

Spatial and Temporal Variability in Pesticide Exposure Downstream of a Heavily Irrigated Cropping Area: Application of Different Monitoring Techniques

O'Brien, D. , Lewis, S. , Davis, A. , Gallen, C. , Smith, R. , Turner, R. , Warne, M. St. J. , Turner, S. , Caswell, S. , Mueller, J. F. and Brodie, J.

Author post-print (accepted) deposited by Coventry University's Repository

Original citation & hyperlink:

O'Brien, D. , Lewis, S. , Davis, A. , Gallen, C. , Smith, R. , Turner, R. , Warne, M. St. J. , Turner, S. , Caswell, S. , Mueller, J. F. and Brodie, J. (2016) Spatial and Temporal Variability in Pesticide Exposure Downstream of a Heavily Irrigated Cropping Area: Application of Different Monitoring Techniques. *Journal of Agricultural and Food Chemistry*, volume 64 (20): 3975–3989

<http://dx.doi.org/10.1021/acs.jafc.5b04710>

DOI 10.1021/acs.jafc.5b04710

ISSN 0021-8561

ESSN 1520-5118

Publisher: American Chemical Society

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Journal of Agricultural and Food Chemistry*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see

<http://dx.doi.org/10.1021/acs.jafc.5b04710>

Copyright © and Moral Rights are retained by the author(s) and/ or other copyright owners. A copy can be downloaded for personal non-commercial research or study, without prior permission or charge. This item cannot be reproduced or quoted extensively from without first obtaining permission in writing from the copyright holder(s). The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the copyright holders.

This document is the author's post-print version, incorporating any revisions agreed during the peer-review process. Some differences between the published version and this version may remain and you are advised to consult the published version if you wish to cite from it.

Article

Spatial and temporal variability in pesticide exposure downstream of a heavily irrigated cropping area: the application of different monitoring techniques

Dominique O'Brien, Stephen Lewis, Aaron Davis, Christie Gallen, Rachael Smith, Ryan D.

Turner, Michael St. J. Warne, Scott Turner, Stewart Carswell, Jochen F. Mueller, and Jon Brodie

J. Agric. Food Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.jafc.5b04710 • Publication Date (Web): 11 Jan 2016

Downloaded from <http://pubs.acs.org> on January 15, 2016

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Publications

Title: Spatial and temporal variability in pesticide exposure downstream of a heavily irrigated cropping area: the application of different monitoring techniques

Dominique O'Brien^{1*}, Stephen Lewis¹, Aaron Davis¹, Christie Gallen², Rachael Smith³, Ryan Turner³, Michael Warne³, Scott Turner⁴, Stewart Caswell⁴, Jochen F. Mueller², and Jon Brodie¹

¹ Catchment to Reef Research Group, TropWATER, ATSIP, DB145, James Cook University, Townsville, Queensland, Australia,

^{*} Corresponding author contact details: dominique.obrien@jcu.edu.au; Ph: (+617) 4781 4680

² The University of Queensland, Entox, 39 Kessels Road, Coopers Plains, QLD 4108, Australia

³ Water Quality and Investigations, Environmental Monitoring and Assessment Science, Science Delivery, Queensland Department of Science, Information Technology and Innovation (DSITI), Dutton Park Queensland 4102, Australia

⁴ Organic Chemistry, Forensic and Scientific Services, Health Support, Queensland Department of Health, Queensland Government, 39 Kessels Road Coopers Plains QLD 4108

Abstract:

Pesticide exposure threatens many freshwater and estuarine ecosystems around the world. This study examined the temporal and spatial trends of pesticide concentrations in a waterway within an agriculturally developed dry-tropics catchment using a combination of grab and passive sampling methods over a continuous two year monitoring program. A total of 43 pesticide residues were detected with seven pesticides exceeding ecologically relevant water quality guidelines/trigger values during the study period and four (ametryn, atrazine, diuron and metolachlor) of these exceeding guidelines for several months. The presence and concentration of the pesticides in the stream coincided with seasonal variability in rainfall, harvest timing/cropping cycle and management changes. Our sampling approach demonstrates that the application of these complementary sampling techniques (both grab and passive sampling) were effective to establish pesticide usage patterns in upstream locations where application data are unavailable.

Keywords

Great Barrier Reef, pesticides, herbicides, passive sampling, sugarcane, irrigation

39 Introduction

40 Pesticide residues are now ubiquitous in many streams that drain agricultural, urban and
41 industrial lands around the globe and concerns regarding their environmental risks have led
42 to the implementation of numerous management regulations and assessment programs¹⁻⁵.
43 However, many monitoring programs are limited by costs associated with sampling and
44 laboratory methods; depending on the monitoring aims, a tradeoff is often made between
45 sampling frequency, spatial coverage and analytical cost⁶. Sampling within tropical areas is
46 further complicated by the variable local weather profiles (i.e. rain driven ephemeral flows),
47 extreme weather events and remote locations, that when combined with monitoring
48 limitations has resulted in limited data available on pesticide concentrations in tropical areas
49 compared to the data available from temperate areas.

50 The application of both grab and passive sampling methods allows for more pesticide
51 residues (and degradation products) to be examined in a cost effective manner and to assess
52 how those concentrations vary in space and time⁷. Such monitoring programs are
53 particularly useful when examining the spatial and temporal variability of pesticide
54 concentrations in streams in response to factors such as timing of application, seasonal
55 variability in rainfall/runoff and management change. However, application of such
56 approaches is rare in tropical catchments.

57 Pesticides, along with nutrient and sediments, transported to the Great Barrier Reef (GBR)
58 have been identified as a key issue for management under the Reef Water Quality Protection
59 Plan⁸⁻¹⁰. In response, the Queensland State and Australian Federal Governments
60 implemented the Paddock to Reef Integrated Monitoring Modelling and Reporting program
61 (Paddock to Reef) which encourages the agricultural industry to adopt best management
62 practices in order to improve water quality in the GBR¹¹. Five herbicides including diuron,
63 atrazine, ametryn, hexazinone and tebuthiuron have been identified as priority herbicides to

64 be targeted for reduction in their offsite transport. Among these five herbicides, diuron has
65 been widely recognised as one that consistently poses the highest ecological risk¹²⁻¹³ which
66 is manifested through regulation on its use introduced by the Australian Pesticides and
67 Veterinary Medicines Authority (APVMA) in 2011 and 2012. As a result, farmers have
68 sought out a range of alternative pesticides as replacements¹² and many of these alternatives
69 are now detectable in several rivers or tributaries that flow into the sea along the GBR
70 coastline¹⁴. Unfortunately, pesticide sales or usage data in the GBR are not publically
71 available and with the exception of ‘anecdotal evidence’ (i.e. farmer/industry stakeholder
72 communications on usage within the region) changes in pesticide use cannot be quantified.
73 Barratta Creek, located in the dry tropics of north-eastern Australia (Figure 1), and with a
74 large proportion of sugarcane cropping in the catchment, has been identified as a high risk
75 area compared to other GBR catchments as pesticide concentrations¹⁵⁻²⁰ exceed both
76 Australian and New Zealand²¹ water quality guideline trigger values and international²²
77 guideline values^{15-20, 23-24}. While previous studies have examined the concentrations and
78 loads of pesticide residues at various sites along Barratta Creek, no systematic and
79 continuous monitoring approach to examine spatial and temporal variations within Barratta
80 Creek has been undertaken. This study has undertaken continuous monitoring of pesticide
81 concentrations over two years (July 2011 to July 2013) at four sites within Barratta Creek
82 with an aim to assess pesticide presence and the temporal and spatial variability of pesticide
83 residues in this intensely developed tropical catchment.

84 **Materials and methods**

85 **Study site.** Barratta Creek drains a large area of the Burdekin-Haughton floodplain and has
86 a total catchment area of 1,167 km² which covers 0.9% of the Burdekin Dry Tropics Natural
87 Resource Management region²⁵. Land use within the Barratta Creek catchment includes

88 grazing on native pastures (60% of area) and irrigated sugarcane production (approximately
89 31%) with the remaining catchment area consisting of wetland/conservation, minimal use
90 and other crops²⁵; other crops includes legumes (i.e. chickpeas, soybeans etc.) grown in
91 fallow sugarcane paddocks as well as mango orchards, mixed horticulture, cotton and rice.
92 Sugarcane within the Barratta catchment accounts for approximately one quarter of the total
93 land area cultivated for sugarcane production across the whole Burdekin Region. The creek
94 network drains into nationally (Australian Nature Conservation Agency; ANCA) and
95 internationally (Ramsar) recognized wetlands and ultimately the World Heritage listed
96 GBR¹⁸⁻¹⁹. The Barratta Creek catchment has been extensively developed for sugarcane
97 supported by furrow irrigation, the introduction of which has altered the previously
98 intermittent flow regime of Barratta Creek to one of constant flow¹⁷ and raised local water
99 tables²³. The sampling sites monitored as part of this study (Figure 1) were all located within
100 the area identified by the directory of important wetlands in Australia²⁶. The three freshwater
101 sites (Upper Barratta Creek, West Barratta Creek, and East Barratta Creek) have been
102 subjected to previous monitoring efforts¹⁶⁻¹⁹ but not at this level of sophistication. The end
103 of catchment estuarine site (Lower Barratta Creek) was within the Bowling Green Bay
104 Ramsar wetland boundary. The percentage contribution of grazing, cropping and
105 conservation/other land uses above the monitored sampling sites are outlined in Table 1²⁵.

106 **Monitoring methods.** Water sampling across the four sites was undertaken through the
107 combination of grab (point in time measurements), time/flow weighted sampling using an
108 automated sampler (multiple point in time measurements; at Upper Barratta Creek only –
109 data provided by Queensland Department of Science, Information Technology and
110 Innovation (DSITI)) and passive sampling techniques (time-integrated measurement).
111 Passive sampling devices facilitate the accumulation of chemicals from water into a sorbent.
112 When calibrated correctly the mass accumulated by a passive sampler can be used to provide

a time weighted average (TWA) measurement of a contaminant during the exposure period. Two passive sampling devices (PSDs) were employed: the Chemcatcher[®] and the polydimethylsiloxane (PDMS) passive samplers. The Chemcatcher[®] passive sampler configured with styrenedivinylbenzene (SDB) Empore Disk (ED) and polyethersulfone (PES) membranes in the original Teflon[®] housing²⁷⁻²⁹ was used for sampling the polar chemicals. The PDMS passive samplers accumulate less polar chemicals and have been employed in assessing the concentrations of hydrophobic organic compounds³⁰⁻³². The PDMS strips (410 μm thick, 2.5 cm wide, 92 cm length; Purple Pig Australia), were deployed inside stainless steel cages. Passive sampling kinetics for each deployment were adjusted to the deployment specific flow conditions using the passive flow monitors (PFM) in replicate³³⁻³⁴. Further, water salinity/conductivity is known to influence the calibration method employed so the water electrical conductivity (EC) was recorded during site visits using a Hydrolab Quanta (ECO Environmental) and the data used to refine the calibration of the passive sampling devices³³.

Passive samplers were deployed in replicate at each site attached to a length of chain on an overhanging tree branch such that the samplers were exposed to the main channel flow and remained submerged for the duration of the deployments. Previous studies show that PSDs can under- or over- estimate the TWA concentrations of certain analytes when fluctuations in both concentration and flow occur during the deployment period³⁵⁻³⁷. As such, each deployment period during this study lasted for approximately four weeks except when a runoff event occurred. When a runoff event occurred samplers were exchanged within the next few days to ascertain that samplers remained in a linear uptake phase^{36, 38}. During each site visit two 1 L grab samples were collected using a 3-5 m extendable sampling pole from ~ 20 cm below the water surface in amber glass bottles. The passive and grab samples were kept on ice during transport and stored at 4 °C prior to analysis.

Rainfall and stream water level data were obtained from Queensland Department of Natural Resources and Mines³⁹ Northcote gauging station (119101A) located ~ 50 metres downstream of the Upper Barratta Creek sampling site. During January 2013, the rain gauge failed and the rainfall associated with ex-Tropical Cyclone Ita was not recorded. To fill in the missing data the rainfall recorded at the nearest gauging site (119003A: Haughton River at Powerline, located ~9 km to the North West) was obtained.

Sample extraction and analysis. Analysis of all grab water samples was undertaken by the Queensland Health Forensic and Scientific Services (QHFSS) using a Varian 3400 gas chromatograph (GC) with a Finnigan A200S liquid autosampler (splitless; injector temperature 295°C; GC column: J&W DB-1, originally 20 m, 0.2 mm id, 0.33 μ m film thickness; temperature program: 65°C (isothermal 2 min), 20°C min⁻¹ to 295°C (isothermal 10 min)) and coupled to a Finnigan SSQ 710 single stage quadrupole mass selective detector. Detection limits were defined as three times blank values or where a compound was not identified in the blanks, as three times signal to noise ratio. The passive samplers were extracted for the quantification of pesticide concentration at the University of Queensland. A full description of the passive sampling extraction and analysis methods employed in this study has been described previously^{28, 30}. Analysis of the extracted samples employed liquid and gas chromatography–mass spectrometry (LC-MS/MS and GCMS). All results have been reported as μ g.L⁻¹ (i.e. equivalent to ppb). Sample replicates were analysed separately to ensure the reproducibility of the measurements obtained.

