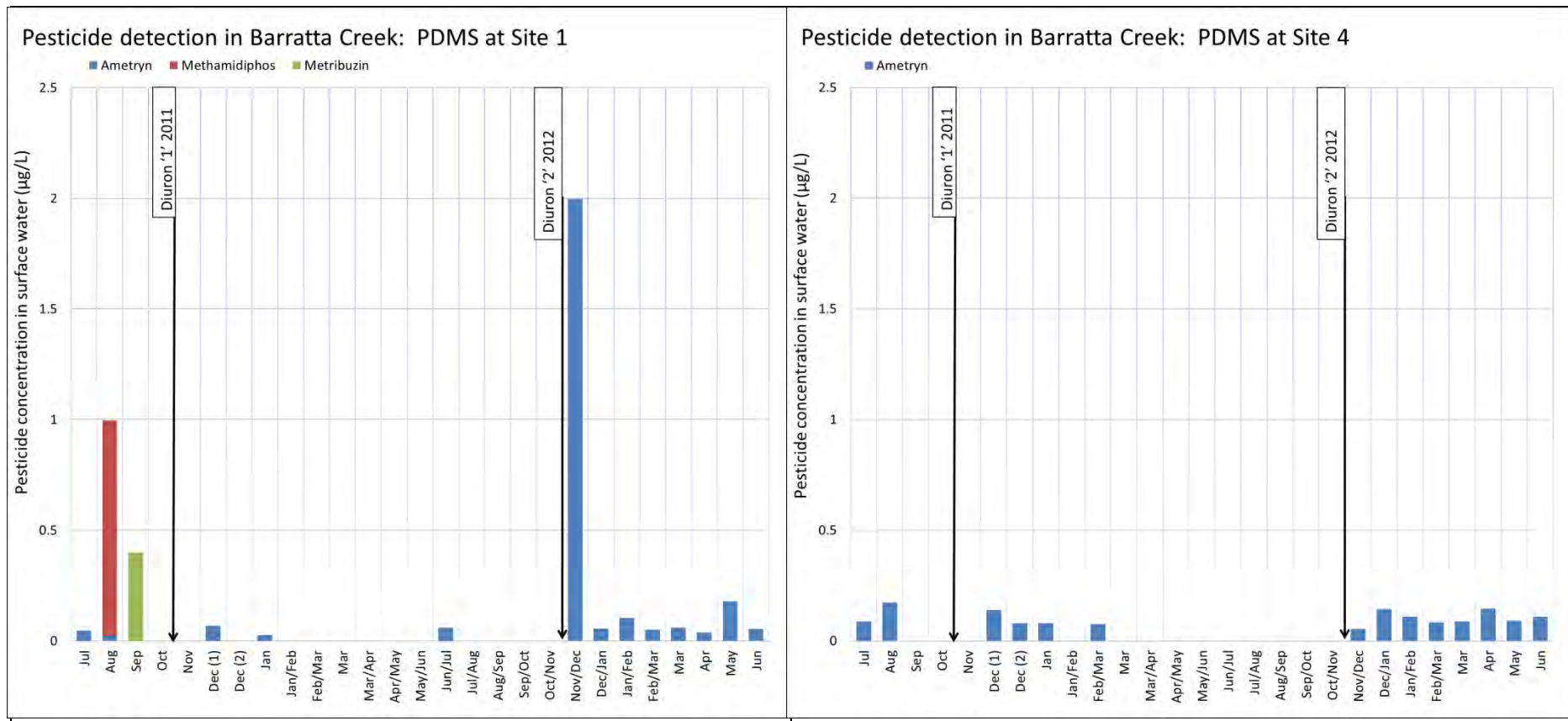


Figure 10 Pesticide concentrations detected using PDMS passive samplers: Ametryn, methamidiphos and metribuzin.

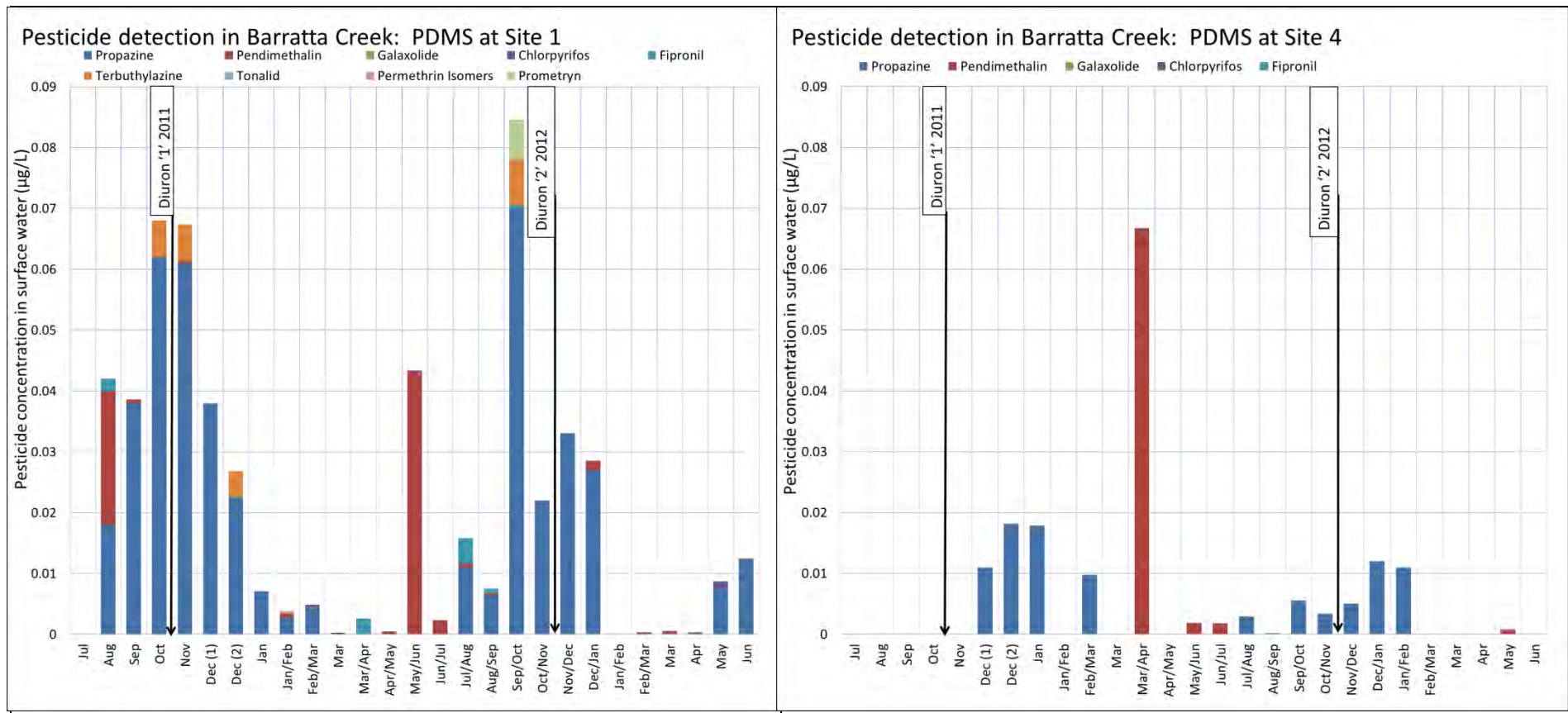


Figure 11 Pesticide concentrations detected using PDMS passive samplers: residues at concentrations of <0.09 µg/L.

