An evaluation of the prevalence of alternate pesticides of environmental concern in Great Barrier Reef catchments: RP57C

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Summary

Poor water quality discharged from rivers of the east coast of Queensland is known to directly impact the health of the Great Barrier Reef (GBR) and its ecosystems. The Reef Water Quality Protection Plan (Reef Plan 2009 and 2013) aims to ensure "that by 2020 the quality of water entering the reef from broadscale land use has no detrimental impact on the health and resilience of the Great Barrier Reef". Pesticides have been targeted as one of the key pollutant types, along with nutrients and sediment, to improve Reef water quality. The aims of Reef Plan are delivered through pollution reduction targets. For Reef Plan 2009, the pesticide reduction target was set at a minimum of 50 per cent of the pesticide load by 2013; for Reef Plan 2013, the pesticide reduction target was set at a minimum of 60 per cent for end-of-catchment pesticide loads in priority areas by 2018. Five photosystem II (PSII) herbicides (ametryn, atrazine, diuron, hexazinone and tebuthiuron) were identified as the priority pesticides for target reduction, as they posed the greatest risk from pesticides to the health and resilience of the GBR.

One component of farming best management practice in the GBR catchment area aims to reduce the use of PSII herbicides in favour of knockdown herbicides (e.g. 2,4-D, paraquat and glyphosate). Additionally, the Australian Pesticides and Veterinary Medicines Authority (APVMA) have recently placed further restrictions on the use of one of the priority PSII herbicides, diuron, due its potential for environmental harm. A focus on reducing the priority PSII herbicides to meet the Reef Plan reduction targets is a desirable long-term goal, however we must also assess what contribution any alternate pesticides (i.e. non-priority pesticides) have to the total pesticide load, and to ensure that their concentrations will not cause adverse ecological effects. It is therefore important to understand whether any alternate pesticides are reaching waterways in potentially harmful concentrations and whether the environmental impact of the alternate pesticides is less than the priority PSII herbicides.

Progress towards Reef Plan targets is measured through the Paddock to Reef Integrated Monitoring, Modelling and Reporting Program (Paddock to Reef Program) which is jointly funded by the Australian and Queensland governments. The Paddock to Reef Program includes catchment scale

water quality monitoring of pollutant loads entering the Great Barrier Reef lagoon which is implemented through the Great Barrier Reef Catchment Loads Monitoring Program (GBRCLMP). In order to achieve a more comprehensive estimate of total pesticide loads discharging to the Reef, the pesticide monitoring component of the GBRCLMP was expanded to include alternate pesticides along with the priority PSII herbicides. Pesticide analysis in six catchments was broadened to include an additional 21 pesticides, some of which were believed to be used as replacements for the priority PSII herbicides e.g. 2,4-D, acifluorfen, imazapic, imazethapyr, isoxaflutole, metribuzin, trifloxysulfuron-Na, metolachlor, trifluralin, pendimethalin.

Altogether, fifteen alternate pesticides were detected, in addition to the priority PSII herbicides. Overall, the priority PSII herbicides had a greater contribution (79–88%) to the total pesticide load than the alternate pesticides (12–21%). Diuron and atrazine were the predominant priority PSII herbicides in most catchments in terms of their concentrations, frequency of detection and load. Of the alternate pesticides, 2,4-D was found at the highest concentrations, highest detection frequency and made the largest contribution to the total pesticide load. Other prevalent alternate pesticides included metribuzin, metolachlor, isoxaflutole, and MCPA. Temporal changes were examined over a period between 2009 – 2013 for the priority PSII herbicides and seven alternate pesticides (fluometuron, metolachlor, prometryn, simazine, terbutryn and metribuzin) where historical data were available. Each catchment varied in the temporal trends of each of the pesticides with both increases and decreases in concentration and detection frequencies observed.

The priority PSII herbicides were found to generally have a higher ecological risk in terms of their concentrations and frequency of detection, particularly diuron, than the alternates. Of the alternate pesticides only metolachlor was found to pose a high risk - in one catchment (Barratta Creek). It was found, however, that some of the alternate pesticides, particularly metsulfuron-methyl and prometryn, had a higher or equivalent toxicity to phototrophic species than the priority PSII herbicides. If the use of these toxic alternate pesticides increases in the future, then their concentrations and frequency of detection are likely to increase and, consequently, their ecological risk will also increase.

The data generated from this project will provide a baseline to compare future loads, concentrations and detection frequencies of the alternate pesticides. Furthermore, the information will be provided for the Paddock to Reef Integrated Monitoring, Modelling and Reporting Program. Lastly, this project will provide important information for assessing the pesticide monitoring, policy and regulatory activities related to achieving the targets of Reef Plan 2009, 2013 and 2018.

Contents

1 Introduction

1.1 Background

It is widely acknowledged that the Great Barrier Reef (GBR) is at significant risk from degraded water quality caused by pollutants exported from catchments adjacent to the GBR (Wachenfeld et al. 1998; State of Queensland and Commonwealth of Australia 2003; DPC 2008; Brodie et al. 2008; Hunter and Walton 2008; Brodie et al. 2009; Packett et al. 2009; Brodie et al. 2010; Brodie et al. 2013a, 2013b; Schaffelke et al. 2013). Evidence of elevated anthropogenic loads of total suspended solids, nutrients and pesticides exported to the GBR lagoon since European settlement have been reported extensively over recent years (e.g. Nicholls 1988; Eyre 1998; Wachenfeld et al. 1998; Fabricius et al. 2005; Hunter and Walton 2008; Packett et al. 2009; Brodie et al. 2010; DPC 2011; Kroon et al. 2011; Smith et al. 2012; Turner et al. 2012; Kroon et al. 2013; Turner et al. 2013; Wallace et al. 2014; Wallace et al. in prep). In order to improve water quality entering from these catchments, the Queensland and Australian Governments cooperatively initiated the Reef Water Quality Protection Plan (Reef Plan 2009 and 2013, Reef Water Quality Protection Plan Secretariat 2009, 2013) with the long term goal "to ensure that by 2020 the quality of water entering the reef from broadscale land use has no detrimental impact on the health and resilience of the Great Barrier Reef" (Reef Water Quality Protection Plan Secretariat 2009, 2013).

Along with nutrients and sediment, pesticides transported in catchments from agricultural areas were targeted by the Queensland and Federal governments to achieve the Reef Plan's (2009, 2013) long-term goal. Five photosystem II inhibiting (PSII) herbicides have been the primary focus for achieving the target set to reduce pesticide loads transported to the GBR. These five priority PSII herbicides (ametryn, atrazine, diuron, hexazinone and tebuthiuron) have been the most widely and frequently detected pesticides in the GBR (e.g. Smith et al. 2012; Turner et al. 2012, 2013; Wallace et al. 2014, in press) and its catchments, and are subsequently considered as being the most threatening pesticides to the health of the marine ecosystems in the GBR (Lewis et al. 2009).

Thirty-five catchments flow into the GBR lagoon, and cover an area of approximately 424,000 (km^2). These catchments extend from the tropics to the subtropics over 1500 km of the Queensland coastline (DPC 2011). In 2009, the monitoring of PSII herbicides in GBR catchments was included in the Great Barrier Reef Catchment Loads Monitoring Program (GBRCLMP), which was established in 2006 for monitoring nutrients and total suspended solids to assist in evaluating the progression towards the water quality targets of Reef Plan. Of the 35 GBR catchments, the GBRCLMP monitors 11 catchments in total, nine of which are monitored for pesticides. These nine catchments are:

- North Johnstone, Tully and Herbert catchments in the Wet Tropics region

- Burdekin and Haughton catchments in the Burdekin region
- Plane and Pioneer catchments in the Mackay Whitsunday region
- Fitzroy catchment in the Fitzroy region
- Burnett catchment in the Burnett-Mary region

As part of farming best management practice, farmers have been encouraged to replace the priority PSII herbicides with knockdown products such as 2,4-D, glyphosate and paraquat (Carroll et al. 2012). Furthermore, recently imposed restrictions on the use of diuron by the Australian Pesticides and Veterinary Medicines Authority (APVMA) are likely to strengthen the changes in pesticide use from the priority PSII herbicides to alternate pesticides. We know (anecdotally) that farmers have begun supplementing the five PSII herbicides with other herbicides as well, and their potential environmental impacts to GBR waterways are currently unknown. In addition to the knockdown products (2,4-D, glyphosate and paraquat), some of the pesticides believed to be used in place of the five priority PSII herbicides include:

- Acifluorfen (e.g. Blazer)
- Imazapic (e.g. Flame)
- Imazethapyr (e.g. Conquest)
- Isoxaflutole (e.g. Balance)
- Metribuzin (e.g. Soccer)
- Trifloxysulfuron-Na (e.g. Krismat)
- Metolachlor (e.g. Dual Gold)
- Trifluralin (e.g. Treflan)
- Pendimethalin (e.g. Stomp Xtra)

Understanding the use of any alternate[1] herbicides, their transport from agricultural land to waterways and their ecotoxicity is required in order to assess whether such pesticides pose a significant risk to the health and resilience of the GBR. Currently the prevalence of these alternate pesticides in waterways draining to the GBR has not been determined and methods for their analysis are not available routinely in Australia. We are also unaware whether any of the alternate pesticides are having environmental impacts.

[1] Alternate pesticides are defined in this report as any herbicide that has been used or could be used by farmers in the GBR catchment area that is not one of the five priority PSII herbicides; ametryn, atrazine, diuron, hexazinone and tebuthiuron. Alternate pesticides do not, in this report, include insecticides or fungicides.

1.2 Objectives

The objectives of this project are to:

1. Provide an initial baseline data set and assessment of the prevalence of alternate pesticides in GBR waterways. In particular, to determine if alternate pesticides (e.g. 2,4-D[2], acifluorfen, imazapic, imazethapyr, isoxaflutole, metribuzin, trifloxysulfuron-Na, metolachlor, trifluralin, pendimethalin) which are being applied in the catchments have the potential to be transported to the GBR?
2. Measure concentrations and calculate loads of the alternate pesticides to inform catchment models, to assess risk to aquatic ecosystems and their likely contribution to reef pollution. Specifically, the following will be calculated:
    a. Annual loads
    b. Mean concentrations
    c. Detection frequency
    d. Trends in the presence of the alternative vs the priority pesticides on a spatial scale
    e. Trends in the presence of alternative vs priority on a temporal scale for: metolachlor, metribuzin, trifluralin and pendimethalin
3. Enable a more comprehensive estimate of total pesticide loads within catchments discharging to the GBR and within the GBR environment.
4. Inform farming best management practices for pesticides of concern that are detected in catchments, to help avoid perverse environmental outcomes.

2 Methods

2.1 Monitoring sites

Six GBR catchments were selected for monitoring alternate pesticides out of the nine catchments routinely monitored for the priority PSII herbicides by the GBRCLMP (Turner et al. 2012, 2013; Wallace et al. 2014, in press). The six sites were the North Johnstone, Tully and Herbert Rivers in the Wet Tropics, Barratta Creek in the Lower Burdekin, and Pioneer River and Sandy Creek in the Mackay-Whitsundays (Figure 2.1). These sites were selected based on previous monitoring data indicating that the priority PSII herbicides were detected frequently at these sites and generally in higher concentrations than the other three catchments routinely monitored as part of the GBRCLMP (i.e. the Burdekin, Fitzroy and Burnett rivers) (Turner et al. 2012, 2013; Wallace et al. 2014, in prep). Summary information on the six monitoring sites selected for this study, including the gauging

[2] While it is known that paraquat and glyphosate are also commonly used as knockdown products in GBR catchments, due to budget constraints, water samples were not analysed for these pesticides.

station identification, location, the surface area of each catchment, the area monitored and the dominant land use types upstream of the gauging station is provided in Table 2.1.