Assessment of ecosystem risk. Guidelines have been established with respect to the percent of species theoretically protected when concentrations are maintained below a certain concentration (PC). Pesticide concentrations across the study sites were compared to the PC95 and PC99 (theoretically protect 95% or 99% of species in the ecosystem being considered) ecological threshold values proposed by Smith et al⁴⁰, then to any existing

ANZECC and ARMCANZ²¹ trigger values (TV). It is general practice that the PC95 values are applied for ecosystems already impacted by anthropogenic activities. However, as the Barratta Creek system is of higher ecological significance as it lies within ANCA⁴¹ (East/West/Upper Barratta sites) and Ramsar (Lower Barratta) listed wetlands, management of this site should aim to maintain pesticide concentrations at levels that protect 99% of species and thus the PC99 values are more appropriate when assessing ecosystem risk of this system. Overall, ecosystem risk per site was assessed through the calculation of the 95th percentile concentration of individual pesticides per sampling year (i.e. the highest concentration that falls within 95% of all samples collected; where concentrations in samples were below the analytical reporting limit values half the detection limits were used in the calculation) to compare to both the PC95 and PC99 guideline values (method described in Smith et al.²⁰).

Results

Environmental condition. Electrical conductivity (EC) and rainfall data were obtained to inform the environmental conditions during the study period relative to long term averages. The study period captured two of the wettest years on record within the catchment with ~1200 mm falling during both sampling years (mean rainfall is ~ 700 mm). The data obtained are presented in more detail in the supporting materials.

Pesticides detected and frequency of detection. A total of 48 organic compound residues were detected over the two year monitoring program including 32 herbicides (including three breakdown products), 10 insecticides (including one breakdown product and the insect repellent DEET) and one fungicide. Non-pesticide organic compound residues detected during the analysis included the fuel and oil additive 2,6-di-t-butyl-p-cresol (BHT), a plasticizer (bisphenol A) and two polycyclic musks (galaxolide and tonalid). In addition to

the known pesticide contaminants of concern, pesticide residues were detected that have not previously been reported within the GBR catchment area (see unshaded chemicals in Table 2). Grab sampling detected 17 residues (14 herbicides, 1 insecticide, 2 non-pesticides) and 45 residues (32 herbicides, 9 insecticides, one fungicide, 3 non-pesticides) were detected using PSDs. Of the PSDs samplers, the Chemcatcher[®] passive sampler detected 33 compounds in total including an additional 22 residues (18 herbicides, 2 insecticides and one fungicide and one herbicide additive) not detected by the grab method. The PDMS passive samplers detected ten residues (4 herbicides, 2 herbicide breakdown products, 2 insecticides one fungicide and one fuel/oil additive) that were not detected by either the grab or Chemcatcher[®] sampling methods. Overall, grab samples detected 3 residues (bifenthrin, bisphenol A and tris (dichloropropyl) phosphate) not detected by the PSDs.

On a concentration and detection frequency basis, the nine key pesticides identified were diuron (0.01 – 12.8 $\mu\text{g.L}^{-1}$; 88% detection in grabs and 100% in PSDs); atrazine (0.017 – 11.5 $\mu\text{g.L}^{-1}$; 96% detection in grabs and 100% in PSDs); ametryn (0.001 – 1.99 $\mu\text{g.L}^{-1}$; 60% detection in grabs and 100% in PSDs); metolachlor (0.003 – 5.31 $\mu\text{g.L}^{-1}$; 48% detection in grabs and 100% in PSDs); hexazinone (0.001 – 0.327 $\mu\text{g.L}^{-1}$; 22% detection in grabs and 100% in PSDs); simazine (below detection limit (BDL) – 0.543 $\mu\text{g.L}^{-1}$; 16% detection in grabs and 98% in PSDs); imidacloprid (BDL – 0.504 $\mu\text{g.L}^{-1}$; 7% detection in grabs and 93% in PSDs); tebuthiuron (BDL– 0.007 $\mu\text{g.L}^{-1}$; 0% detection in grabs and 100% in PSDs) and; prometryn (BDL – 0.03 $\mu\text{g.L}^{-1}$; 2% detection in grabs and 84% in PSDs). Chemical specific detection frequencies are presented in Table 2 with site and method specific detection frequency and concentrations for the nine key pesticides presented in Table 3. Further analysis presented in this paper predominantly focuses on the nine key pesticides identified.

The PSDs employed in this study measure a TWA concentration for the pesticide residues detected and cannot be directly compared to the point in time (PIT) concentration

measurements made using grab sampling without recognising the differences in the two different methods. However, the ranges of pesticide concentrations when detected by two or more sampling methods showed very good agreement (Table 3). Further, there was a similar temporal rise and fall trend in the concentrations measured at each site when comparing the TWA and PIT values (Figure 3-5). While the TWA and PIT values were generally “in range” when detected by both grab and passive sampling methods, the agreement became less clear when the frequency of pesticide detection in the grab water samples fell below the analytical limit of reporting (e.g. ametryn and metolachlor); the PSDs were able to detect these herbicides at lower quantifiable limits for longer periods of time during the study period. The measured TWA and PIT pesticide concentrations have been plotted in Figure 3-5.

Summary concentrations of atrazine, diuron, ametryn, metolachlor, hexazinone and imidacloprid measured using the Chemcatcher[®] PSD are shown in the box plots in Figure 6. The ranges and medians of atrazine, diuron, ametryn and hexazinone concentrations over the two year sampling period were comparable across the three freshwater sampling sites. While the measured concentration ranges of metolachlor were comparable across the three freshwater sites, the median concentration measured at East Barratta was higher than the Upper Barratta and West Barratta sites. Further, while the median concentrations of imidacloprid measured across the three freshwater sites were similar, a greater range was recorded at the Upper Barratta site. The concentrations of all pesticides measured at the Lower Barratta estuarine site were generally between one third and one half the concentrations measured within the freshwater reaches of the creek (Figure 6).

Temporal changes in pesticide concentration. In general, the highest pesticide concentrations detected during this study across all sampling sites (and recorded by the different techniques) occurred from August 2011 to January 2012 and from October 2012 to

January 2013. Peak pesticide concentrations in Barratta Creek coincided with end of the sugarcane harvest period (November-December) and with the onset of the first wet season rains in November 2011 and December 2012, respectively. Consistently, the nine key pesticides were detected at highest levels between July and December. Six of the nine pesticides (diuron, atrazine, ametryn, metolachlor, hexazinone and imidacloprid) are registered for use in sugarcane and the temporal change in concentrations reflected usage patterns within the industry; i.e. the highest concentrations were measured during the sugarcane harvest period (July to December), with concentrations increasing as the harvest period progressed (for example see Figure 2). Concentrations of the herbicides ametryn, atrazine and diuron were highest between August 2011 and February 2012 and September 2012 and February 2013. Concentrations of metolachlor followed a similar trend; however, there were additional fluctuations in the TWA concentrations recorded across the study period. Concentrations of hexazinone and imidacloprid increased in association with rainfall-runoff driven discharge within the creek (Figure 4). The maximum TWA and PIT concentrations of atrazine and diuron recorded during our monitoring program were 11.5 and 12.3 $\mu\text{g atrazine.L}^{-1}$ and 9.2 and 12.8 $\mu\text{g diuron.L}^{-1}$, respectively. Peak concentrations of atrazine and diuron occurred during low flow conditions during October, 2011 and December, 2012 (grab sampling) and during August, 2011, November, 2011 and December, 2012 (passive sampling).

Pesticide concentrations rapidly decreased following each subsequent rainfall event throughout the wet season and then generally increased following the onset of either crop planting or the crop harvest period (June) when pesticides (predominant examples include: pre-emergent herbicides: atrazine, diuron, ametryn, metribuzin, metolachlor and imazapic; knockdown herbicides: 2,4-D and MCPA; and insecticides: imidacloprid, permethrin and bifenthrin) are applied to cane blocks. Exceptions to this pattern included the herbicide

terbuthylazine which is registered for use in legume fallow crops but not in sugarcane; the insecticide bifenthrin and herbicides imazapic and isoxaflutole which are registered for use on sugarcane. The latter herbicides were predominantly detected during the non-harvest period from December through June. Reductions in pesticide concentrations as the wet season progressed were observed with each subsequent rainfall event. During the 2011/2012 water year, rainfall extended into the winter months which led to a delay in the 2012 sugar harvest⁴² and coincided with an increase in the TWA concentrations of metolachlor, ametryn and imidacloprid.

Site-specific differences in the contaminant profiles included the detection of clomazone (herbicide) and imidacloprid urea (insecticide) only at West Barratta; fluometuron (herbicide) at Upper and East Barratta; mecoprop (herbicide) only at Upper Barratta; and the failure to detect bifenthrin (insecticide) at Upper Barratta and bromacil (herbicide) at East Barratta (Table 2).

Overall, both the grab and passive sampling techniques generally displayed similar concentration ranges and seasonal trends. The pesticide concentrations detected in the grab samples followed the same trend over time as the TWA measurements. Average concentrations of atrazine and diuron measured using both the grab and Chemcatcher[®] sampling methods at the three freshwater sampling sites were higher during the June – November harvest period (i.e. when pesticides are being reapplied to plots post-harvest) compared to the non-harvest period (December – May), with t-test p values of <0.05 across all sites. There was little to no difference in the average concentrations of ametryn, metolachlor, prometryn, simazine and tebuthiuron when compared across the same periods (t-test p values varied from between 0.01 and 0.37 for each pesticide across the three freshwater sites). For all other pesticide residues there was no significant difference between the average calculated during both the harvest and non-harvest periods.

Ecosystem risk. Australian water quality guidelines²¹ exist (or have been proposed⁴⁰) for 12 of the detected pesticides. Of those 12 pesticides, the guidelines for 2,4-D, imazethapyr, bromacil, MCPA and tebuthiuron were not exceeded while hexazinone, atrazine, simazine, diuron, ametryn, imidacloprid and metolachlor concentrations exceeded at least one guideline value (TV or 99/95% species protection concentration (PC) values – PC99/PC95) in at least one sample collected across the fresh (Table 4) or estuarine sites (Table 5) using either grab or passive methods. Table 6 outlines the 95th percentile concentrations for each detected pesticide with an established or proposed guideline. Diuron 95th percentile concentrations exceeded both the existing TV and the proposed PC95 guidelines across all fresh and estuarine sites for both years of sampling. The atrazine 95th percentile concentrations did not exceed the existing TV but did exceed the proposed PC95 guideline at Upper and East Barratta sites over both sampling years and at West Barratta during 2012-2013. Atrazine and simazine use has been banned in most European countries⁴³. Ametryn 95th percentile concentrations exceeded the proposed PC95 guideline at Upper and West Barratta in 2012-2013; East Barratta over both sampling years and the proposed marine PC95 guideline at the estuarine site during 2011-2012. Metolachlor 95th percentile concentrations exceeded the existing TV across all freshwater and estuarine sampling sites over all sampling years; however, no proposed PC95 guidelines have been established and no guideline values for metolachlor have been proposed for marine/estuarine systems. The only other 95th percentile concentration to exceed a guideline or TV occurred for imidacloprid at Upper Barratta for the 2011-2012 sampling year. The 95th percentile concentrations of ametryn, atrazine and diuron exceeded the PC99 freshwater values across all freshwater sites; the 95th percentile imidacloprid concentrations exceeded PC99 freshwater values at Upper Barratta during 2011-2012; and the 95th percentile hexazinone concentrations exceeded the PC99 freshwater values at Upper Barratta during 2012-2013

and West Barratta during 2011-2012. The marine PC99 values were exceeded in the samples collected at Lower Barratta (estuarine site) for ametryn and diuron across both sampling years and atrazine (including the estuarine specific guideline) during 2011-2012. The 95th percentile concentrations of simazine across the two sampling years did not exceed any established or proposed guideline values. We note our assessment of ecosystem risk is based on the 95th percentile values; however the TWA values from the PSDs indicate that many of these pesticides were continuously above TV for several months of the year including diuron (7 months), atrazine (4 months), metolachlor (2-7 months) and imidacloprid (1 month), see Figures 3-5.

Discussion

Sampling approach. Our sampling approach allowed for a comprehensive and continuous pesticide profile to be established and illustrates the consistency in the results obtained when using both grab and passive sampling methods. Our monitoring program detected 24 additional contaminants (including 17 pesticides and two breakdown products) that were not previously reported in Barratta Creek or within the wider GBR catchment area^{13, 16, 18-20, 44-46} and as such has highlighted that a wide range of pesticide products are used upstream and are largely sourced to cropping lands (particularly sugarcane). Our results also demonstrate that, while both grab and passive sampling methods offer a few (grab) or many (PSD) additional chemicals not detected by the other method, both methods effectively capture the five priority herbicides which pose the most risk to the GBR. As such a similar monitoring program using either grab or passive sampling methods at any one time could be applied to save resources based on the objective of the monitoring. We note that for monitoring programs of other agricultural areas where a broader (or different) suite of pesticides are applied, the pesticide profiles would first need to be established using both grab and passive

techniques to determine the key pesticides of concern. Specifically, the application of passive samplers would be suitable when seeking to assess the presence of a broader range of pesticides (i.e. the assessment of land use change/management) over a longer period while grab sampling would be best to apply when seeking to assess the key pesticides of concern or to quantify peak concentrations (i.e. during wet season discharge). However, unless collected at high frequency, grab sampling only provides limited information about the concentration profiles over time in a water body which comes at a high price with regards to both sample collection and analysis. Overall, our time-series data indicate the key periods when the bulk pesticide usage occurs, the key exposure (and risk) period in the waterway, and to some degree the main products used in the upstream catchment area.