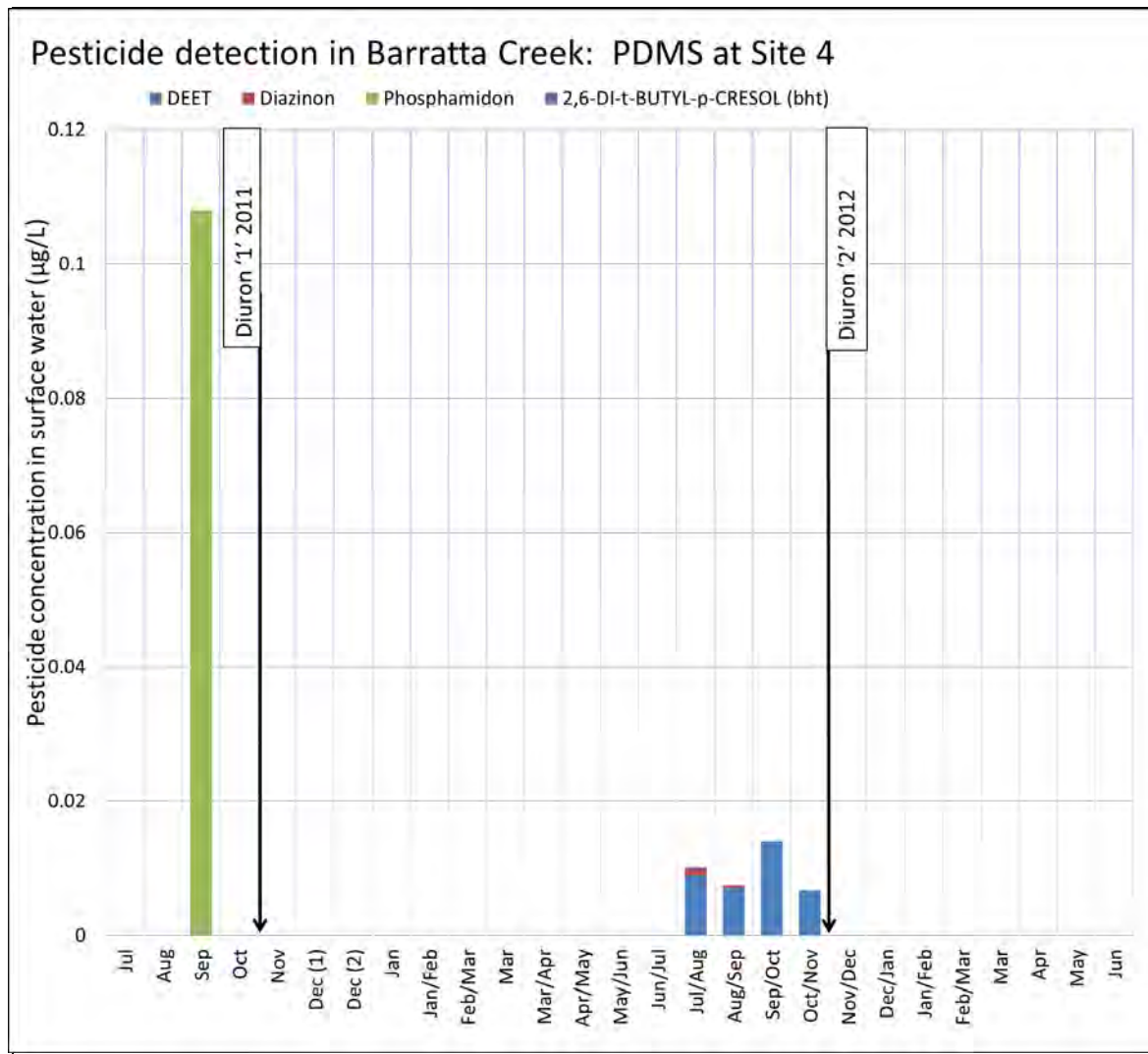


Figure 12 Pesticide concentrations detected using PDMS passive samplers: residues detected only at Site 4

Ecological risk assessment

Diuron and atrazine are two prominent pesticides employed by the sugarcane industry. Considerable research has been undertaken that investigates and demonstrates the impact that these herbicides have upon non target organisms (for reviews see Solomon *et al.* (2008)). The monthly mean concentration of both diuron and atrazine measured through the use of both grab and passive sampling methods have been plotted in Figures 13 and 14, respectively. Concentration data collected at all sites have been plotted against the existing water quality guideline and trigger values established for fresh water. As no guidelines have been established for estuarine systems, both the freshwater and marine guidelines have been used to assess the risks associated with the pesticide concentrations recorded in samples collected from Site 4 within the estuarine reaches of the Barratta Creek as it passes through the Ramsar wetland site.

The freshwater WQ guideline values for atrazine (99% species protection) and the low reliability trigger values for diuron and metolachlor (data presented Table 3 and 4 above) were exceeded in 50 - 55% of samples collected from within the freshwater reaches of Barratta Creek (Sites 1, 2 and 3). Diuron and atrazine concentrations measured within the Ramsar wetland (Site 4) by comparison exceeded the freshwater guidelines/trigger values less frequently, with exceedances recorded in 33-40% of samples. Both atrazine and diuron have specific water quality guidelines for the Great Barrier Reef Marine Park (GBRMPA 2010). The atrazine marine guideline was exceeded in 41% and 37% of samples while the diuron marine guideline was exceeded in 4% and 11% of grab and passive samplers, respectively.

Pesticide exposure within Barratta Creek Catchment

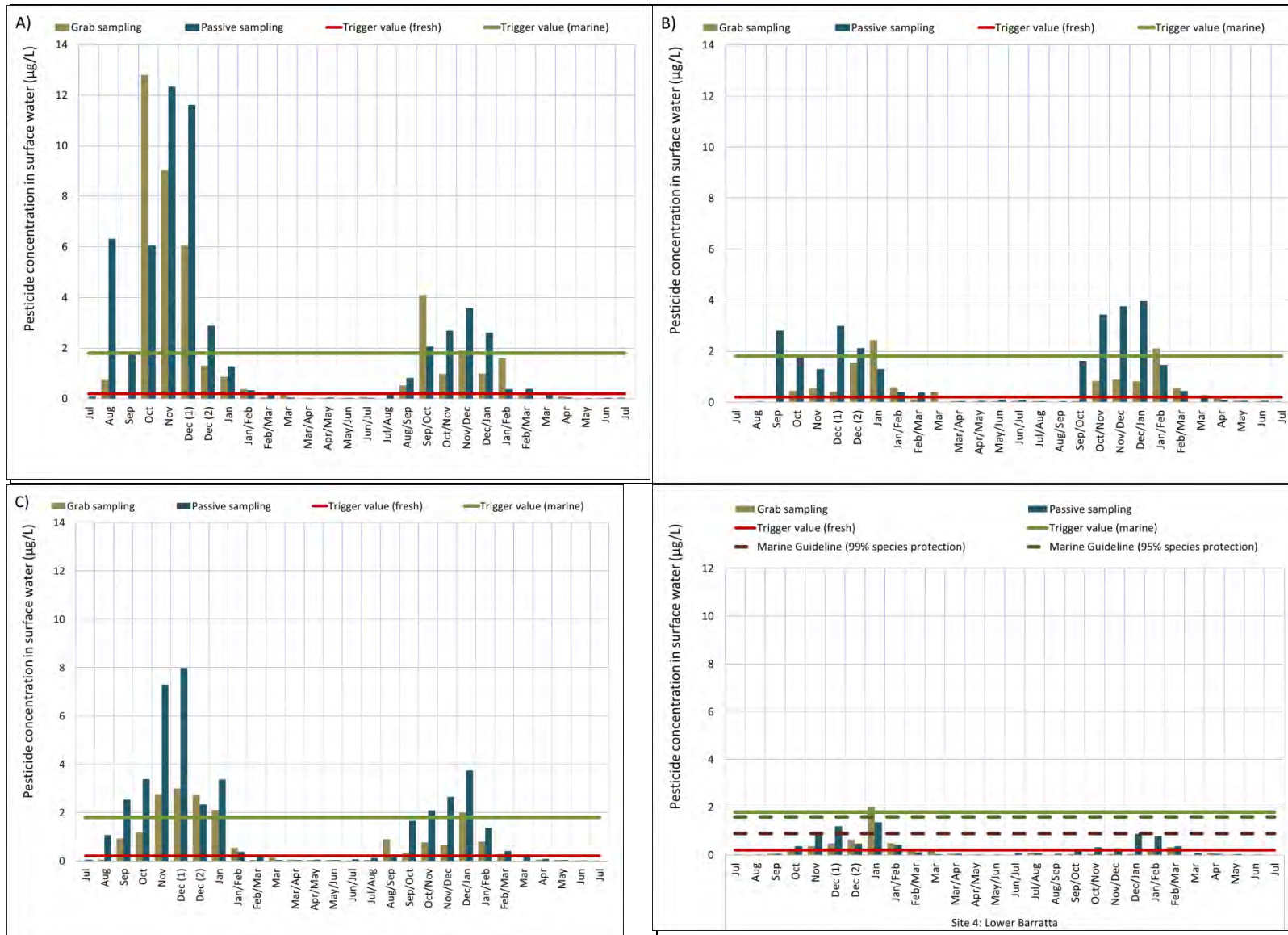


Figure 13 Comparison of Diuron concentrations detected across all sites when employing both grab and passive sampling methods.



Figure 14 Comparison of atrazine concentrations detected across all sites when employing both grab and passive sampling methods.

Comparison of measurements obtained using grab vs passive sampling

A comparison of water concentrations obtained when employing both passive and grab sampling methods for all detected pesticides is provided in Appendix 3: Pesticide concentrations detected during this study.

The results obtained when employing the PSDs shows that the time-weighted average concentrations calculated per deployment period follow a similar trend across the two year study period when compared to grab samples (Figure 15). In some instances the average concentration calculated through the use of the PSDs is considerably higher than the concentrations reported in grab samples taken at the start and end of each deployment. These discrepancies between the two monitoring techniques are likely to occur when the PSDs have been exposed to pulses in contaminant concentrations higher than those captured in the point in time at which the grab samples were collected. Further, the PSD and grab data presented in Figure 15 further illustrates the strong pattern in flow verse concentrations in the Barratta Creek which show, contrary to measurements recorded in rainfed sugarcane districts, pesticides concentrations are measured at higher concentrations during low flow periods.