2.2 Water quality sampling

Water samples were collected according to methods outlined in the Environmental Protection (Water) Policy Monitoring and Sampling Manual (DERM 2010). Water quality samples were collected between 1 July 2012 and 30 June 2013. All pesticide samples were manually collected except in the Pioneer where a refrigerated automatic sampler fitted with glass bottles was installed. Intensive sampling (daily or every few hours) occurred during high flow events and reduced sampling (monthly) was undertaken during ambient (low or base-flow) conditions. The number of samples collected and the number of events covered at each site are reported in Table 2.2. Samples were stored and transported in accordance with the Environmental Protection (Water) Policy Monitoring and Sampling Manual (DERM 2010).

2.3 Pesticide sample analysis

Queensland Health Forensic and Scientific Services (QHFSS) (Coopers Plains, Queensland) undertook the analysis of water samples for pesticides. These laboratories are accredited by the National Association of Testing Authorities (NATA, Australia) for the analyses conducted. Samples were analysed using a combination of solid-phase extraction (SPE) with liquid chromatography-mass spectrometry (LCMS) and a liquid-liquid extraction (LLE) with gas chromatography-mass spectrometry (GCMS) (Turner et al. 2013; Wallace et al. 2014). Due to the extraction processes, chemicals analysed using SPE are considered as a dissolved fraction only, whereas chemicals extracted using LLE are considered as the whole fraction.

The five priority PSII herbicides were analysed using the LCMS method which also detects other polar pesticides including metolachlor (Table 5.1, Appendix 1). The LCMS method is the principal analytical method used in previous years by the GBRCLMP for pesticide analysis. GCMS detects more non-polar pesticides (e.g. organochlorines and organophospates) and includes metribuzin, trifluralin and pendimethalin in the analysis suite (Table 5.2, Appendix 1). The GCMS method has been used only sporadically in previous years of pesticide monitoring by the GBRCLMP.

At the commencement of this study, analytical methods for the detection of a number of the alternate pesticides at environmentally relevant concentrations were not available in laboratories in Australia, i.e. isoxaflutole, imazapic, trifloxysulfuron-Na, imazethapyr, acifluorfen. Therefore, we coordinated with QHFSS to develop new analytical methods for the extraction and analysis of these five alternate pesticides. The resulting analytical method was SPE combined with LCMS, similar to the methods used for the priority PSII herbicides. QHFSS created a second LCMS analysis suite

containing these five alternate pesticides, along with 21 other pesticides that were not previously available in the LCMS suite (Table 5.3, Appendix 1).

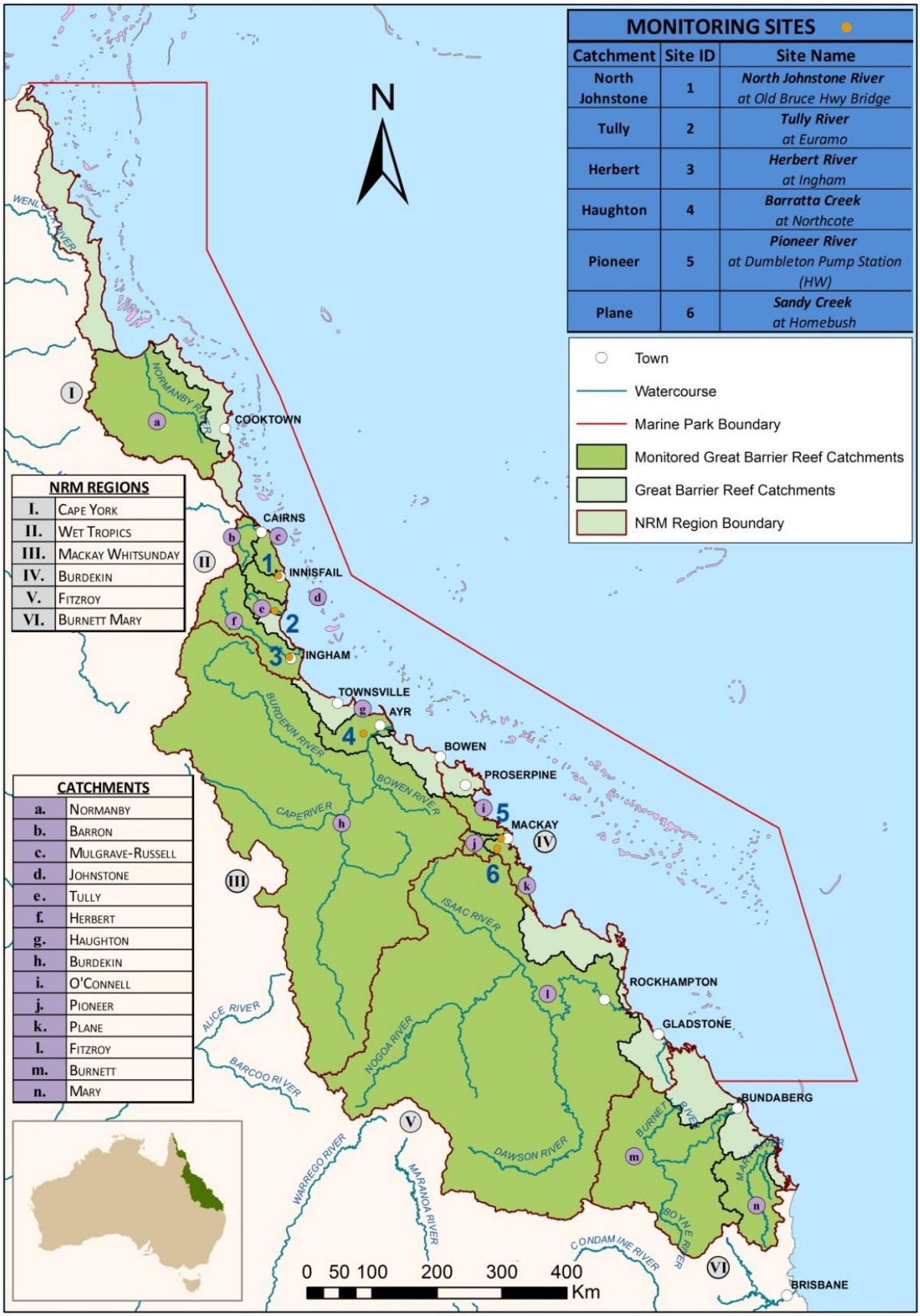

Figure 2.1: Map indicating the natural resource management regions, catchments and sites where priority photosystem II inhibiting herbicides and alternate pesticides were monitored between 1 July 2012 and 30 June 2013

Table 2.1 Summary information on sites monitored for priority photosystem II inhibiting herbicides and alternate pesticides between 1 July 2012 and 30 June 2013.

NRM region	Catchment	Gauging station	River and site name	Site location		Total catchment surface area (km^2)	Monitored surface area (km^2)	Per cent of catchment monitored	Dominant land uses (DPC 2011)
				Latitude	Longitude				
Wet Tropics	**Johnstone**	**112004A**	**North Johnstone River at Tung Oil**	-17.54564	145.93253	2325	925	40	Conservation, grazing, sugarcane, and horticulture
	Tully	**113006A**	**Tully River at Euramo**	-17.99214	145.94247	1683	1450	86	
	Herbert	**116001F**	**Herbert River at Ingham**	-18.63275	146.14267	9844	8581	87	
Burdekin	**Haughton**	**119101A**	**Barratta Creek at Northcote**	-19.69228	147.16879	4051	753	19	Grazing, irrigated sugarcane, horticulture and cropping
Mackay-Whitsundays	**Pioneer**	**125013A**	**Pioneer River at Dumbleton Pump Station**	-21.14407	149.07528	1572	1485	94	Grazing, sugarcane, conservation and forestry
	Plane	**126001A**	**Sandy Creek at Homebush**	-21.28306	149.02278	2539	326	13	

Table 2.2 Pesticide sampling summary, including the number of samples collected and the number of events covered, for monitored for this study between 1 July 2012 and 30 June 2013.

River and site name	Number of samples collected	Number of events sampled (total number of events)
North Johnstone River at Tung Oil	5	1 (11)
Tully River at Euramo	64	6 (7)
Herbert River at Ingham	44	7 (9)
Barratta Creek at Northcote	31	5 (10)
Pioneer River at Dumbleton Pump Station	104	7 (9)
Sandy Creek at Homebush	26	6 (10)

2.4 River discharge

The selected monitoring sites at each catchment were established at existing Queensland Government stream gauging stations (Table 2.1). River discharge data (hourly-interpolated flow, $m^3 s^{-1}$) were extracted from the Department of Natural Resources and Mines, Surface Water Database using the Hydstra pre-programmed script (http://watermonitoring.derm.qld.gov.au/host.htm). The preference was to use data with a quality code of 10 to 30, based on the Department of Natural Resources and Mines hydrographic methodology for quality rating flow data (DERM 2011). If such data were not available due to a gauging station error, flows with a quality code of 60 were used (Turner et al. 2012, 2013; Wallace et al. 2014, in prep). If samples were collected at sites without an operating Department of Natural Resources and Mines gauging station (due to logistic or work health and safety reasons, or decommissioning) a 'timing and flow factor' was calculated based on flow data from the nearest upstream gauging station. Timing and flow factors were applied at Pioneer River at Dumbleton Pump Station estimated from historical discharge data including Mirani Weir GS 125007A. In general, the factors adjust the timing of the flow to account for the delay in time it takes water to flow from the gauging station to the monitoring site. For details on these timing and flow factors refer to Turner et al. 2013 and Wallace et al. 2014.

The method used to calculate discharge by the Surface Water Database is:

Equation 1

$$q = va$$

where, q is the discharge ($m^3 s^{-1}$), a = the cross-sectional area of the river (m^2), and v = average velocity of the flow in the cross-sectional area (ms^{-1}).

Discharge is calculated for sub-sectional areas of the river channel and summed to determine the discharge across the whole cross-sectional area. Sub-sectional areas were calculated from a known width multiplied by the river gauge height at time *t*. River gauge height was recorded by gauging

stations using a float or a pressure sensor at intervals of approximately fifteen minutes. Flow velocity was determined for each cross-sectional area at time *t* using a current meter. Flow records were extracted for each site from the Queensland Government electronic data management system (Hydstra).

The exceedence probability (P_e) of the annual discharge was calculated for each monitored site by:

Equation 2

$$P_e = 1 - \frac{R_i}{N+1}$$

where *R* is the rank of the i^{th} total annual (June to July) discharge, and *N* is the number of annual discharge observations at the monitoring site.