Many of the 43 pesticide residues detected over the monitoring program are registered for multiple land uses. Twenty-two of the detected pesticides are registered for use in the Queensland sugarcane industry, 13 of which are also registered for use in other crops/land uses. Additional agricultural applications for the pesticides detected included legume fallow crops (10 pesticides), cotton (15 pesticides), rice (8 pesticides), sunflower (8 pesticides), mango/lychee (6 pesticides), and grazing (6 pesticides). Local land uses specific for each pesticide detected has been indicated in Table 2. A number of pesticide residues (i.e. bromacil, diazinon, permethrin, mecoprop) detected could not be ascribed to a particular land use source but may be predominately used in the management of weeds and insects around agricultural buildings or roadways. Reliable pesticide usage/application data are not available for the GBR⁴⁷ (or indeed Australia generally) and so this approach also captures some indication of the key pesticides being used in the upstream catchment area. We note that some pesticides known to be used in high amounts in the catchment (e.g. paraquat¹⁶ and glyphosate) were not analysed as part of our program; these pesticides are strongly bound to soils and are not commonly mobilised in paddock runoff (e.g. Davis et al.¹⁸, Oliver et al.⁴⁸).

While the results from the grab and passive sampling methods could not be directly compared due to the differences in their sampling intervals, some broad comparisons could be examined across the techniques. Our monitoring program aimed to establish temporal trends in TWA pesticide concentrations (to examine chronic exposure periods) and thus the sampling could not establish the peak pesticide concentrations within Barratta Creek. Passive sampler devices are not designed to capture the maximum pesticide concentrations during the period of deployment⁴⁹⁻⁵¹ nor are the monthly PIT grab samples collected at the start and end of each passive deployment. PIT grab sampling can provide maximum concentrations provided a) there is a good understanding of pesticide transport within the system and b) there is good sample coverage (and subsequent analysis) during periods when expected peaks in concentrations are anticipated. The inclusion of flow weighted PIT sampling data (see small dot points in Figure 3-5) highlight that the PIT values (particularly with regard to atrazine, hexazinone and imidacloprid) were occasionally at concentrations up to 10 times higher or lower than the corresponding TWA passive measurements.

To visualise the difference in the information obtained when using grab and passive sampling methods, the PIT (excluding flow weighted data), the flow weighted (FE) PIT, and TWA data (and the respective 95th percentile concentration) have been plotted against the average and median concentrations calculated across the whole sampling period for each respective method (Figure 7). While it would expected that grab sampling would provide more information on the “variability” of concentrations/exposure within the system, Figure 7 illustrates that in general the grab and passive sample data match reasonably well. The highest agreement is particularly evident for pesticides for which extensive calibration data are available for validating uptake kinetics (i.e. simazine, atrazine and diuron) as opposed to those chemicals where calibration data are very limited or predicted from other pesticides with similar properties (such as imidacloprid). However, there may be bias in the data as a

result of the different detection limits achieved when using the passive verses grab methods, particularly considering that only positive detections in the grab samples have been used in the comparison and it is possible that concentrations may have been close to the limits of detection. Passive samplers are not 100% accurate as they suffer from lag phases and the single phase model is oversimplifying how chemicals are accumulated which results in some uncertainties. However, they are a cost effective tool for the measurement of temporal changes in the presence of pesticide residues and to gauge relative trends in pesticide concentration over time. The detection of additional pesticides (including 19 herbicides and 8 insecticides and 1 fungicide) through the use of passive sampling methods during this study has demonstrated the utility of PSDs in the screening for the types of pesticides employed within a catchment area.

Pesticide variability in Barratta Creek. Our data show that there were large spatial and temporal variability in pesticide detection and concentrations in Barratta Creek over the two year monitoring program. On a spatial scale, the pesticide concentrations tended to be considerably lower at the Lower Barratta estuarine site, which most likely indicates dilution with seawater. Indeed the mean EC value measured at this site (20.4 mS.cm^{-1}) suggests that the average creek water to seawater ratio is approximately 60:40. This result provides support that the lower pesticide concentrations measured at Lower Barratta are influenced by dilution, particularly in grab samples collected during high tide periods.

Changes in the pesticide profiles across the freshwater sampling sites can be attributed to local land use differences particularly between the West and East Barratta sites. For example, bromacil, fluometuron and clomazone were detected at West Barratta but were not detected at the East Barratta site while imazapic and imazethapyr were detected at West Barratta at twice the frequency recorded at East Barratta. It is believed that most of the catchment runoff discharges through East Barratta Creek¹⁷, however the disparity between

the detection frequencies of pesticides between East and West Barratta would suggest that there is a local runoff source influencing the West Barratta site. The detections of bromacil and fluometuron are possibly associated with use around urban/industrial buildings or weed management in cotton crops, respectively. Clomazone is registered for use in horticulture, legume and rice crops; the detections at West Barratta are likely associated with the management of weeds within fallow legume crops (within the sugarcane crop cycle). Imazapic and imazethapyr are only registered in the sugarcane industry and hence the increased frequency of detection at the West Barratta site might reflect differences in local usage amounts across the catchment.

The pronounced dry season in the lower Burdekin (April to October) means that cropping in this region is almost completely dependent on furrow irrigation methods. This irrigation paddock runoff (and associated pesticide losses) is transported through a network of drains which ultimately discharge into Barratta Creek introducing flow into a normally ephemeral system and explains why pesticide concentrations in Barratta Creek increase prior to the onset of wet season rains¹⁷⁻¹⁹. Several studies have shown that the dominant mechanism driving the amount of pesticide lost from croplands relates to surface runoff following rainfall as well as the timing of pesticide application⁵²⁻⁵³. In contrast, the design of the water supply and discharge network of the Burdekin Water Supply Scheme means that irrigation runoff within the Barratta Creek catchment drives the prolonged and elevated pesticide profile within the stream prior to wet season rains. Our results reflect this and show that the first flush rainfall events also deliver pulses of pesticide concentrations into Barratta Creek that flush the system prior to the onset of the next cropping cycle.

Interestingly, there was a delay in the increase in Barratta Creek pesticide concentrations in the 2012 season (September) compared to the previous (2011 August) and following (2013 July) seasons (Figure 3-5). Unseasonal winter rainfall in June/July, 2012 delayed the harvest

commencement (and hence the preparation of paddocks for the new or ratoon crop) and the subsequent application of pesticides on the cropping lands. However, variable concentrations of certain pesticides (ametryn, atrazine, diuron, hexazinone, metolachlor, imidacloprid, prometryn, tebuthiuron; see Figure 3-5) in the TWA and PIT samples during this period suggest that some application occurred within the catchment prior to this unseasonal rain event. The origin of the tebuthiuron detected in the Barratta catchment is most likely sourced from the irrigation water ultimately delivered from the Burdekin Falls Dam which drains extensive grazing lands where this herbicide has been detected in monitoring programs²⁴; however, local use of tebuthiuron within the grazing lands in the Barratta catchment is also possible.

Our two-year continuous dataset captured the apparent response to changes in pesticide management regulations in the Barratta Creek catchment area. Specifically, during our monitoring period, the Australian Pesticide and Veterinary Medicines Authority (APVMA) imposed two separate diuron restrictions over successive seasons. The first restriction, announced in November 2011, involved a suspension of diuron products within the GBR catchment area in any areas where runoff was not contained. The announcement did not state whether diuron would be available for use after this date, although a subsequent announcement allowed diuron use to recommence from March 28th 2012. The second restriction, announced on the 1st November 2012 declared a no spray window for diuron between December 2012 and March 2013. Our data show that diuron concentrations in Barratta Creek increased considerably (more than doubled) in November 2011, and also became the dominant herbicide in Barratta Creek in the subsequent months (Figure 3). Following the second restriction, the diuron concentrations in Barratta Creek were more than four-fold lower over the same period (compared to the previous year). Taken together with previous monitoring showing atrazine as the dominant pesticide within this system, these

results could imply that the existing diuron stores held by local farmers were being used up prior to the first restriction and that during subsequent pesticide applications within the region local farmers began employing alternative pesticides (i.e. metolachlor and metribuzin as alternative herbicides registered for use in sugarcane⁵⁴).

Our dataset also reveals increases in concentration and detection frequency of other “alternative herbicides” such as isoxaflutole and imazapic over the monitoring period, which coincided with major changes in pesticide management in this catchment. Indeed these “alternative herbicides” have been marketed as suitable replacements for the traditionally-used PSII inhibitors such as diuron, atrazine, ametryn and hexazinone which are under increasing pressure due to the implementation of the Reef Water Quality Protection Plan, government regulations and label restrictions^{12, 55-56}. Furthermore, the implementation of improved pesticide management practices such as the use of banded/shielded spraying techniques will lead to lower amounts of herbicides applied and lost from sugar paddocks⁴⁸. Future pesticide monitoring of the Barratta Creek system is likely to highlight the positive influences associated with the increasing uptake of these improved practices in the absence of catchment-specific sales and usage data.

Pesticide exposure and risk in the Creek. Our continuous monitoring data show the prolonged exposure and risk of multiple pesticides across the Barratta Creek complex. Specifically concentrations of diuron, atrazine, hexazinone, metolachlor, ametryn, simazine and imidacloprid exceed relevant ANZECC and ARMCANZ guidelines²¹ and/or proposed ecological threshold values⁴⁰ for freshwater (Table 4) and/or estuarine systems (Table 5). In particular, the exposure periods where the guidelines or proposed ecological values were exceeded for these pesticides range from 7 months for diuron to 1 month for imidacloprid per year (Figure 3-5).

485 Effects of multiple pesticides in mixtures within Barratta Creek are also of concern as many
486 pesticides have a common mode of action (i.e. the PSII herbicides) which would produce
487 additive toxicity⁴⁴. Previous research investigating the ecological risk of pesticides in
488 freshwater have highlighted that Barratta Creek is at high risk of impaired ecosystem
489 function compared to other lower Burdekin sites¹⁹. An analysis of the likely effects of the
490 more frequently detected herbicides in Barratta Creek (atrazine, ametryn, diuron, hexazinone
491 and 2,4-D) on a range of aquatic community endpoints showed that the major effects would
492 particularly be evident on photosynthetic communities including periphyton, phytoplankton
493 and zooplankton¹⁹. Indeed the risk of pesticides in Barratta Creek in this earlier risk
494 assessment¹⁹ would likely have been conservative given that only 5 herbicides of the total 43
495 pesticides identified in our study were assessed. Future assessments within Barratta Creek
496 should perform *in situ* ecotoxicological investigations to better quality the impacts of
497 pesticide exposure on this system and determine if pollution-induced community tolerance
498 has developed due to the long-term chronic pesticide exposure⁵⁷.

499 A number of pesticides detected within Barratta Creek are known endocrine disrupting
500 compounds (EDCs) (e.g. herbicides atrazine and its metabolite desethyl atrazine,
501 pendimethalin and simazine; insecticides chlorpyrifos, fipronil and permethrin). Kroon et
502 al.⁵⁸ showed that estrogenic effects in coastal fish in GBR catchment waterways were
503 correlated with sugarcane land use and that the level of the biological marker for exposure of
504 EDCs (vitellogenin expression) in the fish barramundi (*Lates calcarifer*) increased at sites
505 with increased concentrations of ametryn, diuron, hexazinone, imidacloprid and simazine.
506 Further, the study found that some of the highest vitellogenin expression was observed in
507 wild barramundi obtained from rivers without sewerage discharge (Haughton Basin =
508 Barratta Creek) or intensive animal production (Tully) leading the authors to conclude that

the pattern of estrogenic exposure more closely reflected agricultural land use and associated pesticide runoff⁵⁸.

We conducted an extensive grab and passive sampling monitoring program to analyse pesticide residues in the Barratta Creek complex. Our sampling approach provides a framework to construct a more complete pesticide profile for waterways to assess spatial and temporal variability and to better appreciate ecosystem risk. The continual discharge of irrigation tail waters from sugarcane cropping into Barratta Creek facilitates the transport of pesticides within the surface waters during the “dry season”. The onset of “wet season” rainfall discharge through the Barratta Creek complex resulted in the dilution of pesticide concentrations within the system and concentrations were only observed to increase again during the subsequent sugarcane crop harvest and associated reapplication of herbicides during the new cropping cycle. The chronic exposure of the local freshwater biota to elevated pesticide concentrations during the “dry season” is distinctly different to the acute short term exposures that are more commonly observed when first flush rainfall-driven events transport pesticides into the environment from the sites of application. The results are broadly applicable across regions and internationally as they demonstrate the impact of management practices on the transport of pesticides into the environment following industry adoption and regulatory changes.

Acknowledgements

Funding for this work was provided through the Australian Government Reef Rescue R&D Program (Project RRRD038). Further, the authors also extend thanks to Chris Paxman and Geoff Eaglesham for sampler preparation and analysis at Entox; Mike Hanks (QDAFF) and Rob Milla (Burdekin Productivity Services) for discussions on data and to the owners and managers of Jerona Station for access to East and West Barratta sites; and local cane growers

533 for the occasional assistance with the extraction of bogged vehicles. We also thank Melany
534 Ginders, Scott Stinson and Phil Mercurio for assistance in the field.