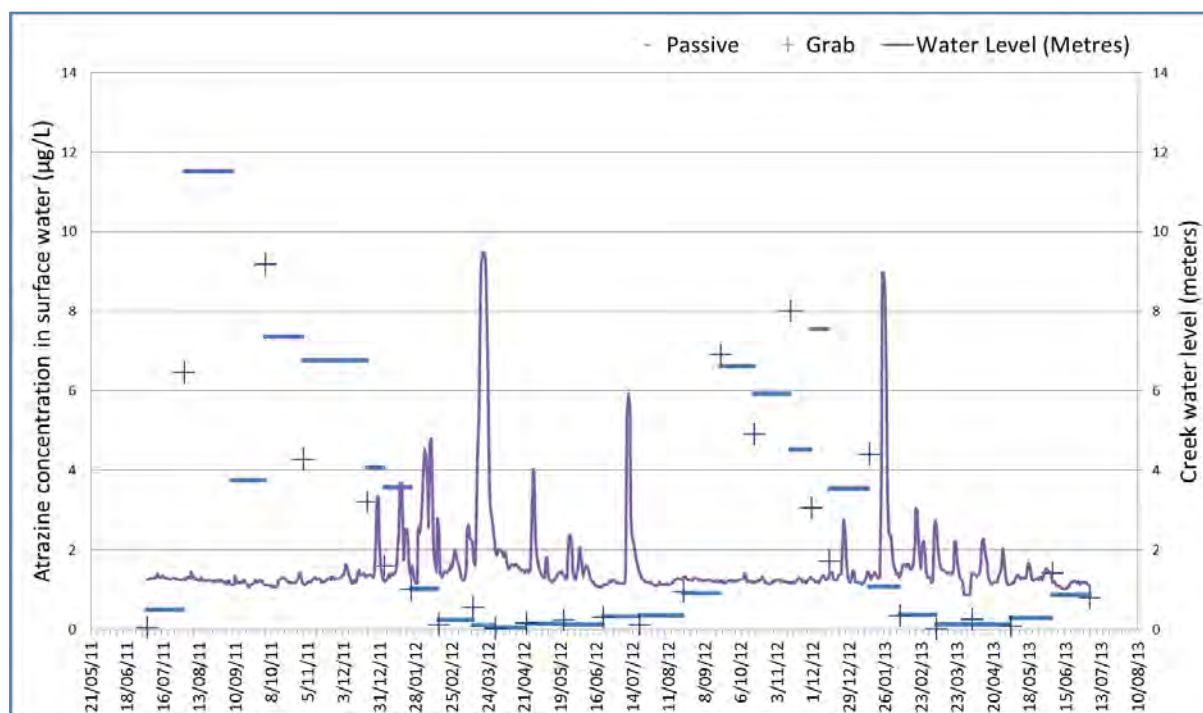


Figure 15: Measurement of atrazine by passive and grab sampling methods between July 2011 and July 2013. The crosses indicate the grab sampling measurements while the bars indicate the time integrated average measurement obtained for each passive sampling deployment undertaken.

Seasonal change in pesticide concentrations

In 2011, pesticide residues in the Barratta Creek system increased markedly from July - August (Figure 9) coinciding with the time of harvesting and remain elevated until January-February when there is a significant decrease following the initial stages of early wet season flow events . This has been observed in pervious monitoring programs (see Davis et al., 2012, 2013). In 2012, concentrations of residues did not increase until September, which reflects the later harvest in this particular year due to unseasonal rainfall in June – July 2012 (Figure 16).

Our data also may provide insight into the change in pesticide concentrations in surface waters during the implementation of diuron regulations in the Burdekin region at the start of the 2011/12 and 2012/13 wet seasons. In November, 2011 the APVMPA announced a ban on diuron use in sugarcane to come into effect in December 2011. The announcement did not state whether diuron would be available for use again after this date. Our data show that diuron concentrations in Barratta Creek increase considerably (more than doubled) in November 2011, and also became the dominant herbicide in Barratta Creek. In comparison, the APVMA announced a no spray window for diuron between December 2012 and March 2013. On this occasion, the diuron concentrations in Barratta Creek were more than four-fold lower over the same period and slightly higher levels of metolachlor were measured at this time (Figure 16).

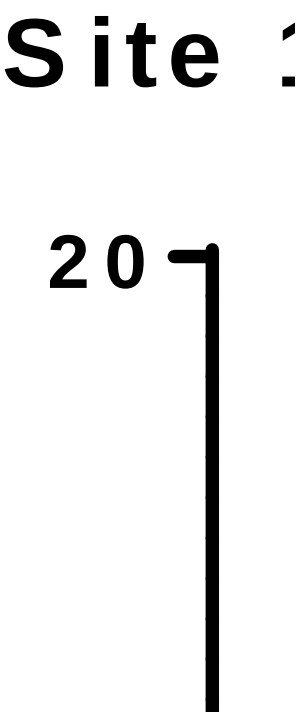


Figure 16 Herbicide concentrations in a) the Upper Barratta Creek site and b) in the Ramsar wetland at the Jerona site. The data show the seasonality of the herbicide exposure in the creek which coincides with the sugarcane harvest period. Also the ineffectiveness of the diuron regulation in November 2011 (diuron '1') is clear from the increasing concentrations in the creek while the second regulation (diuron '2') was more effective. The data show that for 5 – 6 months of the year ecological protection guidelines for diuron and atrazine are exceeded at both sites (this is also reflected at the sites monitored in East and West Barratta Creeks).

Discussion

Since pesticide usage data are unavailable in the upstream catchment area, this research program provides valuable insights into the pesticides in common use in this region beyond what is being promoted for use by suppliers within the local region. Moreover, long-term programs provide insights into changing patterns in pesticide usage. This study found increasing levels of metribuzin and metolachlor in Barratta Creek (compared to earlier monitoring program results) which likely reflects the wider adoption of these 'alternative' herbicides as replacements for diuron in the lower Burdekin region.

The combined use of both passive and grab sampling methods has facilitated the detection of a broad range of pesticide residues during each sampling period. While a number of pesticides were detected within grab samples a range of residues were detected only through the use of PSDs. These pesticides were at concentrations below the analytical detection limit when collecting 1L grab samples for the analysis undertaken and these results further demonstrate the effectiveness of the PSDs for identifying the presence of pesticide residues at trace levels. Further, the use of the PSDs when calculating time-weighted average (TWA) pesticide concentrations at times produced TWA concentrations higher than the concentrations detected within the grab samples collected at the start and end of the deployment period. This would indicate that a spike in pesticide concentrations occurred during the deployment of the PSDs which were missed by the grab samples collected. As such, the passive sampling technology provides a means to more accurately assess the "chronic" exposure of pesticides within the Barratta Creek catchment, particularly during the dry season when stream flow is dominated by irrigation tail waters.

Of the pesticides detected, diuron and atrazine were the most frequently detected and at the highest concentrations. There was an apparent decrease in diuron concentrations corresponding with the second change to diuron use regulation (2012) corresponding with an observable increase in the concentrations of metolachlor and metribuzin. This suggests that metolachlor and metribuzin are being employed as alternatives to diuron. The work undertaken by Lewis *et al.* (2013) as part of the Reef Rescue Water Quality Research and Development Program has shown that metolachlor and metribuzin have a similar toxicity as diuron in the GBR ecosystems and a greater risk than atrazine and as such they may not be the acceptable replacements for diuron as was previously thought.

Further, paddock scale research undertaken over the same period has shown that the management of atrazine and diuron runoff through banded spraying methods and the capture of irrigation tailwater in recycle pits would effectively reduce the loss of these herbicides from paddocks by ~90% (Oliver *et al.* 2014). A reduction of the observed herbicide residue concentrations in Barratta Creek by 90% would reduce the exposure of the Bowling Green Bay Ramsar site to PSII herbicides such that for the majority of the year the measured values would likely fall below the ecological protection guidelines.

Conclusions

A 24 month monitoring program was run from July 2011 to July 2013 in the Barratta Creek complex of the lower Burdekin floodplain. The monitoring undertaken included 28 sampling time points at four separate sites with 27 passive sampler deployments at each site. Monitoring of this intensity and duration has not been undertaken previously and the dataset obtained represents a significant resource that describes the environmental presence many of the pesticides currently employed by the local industry, particularly sugarcane. Further, this monitoring program has captured two changes in the regulation of diuron use within the sugarcane industry. As such this dataset provides valuable insight into the response of the sugarcane industry to changes in regulation. Both diuron and atrazine were shown to be found at the highest concentrations and at the highest frequency.

Future directions

This study has provided valuable data on the delivery of pesticides to surface waters within the Barratta Creek catchment located in the lower Burdekin region. The results have allowed us to observe the change in pesticide use in response to changes in pesticide use regulation and to tangibly record the pesticides that are being used in this region. We recommend the following:

- That monitoring of pesticide concentrations and detection frequencies continue at some or all of the sites included in this study. Future monitoring within the Barratta Creek catchment ensures that any further changes in pesticide usage are captured and that newly introduced pesticides are not being transported into the receiving environments at concentrations likely to put valuable species or ecosystems at risk.
- That relevant ecotoxicological data (i.e. freshwater plants and macro algae, seagrass, coral, phytoplankton) be developed so that the relative toxicity of the new/alternative herbicides and currently employed herbicides (where insufficient data are currently available) can be more thoroughly understood. Delivery of this information to the industry will aid in supporting any changes in pesticide use and the management of any associated environmental impacts. Based on the pesticide residues being detected in this study it is recommended that priority be placed on developing ecotoxicological data for metolachlor, hexazinone, metribuzin and imadiclopid.