2.5 Data analysis

2.5.1 Loads estimation

The annual pesticide load is defined as the total amount of a pesticide transported past the gauging station. The loads do not represent the total load discharged to the Great Barrier Reef lagoon[3]. Annual load estimations were calculated using the Loads Tool component of the Water Quality Analyser 2.1.1.4 (eWater 2011) as per the methods outlined in (Turner et al. 2012, 2013; Wallace et al. 2014, in prep). In summary, one of two load calculation models was used to calculate the annual load for each pesticide at each site: average load (linear interpolation of concentration) or the Beale ratio. The average load (linear interpolation of concentration) and Beale ratio methods were calculated using equations 3 and 4, respectively:

Equation 3

$$Load = \sum_{j=1}^{n} \frac{c_j + c_{j+1}}{2} \times q_j$$

where c_j is the j^{th} sample concentration, and q_j is the inter-sample mean flow (eWater 2011).

Equation 4

$$Load = Q\left(\frac{\bar{l}}{\bar{q}}\right)\left\{\frac{1+\frac{1}{N}\frac{\rho\sigma L\sigma Q}{\bar{l}\bar{q}}}{1+\frac{1}{N}\frac{\sigma^2 Q}{\bar{q}^2}}\right\}$$

[3] The end-of-system monitoring sites are not located at the mouth of the river or creek (refer to Section 2.1) and this unmonitored portion of the catchment or sub-catchment may contribute, remove or degrade pesticides.

where Q is the total discharge for the period, $\bar{l}$ is the average load for a sample, L is the observed load, $\bar{q}$ is the average of *N* discharge measurements, σ is the standard error of L and ρ is the correlation coefficient for L and Q (eWater 2011; Joo et al. 2012).

The most appropriate method (average load (linear interpolation of concentration) or Beale ratio) to calculate the annual load was determined using the following criteria (Turner et al. 2012, 2013; Wallace et al. 2014, in prep):

- if the majority of major events were sampled with sampling points on both the rise and fall, then the average load (linear interpolation of concentration) method was applied
- if the majority of the events were not adequately sampled the Beale ratio was applied.

At some sites, the average load (linear interpolation of concentration) method was determined to be the most appropriate calculation method, but inadequate ambient sampling points were available to calculate annual loads using Water Quality Analyser 2.1.1.4 (eWater 2011). In these cases, calculated data points that were 50 per cent of the lowest reported concentration were inserted into the dataset at 1 July 2011 and the lowest reported concentration was inserted into the dataset at 30 June 2012 to provide tie-down concentrations for calculations (eWater 2011).

2.5.2 Limit of reporting

The limits of reporting (LORs) for each pesticide measured in the current study are presented in Appendix 1. The method for dealing with < LOR concentration data adopted in this study was based on the methods of Turner et al. (2012; 2013). The exact concentration of < LOR samples is not known, it could be any concentration between zero and the LOR. If a pesticide was present at a non-zero concentration then they will contribute to the load for that pesticide. When a pesticide was detected (> LOR) in the same event as < LOR values it is possible that the concentration of the pesticide in the < LOR sample was not zero. For such data, half the LOR (½ LOR) was adopted so that a standard estimate of the load could be made. However, when there was no evidence that a pesticide was present (i.e. all concentrations for the pesticide were < LOR during an event) then all < LOR values were assumed to be zero and so they do not contribute to the estimate of the load for the pesticide.

Boxplots were created based on a log-scale and therefore a value of 0 µg/L could not be used. Therefore, for the boxplots the < LOR values were converted to ½ LOR for pesticides in which at least one sample was detected above the LOR. Pesticides were excluded from the analysis if all samples at a site were < LOR.

It should be noted that not all pesticides have the same LOR (Appendix 1). This has a number of implications. A pesticide with a high LOR means that when converting the < LOR to ½ LOR, the resulting loads and concentration averages may be higher than for other pesticides which have a lower LOR. For example, metribuzin has an LOR of 0.1 µg/L compared to the PSII herbicides which

have an LOR of 0.01 µg/L, thus when converting the < LOR to ½ LOR, the metribuzin < LOR will be converted to 0.05 µg/L, which is ten times the ½ LOR of the PSII herbicides (0.005 µg/L). Thus when the loads and concentration averages are calculated, metribuzin could have a higher load based on the above methodology.

2.5.3 Statistical Analysis

All descriptive statistics were performed using Microsoft Excel® 2010. Box plots were created using SigmaPlot 12.5 (SYSTAT software Inc.).

2.6 Ecotoxicity Assessment

The alternate pesticides and priority PSII herbicides were compared with the Australian and New Zealand water quality guideline trigger values (TV) for the default level of protection of freshwater ecosystems (i.e. the concentration that should theoretically protect 95% of species – PC95) (ANZECC and ARMCANZ 2000) and recently derived Ecotoxicity Threshold Values (ETVs) (Smith et al. in prep). The ETVs were calculated using the proposed new method for deriving water quality guideline values (Batley et al. 2013; Warne et al. in review). However, it should be noted, that although the ETVs were calculated using the same method as guideline values and should provide the same level of protection, they are termed Ecotoxicity Threshold Values because, at the time of reporting, they had not been nationally endorsed or have any official status.

Not all of the alternate pesticides have a TV or ETV available for comparison, therefore, toxicity ranges were derived. Ecotoxicity data for each alternate pesticide were collated using the USEPA ECOTOX Database (USEPA 2014). The data were selected using similar methods as those used to derive the ETVs; i.e. one chronic NOEC (no observed effective concentration) or EC10 (the concentration which causes a 10% effect) value was selected per phototrophic[4] species. If there were multiple values per species, these were averaged. The phototrophic species with the minimum and maximum values were then selected to report the range of toxicity values for each pesticide. The maximum and minimum values for the priority PSII herbicides were taken from the data used to derive the ETVs (Smith et al, in prep).

Hazard units (HU) were calculated as a measure of the risk of the concentrations detected in catchments. The HU was calculated based on the following equation:

Equation 5

[4] Only phototrophic species were used as all the pesticides in this study are herbicides which have a direct impact on phototrophic species. In addition, we wanted to maintain consistency with the methods used to calculate the ETVs for the priority pesticides. It should be noted that some of the alternate pesticides may have a high toxicity to non-phototrophic species.

$$HU = \frac{C_i}{\min NOEC_i}$$

where, C_i is the 95th percentile of the measured environmental concentration of pesticide *i*, and *min NOECi* is the minimum no observed effect concentration of pesticide *i*.

3 Results & Discussion

3.1 Alternate pesticides detected

For this report all herbicides detected in addition to the five priority PSII herbicides (i.e. ametryn, total atrazine, diuron, hexazinone and tebuthiuron) were classed as alternate pesticides. Fifteen alternate pesticides, along with the five priority PSII herbicides were detected (

Table 3.1). Monitoring at North Johnstone River was limited due to logistical problems with only five samples collected in total over the sampling period. From these five samples, only one alternate (2,4-D) and one priority pesticide (diuron) were detected.

The alternate pesticides detected in GBR catchments included 2,4-D, acifluorfen, bromacil, fluometuron, fluroxypyr, haloxyfop, isoxaflutole, MCPA, metribuzin metsulfuron-methyl, metolachlor, prometryn, propazine-2-hydroxy (a metabolite of propazine), simazine and triclopyr. Although it was believed that imazapic, imazethapyr, trifloxysulfuron-Na, trifluralin and pendimethalin were being used by farmers, these pesticides were not detected in any of the six monitored catchments. All 20 of the pesticides detected, priority and alternates, were detected at Barratta Creek, 14 were detected at Tully River, 12 at Pioneer River, 11 at Sandy Creek, and 8 at Herbert River. Diuron and 2,4-D were the only pesticides detected at all six sites, but this may be a factor of the limited sampling at North Johnstone as atrazine, hexazinone, simazine and tebuthiuron have also been detected at this site in previous years (e.g. Turner et al., 2013; Wallace et al. 2013, in prep). Of the priority pesticides, ametryn, atrazine and hexazinone were detected at all sites, apart from the North Johnstone River. Triclopyr and metolachlor were the only alternate pesticides detected at all sites, apart from the North Johnstone River. Isoxaflutole and metribuzin were detected at four sites, i.e. all except North Johnstone and Herbert rivers. The fifth priority pesticide, tebuthiuron, was detected at only half of the sites monitored (i.e. at 3 sites), along with metsulfuron-methyl, MCPA and simazine. Haloxyfop, bromacil, and fluometuron were detected at only two sites, and fluroxypyr, acifluorfen, prometryn and propazine-2 hydroxy were all only detected at Barratta Creek.

The alternate pesticides detected varied in their mode of action. There were six alternate PSII herbicides (11 in total with the priority PSII herbicides), one amino acid inhibitor, four auxin growth regulators, one cell membrane disruptor, one inhibitor of meristematic tissue growth, one inhibitor of carotenoid biosynthesis and one inhibitor of long chain fatty acids. Having such an array of pesticides with both similar and non-similar modes of action has implications in terms of the potential toxicity exerted by mixtures of these pesticides. This will be discussed in more detail in Section 3.5.

Table 3.1 The pesticides detected in the six monitored Great Barrier Reef catchments, their mode of action and where they were detected.

Mode of Action	Pesticide	Catchments where detected
Priority PSII Herbicides		
PSII inhibitors	Ametryn	Tully, Herbert, Barratta, Pioneer, Sandy
	Atrazine	Tully, Herbert, Barratta, Pioneer, Sandy
	Diuron	Nth Johnstone, Tully, Herbert, Barratta, Pioneer, Sandy
	Hexazinone	Tully, Herbert, Barratta, Pioneer, Sandy
	Tebuthiuron	Barratta, Sandy
Alternate Pesticides		
Amino acid inhibitor	Metsulfuron-methyl	Tully, Herbert, Barratta
Auxin growth regulators	2,4-D	Nth Johnstone, Tully, Herbert, Barratta, Pioneer, Sandy
	Fluroxypyr	Barratta
	MCPA	Barratta, Pioneer, Sandy
	Triclopyr	Tully, Herbert, Barratta, Pioneer, Sandy
Cell membrane disruptor	Acifluorfen	Barratta
Inhibitor of meristematic tissue growth	Haloxyfop	Tully, Barratta
Inhibitor of carotenoid biosynthesis	Isoxaflutole	Tully, Barratta, Pioneer, Sandy
PSII inhibitors	Bromacil	Tully, Barratta
	Fluometuron	Barratta, Pioneer
	Metribuzin	Tully, Barratta, Pioneer, Sandy
	Prometryn	Barratta
	Simazine	Tully, Barratta, Pioneer
	Propazine-2-hydroxy[†]	Barratta
Inhibitor of long-chain fatty acids	Metolachlor	Tully, Herbert, Barratta, Pioneer, Sandy

[†] Metabolite of propazine

3.2 Pesticide concentration trends

3.2.1 Comparison of the alternate pesticides to the priority PSII herbicides

The detection frequency (i.e. per cent of samples with pesticide concentrations > LOR) and the annual average pesticide concentrations recorded in 2012–13 were calculated in order to compare the alternate pesticides to the priority PSII herbicides. The trends are presented below for each catchment.

North Johnstone River

As previously stated, only two pesticides were detected in the North Johnstone catchment, one of the priority PSII herbicides, diuron, and an alternate pesticide, 2,4-D. 2,4-D had a markedly higher detection frequency than diuron (Figure 3.1). The distributions of diuron and 2,4-D concentrations (Figure 3.2) demonstrated a similar trend to the detection frequencies, i.e. the distribution of 2,4-D concentrations were higher than for diuron. It should be remembered however, as there were only five samples collected, there is a high level of uncertainty in the concentrations that occur in this catchment for 2012–2013.