535 **Supporting information**

536 Information on the environmental condition (rainfall and water electrical conductivity) across
537 the sampling sites during the study period are made summarised in the supporting material.
538 Additional figures are also provided to present the temporal change in the nine key pesticides
539 identified (atrazine, diuron, hexazinone, ametryn, imidacloprid, metolachlor, simazine,
540 prometryn and tebuthiuron) at the Lower Barratta estuarine sampling site.

Tables and figures:

Table 1: Site coordinates and the percent land use contribution above each sampling site.

| | Barratta sampling sites | | | |
|--|---------------------------------|-------------------------------|---------------------------------|---------------------------------|
| | Upper | West | East | Lower |
| | 19°41'23.15"S 147°10'13.69"E | 19°32'9.94"S 147°13'3.07"E | 19°33'42.37"S 147°13'16.71"E | 19°28'41.55"S 147°13'57.66"E |
| Percent land use contribution above site (%) | | | | |
| Grazing | 84 | | 72 | 60 |
| Cropping | 15 | | 25 | 31 |
| Conservation/Other | 1 | | 3 | 9 |

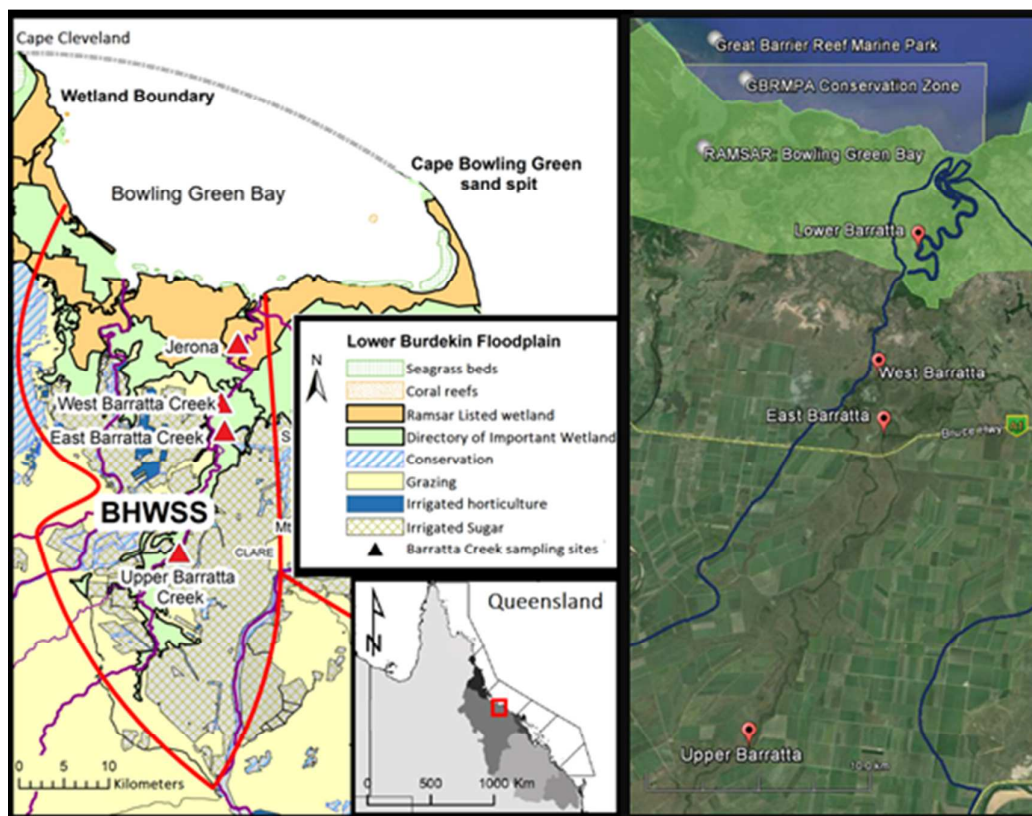


Figure 1: Sampling sites in the Barratta Creek Complex. The Left map shows the location of the sampling sites (red triangles) in relation to the surrounding land use in the area supplied with irrigation water from the Burdekin Haughton Water Supply Scheme (BHWSS; red lines). Land use classifications are based on the 2004 Queensland Land Use Mapping shape files obtained from the Queensland Department of Natural Resources and Mines (DNRM). The right satellite image shows the locations of the four sampling sites in relation to the sugarcane croplands surrounding the wetlands supported by the Barratta Creek (catchment boundary indicated by the blue line⁵⁹); the Ramsar wetland (green shaded area), the GBRMP and conservation zone.

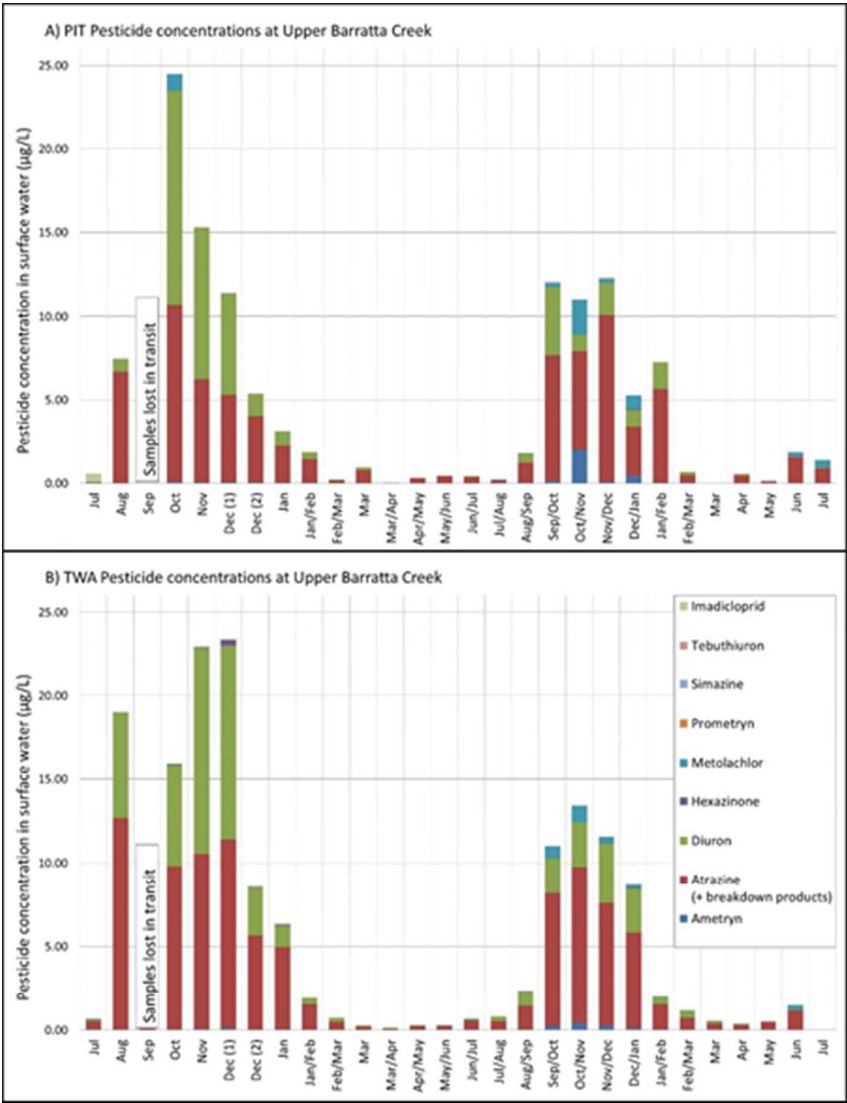


Figure 2: PIT (A) and TWA (B) concentrations of the nine key pesticide measured at Upper Barratta Creek between July 2011 and July 2013.

Table 2: Frequency (%) at which a contaminant was detection per sampling period (~1 month intervals) irrespective of sampling method (i.e. grab or passive sampling).

| | Sampling method: | All sites | Upper | West | East | Lower | Registered land use: |
|---|------------------|-----------|-------|------|------|-------|--------------------------------|
| 2,4 D ^a | ED | 68 | 67 | 73 | 67 | 67 | SC, H, L, C, R, U/I |
| 3,4 Di Cl Aniline ^{a#} | PDMS | 11 | 11 | 12 | 11 | 11 | SC |
| Acifluorfen ^a | ED | 9 | 4 | 15 | 15 | 4 | H, L |
| Ametryn ^a | ED | 100 | 100 | 100 | 100 | 100 | SC, H |
| Atrazine ^a | Grab, ED, PDMS | 100 | 100 | 100 | 100 | 100 | SC, H, C, U/I |
| Atrazine desethyl ^{a#} | Grab, ED, PDMS | 100 | 100 | 100 | 100 | 100 | SC |
| Bromacil ^a | Grab, ED | 8 | 11 | 19 | ND | 4 | U/I |
| Clomazone ^a | Grab | 2 | ND | 8 | ND | ND | H, L, R |
| Desisoproyl atrazine ^{a#} | Grab | 100 | 100 | 100 | 100 | 100 | SC |
| Diuron ^a | ED | 100 | 100 | 100 | 100 | 100 | SC, H, C, U/I |
| Fluometuron ^a | PDMS | 6 | 4 | 19 | ND | ND | C |
| Fluroxypyr ^a | ED | 22 | 26 | 27 | 26 | 11 | SC |
| Flusilazole ^c | PDMS | 8 | 15 | 12 | 4 | 4 | SC |
| Haloxypop ^a | Grab, ED | 38 | 48 | 35 | 44 | 26 | H, C, U, |
| Hexazinone ^a | PDMS | 100 | 100 | 100 | 100 | 100 | SC, H, U/I |
| Imazapic ^a | Grab, ED | 40 | 7 | 62 | 37 | 56 | SC |
| Imazethapyr ^a | PDMS | 34 | 15 | 62 | 33 | 26 | SC |
| Imidacloprid ^b | ED | 93 | 100 | 81 | 100 | 93 | SC, H, L, C, R, S, M/L, U/I, G |
| Imidacloprid urea ^b | ED | 4 | 7 | ND | 7 | ND | |
| Isoxaflutole ^a | ED | 46 | 44 | 50 | 44 | 44 | SC |
| MCPA ^a | PDMS | 64 | 67 | 65 | 67 | 59 | SC, R, U/I |
| Mecoprop ^a | ED | 1 | 4 | ND | ND | ND | U/I |
| Metolachlor ^a | Grab, ED | 100 | 100 | 100 | 100 | 100 | SC, H, C, S |
| Metribuzin ^a | Grab | 11 | 11 | 12 | 11 | 11 | SC |
| Metsulfuron methyl ^b | Grab | 47 | 48 | 50 | 48 | 41 | H, L, G |
| Prometryn ^a | Grab, ED | 84 | 85 | 69 | 93 | 89 | H, L, C, S |
| Propazin-2-hydroxy ^a | ED | 74 | 74 | 73 | 74 | 74 | |
| Simazine ^a | ED | 98 | 100 | 92 | 100 | 100 | H, U/I, F |
| Tebuthiuron ^a | ED | 100 | 100 | 100 | 100 | 100 | H, C, U/I, G |
| Terbutylazine ^a | ED | 29 | 37 | 23 | 33 | 22 | L,G |
| Terbutylazine desethyl ^{a#} | PDMS | 7 | 7 | 4 | 11 | 4 | L,G |
| Terbutryn ^a | Grab, ED, PDMS | 36 | 37 | 35 | 44 | 26 | SC, U/I |
| Triclopyr ^a | Grab, ED, PDMS | 52 | 56 | 46 | 63 | 44 | M/L, U/I |
| Pendimethalin ^a | ED | 30 | 44 | NA | NA | 15 | SC, H, C, R, M/L |
| Propazine ^a | Grab, PDMS | 50 | 63 | NA | NA | 37 | |
| Chlorpyrifos ^b | PDMS | 13 | 22 | NA | NA | 4 | SC, H, L, C, R, S, M/L, U/I, G |
| DEET | Grab | 7 | ND | NA | NA | 15 | U/I |
| Diazinon ^b | Grab, ED, PDMS | 4 | ND | NA | NA | 7 | H, L, C, R, U/I, G |
| Fipronil ^b | ED | 11 | 19 | NA | NA | 4 | C, R, S, F |
| Methamidophos ^b | Grab, PDMS | 2 | 4 | NA | NA | ND | |
| Permethrin ^b | Grab, ED | 2 | 4 | NA | NA | ND | C |
| Phosphamidon ^b | Grab, ED | 2 | ND | NA | NA | 4 | |
| BHT ^d | PDMS | 2 | ND | NA | NA | 4 | |
| Galaxolide ^f | Grab, ED | 19 | 22 | NA | NA | 15 | |
| Tonalid ^f | ED, PDMS | 2 | 4 | NA | NA | ND | |
| Bifenthrin ^{a#} | PDMS | 9 | ND | 11 | 14 | 11 | SC, H, C, M/L, U/I |
| Bisphenol A | ED | 4 | ND | 7 | 4 | 4 | U/I |
| Tris(dichloropropyl) phosphate ^e | Grab | 6 | ND | 4 | 11 | 11 | |

a = Herbicide; b = Insecticide; c = Fungicide; d = a fuel and oil additive; e = Flame retardant and pesticide; f = Polycyclic musks; # = Breakdown product; BHT = 2,6-Di-t-BUTYL-p-CRESOL; ND = not detected; N/A = not analysed; SC = Sugar, H = Horticulture, L = Legume, C = Cotton, R = Rice, S = Sunflower, M/L = Mango/Lychee, U/I = Urban/industrial, G = Grazing, F = Forestry

Shaded cells indicate chemicals that have been reported previously in the GBR catchment area ^{13, 16, 18-20, 44-46}.