Appendix 1: Water quality guidelines established for the chemicals detected using EDs during this study:

	AUSTRALIAN AND NEW ZEALAND WATER QUALITY GUIDELINES (µg/L)								GBR guidelines (µg/L)				International guideline (µg/L)		
	Species protection in fresh water						Marine water		Marine species protection				Canadian: Protection of aquatic life	EU: inland surface waters	
	0.99 (%)	0.95 (%)	0.9 (%)	0.8(%)	trigger	reliability	trigger	reliability	0.99 (%)	0.95 (%)	0.9 (%)	reliability		Annual average	Maximum allowable concentration
Ametryn	--	--	--	--	--	--	--	--	0.5	1	1.6	M	--	--	--
Atrazine	0.7	13	45 ^C	150 ^C	13	M	13	L	0.6	1.4	2.5	M	1.8	0.6	2
Bromacil	ID	ID	ID	ID	180	L	180	L	--	--	--	--	5	--	--
Diuron	ID	ID	ID	ID	0.2	L	1.8	L	0.9	1.6	2.3	M	--	0.2	1.8
Flumeturon	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Hexazinone	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Mecoprop	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Metolachlor	ID	ID	ID	ID	0.02	L	--	--	--	--	--	--	7.8	--	--
Prometryn	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Simazine	0.2	3.2	11	35	3.2	M	3.2	L	0.2	3.2	11	L	--	1	4
Tebuthiuron	0.02	2.2	20	160 ^C	2.2	H	2.2	L	0.02	2	20	L	1.6	--	--
Terbutryn	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Terbutylazine	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Imadicloprid	--	--	--	--	--	--	--	--	--	--	--	--	0.23	--	--
MCPA	ID	ID	ID	ID	1.4	L	1.4	L	--	--	--	--	2.6	--	--
2,4-D	140	280	450	830	280	M	280	L	0.8	30.8	152	M	--	--	--
Triclopyr	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Haloxypop	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Fluroxypyr	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Propazin-2-hydroxy	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Terbutylazine desethyl	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Imazethapyr	ID	ID	ID	ID	240	L	240	L	--	--	--	--	--	--	--
Imazapic	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Acifluorfen	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Isoxaflutole	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Propazin-2-e	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Clomazone	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Metsulfuron	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Flusilazole	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

L = low, M = moderate, H = high, C = Figure may not protect key test species from chronic toxicity (this refers to experimental chronic figures or geometric mean for species)

Pesticide exposure within Barratta Creek Catchment

Appendix 2: Pesticide residues analyzed for but not detected when employing the Empore Disk PSDs. Note: no LOD has been listed as any limit would be theoretical and subject to change depending on chemical properties, the capacity of the sampler employed and the variable sampling rates experienced during exposure.

Empore Disk/chemcatcher:
Carbendazim
2,4-DB
Bifenthrin
Bisphenol A
Diazinon
Diclofenac
Fipronil
Flusilazole
Irgarol
Isoproturon
Mecoprop
Pendimethalin
Sulfamethoxazole
Tris(dichloropropyl) phosphate

Appendix 3: Pesticide concentrations detected during this study.

Table 7: Pesticide concentrations detected in grab samples at Site 1 between July 2011 and July 2013.

	Frequency of detection (%)	Site1: Upper Barratta																															
				2011										2012										2013									
		Jul	Aug	Sep	Oct	Nov	Dec (1)	Dec (2)*	Jan*	Jan/Feb*	Feb/Mar*	Mar*	Mar/Apr*	Apr/May*	May/Jun*	Jun/Jul	Jul/Aug	Aug/Sep	Sep/Oct	Oct/Nov	Nov/Dec	Dec/Jan	Jan/Feb	Feb/Mar	Mar	Apr	May	Jun	Jul				
Ametryn	54				0.0916	0.0500	0.0500	0.0500	0.0400	0.0340						0.0200	0.0300	0.1300	2.0000	0.0900	0.4600	0.0300	0.0300					0.0300					
Atrazine	93	0.0329	6.4500		9.1650	4.2600	3.0600	3.2000	1.6000	1.0000	0.1100	0.5400	0.0170	0.1500	0.2200	0.3000	0.1200	0.9400	6.9000	4.9000	8.0000	1.7000	4.4000	0.3400			0.2500	0.0800	1.4000	0.7800			
Atrazine desethyl	89	0.0258	0.1690		1.1364	1.5700	1.7200	0.4900	0.4400	0.2900	0.0450	0.1800		0.1000	0.1500	0.0600	0.0500	0.1900	0.4700	0.7900	1.5000	1.0000	0.9400	0.1000		0.1900	0.0700	0.1300	0.1000				
Desisoproyl atrazine	61		0.0559		0.3090	0.3600	0.4700	0.3000	0.1600	0.0980	0.0180	0.0610		0.0340	0.0420			0.0500	0.1500	0.2000	0.4900	0.2500	0.2600										
Diuron	86	0.0153	0.7470		12.8070	9.0400	6.0500	1.3000	0.8700	0.3900	0.0530	0.1500	0.0200	0.0430	0.0380	0.0700		0.5300	4.1000	0.9800	1.9000	1.0000	1.6000	0.2200		0.1000		0.0200	0.0500				
Hexazinone	21				0.0107		0.0100	0.0200	0.0300	0.0240											0.0300												
Mecoprop	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Metolachlor	32				0.9862												0.0300	0.0600	0.2200	2.1000	0.2300	0.8300						0.2700	0.4500				
Prometryn	4																			0.0300													
Simazine	18		0.0153				0.0300	0.0100											0.1000		0.0300												
Tebuthiuron	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Terbutryn	0																																
Terbutylazine	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Imadicloprid	11	0.5040																		0.0200	0.0800												
MCPA	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
2,4-D	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Triclopyr	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Haloxfop	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Fluroxypyr	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Propazin-2-hydroxy	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Terbutylazine desethyl	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Imazethapyr	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Imazapic	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Acifluorfen	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Isoxaflutole	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Bromacil	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Flumeturon	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Clomazone	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Metsulfuron methyl	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Flusilazole	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Metribuzin	21				0.6900	0.1770	0.3290														0.4000	0.3000							0.3000				
Imidacloprid urea	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
3,4 Di Cl Aniline	0	NR	NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR			
Tris(dichloropropyl) ph	0																																
Bisphenol A	0																																
Bifenthrin	0																																
Pendimethalin	0																																
Propazine	0																																

Samples lost in transport

NR not reported,  not detected, *analysis undertaken by DSITIA, the cells are coloured on a gradient from yellow (indicating the lowest detected concentrations) to orange (indicating median concentrations or 50th percentile) to maroon (indicating the highest concentrations recorded).

Pesticide exposure within Barratta Creek Catchment

Table 8: Pesticide concentrations detected in ED passive samplers at Site 1 between July 2011 and July 2013.