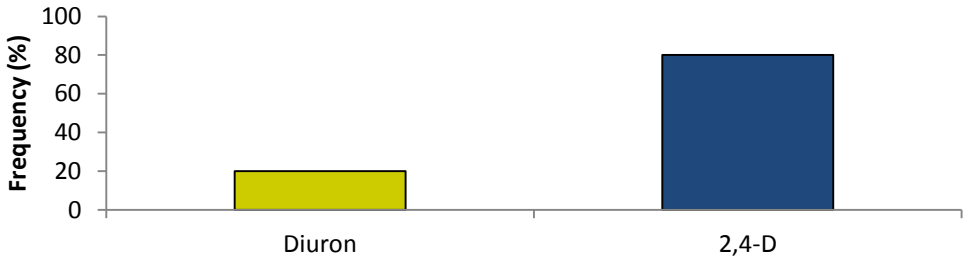

Figure 3.1: Detection frequency of pesticide concentrations greater than the limit of reporting at North Johnstone River between 1 July 2012 and 30 June 2013. Yellow bars represent the priority photosystem II inhibiting herbicides and the blue bars represent the alternate pesticides (n = 5).

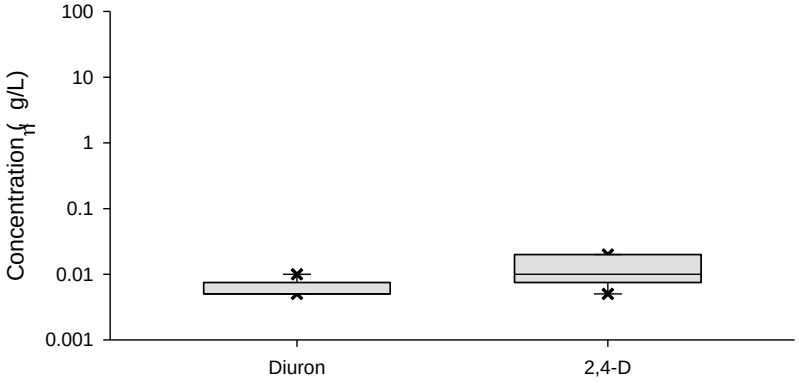

Figure 3.2: Box plots representing the distribution of pesticide concentrations detected in the North Johnstone River between 1 July 2012 and 30 June 2013. The top and bottom boundary lines of the box represent the 75th and 25th percentiles (respectively); the straight line within the box represents the median; the error bars represent the 90th and 10th percentiles; and the X symbol represents the 5th and 95th percentiles (n = 5).

Tully River

Four out of the five priority PSII herbicides (ametryn, atrazine, diuron and hexazinone) were detected at Tully River. The alternate pesticides that were detected were 2,4-D, haloxyfop, isoxaflutole, metolachlor, metribuzin, metsulfuron-methyl, simazine and triclopyr (Figure 3.3). Three of the priority PSII herbicides and one of the alternate pesticides were detected in at least 50% of samples (Figure 3.3); diuron was detected at the greatest frequency (65%), followed by 2,4-D (64%), hexazinone (55%) and atrazine (52%). The remaining alternate pesticides all had a detection frequency of less than 10% (isoxaflutole, 8%; metribuzin, 6%; metolachlor, 6%; metsulfuron-methyl, 5%; simazine, 5%; triclopyr, 5%; and haloxyfop,2%), which was comparable to the ametryn detection frequency (6%).

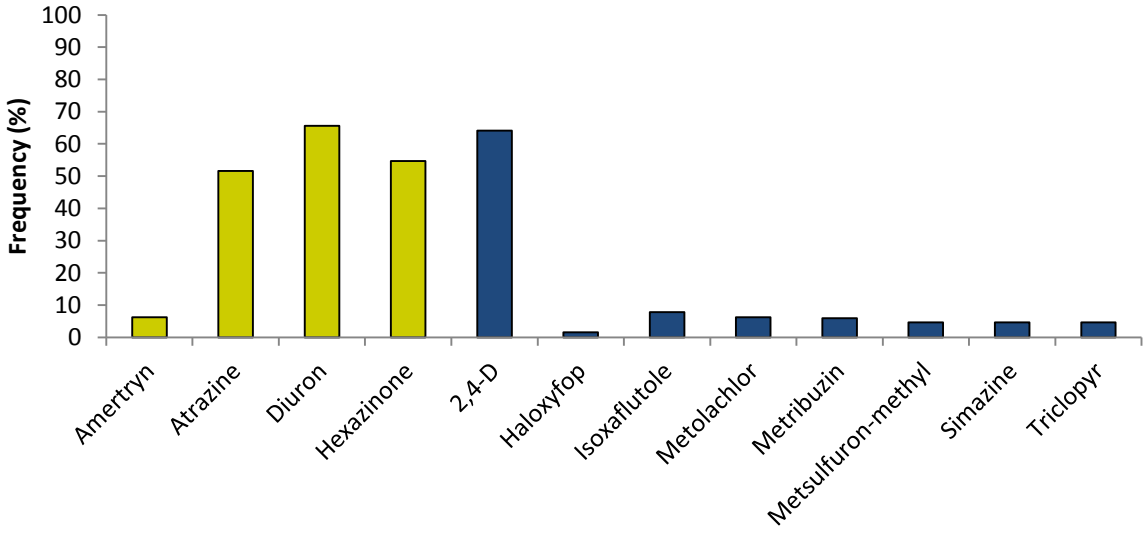

Figure 3.3: Detection frequency of pesticide concentrations greater than the limit of reporting in the Tully River between 1 July 2012 and 30 June 2013. Yellow bars represent the priority photosystem II inhibiting herbicides and the blue bars represent the alternate pesticides (n = 64).

Diuron was also present at the highest concentrations (Figure 3.4). 2,4-D was detected at a greater frequency than atrazine and hexazinone (Figure 3.3), however they all had similar concentration distributions. The metribuzin boxplot indicates a higher range of concentrations, however, this is an artefact of the higher limit of reporting (LOR = 0.1 µg/L) compared to the other pesticides detected (LOR = 0.01 µg/L). The majority of the metribuzin distribution sits below the LOR, which is consistent with the low detection frequency. Similarly, the low detection frequencies of the remaining pesticides also meant that the majority of the concentration distributions sat below the LOR with only the 95th percentile being above the LOR.

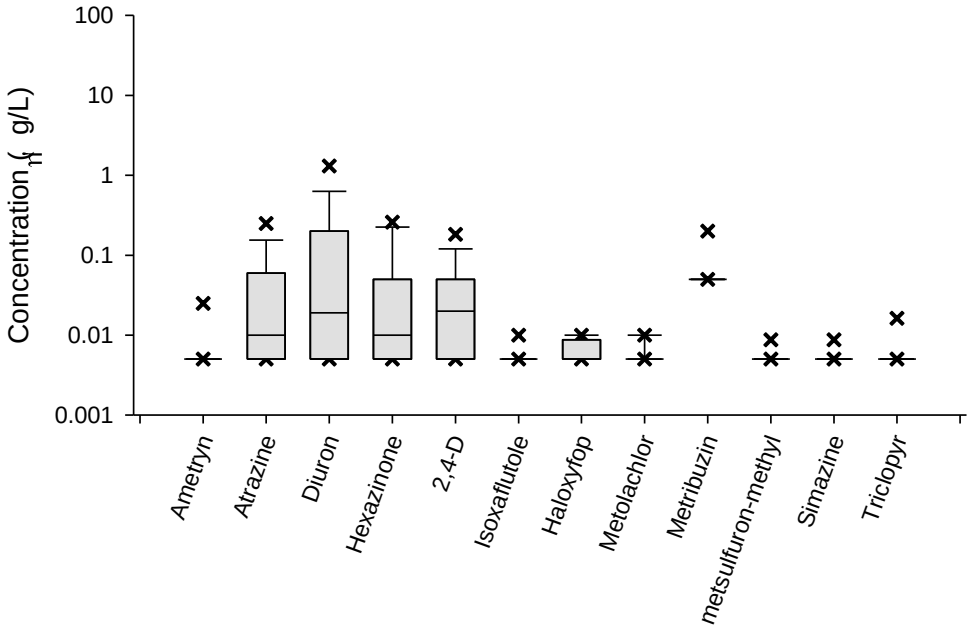

Figure 3.4: Box plots representing the distribution of pesticide concentrations (greater than the limit of reporting) detected at Tully River between 1 July 2012 and 30 June 2013. The top and bottom boundary lines of the box represent the 75th and 25th percentiles (respectively); the straight line within the box represents the median; the error bars represent the 90th and 10th percentiles; and the X symbol represents the 5th and 95th percentiles (n = 64).

Herbert River

All of the priority PSII herbicides were detected in the Herbert River, except for tebuthiuron (Figure 3.5). In addition, four alternate pesticides were detected, 2,4-D, metolachlor, metsulfuron-methyl and triclopyr. The highest detection frequencies were recorded for two of the priority PSII herbicides, hexazinone (63%) and diuron (60%). The only alternate pesticide with a high detection frequency was 2,4-D (52%) which was comparable to atrazine (50%). Ametryn was only detected in

14% of samples, while the remaining alternate pesticides were each detected in less than 10% of samples (metolachlor in 7%, and metsulfuron-methyl and triclopyr in 2% of samples).

Diuron had the highest concentration distributions, followed by hexazinone and atrazine and then 2,4-D (Figure 3.6). Ametryn, metolachlor, metsulfuron-methyl and triclopyr were all present at low concentrations (Figure 3.6).

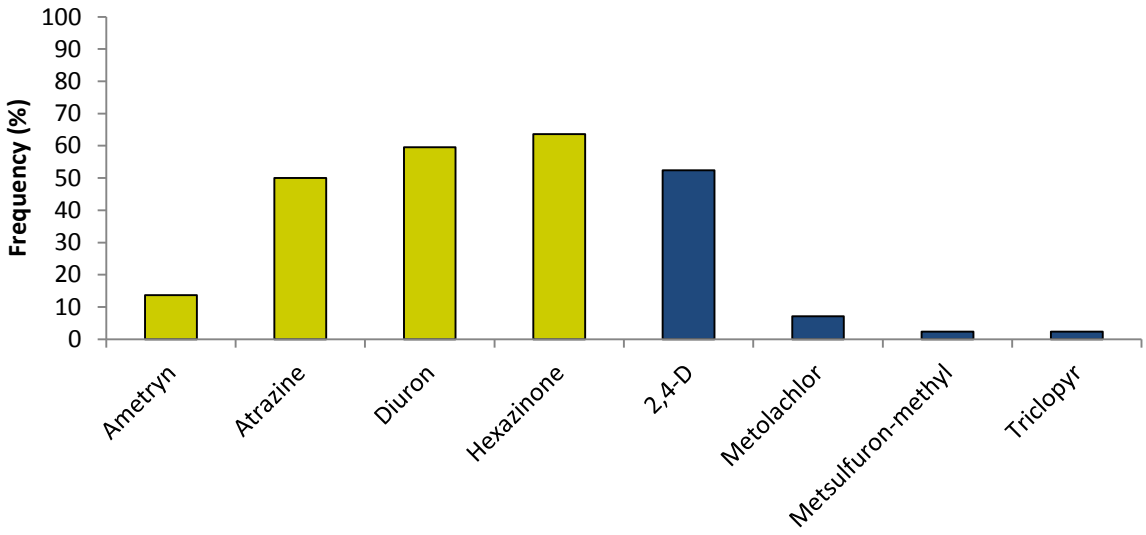

Figure 3.5: Detection frequency of pesticide concentrations greater than the limit of reporting in the Herbert River between 1 July 2012 and 30 June 2013. Yellow bars represent the priority photosystem II inhibiting herbicides and the blue bars represent the alternate pesticides (n = 44).