Table 3: Frequency (%) and concentration (µg.L⁻¹) range for the nine most frequently detected pesticides during this study across all sampling sites.

| | Sampling method | All sites | | | Upper | | | West | | | East | | | Lower | | |
|--------------|-----------------|---------------------|---------|---------|---------------------|---------|---------|---------------------|---------|---------|---------------------|---------|---------|---------------------|---------|---------|
| | | Detection frequency | Minimum | Maximum | Detection frequency | Minimum | Maximum | Detection frequency | Minimum | Maximum | Detection frequency | Minimum | Maximum | Detection frequency | Minimum | Maximum |
| Ametryn | GRAB | 60 | 0.02 | 2 | 56 | 0.02 | 2 | 48 | 0.02 | 0.17 | 61 | 0.02 | 1.02 | 75 | 0.02 | 0.09 |
| | ED | 100 | 0.001 | 0.505 | 100 | 0.001 | 0.403 | 100 | 0.002 | 0.348 | 100 | 0.002 | 0.505 | 100 | 0.001 | 0.118 |
| | PDMS | 50 | 0.022 | 1.99 | 48 | 0.022 | 1.99 | N/A | -- | -- | N/A | -- | -- | 52 | 0.054 | 0.173 |
| Atrazine | GRAB | 96 | 0.017 | 9.17 | 96 | 0.017 | 9.17 | 96 | 0.043 | 4.84 | 96 | 0.068 | 8.06 | 96 | 0.079 | 4.19 |
| | ED | 100 | 0.034 | 11.5 | 100 | 0.034 | 11.5 | 100 | 0.064 | 9.03 | 100 | 0.09 | 7.28 | 100 | 0.06 | 2.16 |
| | PDMS | 100 | 0.076 | 10.9 | 100 | 0.076 | 10.9 | N/A | -- | -- | N/A | -- | -- | 100 | 0.134 | 4.23 |
| Diuron | GRAB | 88 | 0.01 | 12.8 | 89 | 0.015 | 12.8 | 93 | 0.01 | 2.43 | 96 | 0.017 | 2.99 | 75 | 0.011 | 2.02 |
| | ED | 100 | 0.018 | 12.4 | 100 | 0.024 | 12.3 | 100 | 0.019 | 3.97 | 100 | 0.021 | 7.98 | 100 | 0.018 | 1.37 |
| | PDMS | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- |
| Hexazinone | GRAB | 22 | 0.01 | 0.259 | 22 | 0.01 | 0.03 | 26 | 0.026 | 0.259 | 18 | 0.019 | 0.107 | 21 | 0.01 | 0.097 |
| | ED | 100 | 0.001 | 0.327 | 100 | 0.001 | 0.327 | 100 | 0.001 | 0.171 | 100 | 0.001 | 0.223 | 100 | 0.001 | 0.042 |
| | PDMS | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- |
| Imidacloprid | GRAB | 7 | 0.02 | 0.504 | 11 | 0.02 | 0.504 | 7 | 0.02 | 0.04 | 7 | 0.03 | 0.04 | 4 | 0.02 | 0.02 |
| | ED | 93 | 0 | 0.041 | 100 | 0.001 | 0.041 | 81 | 0.001 | 0.03 | 100 | 0.001 | 0.037 | 93 | 0 | 0.013 |
| | PDMS | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- |
| Metolachlor | GRAB | 48 | 0.013 | 2.1 | 33 | 0.03 | 2.1 | 56 | 0.013 | 0.57 | 57 | 0.04 | 1.04 | 46 | 0.013 | 0.19 |
| | ED | 100 | 0 | 0.964 | 100 | 0 | 0.964 | 100 | 0.001 | 0.392 | 100 | 0.002 | 0.699 | 100 | 0.001 | 0.098 |
| | PDMS | 96 | 0.003 | 5.31 | 93 | 0.003 | 5.313 | N/A | -- | -- | N/A | -- | -- | 100 | 0.01 | 0.509 |
| Prometryn | GRAB | 2 | 0.02 | 0.03 | 4 | 0.03 | 0.03 | ND | -- | -- | 4 | 0.02 | 0.02 | ND | -- | -- |
| | ED | 84 | 0 | 0.003 | 85 | 0 | 0.002 | 69 | 0 | 0.003 | 93 | 0 | 0.002 | 89 | 0 | 0.001 |
| | PDMS | 2 | 0.007 | 0.007 | 4 | 0.007 | 0.007 | N/A | -- | -- | N/A | -- | -- | ND | -- | -- |
| Simazine | GRAB | 16 | 0.01 | 0.1 | 19 | 0.01 | 0.1 | 7 | 0.011 | 0.03 | 29 | 0.01 | 0.03 | 11 | 0.02 | 0.06 |
| | ED | 98 | 0 | 0.543 | 100 | 0 | 0.013 | 92 | 0 | 0.011 | 100 | 0 | 0.543 | 100 | 0 | 0.1 |
| | PDMS | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- |
| Tebuthiuron | GRAB | ND | -- | -- | ND | -- | -- | ND | -- | -- | ND | -- | -- | ND | -- | -- |
| | ED | 100 | 0 | 0.007 | 100 | 0.001 | 0.006 | 100 | 0.001 | 0.007 | 100 | 0.001 | 0.006 | 100 | 0 | 0.004 |
| | PDMS | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- | N/A | -- | -- |

Table 4: Established Australian pesticide guideline values ($\mu\text{g.L}^{-1}$) for freshwater and the rate at which guidelines were exceeded in samples collected during this study across the three freshwater sampling sites (Upper, East and West Barratta).

Note: data is shown only for pesticides where concentrations exceeded any established guidelines

| Guideline | | Values | Sampling method | Guideline exceedance frequency/ timing/location: | | | | |
|-------------------|-------------------|--------|-----------------|--|----|---|---|-----|
| | | | | No. | % | Months | Sites | |
| Ametryn | PC99 ^a | 0.02 | ED | 45 | 56 | Jul-Nov 2011; May, Jun, Aug 2012-Jan, June 2013 | All | |
| | | | Grab | 59 | 73 | July 2011-Jan 2012; May-July, Aug 2012-Feb 2013; May-Jul 2013 | All | |
| | PC95 ^a | 0.10 | ED | 13 | 16 | Jul, Aug, Nov 2011; May, Aug-Dec 2012 | | |
| | | | Grab | 11 | 14 | Aug-Nov 2011; Aug-Dec 2012; | All | |
| Atrazine | PC99 | 0.70 | ED | 44 | 54 | Jul 2011-Feb 2012; Aug 2012-Jan 2013 | All | |
| | | | Grab | 44 | 54 | Aug, Oct 2011-Jan 2012; Aug 2012-Jan 2013; Jun-Jul 2013 | All | |
| | PC95 | 13.00 | ED | 0 | 0 | -- | -- | |
| | | | Grab | 0 | 0 | Aug, Oct -Nov 2011; Sep-Nov 2012; Jan 2013 | All | |
| | PC99 ^a | 3.70 | ED | 20 | 25 | Aug-Dec 2011; Sept-Nov 2012-Jan 2013 | All | |
| | | | Grab | 14 | 17 | Aug, Oct-Nov 2011; Sep, Nov 2012 | Upper, West | |
| | PC95 ^a | 6.00 | ED | 7 | 9 | Aug-Nov 2011; Sept 2013 | Upper, East | |
| | | | Grab | 6 | 7 | Aug, Oct, Nov 2011; Sep, Nov 2012 | Upper, West | |
| | Diuron | TV | 0.20 | ED | 49 | 60 | Aug 2011-Feb 2012; July 2012-March 2013 | All |
| | | | | Grab | 40 | 49 | Aug, Oct 2011-Jan 2012; Aug 2012-Feb 2013 | All |
| PC99 ^a | | 0.20 | ED | 49 | 60 | Aug 2011-Feb 2012; July 2012-March 2013 | All | |
| | | | Grab | 40 | 49 | Aug, Oct 2011-Jan 2012; Aug 2012-Feb 2013 | All | |
| PC95 ^a | | 0.30 | ED | 43 | 53 | Aug 2011-Feb 2012; Aug 2012-Feb 2013 | All | |
| | | | Grab | 38 | 47 | Aug, Oct 2011-Jan 2012; Aug 2012-Feb 2013 | All | |
| Hexazinone | TV | 75.00 | ED | 0 | 0 | -- | -- | |
| | | | Grab | 0 | 0 | -- | -- | |
| | PC99 ^a | 0.20 | ED | 2 | 2 | Nov-11 | Upper, West | |
| | | | Grab | 1 | 1 | Nov-11 | East | |
| | PC95 ^a | 0.70 | ED | 0 | 0 | -- | -- | |
| | | | Grab | 0 | 0 | -- | -- | |
| Imidacloprid | Canadian | 0.23 | ED | 0 | 0 | -- | -- | |
| | | | Grab | 1 | 1 | Jul 2011 | | |
| | PC99 ^a | 0.03 | ED | 4 | 5 | Jul, 2011; Jan, Aug 2012 | All | |
| | | | Grab | 4 | 5 | July 2011; Jan, Oct, Nov 2012 | Upper, East | |
| | PC95 ^a | 0.10 | ED | 0 | 0 | -- | -- | |
| | | | Grab | 1 | 1 | Jul 2011 | | |
| Metolachlor | TV | 0.02 | ED | 44 | 54 | Jul 2011-Jan 2012; Jun 2012-Feb 2013; May-Jun 2013 | All | |
| | | | Grab | 35 | 43 | Aug 2011-Jan 2012; Mar, May-Dec 2012; Jun-Jul 2013 | All | |
| Simazine | PC99 | 0.20 | ED | 1 | 1 | Aug-11 | West | |
| | | | Grab | 0 | 0 | -- | -- | |
| | PC95 | 3.20 | ED | 0 | 0 | -- | -- | |
| | | | Grab | 0 | 0 | -- | -- | |

^a Proposed guideline values established for Great Barrier Reef and its adjacent catchments⁴⁰.

Table 5: Established Australian pesticide guideline values ($\mu\text{g}\cdot\text{L}^{-1}$) for marine/estuarine waters and the rate (%) at which guidelines were exceeded in samples collected during this study (Note: data is shown only for pesticides where concentrations exceeded any established guidelines)

| | Guideline | Values | | Sampling method | Guideline exceedance frequency: | | |
|-------------|-------------------|--------|-----------|-----------------|---------------------------------|----------------|--|
| | | Marine | Estuarine | | No. | % | Months detected |
| Ametryn | PC99 | 0.50 | NIL | ED | 0 | 0 | -- |
| | | | | Grab | 0 | 0 | -- |
| | PC95 | 1.00 | NIL | ED | 0 | 0 | -- |
| | | | | Grab | 0 | 0 | -- |
| | PC99 ^a | 0.02 | NIL | ED | 14 | 52 | Jul, Aug, Nov 2011; Jan, May-Jun, Sep-Dec 2012; May-Jun 2013 |
| | | | | Grab | 18 | 67 | July 2011-Mar 2012; May, Jul-Sep 2012; Jan-Feb, Apr-May 2013 |
| | PC95 ^a | 0.10 | NIL | ED | 1 | 1 | Aug 2011 |
| | | | | Grab | 0 | 0 | -- |
| Atrazine | PC99 | 0.60 | NIL | ED | 10 | 37 | Aug, Oct-Nov 2011; Jan 2012; Sep, Nov-Dec 2012 |
| | | | | Grab | 10 | 37 | Sep 2011-Jan 2012; Mar, July 2012; Jan-Feb 2013 |
| | PC95 | 1.40 | NIL | ED | 4 | 15 | Aug 2011; Jan, Dec 2012; Jan 2013 |
| | | | | Grab | 1 | 4 | Jan 2012 |
| | PC99 ^a | 2.80 | 2.20 | ED | 0 ^b | 0 ^b | -- |
| | | | | Grab | 1 ^b | 4 ^b | Jan 2012 |
| | PC95 ^a | 3.80 | 3.40 | ED | 0 ^b | 0 ^b | -- |
| | | | | Grab | 1 ^b | 4 ^b | Jan 2012 |
| Diuron | TV | 0.20 | NIL | ED | 11 | 41 | Oct 2011-Jan 2012; Oct 2012-Feb 2013 |
| | | | | Grab | 0 | 0 | -- |
| | PC99 | 0.90 | NIL | ED | 3 | 11 | Nov 2011 Jan 2012 |
| | | | | Grab | 1 | 4 | Jan 2012 |
| | PC95 | 1.60 | NIL | ED | 0 | 0 | -- |
| | | | | Grab | 1 | 4 | Jan 2012 |
| | PC99 ^a | 0.08 | NIL | ED | 14 | 52 | Oct 2011-Feb 2012; Sep 2012-March 2013 |
| | | | | Grab | 12 | 44 | Oct 2011-March 2012; Jul 2012; Jan, Feb, Apr 2013 |
| Metolachlor | TV | NIL | NIL | ED | 10 | 37 | Jul, Oct, Nov 2011; May-Jul, Oct-Dec 2012; Jun 2013 |
| | | | | Grab | 11 | 41 | Sep-Nov 2011, Jan, May-Sep, Nov 2012 |

^a Proposed guideline values established for Great Barrier Reef and its adjacent catchments⁴⁰.

^b calculated using the estuarine guideline.