	Frequency of detection (%)	Site1: Upper Barratta																										
		2011							2012													2013						
		Jul	Aug	Sep	Oct	Nov	Dec (1)	Dec (2)	Jan	Jan/Feb	Feb/Mar	Mar	Mar/Apr	Apr/May	May/Jun	Jun/Jul	Jul/Aug	Aug/Sep	Sep/Oct	Oct/Nov	Nov/Dec	Dec/Jan	Jan/Feb	Feb/Mar	Mar	Apr	May	Jun
Ametryn	100	0.0075	0.0065	0.0014	0.0058	0.0648	0.1183	0.0067	0.0139	0.0091	0.0094	0.0021	0.0025	0.0039	0.0031	0.0280	0.0068	0.0318	0.2171	0.4030	0.2740	0.1315	0.0313	0.0130	0.0090	0.0080	0.0174	0.0124
Atrazine	100	0.4816	11.5011	3.7451	7.3525	6.7629	7.5395	4.0601	3.5662	1.0158	0.2262	0.0956	0.0338	0.1268	0.1174	0.3138	0.3421	0.8953	6.6080	5.9231	4.5125	3.5429	1.0730	0.3579	0.1197	0.1073	0.2854	0.8711
Atrazine desethyl	100	0.0209	0.5543	0.3323	1.0195	1.5555	1.6373	0.6351	0.5984	0.2101	0.0997	0.0455	0.0226	0.0377	0.0437	0.0908	0.0689	0.2079	0.5359	1.3974	1.1594	0.8669	0.1754	0.1456	0.0993	0.0823	0.0649	0.1122
Desisoproyl atrazine	100	0.0085	0.0203	0.1049	0.2070	0.3101	0.2333	0.1577	0.0953	0.0538	0.0210	0.0109	0.0057	0.0081	0.0090	0.0222	0.0196	0.0455	0.1544	0.3091	0.2466	0.2078	0.0480	0.0334	0.0209	0.0103	0.0110	0.0209
Diuron	100	0.0774	6.3254	1.7723	6.0693	12.3386	11.6191	2.8855	1.2828	0.3425	0.2270	0.0522	0.0291	0.0494	0.0367	0.0464	0.2597	0.8291	2.0637	2.6892	3.5752	2.6141	0.3877	0.3935	0.1393	0.0561	0.0237	0.0391
Hexazinone	100	0.0107	0.0055	0.0016	0.0021	0.0289	0.3270	0.0237	0.0563	0.0117	0.0044	0.0011	0.0008	0.0016	0.0014	0.0020	0.0032	0.0083	0.0077	0.0089	0.0108	0.0495	0.0015	0.0104	0.0148	0.0024	0.0014	0.0020
Mecoprop	4	NR	NR	NR	0.0000																							
Metolachlor	100	0.0177	0.0130	0.1276	0.0740	0.0137	0.0068	0.0028	0.0027	0.0017	0.0010	0.0005	0.0009	0.0020	0.0023	0.0528	0.0069	0.0584	0.7146	0.9637	0.3678	0.2025	0.0401	0.0236	0.0069	0.0086	0.0296	0.2818
Prometryn	85					0.0009	0.0011	0.0001	0.0002	0.0002	0.0002	0.0000	0.0000	0.0001	0.0001	0.0004	0.0001	0.0005	0.0014	0.0023	0.0020	0.0011	0.0003	0.0002	0.0001	0.0001	0.0004	0.0002
Simazine	100	0.0007	0.0034	0.0010	0.0017	0.0054	0.0117	0.0072	0.0037	0.0011	0.0008	0.0003	0.0001	0.0003	0.0003	0.0009	0.0010	0.0045	0.0132	0.0067	0.0071	0.0071	0.0025	0.0015	0.0007	0.0008	0.0010	0.0018
Tebuthiuron	100	0.0030	0.0029	0.0006	0.0008	0.0031	0.0042	0.0011	0.0014	0.0012	0.0060	0.0015	0.0028	0.0038	0.0024	0.0024	0.0016	0.0056	0.0023	0.0053	0.0064	0.0033	0.0017	0.0035	0.0027	0.0028	0.0029	0.0032
Terbutryn	37				0.0010	0.0014	0.0003		0.0046	0.0122									0.0000	0.0000	0.0001			0.0144	0.0035			
Terbutylazine	37	NR	NR	NR	NR	NR	NR	NR	0.0007	0.0007	0.0003	0.0001	0.0000	0.0001	0.0000			0.0002	0.0024	0.0015								
Imadicloprid	100	0.0407	0.0042	0.0007	0.0017	0.0048	0.0046	0.0056	0.0087	0.0109	0.0041	0.0027	0.0012	0.0051	0.0044	0.0135	0.0068	0.0085	0.0357	0.0269	0.0191	0.0071	0.0050	0.0008	0.0008	0.0057	0.0043	0.0275
MCPA	67	NR	0.0210	0.0007	0.0179	0.0020	0.0066	0.0051	0.0060	0.0129						0.0039	0.0006	0.0011	0.0531	0.0078	0.0040	0.0019	0.0048	0.0015	0.0017			
2,4-D	67	NR	0.2133	0.0417	0.0624	0.0136	0.0203	0.0174	0.0027	0.0013						0.0056	0.0259	0.1573	0.0783	0.0389	0.0180	0.0083	0.0097	0.0067	0.0047			
Triclopyr	56	NR	0.0017	0.0002	0.0020	0.0005	0.0251	0.0055	0.0048	0.0018						0.0004	0.0015			0.0009	0.0011	0.0013	0.0007	0.0007				
Haloxypol	48	NR	NR	0.0005	0.0013	0.0005	0.0003	0.0002	0.0009	0.0007									0.0001	0.0002		0.0004	0.0040	0.0149	0.0016			
Fluroxypyr	26	NR	NR	0.0007	0.0007	0.0005	0.0003	0.0009	0.0007	0.0007																		
Propazin-2-hydroxy	74	NR	NR	NR	NR	NR	NR	NR	0.0025	0.0010	0.0010	0.0004	0.0003	0.0006	0.0003	0.0011	0.0009	0.0020	0.0022	0.0077	0.0100	0.0058	0.0019	0.0015	0.0023	0.0011	0.0007	0.0014
Terbutylazine desethyl	7	NR	NR	NR	NR	NR	NR	NR	0.0004		0.0001																	
Imazethapyr	15	NR	NR	NR	NR	NR	NR	NR													0.0001	0.0005	0.0001	0.0000				
Imazapic	7	NR	NR	NR	NR	NR	NR	NR		0.0001												0.0008						
Acifluorfen	4	NR	NR	NR	NR	NR	NR	NR																	0.0039			
Isoxaflutole	44	NR	NR	NR	NR	NR	NR	NR	0.2006	0.0709						0.0151	0.0109	0.0181	0.0095	0.0968	0.1121	0.1982	0.0157	0.0076	0.0021			
Bromacil	11																		0.0003	0.0004		0.0002						
Flumeturon	4																	0.0003										
Clomazone	0	NR	NR	NR	NR	NR	NR	NR	NR		NR																	
Metsulfuron methyl	48	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0023	0.0013	0.0012	0.0006	0.0004	0.0004	0.0028	0.0014	0.0015	0.0023	0.0029	0.0091	0.0041
Flusilazole	15	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0000	0.0000	0.0000	0.0000									
Metribuzin	11	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0029	0.0590	0.0699
Imidacloprid urea	7	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0003		0.0019
3,4 Di Cl Aniline	11	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0111	0.0051	0.0041

NR not reported,  not detected, the cells are coloured on a gradient from yellow (indicating the lowest detected concentrations) to orange (indicating median concentrations or 50th percentile) to maroon (indicating the highest concentrations recorded).

NR not reported,  not detected, *analysis undertaken by DSITIA, the cells are coloured on a gradient from yellow (indicating the lowest detected concentrations) to orange (indicating median concentrations or 50th percentile) to maroon (indicating the highest concentrations recorded).

Pesticide exposure within Barratta Creek Catchment

Table 10: Pesticide concentrations detected in ED passive samplers at Site 2 between July 2011 and July 2013.

	Frequency of detection (%)	Site 2: West Barratta																												
		2011										Mar	2012										2013							
		Jul	Aug	Sep	Oct	Nov	Dec (1)	Dec (2)	Jan	Jan/Feb	Feb/Mar		Mar/Apr	Apr/May	May/June	June/July	July/Aug	Aug/Sep	Sep/Oct	Oct/Nov	Nov/Dec	Dec/Jan	Jan/Feb	Feb/Mar	Mar	Apr	May	June	July	
Ametryn	96	0.0063	0.0046	0.0021	0.0026	0.0046	0.0092	0.0144	0.0112	0.0036	0.0058		0.0030	0.0054	0.1109	0.0408	0.0176	0.0200	0.0726	0.1152	0.0677	0.3479	0.0371	0.0052	0.0067	0.0092	0.0094	0.0137		
Atrazine	96	0.0648	0.3281	9.0268	3.9383	1.2388	5.8599	3.5129	2.2825	0.9149	1.0872		0.0640	0.2159	1.6903	0.5483	0.1891	0.2107	2.6873	2.5625	2.4007	5.1052	1.5525	0.5994	0.1875	0.1305	0.1079	0.0823		
Atrazine desethyl	96	0.0226	0.0201	0.7461	1.1801	0.7433	1.4056	0.6165	0.5282	0.2712	0.2443		0.0393	0.0522	0.1360	0.1211	0.0808	0.0956	0.2663	0.7973	1.7071	1.1513	0.5195	0.1876	0.1235	0.1072	0.1121	0.0691		
Desisoproyl atrazine	96	0.0066	0.0050	0.2297	0.1769	0.1920	0.2937	0.1455	0.1065	0.0793	0.0600		0.0073	0.0110	0.0299	0.0294	0.0165	0.0167	0.0755	0.1900	0.4074	0.2686	0.1226	0.0446	0.0303	0.0184	0.0145	0.0117		
Diuron	96	0.0187	0.0224	2.7975	1.7653	1.2969	2.9859	2.1212	1.2999	0.4060	0.3857		0.0402	0.0563	0.1019	0.0648	0.0390	0.0393	1.6106	3.4300	3.7566	3.9687	1.4599	0.4443	0.2691	0.0777	0.0612	0.0528		
Hexazinone	96	0.0032	0.0022	0.0159	0.1530	0.1531	0.0977	0.0302	0.0250	0.0142	0.0056		0.0013	0.0023	0.0021	0.0018	0.0017	0.0020	0.0016	0.0022	0.1713	0.0637	0.0387	0.0086	0.0087	0.0072	0.0064	0.0078		
Mecoprop	0	NR	NR	NR																										
Metolachlor	96	0.0634	0.0682	0.0119	0.0057	0.0024	0.0145	0.0315	0.0216	0.0118	0.0115		0.0013	0.0082	0.3920	0.1035	0.0482	0.0282	0.1639	0.2266	0.1444	0.3652	0.1187	0.0174	0.0092	0.0104	0.0047	0.0046		
Prometryn	67								0.0001	0.0001	0.0001		0.0001	0.0001	0.0012	0.0005	0.0002	0.0003	0.0006	0.0011	0.0005	0.0029	0.0003	0.0001	0.0001		0.0002	0.0003		
Simazine	89			0.0047	0.0024	0.0018	0.0067	0.0109	0.0043	0.0019	0.0037		0.0003	0.0006	0.0067	0.0023	0.0006	0.0006	0.0042	0.0039	0.0036	0.0091	0.0035	0.0016	0.0008	0.0007	0.0006	0.0005		
Tebuthiuron	96	0.0028	0.0019	0.0011	0.0009	0.0014	0.0039	0.0009	0.0006	0.0007	0.0027		0.0013	0.0016	0.0020	0.0018	0.0010	0.0025	0.0012	0.0025	0.0050	0.0070	0.0015	0.0028	0.0023	0.0022	0.0028	0.0039		
Terbutryn	33								0.0155	0.0185									0.0000	0.0000		0.0000	0.0000	0.0049	0.0053					
Terbutylazine	22	NR	NR	NR	NR	NR	NR	NR	0.0008	0.0005	0.0005		0.0000	0.0001	0.0002															
Imadicloprid	78				0.0030	0.0083	0.0116	0.0301	0.0156	0.0082			0.0014	0.0073	0.0058	0.0078	0.0051	0.0008	0.0014	0.0016	0.0025	0.0122	0.0065	0.0006	0.0012	0.0026	0.0009			
MCPA	63	NR	0.0080	0.0054	0.0312	0.0023	0.0350	0.0111	0.0144	0.0587					0.0178	0.0043	0.0015	0.0015		0.0892	0.0042	0.0031	0.0040	0.0174						
2,4-D	70	NR	0.0040	0.1091	0.0571	0.0323	2.2335	0.0759	0.0009	0.0006	0.0005				0.0066	0.0019	0.0008	0.0771	0.0127	0.0135	0.0116	0.0058	0.0042	0.0150						
Triclopyr	44	NR			0.0006	0.3020	0.0209	0.0043	0.0019						0.0009	0.0010	0.0005	0.0005				0.0008	0.0006	0.0004						
Haloxypfop	33	NR	NR		0.0001		0.0008	0.0049	0.0014						0.0004							0.0010	0.0025	0.0024	0.0032					
Fluroxypyr	26	NR	NR	0.0009	0.0004	0.0012	0.0350	0.0116	0.0049	0.0014																				
Propazin-2-hydroxy	70	NR	NR	NR	NR	NR	NR	NR	0.0018	0.0007	0.0014		0.0005	0.0005	0.0008	0.0007	0.0006	0.0011	0.0013	0.0052	0.0113	0.0081	0.0052	0.0013	0.0051	0.0012	0.0014	0.0016		
Terbutylazine desethyl	4	NR	NR	NR	NR	NR	NR	NR	0.0004				0.0001	0.0001	0.0005	0.0003	0.0003	0.0005	0.0006	0.0004	0.0008	0.0001	0.0006	0.0002	0.0003					
Imazethapyr	59	NR	NR	NR	NR	NR	NR	NR	0.0026	0.0019	0.0007		0.0001	0.0001	0.0005	0.0003	0.0003	0.0005	0.0006	0.0004	0.0008	0.0001	0.0006	0.0002	0.0003					
Imazapic	59	NR	NR	NR	NR	NR	NR	NR	0.0011	0.0005	0.0013		0.0001	0.0001	0.0002	0.0002	0.0001		0.0004	0.0006	0.0009	0.0008	0.0012	0.0007	0.0009	0.0012				
Acifluorfen	15	NR	NR	NR	NR	NR	NR	NR	0.0005	0.0006														0.0033	0.0014					
Isoxaflutole	48	NR	NR	NR	NR	NR	NR	NR	0.2423	0.1410	0.0001				0.0159	0.0196	0.0236	0.1425	0.0857	0.2445	0.1802	0.1587	0.0185	0.0077						
Bromacil	19								0.0004	0.0008								0.0005	0.0005					0.0018						
Flumeturon	19												0.0038	0.0007	0.0002	0.0002	0.0004													
Clomazone	7	NR	NR	NR	NR	NR	NR	NR	NR		NR			0.0001	0.0001															
Metsulfuron methyl	48	NR	NR	NR	NR	NR	NR	NR	NR		NR		NR	NR	NR	0.0038	0.0020	0.0013	0.0145	0.0104	0.0133	0.0054	0.0022	0.0013	0.0051	0.0028	0.0012	0.0012		
Flusilazole	11	NR	NR	NR	NR	NR	NR	NR	NR		NR		NR	NR	NR	0.0000	0.0000		0.0000											
Metribuzin	11	NR	NR	NR	NR	NR	NR	NR	NR		NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0082	0.0039	0.0020	
Imidacloprid urea	0	NR	NR	NR	NR	NR	NR	NR	NR		NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR				
3,4 Di Cl Aniline	11	NR	NR	NR	NR	NR	NR	NR	NR		NR		NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0201	0.0150	0.0085	