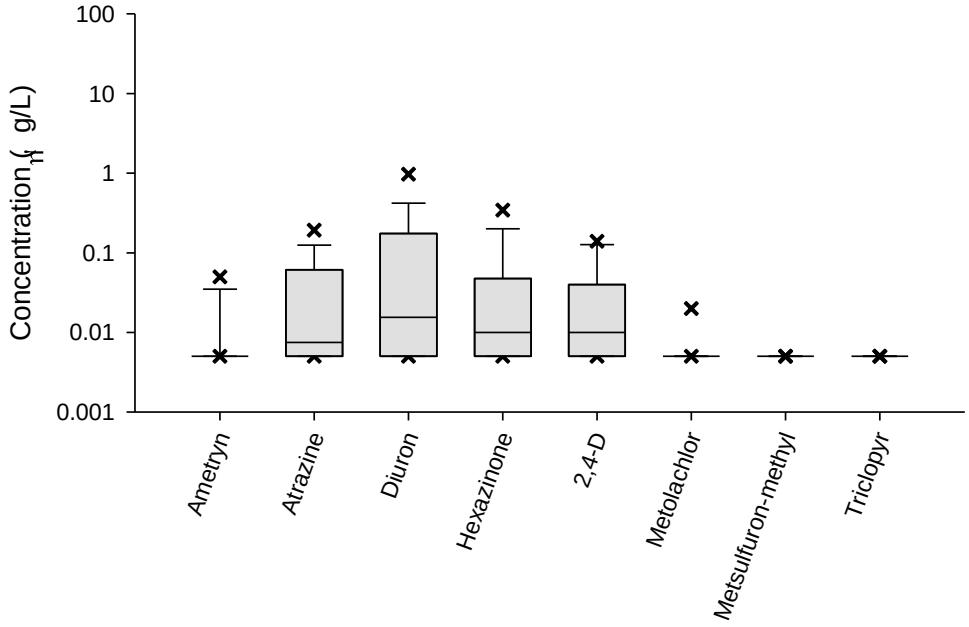

Figure 3.6: Box plots representing the distribution of pesticide concentrations (greater than the limit of reporting) detected in the Herbert River between 1 July 2012 and 30 June 2013. The top and bottom boundary lines of the box represent the 75th and 25th percentiles (respectively); the straight line within the box represents the median; the error bars represent the 90th and 10th percentiles; and the X symbol represents the 5th and 95th percentiles (n = 44).

Barratta Creek

Priority PSII herbicides also had the highest detection frequencies in Barratta Creek (Figure 3.7). Diuron and atrazine had detection frequencies of 100% and ametryn not much less at 94%. The detection frequency of 2,4-D was comparable at 90% and MCPA and metolachlor were also detected in greater than 80% of samples. Isoxaflutole, metribuzin and acifluorfen were detected at a slightly lower rate; 55, 42 and 29% of samples, respectively, but at a greater frequency than haloxyfop, propazine-2-hydroxy, simazine and hexazinone (23–26% of samples). Tebuthiuron was detected only occasionally (3% of samples), along with the alternates herbicides; fluroxypyr, prometryn and triclopyr (6% of samples), bromacil, fluometuron and metsulfuron-methyl (3% of samples).

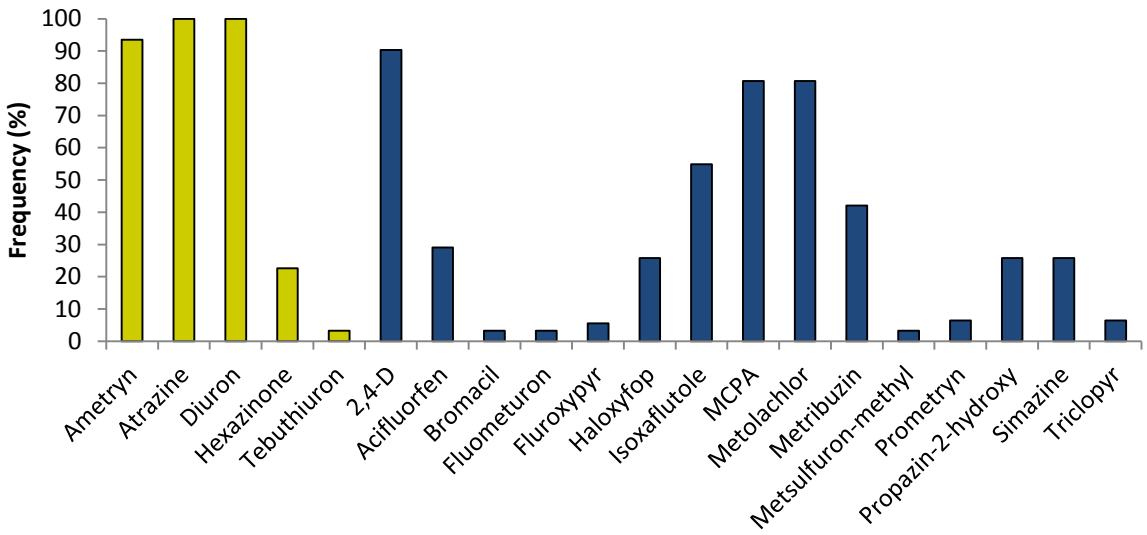

Figure 3.7: Detection frequency of pesticide concentrations greater than the limit of reporting in Barratta Creek between 1 July 2012 and 30 June 2013. Yellow bars represent the priority photosystem II inhibiting herbicides and the blue bars represent the alternate pesticides (n = 31).

Atrazine was present at the highest concentrations with the 95th percentile greater than 10 µg/L (Figure 3.8). The alternate pesticides, 2,4-D and metolachlor also had high 95th percentile concentrations compared to the other alternate pesticides, followed by ametryn and diuron, although the box (25th – 75th percentiles) of the diuron concentrations was higher than the ametryn, 2,4-D and metolachlor boxes. Isoxaflutole, MCPA and metribuzin had lower concentrations compared to atrazine and diuron. Two of the priority PSII herbicides, hexazinone and tebuthiuron, had comparatively low concentrations, along with bromacil, fluroxyyr, fluometuron, haloxyfop, metsulfuron-methyl, prometryn, propazine-2-hydroxy, simazine and triclopyr.

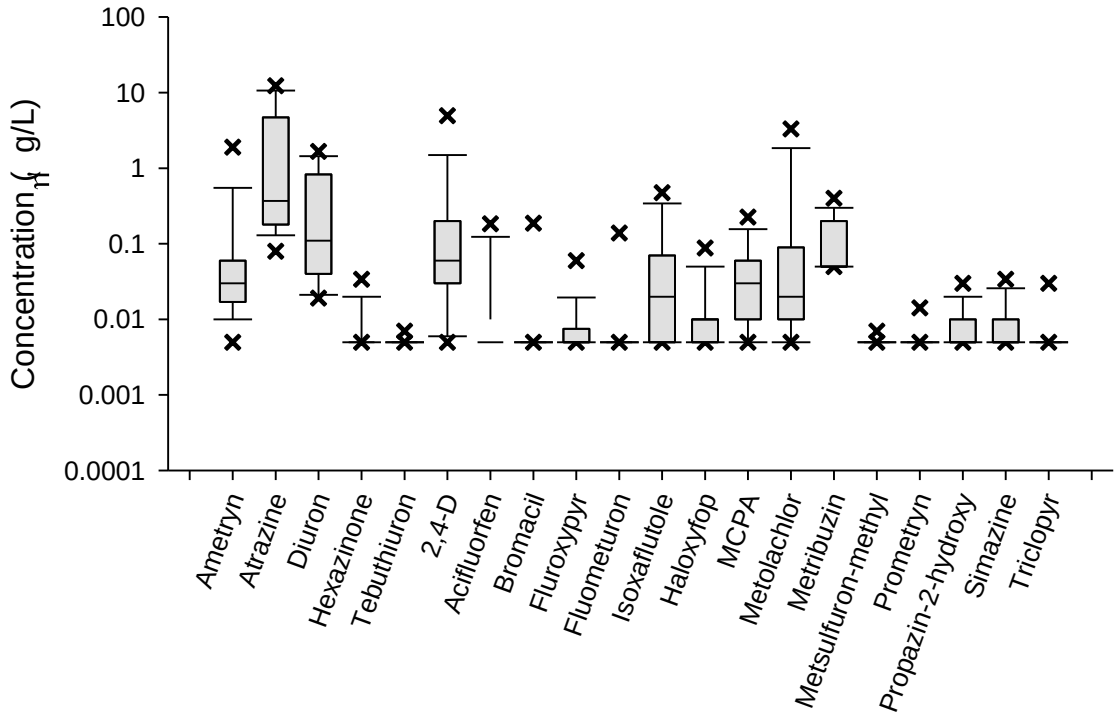

Figure 3.8: Box plots representing the distribution of pesticide concentrations (greater than the limit of reporting) detected in Barratta Creek between 1 July 2012 and 30 June 2013. The top and bottom boundary lines of the box represent the 75th and 25th percentiles (respectively); the straight line within the box represents the median; the error bars represent the 90th and 10th percentiles; and the X symbol represents the 5th and 95th percentiles (n = 31).

Pioneer River

The priority PSII herbicides, diuron, atrazine and hexazinone, were detected at the highest frequency (94, 92 and 85% of samples, respectively) (Figure 3.9). Once again, 2,4-D was detected at a comparable frequency (81% of samples). Ametryn was detected 41% of the time and isoxaflutole, MCPA and metolachlor were detected in about one third of samples and metribuzin in approximately 20% of samples. The three remaining alternate pesticides were detected at a very low frequency; triclopyr (3% of samples), fluometuron (1% of samples) and simazine (1% of samples).