Table 6: 95th percentile pesticide concentrations ($\mu\text{g/L}$) calculated per sampling year across all sites sampled. Values were compared to ANZECC and ARMCANZ (2000) water quality guidelines²¹ and proposed by Smith et al.⁴⁰. Values in bold indicate concentrations that exceed the proposed PC95 values⁴⁰. Underline values are those that exceed the ANZECC and ARMCANZ (2000) TVs. Shaded cells indicate concentrations that exceeded proposed PC99 values⁴⁰.

| | | Ametryn | Atrazine | Diuron | Hexazinone | Imidacloprid | Metolachlor | Simazine |
|----------------------|-----------|--------------|---------------|----------------------|------------|--------------|--------------|----------|
| All Freshwater sites | 2011-2012 | 0.139 | 7.883 | <u>7.054</u> | 0.106 | 0.035 | <u>0.366</u> | 0.030 |
| | 2012-2013 | 0.348 | 6.871 | <u>4.093</u> | 0.109 | 0.027 | <u>0.818</u> | 0.013 |
| Upper Barratta | 2011-2012 | 0.080 | 10.450 | <u>12.596</u> | 0.044 | 0.295 | <u>0.600</u> | 0.023 |
| | 2012-2013 | 1.384 | 7.816 | <u>9.670</u> | 0.216 | 0.062 | <u>1.645</u> | 0.072 |
| West Barratta | 2011-2012 | 0.083 | 7.143 | <u>2.632</u> | 0.211 | 0.036 | <u>0.346</u> | 0.024 |
| | 2012-2013 | 0.286 | 5.558 | <u>3.884</u> | 0.147 | 0.011 | <u>0.488</u> | 0.007 |
| East Barratta | 2011-2012 | 0.788 | 7.502 | <u>5.539</u> | 0.104 | 0.034 | <u>0.796</u> | 0.312 |
| | 2012-2013 | 0.238 | 6.313 | <u>6.286</u> | 0.156 | 0.029 | <u>1.960</u> | 0.015 |
| Lower Barratta | 2011-2012 | 0.107 | 3.275 | 1.825 | 0.085 | 0.018 | 0.140 | 0.082 |
| | 2012-2013 | 0.084 | 1.524 | 1.091 | 0.037 | 0.005 | 0.508 | 0.003 |

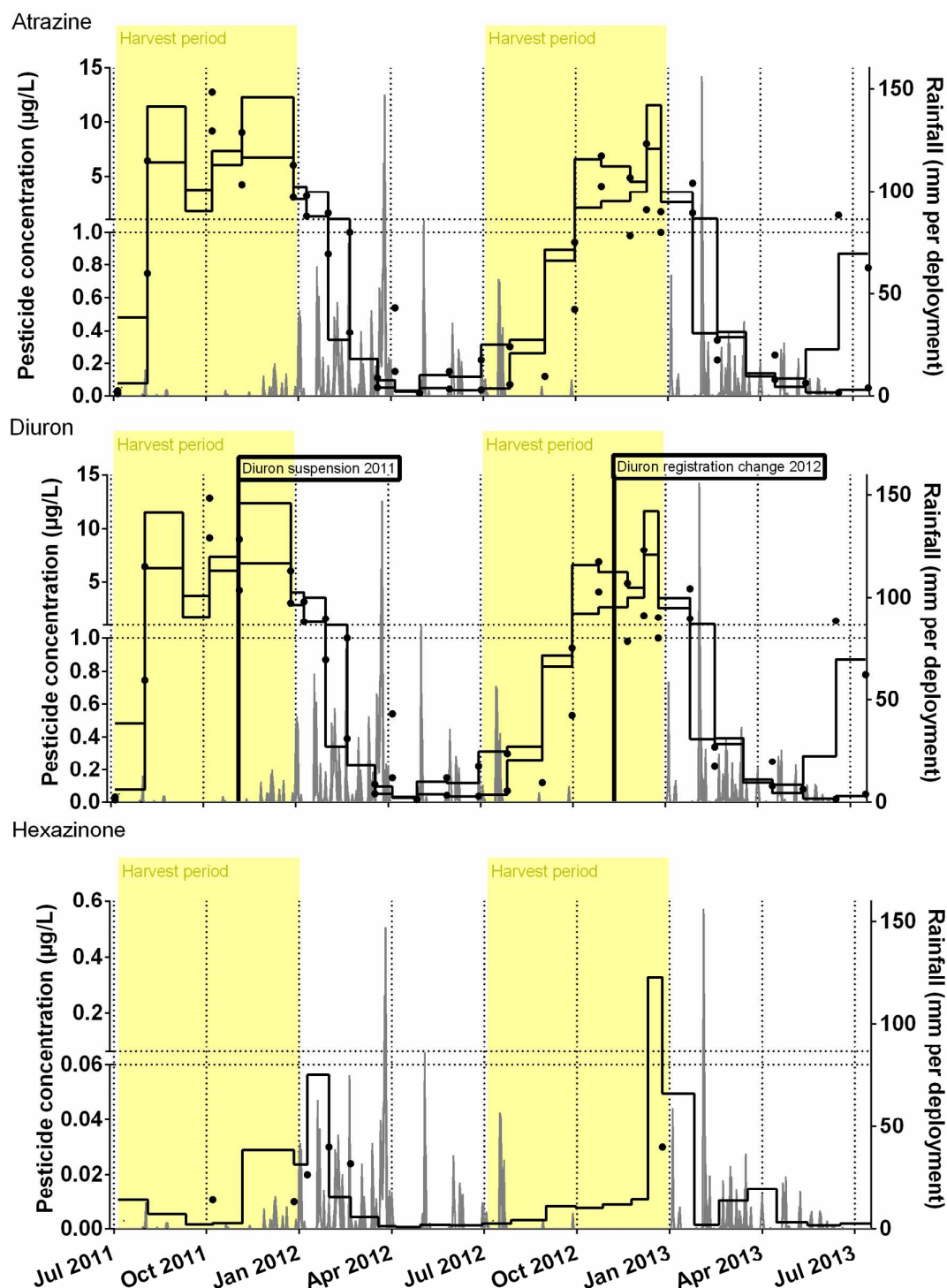


Figure 3: Temporal change in atrazine, diuron and hexazinone concentrations at Upper Barratta Creek when measured in grab samples (dot points: point in time measurements of concentration) and the time weighted average concentration measured using the passive sampling devices (lines) within the catchment during the sampling period (data obtained from DNRM³⁹) and pesticide data obtained by DSITI (small dot points). Plots for concentrations obtained at the Lower Barratta estuarine site are available for comparison in the supplementary material. Vertical spikes indicate daily rainfall (mm).

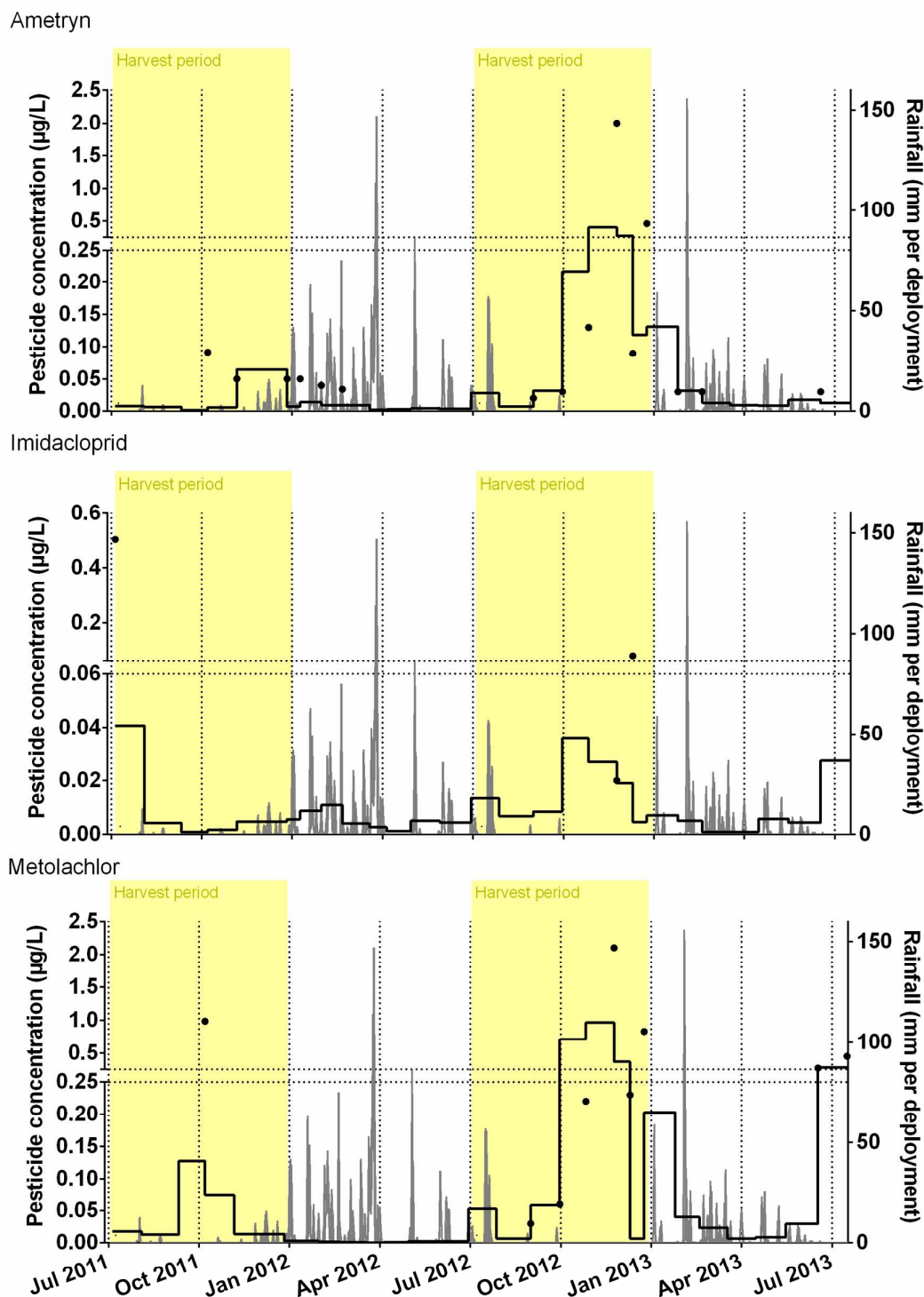


Figure 4: Temporal change in ametryn, imidacloprid and metolachlor concentrations at Upper Barratta Creek when measured in grab samples (dot points: point in time measurements of concentration) and the time weighted average concentration measured using the passive sampling devices (lines) within the catchment during the sampling period (data obtained from DNRM³⁹) and pesticide data obtained by DSITI (small dot points). Plots for concentrations obtained at the Lower Barratta estuarine site are available for comparison in the supplementary material. Vertical spikes indicate daily rainfall (mm).

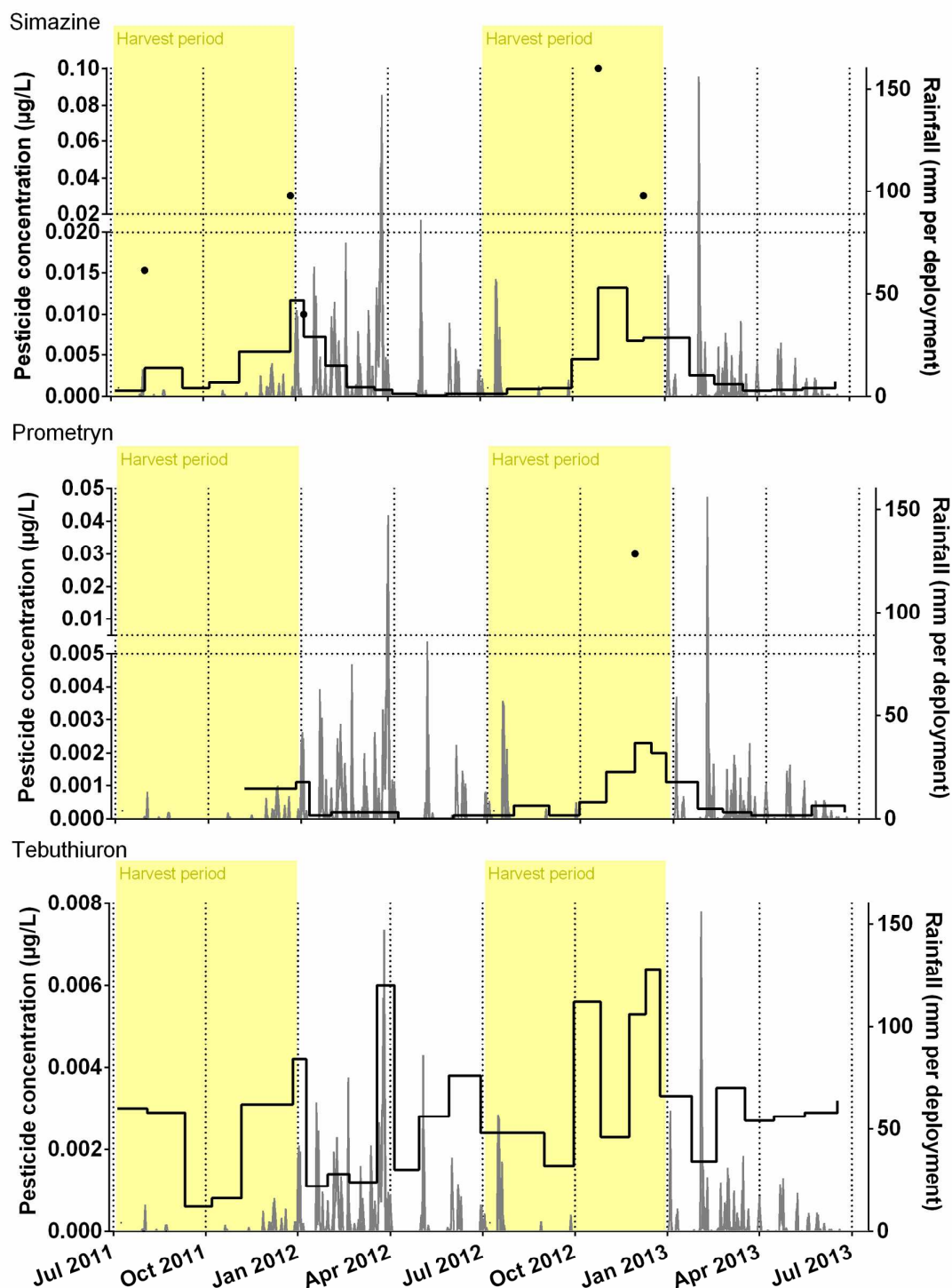


Figure 5: Temporal change in simazine, prometryn and tebuthiuron concentrations at Upper Barratta Creek when measured in grab samples (dot points: point in time measurements of concentration) and the time weighted average concentration measured using the passive sampling devices (lines) within the catchment during the sampling period (data obtained from DNRM³⁹) and pesticide data obtained by DSITI (small dot points). Plots for concentrations obtained at the Lower Barratta estuarine site are available for comparison in the supplementary material. Vertical spikes indicate daily rainfall (mm).