Samplers lost when tree swept away

NR not reported,  not detected, the cells are coloured on a gradient from yellow (indicating the lowest detected concentrations) to orange (indicating median concentrations or 50th percentile) to maroon (indicating the highest concentrations recorded).

Table 11: Pesticide concentrations detected in grab samples at Site 3 between July 2011 and July 2013.

	Frequency of detection (%)	Site 3: East Barratta																												
		2011								2012										2013										
		Jul	Aug	Sep	Oct	Nov	Dec (1)	Dec (2)	Jan	Jan/Feb	Feb/Mar	Mar	Mar/Apr	Apr/May	May/Jun	Jun/Jul	Jul/Aug	Aug/Sep	Sep/Oct	Oct/Nov	Nov/Dec	Dec/Jan	Jan/Feb	Feb/Mar	Mar	Apr	May	Jun	Jul	
Ametryn	61		1.0200	0.1330	0.1410	0.0800	0.1100	0.0500	0.0400							0.0200	0.1300		0.0400	0.1200	0.1500	0.0300	0.0300				0.0400	0.0500	0.1900	
Atrazine	96	0.0684	8.0600	2.8297	3.6995	6.8200	3.5000	2.3300	3.8520	1.2100	0.1700	0.9200	0.1300	0.1900	0.2000	0.2600	0.2900	3.0000	0.3100	4.7000	3.4000	1.8000	2.6000	0.8000			0.1400	0.3000	1.1000	4.2000
Atrazine desethyl	96	0.0685	1.1400	0.3980	0.9228	1.3400	1.1400	1.4700	0.9970	0.4000	0.0600	0.2400	0.0400	0.1000	0.0800	0.0900	0.0700	0.3900	0.1100	0.8100	0.7000	0.8000	0.7300	0.1700			0.1300	0.1300	0.1200	0.3000
Desisopropyl atrazine	57	0.0147	0.3210	0.1270	0.3710	0.3800	0.3100	0.3100	0.2460	0.0900		0.0500						0.1000		0.1900	0.2000	0.2200	0.1600						0.0600	
Diuron	96	0.0171	0.0487	0.9321	1.1652	2.7700	2.9900	2.7520	2.1000	0.5300	0.0300	0.1400	0.0500	0.0400	0.0300	0.0200	0.0300	0.9000	0.3400	0.7700	0.6500	2.0000	0.7900	0.2800			0.0500	0.0300	0.0200	0.0200
Hexazinone	18				0.0191	0.1070		0.0300	0.0700	0.0500																				
Mecoprop	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Metolachlor	57				0.2100	0.4982	0.1400	0.0500	1.0400	0.1250						0.0400	0.0700	0.0800	0.5100	0.0400	0.2100	0.3100	0.6700						0.1400	2.8000
Prometryn	4		0.0202																											
Simazine	29	0.0102	0.0299	0.0165		0.0300	0.0200	0.0100	0.0100									0.0200												
Tebuthiuron	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Terbutryn	4					0.0100																								
Terbutylazine	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Imadicloprid	7								0.0300											0.0400										
MCPA	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
2,4-D	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Triclopyr	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Haloxypof	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Fluroxypyr	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Propazin-2-hydroxy	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Terbutylazine desethyl	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Imazethapyr	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Imazapic	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Acifluorfen	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Isoxaflutole	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Bromacil	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Flumeturon	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Clomazone	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Metsulfuron methyl	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Flusilazole	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
Metribuzin	32					0.6400	0.4860	0.2700	0.3880	3.0000	1.0000	1.0000	2.0000					0.4000												
Imidacloprid urea	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
3,4 Di Cl Analine	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR								

NR not reported,  not detected, *analysis undertaken by DSITIA, the cells are coloured on a gradient from yellow (indicating the lowest detected concentrations) to orange (indicating median concentrations or 50th percentile) to maroon (indicating the highest concentrations recorded).

Pesticide exposure within Barratta Creek Catchment

Table 12: Pesticide concentrations detected in ED passive samplers at Site 3 between July 2011 and July 2013.