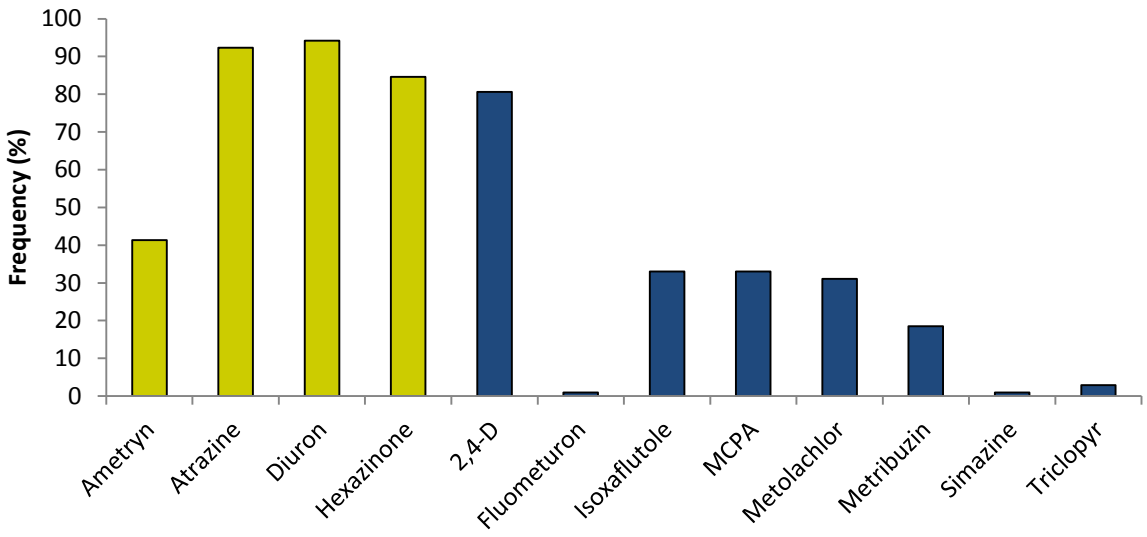

Figure 3.9: Detection frequency of pesticide concentrations greater than the limit of reporting in the Pioneer River between 1 July 2012 and 30 June 2013. Green bars represent the priority photosystem II inhibiting herbicides and the blue bars represent the alternate pesticides (n = 104).

Boxplots of the pesticide concentration distributions are presented in Figure 3.10. The trends in the concentration distributions followed closely to the trends seen with the detection frequencies at this site. That is, three of the priority PSII herbicides, diuron, atrazine and ametryn, had the highest concentration distributions, followed by 2,4-D. The main difference was the distribution of metribuzin concentrations, which are influenced by the higher LOR for metribuzin, but the 95th percentile concentration was still greater than the equivalent 2,4-D concentration. Ametryn also had lower concentrations than metribuzin. Isoxaflutole, MCPA, metolachlor had low concentrations, but these were slightly greater than the concentrations of fluometuron, simazine and triclopyr, which also corresponds with the detection frequencies.

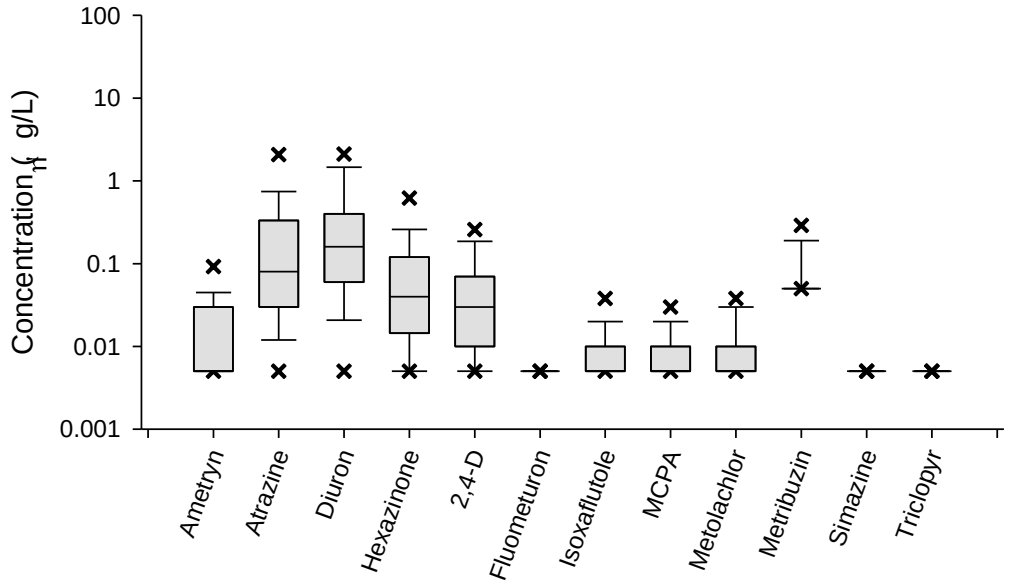

Figure 3.10: Box plots representing the distribution of pesticide concentrations (greater than the limit of reporting) detected in the Pioneer River between 1 July 2012 and 30 June 2013. The top and bottom boundary lines of the box represent the 75th and 25th percentiles (respectively); the straight line within the box represents the median; the error bars represent the 90th and 10th percentiles; and the X symbol represents the 5th and 95th percentiles (n = 104).

Sandy Creek

Four of the priority PSII herbicides and six alternate pesticides were detected at Sandy Creek (Figure 3.11). Of the pesticides detected, seven were detected in more than 60% of samples. Atrazine, diuron and hexazinone had a 100% detection frequency, and 2,4-D, MCPA, metolachlor and isoxaflutole were detected in 73, 77, 69 and 65% of samples, respectively. In addition, ametryn was detected in 46% of samples, metribuzin in 32% and triclopyr had the lowest detection frequency of 8%.

Diuron and atrazine had the highest concentration distributions (Figure 3.12). The metribuzin boxplot also indicated a higher concentration distribution, however, it must be remembered that the high LOR for metribuzin would skew the distribution above 0.05 µg/L. The alternate pesticides had lower concentration distributions more aligned with the distributions of hexazinone and ametryn. The exception to this was Triclopyr which had markedly lower concentrations.

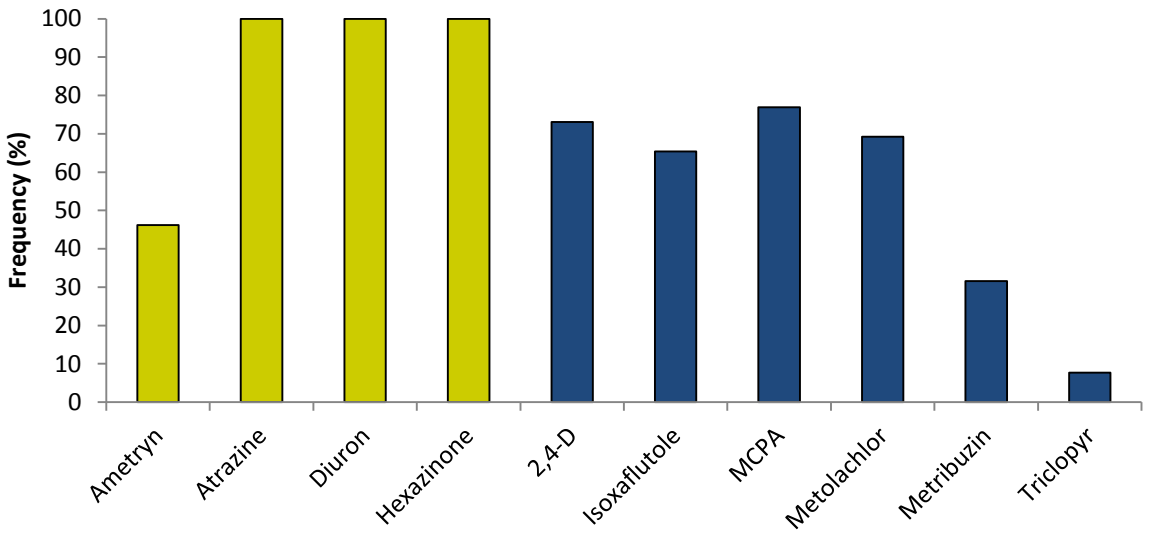

Figure 3.11: Detection frequency of pesticide concentrations greater than the limit of reporting in Sandy Creek between 1 July 2012 and 30 June 2013. Green bars represent the priority PSII herbicides and the blue bars represent the alternate pesticides (n = 26).

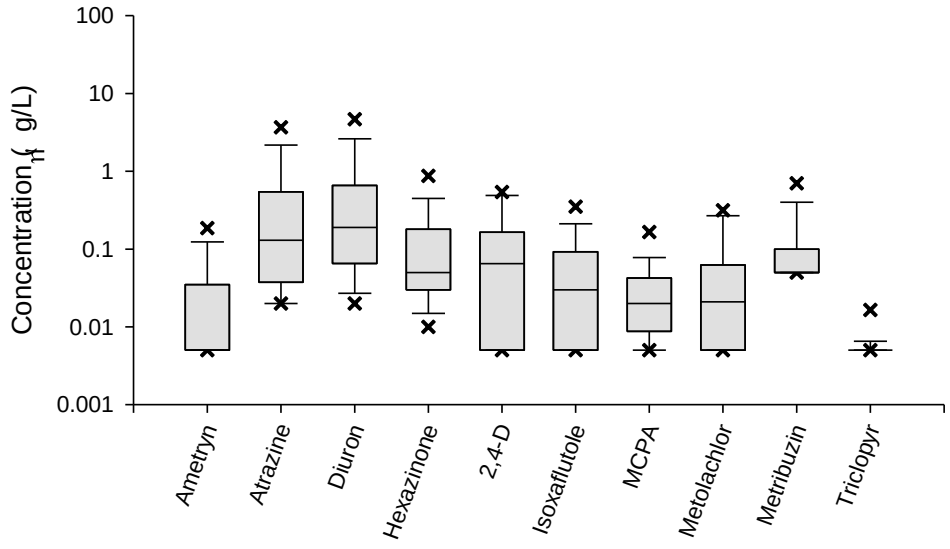

Figure 3.12: Box plots representing the distribution of pesticide concentrations detected in Sandy Creek between 1 July 2012 and 30 June 2013. The top and bottom boundary lines of the box represent the 75th and 25th percentiles (respectively); the straight line within the box represents the median; the error bars represent the 90th and 10th percentiles; and the X symbol represents the 5th and 95th percentiles (n = 26).

3.2.2 Temporal trends

Temporal trends in the five priority PSII herbicides and alternate pesticides, based on the frequency of detection and the annual average concentration, were examined where historical data were available. Temporal trends could be examined for all five priority PSII herbicides, but not necessarily for all sites. Of the alternate pesticides, historical data allowed for temporal trends to be examined for metolachlor, bromacil, fluometuron, prometryn, simazine and metribuzin.

The temporal trends are presented below for each catchment.

North Johnstone

Historical concentration data were available for the North Johnstone River from 2010 (Figure 3.13). Atrazine, diuron, hexazinone, simazine and tebuthiuron were all detected, however only diuron was detected in all three years of monitoring and atrazine in the first two years. The detection frequency of diuron and hexazinone indicated a decreasing trend over time. While the detection frequency of atrazine increased between 2010–11 and 2011–12, it was not detected in 2012–13, indicating that there was no consistent pattern over time. However, this may be a factor of the limited sampling coverage at this site during 2012–2013 that was previously mentioned. Simazine and tebuthiuron were only detected in 2011–2012 – so there is no discernible trend. The annual average concentrations of diuron and atrazine followed the same trends as was seen for the detection frequencies (

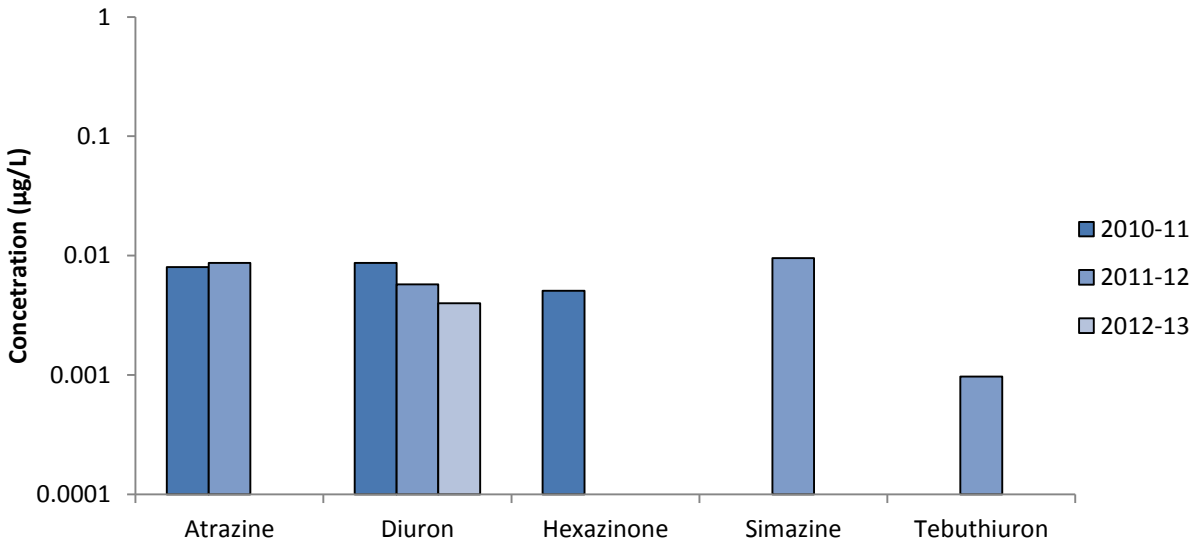

Figure 3.14).