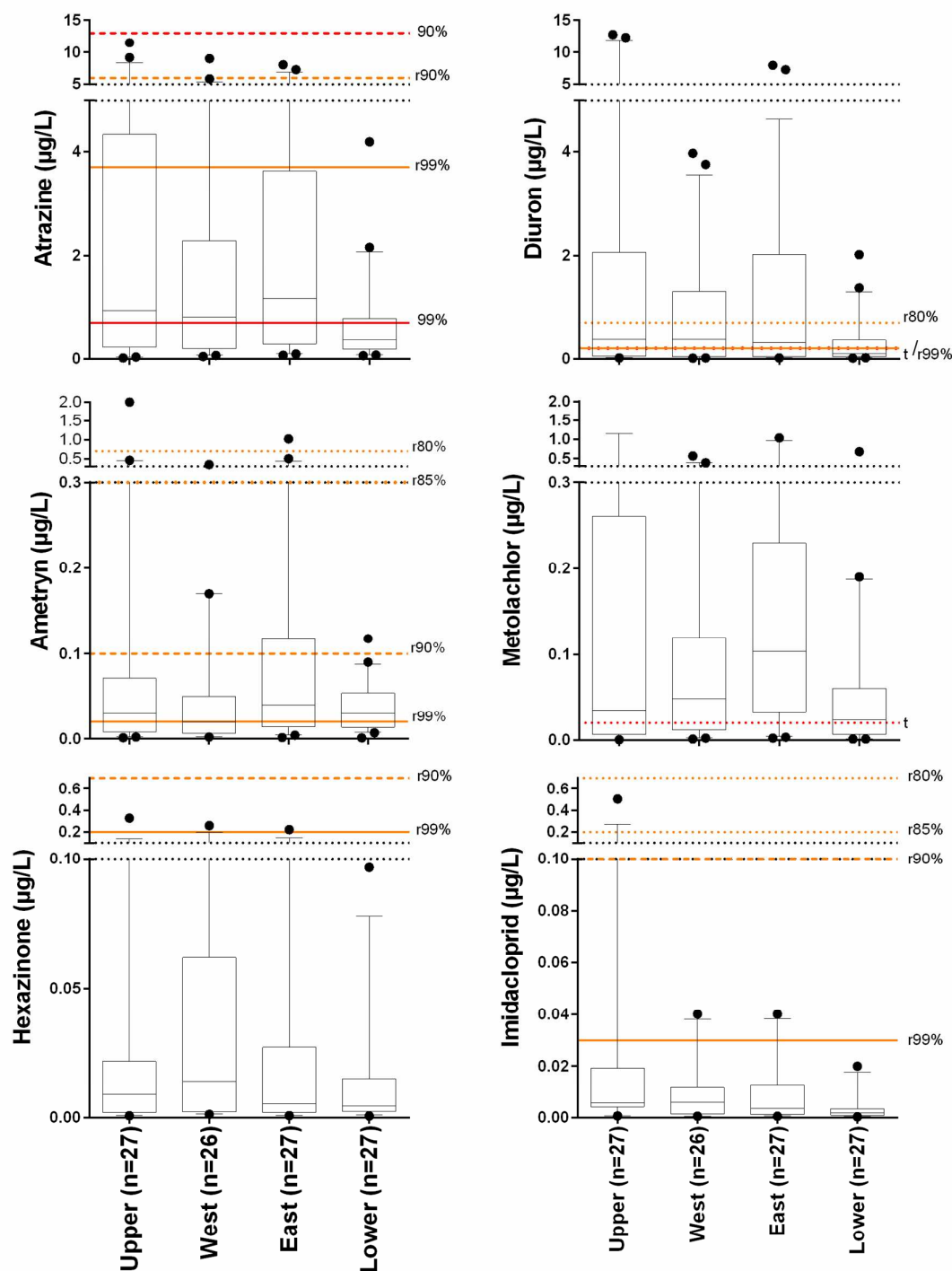


Figure 6: Boxplots of the concentrations of atrazine, diuron, ametryn, metolachlor, hexazinone and imidacloprid across the four monitoring sites measured using the Chemcatcher[®] passive samplers. Within the box plot, boxes represent the 25-75th percentile, the whiskers presents the 5-95th percentile, the median is indicated by the + and the outliers are presented as dot points. The lines on each graph indicate the existing trigger (t) or guideline for species protection (90 and 99) with respect to atrazine, diuron and metolachlor concentrations in surface waters. Revised guidelines have been proposed by Smith et al.⁴⁰ that provide revised guidelines for atrazine, diuron and hexazinone and new guidelines for ametryn and imidacloprid (these guidelines are for 80, 85, 90 and 99 species protection and are indicated by the prefix “r”).

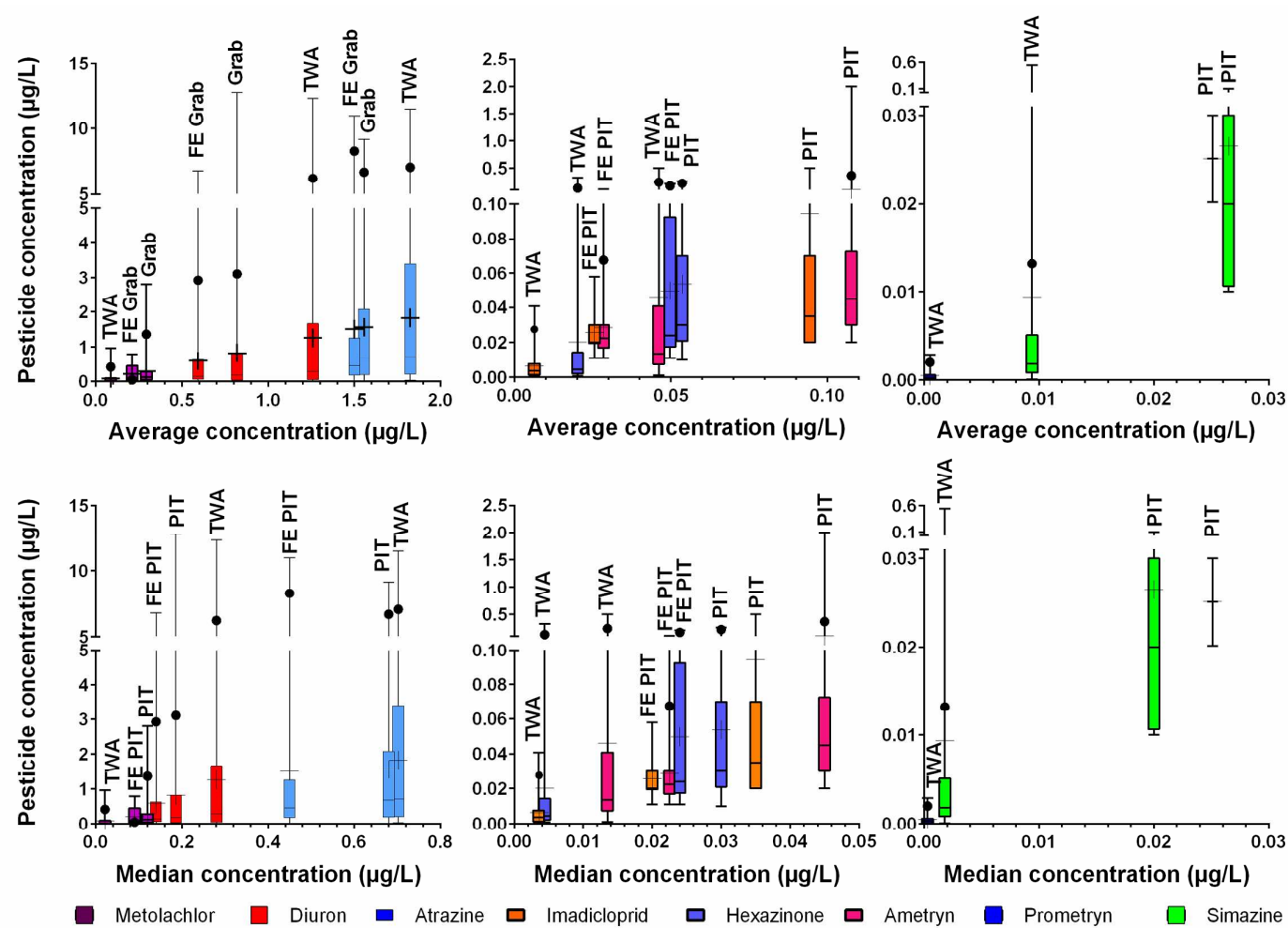


Figure 7: Comparison of the concentrations of atrazine, diuron, ametryn, metolachlor, hexazinone, imadiclopid, prometryn and simazine detected using grab and passive sampling. Boxplots represent the range in the concentrations detected and are plotted against both the average and median concentrations recorded using the sampling method type. Dot points indicate the 95th percentile concentrations.

References

1. Davis, C. C., Environmental concerns about pesticide use in Philippine agriculture. *Science of The Total Environment* **1993**, 134, Supplement 1 (0), 293-306.
2. Praneetvatakul, S.; Schreinemachers, P.; Pananurak, P.; Tipraqsa, P., Pesticides, external costs and policy options for Thai agriculture. *Environmental Science & Policy* **2013**, 27 (0), 103-113.
3. Sattler, C.; Kächele, H.; Verch, G., Assessing the intensity of pesticide use in agriculture. *Agriculture, Ecosystems & Environment* **2007**, 119 (3-4), 299-304.
4. Travisi, C. M.; Nijkamp, P., Valuing environmental and health risk in agriculture: A choice experiment approach to pesticides in Italy. *Ecological Economics* **2008**, 67 (4), 598-607.
5. Yadav, I. C.; Devi, N. L.; Syed, J. H.; Cheng, Z.; Li, J.; Zhang, G.; Jones, K. C., Current status of persistent organic pesticides residues in air, water, and soil, and their possible effect on neighboring countries: A comprehensive review of India. *Science of The Total Environment* **2015**, 511 (0), 123-137.
6. Bundschuh, M.; Goedkoop, W.; Kreuger, J., Evaluation of pesticide monitoring strategies in agricultural streams based on the toxic-unit concept — Experiences from long-term measurements. *Science of The Total Environment* **2014**, 484 (0), 84-91.
7. Huckins, J. N.; Manuweera, G. K.; Petty, J. D.; Mackay, D.; Lebo, J. A., Lipid containing semipermeable membrane devices for monitoring organic contaminants in water. *Environmental Science and Technology* **1993**, 27, 2489-2496.
8. The State of Queensland and Commonwealth of Australia *Reef Water Quality Protection Plan 2009 – For the Great Barrier Reef World Heritage Area and adjacent catchments*. The State of Queensland, Brisbane; Brisbane., 2009.
9. The State of Queensland and Commonwealth of Australia *Reef Water Quality Protection Plan 2013 – Securing the health and resilience of the Great Barrier Reef World Heritage Area and adjacent catchments*. The State of Queensland, Brisbane.; Brisbane, 2013.
10. The State of Queensland and Commonwealth of Australia *Reef Water Quality Protection Plan - For catchments adjacent to the Great Barrier Reef World Heritage Area*. The State of Queensland, Brisbane.; Brisbane, 2003.
11. Carroll, C.; Waters, D.; Vardy, S.; Silburn, D.; Attard, S.; Thorburn, P.; Davis, A.; Halpin, N.; Schmidt, M.; Wilson, B.; Clark, A., A Paddock to Reef Monitoring and Modelling framework for the Great Barrier Reef: Paddock and Catchment component. *Marine Pollution Bulletin. Special Issue: Catchments and coral reef*. **2012**, 65, 136-149.
12. Davis, A. M.; Lewis, S. E.; Brodie, J. E.; Benson, A., The potential benefits of herbicide regulation: A cautionary note for the Great Barrier Reef catchment area. *Science of The Total Environment* **2014**, 490 (0), 81-92.
13. Kennedy, K.; Schroeder, T.; Shaw, M.; Haynes, D.; Lewis, S.; Bentley, C.; Paxman, C.; Carter, S.; Brando, V. E.; Bartkow, M.; Hearn, L.; Mueller, J. F., Long term monitoring of photosystem II herbicides – Correlation with remotely sensed freshwater extent to monitor changes in the quality of water entering the Great Barrier Reef, Australia. *Marine Pollution Bulletin* **2012**, 65 (4-9), 292-305.
14. Smith, R.; Turner, R.; Vardy, S.; Huggins, R.; Wallace, R.; M.St.J., W., An evaluation of the prevalence of alternate pesticides of environmental concern in Great Barrier Reef catchments: RP57C. Queensland Department of Science, Information Technology, Innovation and the Arts report for the Reef Water Quality Program.: 2015.
15. Brodie, J.; Waterhouse, J.; Schaffelke, B.; Johnson, J. E.; Kroon, F.; Thorburn, P.; Rolfe, J.; Lewis, S.; Warne, M.; Fabricius, K.; McKenzie, L.; Devlin, M., Reef Water Quality

Scientific Consensus Statement 2013. Department of the Premier and Cabinet, Q. G., Brisbane., Ed. Queensland Government, Brisbane: 2013.