	Frequency of detection (%)	Site 3: East Barratta																													
		2011								2012										2013											
		Jul	Aug	Sep	Oct	Nov	Dec (1)	Dec (2)	Jan	Jan/Feb	Feb/Mar	Mar	Mar/Apr	Apr/May	May/Jun	Jun/Jul	Jul/Aug	Aug/Sep	Sep/Oct	Oct/Nov	Nov/Dec	Dec/Jan	Jan/Feb	Feb/Mar	Mar	Apr	May	Jun	Jul		
Ametryn	100	0.1895	0.5047	0.0367	0.0282	0.0626	0.0752	0.0145	0.0377	0.0049	0.0076	0.0015	0.0043	0.0233	0.0087	0.0203	0.0135	0.0103	0.0460	0.1957	0.0892	0.2610	0.0073	0.0052	0.0099	0.0104	0.0145	0.0456			
Atrazine	100	3.5801	4.5104	5.2208	4.1935	5.3013	7.2753	2.0736	5.5597	0.9959	0.6350	0.1049	0.0897	0.3192	0.3242	0.3576	0.2733	0.4639	3.6034	3.5873	3.3966	4.8707	2.2373	0.4383	0.1962	0.1635	0.1863	1.1250			
Atrazine desethyl	100	0.1446	0.6692	0.5934	0.7494	1.6640	1.7463	0.5303	1.4481	0.2285	0.1593	0.0488	0.0477	0.0591	0.0533	0.1378	0.0727	0.1402	0.4152	1.0505	1.0604	1.1946	0.3848	0.1546	0.1558	0.1238	0.0984	0.0626			
Desisoproyl atrazine	100	0.0723	0.0186	0.1899	0.2132	0.3301	0.3509	0.1429	0.2633	0.0620	0.0384	0.0122	0.0095	0.0117	0.0106	0.0252	0.0172	0.0335	0.1144	0.2297	0.2221	0.2370	0.0697	0.0368	0.0304	0.0130	0.0134	0.0156			
Diuron	100	0.0467	1.0632	2.5415	3.3896	7.2974	7.9844	2.3298	3.3741	0.3778	0.2100	0.0391	0.0389	0.0553	0.0338	0.0579	0.1165	0.2459	1.6631	2.0939	2.6469	3.7376	1.3565	0.4067	0.2181	0.0758	0.0402	0.0213			
Hexazinone	100	0.0043	0.0011	0.0034	0.0038	0.0405	0.2227	0.0185	0.1013	0.0119	0.0034	0.0008	0.0010	0.0017	0.0014	0.0023	0.0014	0.0024	0.0051	0.0091	0.0077	0.0552	0.0057	0.0099	0.0176	0.0026	0.0021	0.0012			
Mecoprop	0	NR	NR	NR																											
Metolachlor	100	0.0991	0.2112	0.2294	0.2864	0.2093	0.1313	0.1019	0.0593	0.0093	0.0102	0.0024	0.0034	0.0354	0.1037	0.0854	0.0255	0.0224	0.2093	0.6993	0.2285	0.4464	0.0325	0.0148	0.0091	0.0091	0.0198	0.4320			
Prometryn	93	0.0020	0.0020	0.0002		0.0009	0.0009	0.0004	0.0006	0.0001	0.0001		0.0001	0.0003	0.0002	0.0002	0.0002	0.0001	0.0004	0.0014	0.0007	0.0019	0.0001	0.0001	0.0002	0.0002	0.0004	0.0019			
Simazine	100	0.0075	0.5429	0.0201	0.0039	0.0132	0.0178	0.0062	0.0097	0.0015	0.0024	0.0006	0.0005	0.0009	0.0011	0.0018	0.0013	0.0019	0.0065	0.0053	0.0072	0.0068	0.0054	0.0016	0.0010	0.0009	0.0011	0.0051			
Tebuthiuron	100	0.0019	0.0010	0.0010	0.0007	0.0035	0.0042	0.0011	0.0027	0.0013	0.0038	0.0009	0.0036	0.0037	0.0021	0.0042	0.0013	0.0020	0.0026	0.0038	0.0062	0.0048	0.0038	0.0035	0.0032	0.0026	0.0046	0.0020			
Terbutryn	44				0.0002	0.0016	0.0004		0.0196	0.0108									0.0000	0.0000	0.0000	0.0000	0.0046	0.0121	0.0034						
Terbutylazine	33	NR	NR	NR	NR	NR	NR	NR	0.0017	0.0005	0.0004	0.0001	0.0000	0.0001	0.0000				0.0003	0.0009											
Imadicloprid	100	0.0170	0.0008	0.0009	0.0010	0.0034	0.0028	0.0065	0.0367	0.0157	0.0032	0.0024	0.0012	0.0033	0.0036	0.0145	0.0038	0.0015	0.0117	0.0132	0.0074	0.0077	0.0011	0.0006	0.0011	0.0035	0.0045	0.0046			
MCPA	67	NR	0.0032	0.0033	0.0031	0.0032	0.0111	0.0086	0.0218	0.0193						0.0055	0.0017	0.0004	0.0112	0.0072	0.0048	0.0009	0.0021	0.0021	0.0022						
2,4-D	67	NR	0.0227	0.0234	0.0129	0.0175	0.0277	0.0241	0.0012	0.0015						0.0055	0.0111	0.0158	0.0296	0.0237	0.0246	0.0045	0.0049	0.0104	0.0045						
Triclopyr	63	NR	0.0004	0.0003	0.0013	0.0011	0.0513	0.0087	0.0076	0.0025						0.0017	0.0060	0.0008		0.0003	0.0003	0.0031	0.0008	0.0006	0.0015						
Haloxypol	44	NR	NR		0.0006	0.0004	0.0004	0.0003	0.0028	0.0014						0.0002				0.0001		0.0008	0.0027	0.0085	0.0023						
Fluroxypyr	26	NR	NR	0.0009	0.0032	0.0015	0.0016	0.0029	0.0028	0.0014																					
Propazin-2-hydroxy	74	NR	NR	NR	NR	NR	NR	NR	0.0064	0.0008	0.0012	0.0004	0.0005	0.0009	0.0003	0.0015	0.0010	0.0009	0.0027	0.0061	0.0090	0.0083	0.0029	0.0023	0.0051	0.0010	0.0013	0.0011			
Terbutylazine desethyl	11	NR	NR	NR	NR	NR	NR	NR	0.0011		0.0002					0.0001							0.0014								
Imazethapyr	33	NR	NR	NR	NR	NR	NR	NR	0.0001	0.0001	0.0001	0.0000				0.0001						0.0001	0.0003	0.0001	0.0000						
Imazapic	37	NR	NR	NR	NR	NR	NR	NR	0.0003	0.0002	0.0002	0.0001	0.0001	0.0001		0.0002	0.0001	0.0001					0.0000								
Acifluorfen	15	NR	NR	NR	NR	NR	NR	NR	0.0006	0.0008													0.0134	0.0088							
Isoproturon	44	NR	NR	NR	NR	NR	NR	NR	0.4024	0.0766						0.0258	0.0130	0.0079	0.0080	0.0337	0.0776	0.1287	0.0302	0.0113	0.0044						
Bromacil	0																														
Flumeturon	0																														
Clomazone	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0035	0.0032	0.0009	0.0006	0.0024	0.0024	0.0029	0.0035	0.0023	0.0051	0.0041	0.0102	0.0019			
Metsulfuron methyl	48	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0000															
Flusilazole	4	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0000															
Metribuzin	11	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0024	0.0286	0.0214			
Imidacloprid urea	7	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0002	0.0004		
3,4 Di Cl Aniline	11	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0131	0.0104	0.0037		

NR not reported,  not detected, the cells are coloured on a gradient from yellow (indicating the lowest detected concentrations) to orange (indicating median concentrations or 50th percentile) to maroon (indicating the highest concentrations recorded).

NR not reported,  not detected, *analysis undertaken by DSITIA, the cells are coloured on a gradient from yellow (indicating the lowest detected concentrations) to orange (indicating median concentrations or 50th percentile) to maroon (indicating the highest concentrations recorded).

Pesticide exposure within Barratta Creek Catchment

Table 14: Pesticide concentrations detected in ED passive samplers at Site 4 between July 2011 and July 2013.