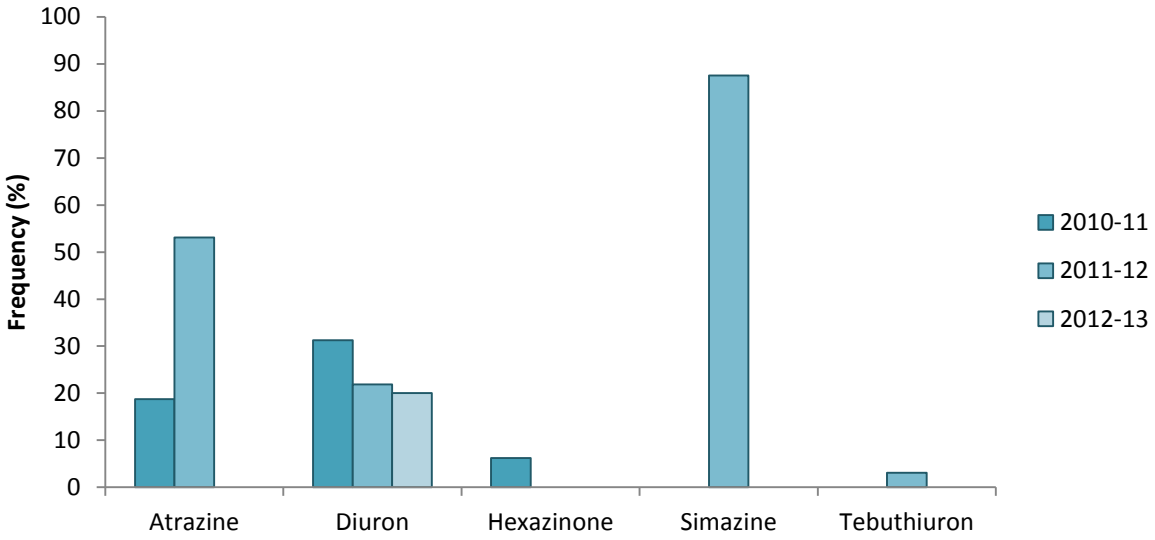

Figure 3.13: Temporal trends in the detection frequency of pesticides (greater than the limit of reporting) in the North Johnstone River for the years 2010–11 (n = 16), 2011–12 (n = 32) and 2012–13 (n = 5).

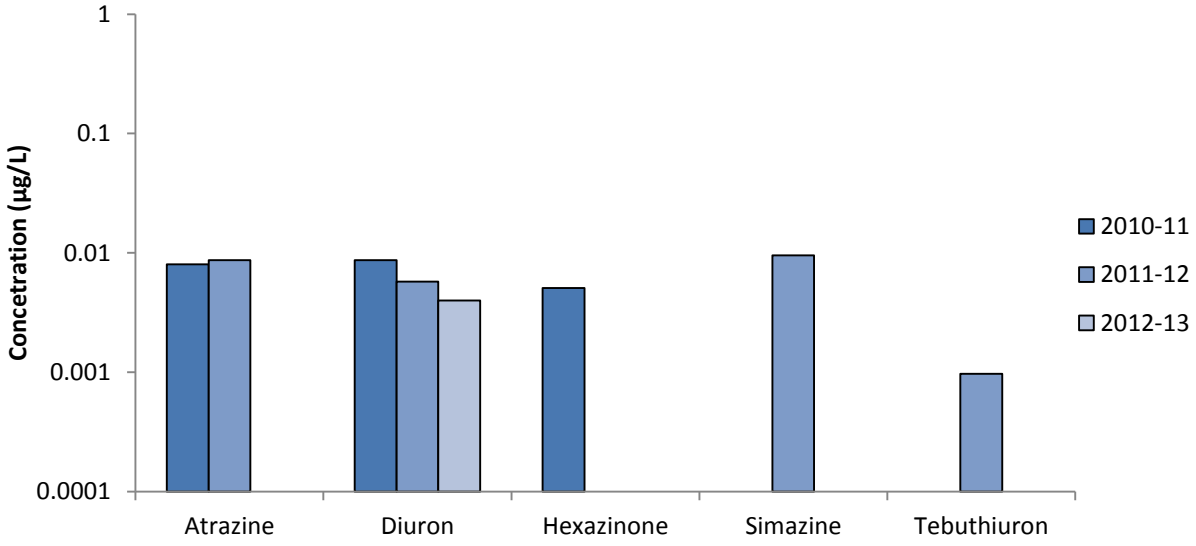

Figure 3.14: Temporal trends in the annual average concentration of pesticides (greater than the limit of reporting) in the North Johnstone River for the years 2010–11 (n = 16), 2011–12 (n = 32) and 2012–13 (n = 5).

Tully River

Monitoring data were available for the Tully River from 2009. Changes in the detection frequency of eight pesticides over four years at Tully River are presented in Figure 3.15. A decreasing trend over time was found for diuron and hexazinone. An increasing trend may be present for ametryn and metolachlor that were not detected in the first two years but were detected at a low frequency in the last two years. The frequencies of atrazine and simazine did not show a consistent increasing or decreasing trend over time, nor did bromacil or tebuthiuron both of which were only detected in 2011-12.

The concentration trends of diuron and hexazinone (Figure 3.16) were not consistent with the trends observed with the detection frequencies, i.e. the concentrations were relatively stable compared with a clear decrease in detection frequency over time. Similarly there was no trend in the atrazine, simazine, bromacil and tebuthiuron concentrations over time. An increasing concentration trend, was observed for ametryn and metolachlor, similar to the trend in detection frequency. However the increasing concentration trend should be judged with caution given the low detection frequencies.

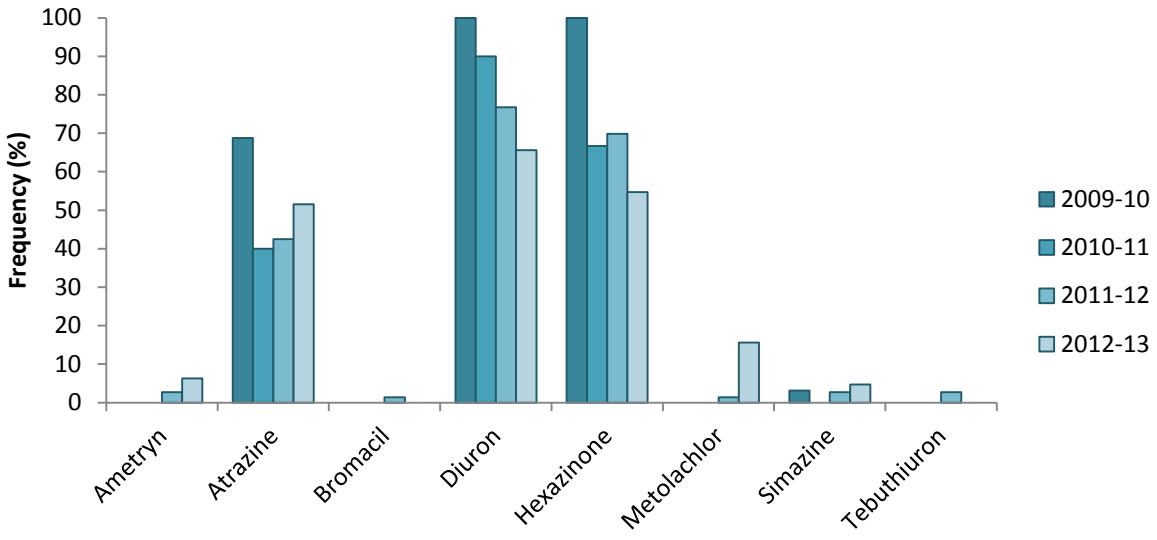

Figure 3.15: Temporal trends in the detection frequency of pesticides (greater than the limit of reporting) in the Tully River for the years 2009–10 (n = 32), 2010–11 (n = 30), 2011-12 (n = 73) and 2012–13 (n = 64).

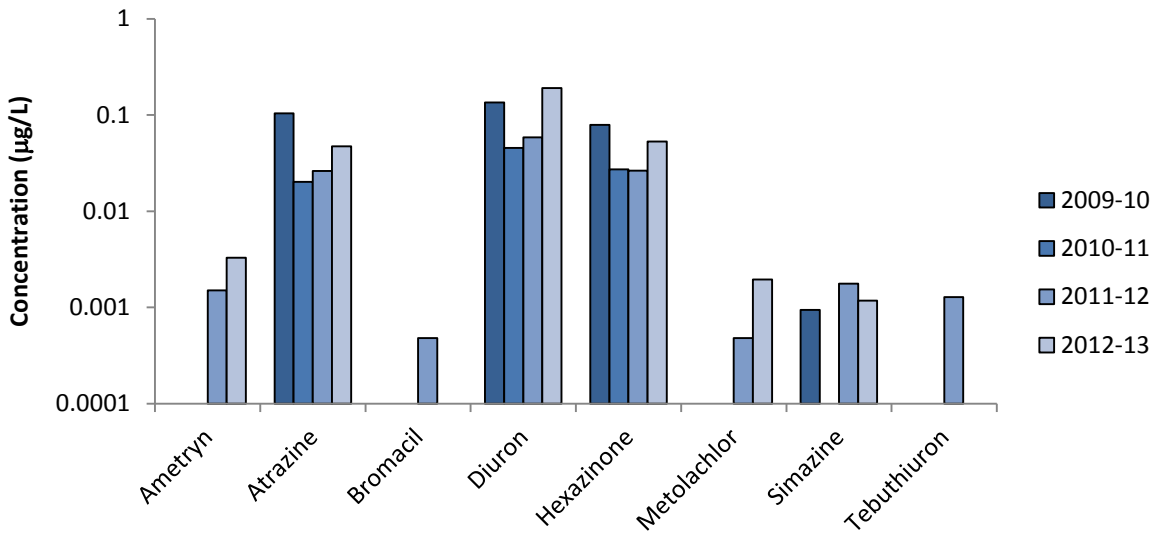

Figure 3.16: Temporal trends in the annual average concentration of pesticides (greater than the limit of reporting) in the Tully River for the years 2009–10 (n = 32), 2010–11 (n = 30), 2011–12 (n = 73) and 2012–13 (n = 64).