16. Davis, A.; Lewis, S.; Bainbridge, Z.; Brodie, J.; Shannon, E., Pesticide residues in waterways of the lower Burdekin region: challenges in ecotoxicological interpretation of monitoring data. *Australasian Journal of Ecotoxicology* **2008**, *14*, 89-108.
17. Davis, A.; Lewis, S.; O'Brien, D.; Bainbridge, Z.; Bentley, C.; Mueller, J.; Brodie, A., Water resources development and high value coastal wetlands on the lower Burdekin floodplain, Australia. In *Estuaries of Australia in 2050 and Beyond, Estuaries of the World.* , Wolanski, E., Ed. Springer 2014; pp 223-245.
18. Davis, A. M.; Lewis, S. E.; Bainbridge, Z. T.; Glendenning, L.; Turner, R. D. R.; Brodie, J. E., Dynamics of herbicide transport and partitioning under event flow conditions in the lower Burdekin region, Australia. *Marine Pollution Bulletin* **2012**, *65* (4–9), 182-193.
19. Davis, A. M.; Thorburn, P. J.; Lewis, S. E.; Bainbridge, Z. T.; Attard, S. J.; Milla, R.; Brodie, J. E., Environmental impacts of irrigated sugarcane production: Herbicide run-off dynamics from farms and associated drainage systems. *Agriculture, Ecosystems & Environment* **2013**, *180*, 123–135.
20. Smith, R.; Middlebrook, R.; Turner, R.; Huggins, R.; Vardy, S.; Warne, M., Large-scale pesticide monitoring across Great Barrier Reef catchments – Paddock to Reef Integrated Monitoring, Modelling and Reporting Program. *Marine Pollution Bulletin* **2012**, *65* (4–9), 117-127.
21. ANZECC; ARMCANZ *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*; Australian and New Zealand Environment and Conservation Council, and Agriculture and Resource Management Council of Australia and New Zealand. Environment Australia, Canberra: 2000; p Available at: <http://www.environment.gov.au/water/publications/quality/index.html#nwqmsguidelines>.
22. Canadian_Council_of_Ministers_of_the_Environment, Canadian Water Quality Guidelines for the Protection of Aquatic Life: Imidacloprid. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the environment, Winnipeg. 2007.
23. Shannon, E.; Ham, G.; Haller, A.; Cox, D., The Davco groundwater project - a grower initiated multidisciplinary approach to groundwater management in the Burdekin district. *Proceedings of the Australian Society of Sugar Cane Technologists* **2011**, *33*.
24. Turner, R.; Huggins, R.; Wallace, R.; Smith, R.; Vardy, S.; Warne, M., Sediment, Nutrient and Pesticide Loads: Great Barrier Reef Catchment Loads Monitoring 2009-2010. Department of Science, I. T., Innovation and the Arts, Ed. Brisbane, 2012.
25. Dight, I., Burdekin Water Quality Improvement Plan Catchment Atlas. NQ Dry Tropics, T., Ed. 2009; p 148pp.
26. Environment_Australia, A Directory of Important Wetlands in Australia, Third Edition. Environment Australia, Canberra, 2001.
27. Shaw, M.; Eaglesham, G.; Mueller, J. F., Uptake and release of polar compounds in SDB-RPS Empore™ disks; implications for their use as passive samplers. *Chemosphere* **2009**, *75* (1), 1-7.
28. O'Brien, D.; Bartkow, M.; Mueller, J. F., Determination of deployment specific chemical uptake rates for SDB-RPD Empore disk using a passive flow monitor (PFM). *Chemosphere* **2011**, *83* (9), 1290-1295.
29. Vrana, B.; Mills, G. A.; Dominiak, E.; Greenwood, R., Calibration of the Chemcatcher passive sampler for the monitoring of priority organic pollutants in water. *Environmental Pollution* **2006**, *142* (2), 333-343.

30. O'Brien, D.; Komarova, T.; Mueller, J. F., Determination of deployment specific chemical uptake rates for SPMD and PDMS using a passive flow monitor. *Marine Pollution Bulletin* **2012**, *64* (5), 1005-1011.
31. Esteve-Turrillas, F. A.; Pastor, A.; Yusà, V.; de la Guardia, M., Using semi-permeable membrane devices as passive samplers. *TrAC Trends in Analytical Chemistry* **2007**, *26* (7), 703-712.
32. Shaw, M.; Furnas, M. J.; Fabricius, K.; Haynes, D.; Carter, S.; Eaglesham, G.; Mueller, J. F., Monitoring pesticides in the Great Barrier Reef. *Marine Pollution Bulletin* **2010**, *60* (1), 113-122.
33. O'Brien, D. S.; Booij, K.; Hawker, D. W.; Mueller, J. F., Method for the in situ calibration of a passive phosphate sampler in estuarine and marine waters. *Environ. Sci. Technol.* **2011**, *45*, 2871-2877.
34. O'Brien, D. S.; Chiswell, B.; Mueller, J. F., Evaluation of an in-field calibration technique for evaluating the influencing of flow on passive sampling uptake rates through the use of a phosphate passive sampler. *J. Environ. Monit.* **2009**, *11*, 212 - 219.
35. O'Brien, D.; Hawker, D.; Shaw, M.; Mueller, J. F., The performance of passive flow monitors and phosphate accumulating passive samplers when exposed to pulses in external water flow rate and/or external phosphate concentrations. *Environmental Pollution* **2011**, *159* (5), 1435-1441.
36. Shaw, M.; Mueller, J. F., Time Integrative Passive Sampling: How Well Do Chemcatchers Integrate Fluctuating Pollutant Concentrations? *Environmental Science & Technology* **2009**, *43* (5), 1443-1448.
37. Gourlay-Francé, C.; Lorgeoux, C.; Tusseau-Vuillemin, M.-H., Polycyclic aromatic hydrocarbon sampling in wastewaters using semipermeable membrane devices: Accuracy of time-weighted average concentration estimations of truly dissolved compounds. *Chemosphere* **2008**, *73* (8), 1194-1200.
38. O'Brien, D. S.; Hawker, D. W.; Shaw, M.; Mueller, J., The performance of Passive Flow Monitors and phosphate accumulating passive samplers when exposed to pulses in external water flow rate and/ or external phosphate concentrations. *Environ. Pollut.* **2011**, *159* (5), 1435-41.
39. DNRM Water Monitoring Data Portal. <http://watermonitoring.derm.qld.gov.au/host.htm> (accessed ongoing access).
40. Smith, R.; Warne, M. S. J.; Delaney, K.; Turner, R.; Seery, C.; Pradella, N.; Vardy, S.; Rogers, B.; Arango, C.; Edge, K.; Julli, M. *Proposed guideline values for six priority pesticides of the Great Barrier Reef and its adjacent catchments.*; in prep.
41. Australian Government Directory of Important Wetlands in Australia. <http://www.environment.gov.au/topics/water/water-our-environment/wetlands/australian-wetlands-database/directory-important>.
42. CANEGROWERS Sugarcane harvest starts: Revised start dates listed. http://www.canegrowers.com.au/page/Industry_Centre/Media_Centre/Media_Releases/Sugar_cane_harvest_starts_Monday_Hopes_for_sweeter_times_ahead/.
43. Commission, E. *Review report for the active substance atrazine; Finalized in the Standing Committee on the Food Chain and Animal Health at its meeting on 3 October 2003 in support of a decision concerning the non-inclusion of atrazine in Annex I of Directive 91/414/EEC and the withdrawal of authorisation for plant protection products containing this active substance.*; European Commission Health and Consumer Protection Directorate General: 2003.
44. Lewis, S. E.; Schaffelke, B.; Shaw, M.; Bainbridge, Z. T.; Rohde, K. W.; Kennedy, K.; Davis, A. M.; Masters, B. L.; Devlin, M. J.; Mueller, J. F.; Brodie, J. E., Assessing the

additive risks of PSII herbicide exposure to the Great Barrier Reef. *Marine Pollution Bulletin* **2012**, *65* (4–9), 280-291.

45. Kennedy, K.; Devlin, M.; Bentley, C.; Lee-Chue, K.; Paxman, C.; Carter, S.; Lewis, S. E.; Brodie, J.; Guy, E.; Vardy, S.; Martin, K. C.; Jones, A.; Packett, R.; Mueller, J. F., The influence of a season of extreme wet weather events on exposure of the World Heritage Area Great Barrier Reef to pesticides. *Marine Pollution Bulletin* **2012**, *64* (7), 1495-1507.
46. Kennedy, K.; Bentley, C.; Paxman, C.; Heffernan, A.; Dunn, A.; Kaserzon, S.; Mueller, J. *Final Report - Monitoring of organic chemicals in the Great Barrier Reef Marine Park using time integrated monitoring tools (2009-2010)*; The University of Queensland, The National Research Centre for Environmental Toxicology (Entox). 2010.
47. King, J.; Alexander, F.; Brodie, J., Regulation of pesticides in Australia: The Great Barrier Reef as a case study for evaluating effectiveness. *Agriculture, Ecosystems & Environment* **2013**, *180* (0), 54-67.
48. Oliver, D. P.; Anderson, J. S.; Davis, A.; Lewis, S.; Brodie, J.; Kookana, R. S., Banded applications are highly effective in minimising herbicide migration from furrow-irrigated sugar cane. *Science of The Total Environment* **2014**, *466-467*, 841–848.
49. Seethapathy, S.; Górecki, T.; Li, X., Passive sampling in environmental analysis. *Journal of Chromatography A* **2008**, *1184* (1–2), 234-253.
50. Stuer-Lauridsen, F., Review of passive accumulation devices for monitoring organic micropollutants in the aquatic environment. *Environmental Pollution* **2005**, *136* (3), 503-524.
51. Vrana, B.; Allan, I. J.; Greenwood, R.; Mills, G. A.; Dominiak, E.; Svensson, K.; Knutsson, J.; Morrison, G., Passive sampling techniques for monitoring pollutants in water. *TrAC Trends in Analytical Chemistry* **2005**, *24* (10), 845-868.
52. Steinheimer, T. R.; Ross, L.; Spittler, T., Agrochemical Movement: Perspective and Scale-of-Study Overview In *Agrochemical Fate and Movement: Perspectives and Scale of Study*, Society, A. C., Ed. Oxford University Press: Northamptonshire, 2000; pp 2-18.
53. Zanardo, S.; Basu, N. B.; Botter, G.; Rinaldo, A.; Rao, P. S. C., Dominant controls on pesticide transport from tile to catchment scale: Lessons from a minimalist model. *Water Resources Research* **2012**, *48* (4), W04525.
54. APVMA Australian Pesticides and Veterinary Medicines Authority.
55. Fillols, E.; Callow, B., Efficacy of pre-emergent herbicides on fresh trash blankets - Results on early-harvested ratoons. *Proceedings of the Australian Society of Sugar Cane Technologists* **2010**, 33.
56. Seeruttun, C.; Barbe, C.; Gaungoo, A., Lumaz: an alternative to atrazine for pre- and post-emergence control of weeds in sugarcane. *Proceedings of the Australian Society of Sugar Cane Technologists* **2010**, 27.
57. Magnusson, M.; Heimann, K.; Ridd, M.; Negri, A. P., Chronic herbicide exposures affect the sensitivity and community structure of tropical benthic microalgae. *Marine Pollution Bulletin* **2012**, *65* (4–9), 363-372.
58. Kroon, F. J.; Hook, S. E.; Jones, D.; Metcalfe, S.; Henderson, B.; Smith, R.; Warne, M. S. J.; Turner, R. D.; McKeown, A.; Westcott, D. A., Altered transcription levels of endocrine associated genes in two fisheries species collected from the Great Barrier Reef catchment and lagoon. *Marine Environmental Research* **2015**, *104* (0), 51-61.
59. NQ Dry Tropics, T. Barratta Creek. http://wiki.bdnrm.org.au/index.php?title=Barratta_Creek (accessed June).

Graphic for table of contents:

Burdekin Sugarcane

Funding source:

The presented work was funded as part of the Reef Rescue Research and Development Water Quality Program (Reef Rescue R&D); a sub component of the Australian Government's Caring for our Country program.