	Frequency of detection (%)	Site 4: Lower Barratta																													
		2011							2012										2013												
		Jul	Aug	Sep	Oct	Nov	Dec (1)	Dec (2)	Jan	Jan/Feb	Feb/Mar	Mar	Mar/Apr	Apr/May	May/June	June/Jul	Jul/Aug	Aug/Sep	Sep/Oct	Oct/Nov	Nov/Dec	Dec/Jan	Jan/Feb	Feb/Mar	Mar	Apr	May	June	Jul		
Ametryn	100	0.0349	0.1179	0.0133	0.0079	0.0553	0.0852	0.0132	0.0240	0.0131	0.0100	0.0011	0.0071	0.0120	0.0207	0.0236	0.0284	0.0088	0.0219	0.0564	0.0816	0.0696	0.0118	0.0132	0.0109	0.0150	0.0324	0.0263			
Atrazine	100	0.2573	2.1556	0.2297	0.7574	0.8779	0.7782	0.4254	2.0500	0.7836	0.2403	0.0828	0.0602	0.1282	0.3838	0.3372	0.2698	0.1860	0.9153	0.3235	0.7023	1.5780	1.4439	0.5214	0.0700	0.1207	0.0966	0.1966			
Atrazine desethyl	100	0.0190	0.1309	0.0682	0.3602	0.5045	0.4025	1.5046	0.4999	0.1978	0.0598	0.0352	0.0321	0.0366	0.0605	0.0839	0.0731	0.0801	0.1358	0.0355	0.4760	0.4389	0.2945	0.1274	0.0486	0.0709	0.0591	0.0409			
Desisoproyl atrazine	100	0.0051	0.0118	0.0115	0.0149	0.0597	0.0731	0.0228	0.0770	0.0365	0.0120	0.0078	0.0050	0.0059	0.0107	0.0186	0.0144	0.0155	0.0224	0.0030	0.0787	0.0882	0.0585	0.0245	0.0080	0.0062	0.0083	0.0050			
Diuron	100	0.0189	0.0194	0.0559	0.3658	0.9552	1.2040	0.4775	1.3689	0.4370	0.1098	0.0416	0.0564	0.0300	0.0285	0.0796	0.0794	0.0578	0.1839	0.3238	0.2803	0.8813	0.7974	0.3784	0.1039	0.0475	0.0337	0.0182			
Hexazinone	100	0.0035	0.0020	0.0017	0.0029	0.0154	0.0415	0.0151	0.0248	0.0187	0.0019	0.0007	0.0017	0.0017	0.0015	0.0035	0.0041	0.0030	0.0034	0.0044	0.0052	0.0079	0.0064	0.0047	0.0074	0.0063	0.0032	0.0014			
Mecoprop	0	NR	NR	NR																											
Metolachlor	100	0.0212	0.0094	0.0068	0.0222	0.0254	0.0100	0.0054	0.0179	0.0030	0.0016	0.0013	0.0013	0.0069	0.0925	0.0573	0.0340	0.0106	0.0137	0.0839	0.0618	0.0975	0.0183	0.0060	0.0015	0.0039	0.0049	0.0305			
Prometryn	89	0.0007	0.0010	0.0002		0.0006	0.0009		0.0004	0.0002	0.0002		0.0001	0.0002	0.0004	0.0003	0.0004	0.0001	0.0003	0.0005	0.0006	0.0005	0.0002	0.0002	0.0002	0.0003	0.0006	0.0005			
Simazine	100	0.0124	0.0996	0.0051	0.0023	0.0026	0.0023	0.0012	0.0045	0.0013	0.0008	0.0004	0.0003	0.0005	0.0013	0.0013	0.0011	0.0010	0.0014	0.0003	0.0013	0.0021	0.0028	0.0013	0.0004	0.0006	0.0006	0.0006			
Tebuthiuron	100	0.0019	0.0009	0.0007	0.0005	0.0024	0.0018	0.0004	0.0008	0.0009	0.0009	0.0006	0.0019	0.0021	0.0021	0.0017	0.0013	0.0017	0.0023	0.0019	0.0027	0.0017	0.0022	0.0021	0.0014	0.0020	0.0037	0.0023			
Terbutryn	26					0.0005	0.0004		0.0033	0.0041													0.0038	0.0019							
Terbutylazine	22	NR	NR	NR	NR	NR	NR	NR	0.0007	0.0003	0.0001	0.0000				0.0001	0.0001														
Imadicloprid	93	0.0029	0.0008			0.0005	0.0008	0.0004	0.0131	0.0112	0.0008	0.0011	0.0010	0.0019	0.0023	0.0041	0.0062	0.0010	0.0011	0.0032	0.0020	0.0021	0.0040	0.0014	0.0017	0.0011	0.0023	0.0010			
MCPA	59	NR		0.0004	0.0001		0.0004	0.0007	0.0082	0.0299						0.0092	0.0013	0.0002	0.0004	0.0010	0.0003	0.0015	0.0054	0.0025	0.0046						
2,4-D	67	NR	0.0009	0.0015	0.0005	0.0006	0.0020	0.0023	0.0003	0.0004						0.0160	0.0019	0.0006	0.0012	0.0019	0.0012	0.0050	0.0064	0.0024	0.0018						
Triclopyr	44	NR		0.0002	0.0002		0.0035	0.0031	0.0028	0.0019						0.0010	0.0010	0.0008				0.0020	0.0005	0.0005							
Haloxypol	26	NR	NR		0.0002			0.0014	0.0011													0.0005	0.0022	0.0027	0.0023						
Fluroxypyr	11	NR	NR					0.0004	0.0014	0.0011																					
Propazin-2-hydroxy	74	NR	NR	NR	NR	NR	NR	NR	0.0043	0.0013	0.0008	0.0002	0.0008	0.0009	0.0009	0.0012	0.0016	0.0017	0.0025	0.0038	0.0053	0.0049	0.0019	0.0006	0.0018	0.0016	0.0025	0.0014			
Terbutylazine desethyl	4	NR	NR	NR	NR	NR	NR	NR	0.0004																						
Imazethapyr	26	NR	NR	NR	NR	NR	NR	NR	0.0001	0.0001	0.0000	0.0000											0.0004	0.0003	0.0001						
Imazapic	56	NR	NR	NR	NR	NR	NR	NR	0.0004	0.0005	0.0002	0.0001	0.0000	0.0001	0.0001	0.0002	0.0002	0.0001				0.0001	0.0002	0.0002	0.0001		0.0002				
Acifluorfen	4	NR	NR	NR	NR	NR	NR	NR		0.0002																					
Isoxaflutole	44	NR	NR	NR	NR	NR	NR	NR	0.2737	0.0744						0.0206	0.0227	0.0223	0.0029	0.0138	0.0626	0.0965	0.0978	0.0247	0.0082						
Bromacil	4																		0.0004												
Flumeturon	0																														
Clomazone	0	NR	NR	NR	NR	NR	NR	NR	NR		NR																				
Metsulfuron methyl	41	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0018	0.0019	0.0012		0.0008		0.0006	0.0012	0.0006	0.0018	0.0021	0.0023	0.0021			
Flusilazole	4	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR		0.0000														
Metribuzin	11	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0016	0.0030	0.0125			
Imidacloprid urea	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	
3,4 Di Cl Aniline	11	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.0105	0.0082	0.0028		

NR not reported,  not detected, the cells are coloured on a gradient from yellow (indicating the lowest detected concentrations) to orange (indicating median concentrations or 50th percentile) to maroon (indicating the highest concentrations recorded).

Table 15: Pesticide concentrations detected in PDMS passive samplers at Site 1 and Site 4 between July 2011 and July 2013.

		Frequency of detection (%)	Site 1: Upper Barratta																																			
			2011												2012												2013											
			Jul	Aug	Sep	Oct	Nov	Dec (1)	Dec (2)	Jan	Jan/Feb	Feb/Mar	Mar	Mar/Apr	Apr/May	May/Jun	Jun/Jul	Jul/Aug	Aug/Sep	Sep/Oct	Oct/Nov	Nov/Dec	Dec/Jan	Jan/Feb	Feb/Mar	Mar	Apr	May	Jun									
Atrazine	100	1.1799	2.7980	9.1460	6.4910	5.4310	2.8550	3.3864	1.1615	0.2678	0.4737	0.0755	0.2814	0.7361	0.5279	0.7124	2.5800	2.4540	10.9890	4.8080	3.7420	5.2910	0.5950	0.2660	0.2060	0.2080	2.0800	2.7275										
Metolachlor	93	0.0653	0.0200	1.1220	0.0410	0.0170	0.0300	0.0138	0.0078		0.0034		0.0163	0.0243	0.0356	0.3379	0.0605	0.1250	5.3130	0.4340	1.2560	0.1255	0.0635	0.0245	0.0270	0.0280	0.3100	1.7055										
Ametryn	48	0.0453	0.0220				0.0680		0.0269							0.0591				1.9960	0.0560	0.1020	0.0505	0.0600	0.0370	0.1780	0.0535											
Methamidiphos	4		0.9730																																			
Metribuzin	4			0.3990																																		
Propazine	63		0.0180	0.0380	0.0620	0.0610	0.0380	0.0225	0.0071	0.0027	0.0043					0.0110	0.0064	0.0700	0.0220	0.0330	0.0270				0.0077	0.0125												
Pendimethalin	44		0.0220	0.0007		0.0004				0.0006				0.0005	0.0434	0.0023	0.0005	0.0003			0.0016		0.0003	0.0005														
Galaxolide	22							0.0002		0.0001	0.0001					0.0001	0.0001			0.0001																		
Chlorpyrifos	22										0.0005	0.0003				0.0001	0.0001								0.0003	0.0011												
Fipronil	19		0.0020									0.0026					0.0041	0.0006	0.0005																			
Terbutylazine	15				0.0060	0.0060		0.0041										0.0076																				
Tonalid	4										0.0004							0.0000																				
Permethrin Isomers	4																		0.0065																			
Prometryn	4																																					
DEETe	0																																					
Diazinone	0																																					
Phosphamidon	0																																					
2,6-Di-t-BUTYL-p-CRESOL (bht)e	0																																					

		Frequency of detection (%)	Site 4: Lower Barratta																																			
			2011												2012												2013											
			Jul	Aug	Sep	Oct	Nov	Dec (1)	Dec (2)	Jan	Jan/Feb	Feb/Mar	Mar	Mar/Apr	Apr/May	May/Jun	Jun/Jul	Jul/Aug	Aug/Sep	Sep/Oct	Oct/Nov	Nov/Dec	Dec/Jan	Jan/Feb	Feb/Mar	Mar	Apr	May	Jun									
Atrazine	100	0.3645	0.7970	0.7550	0.5940	0.4690	1.4490	4.2325	3.2074	0.3805	1.5895	0.1337	0.2053	0.8099	1.3554	1.1442	0.4380	0.6700	1.5650	0.5950	0.7600	2.8430	1.2690	0.2670	0.4200	0.4840	0.1990	1.1240										
Metolachlor	100	0.0859	0.0660	0.0560	0.0930	0.0600	0.0370	0.1918	0.0936	0.0160	0.0156	0.0098	0.0163	0.1014	0.4289	0.5087	0.1230	0.1490	0.0570	0.2490	0.1400	0.2430	0.0740	0.0150	0.0270	0.0240	0.2160											
Ametryn	52	0.0888	0.1730				0.1390	0.0795	0.0799		0.0757										0.0540	0.1440	0.1100	0.0850	0.0880	0.1450	0.0930	0.1110										
Methamidiphos	0																																					
Metribuzin	0																																					
Propazine	37						0.0110	0.0181	0.0179		0.0098					0.0029		0.0056	0.0034	0.0050	0.0120	0.0110																
Pendimethalin	15											0.0668			0.0019	0.0018										0.0008												
Galaxolide	15							0.0001								0.0001	0.0001			0.0001																		
Chlorpyrifos	4																0.0000																					
Fipronil	4																0.0001																					
Terbutylazine	0																																					
Tonalid	0																																					
Permethrin Isomers	0																																					
Prometryn	0																																					
DEET	15															0.0089	0.0070	0.0140	0.0067																			
Diazinon	7															0.0009	0.0004																					
Phosphamidon	4			0.1080																																		
2,6-Di-t-BUTYL-p-CRESOL (bht)	4															0.0004																						

NR not reported,  not detected, the cells are coloured on a gradient from yellow (indicating the lowest detected concentrations) to orange (indicating median concentrations or 50th percentile) to maroon (indicating the highest concentrations recorded).

References

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