Herbert River

Monitoring data were available for temporal trend analysis for the Herbert River from 2010. Increases in detection frequency were observed for atrazine and hexazinone (Figure 3.17). An overall increase in the detection frequency of diuron was observed in 2011–12 and 2012–13 from 2010–11, however the increase was not sequential. An overall decreasing trend was observed for detections of ametryn and metolachlor. Simazine was only detected in the first year of monitoring and therefore may indicate a decreasing trend in this pesticide also.

Changes in the average annual concentrations between 2010 and 2013 are depicted in Figure 3.18. Increases over time in concentrations were observed for diuron and hexazinone. Ametryn, atrazine, and metolachlor showed no trend over time. Similar to the trend in detection frequency, a decreasing trend in concentrations may have occurred for simazine.

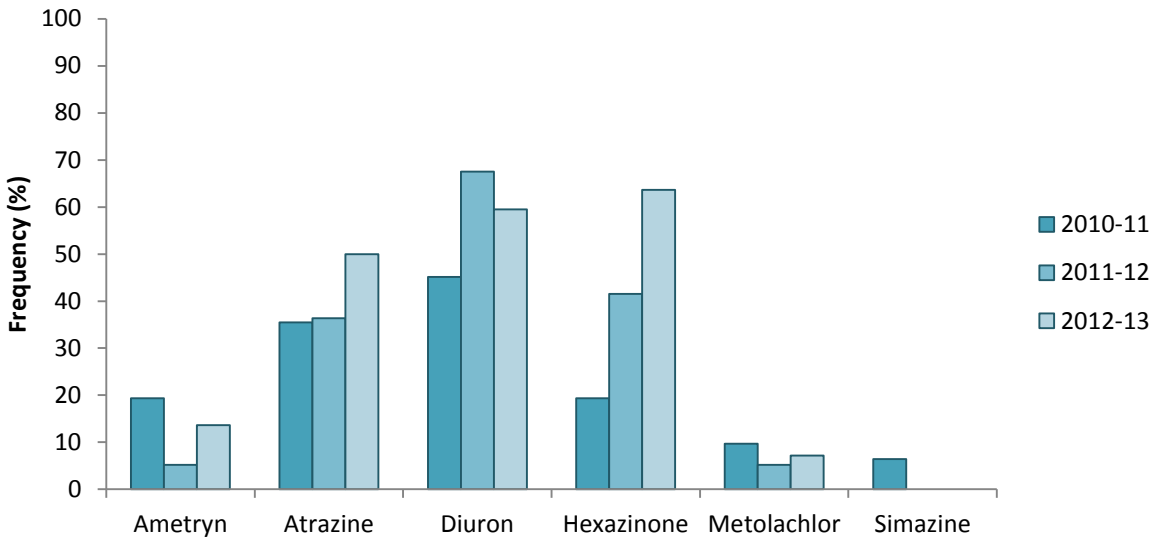

Figure 3.17: Temporal trends in the detection frequency of pesticides (greater than the limit of reporting) in the Herbert River for the years 2010–11 (n = 31), 2011–12 (n = 77) and 2012–13 (n = 44).

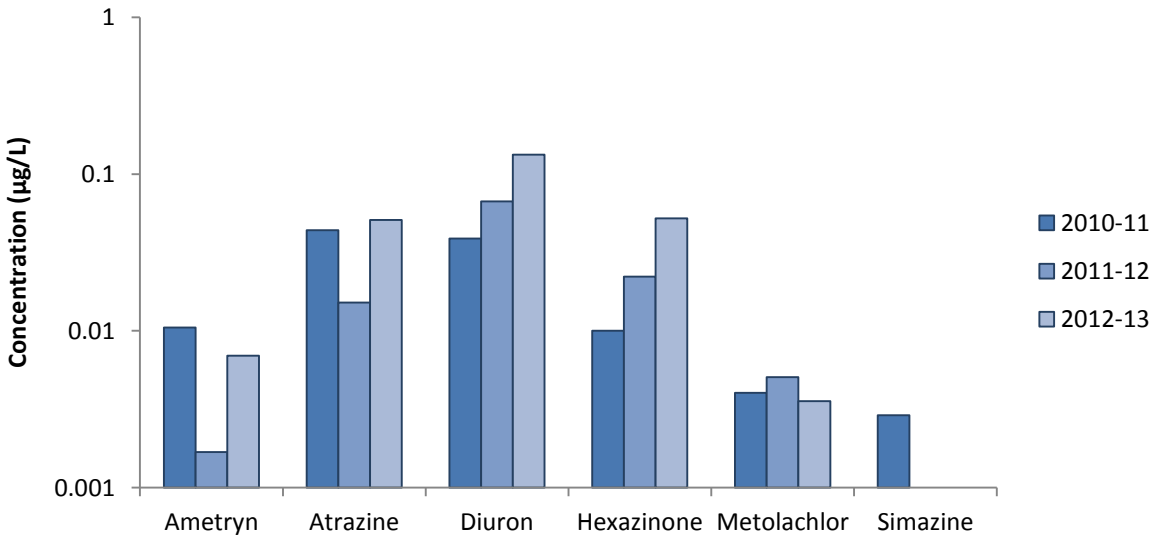

Figure 3.18: Temporal trends in the annual average concentration of pesticides (greater than the limit of reporting) in the Herbert River for the years 2010–11 (n = 31), 2011–12 (n = 77) and 2012–13 (n = 44).

Barratta Creek

Historical data were available from Barratta Creek from 2009 to 2013 (Figure 3.19). Very little variation was observed in the detection frequencies of atrazine and diuron over the four years. Detection frequencies for atrazine and diuron did slightly increase over time, as detections could

only increase by up to 10% before reaching the maximum (100%). Large increases were observed in 2012–13 for ametryn, metolachlor and simazine, along with the first detections of fluometuron and prometryn. Hexazinone and tebuthiuron were the only two pesticides that indicated a decreasing trend in detection frequency. Bromacil appeared to increase but the trend was mixed with two years of no detections.

Some differences were observed for the temporal trends in average concentrations (Figure 3.20). A marked increase in the average concentration was observed in 2012–13 for ametryn and metolachlor. Atrazine also increased in 2012–2013, but it was not a large increase. A steady increase over the four year period was observed for simazine average concentrations, mirroring the trend in detection frequencies. The noted increase in concentration in bromacil, fluometuron and prometryn should be treated with caution due to the low detection frequencies. Average concentrations of diuron and tebuthiuron decreased over the four-year period, whereas hexazinone showed no consistent trend over the four years.

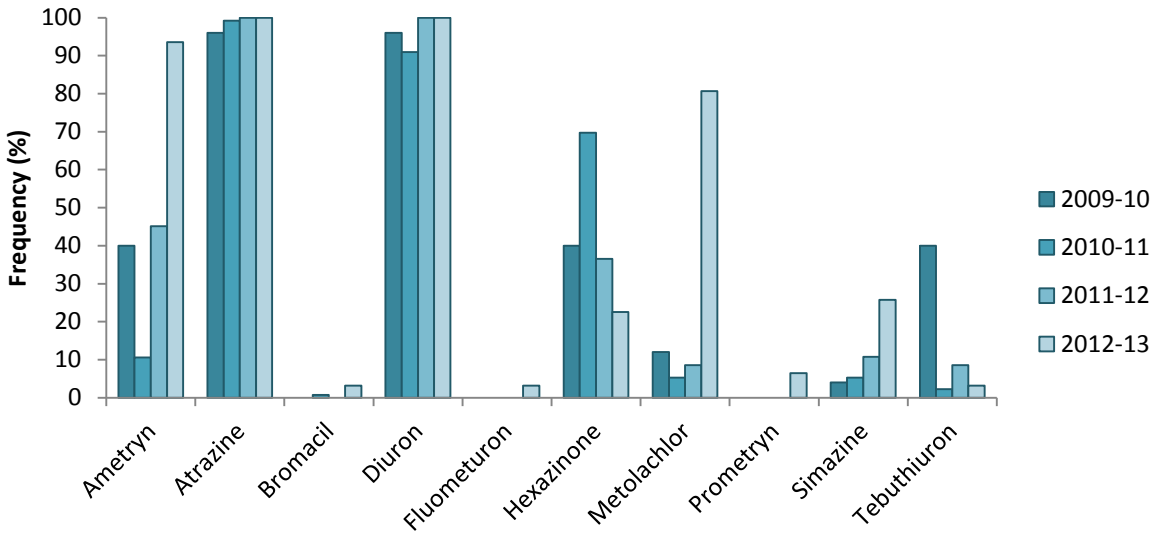

Figure 3.19: Temporal trends in the detection frequency of pesticides (greater than the limit of reporting) in Barratta Creek for the years 2009–10 (n = 25), 2010–11 (n = 132), 2011–12 (n = 93) and 2012–13 (n = 31).

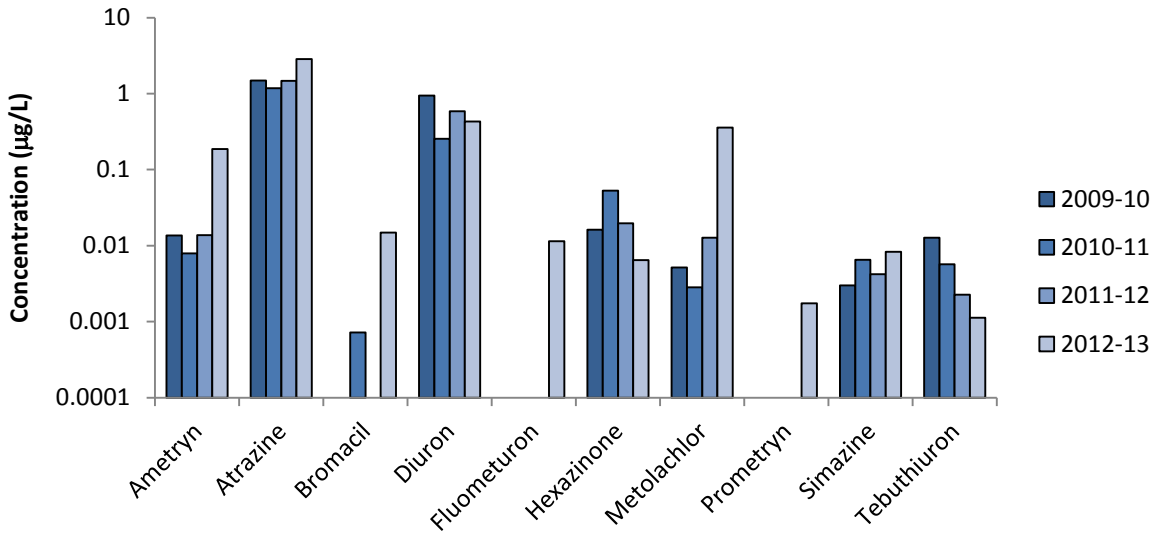

Figure 3.20: Temporal trends in the annual average concentration of pesticides (greater than the limit of reporting) in Barratta Creek for the years 2009–10 (n = 25), 2010–11 (n = 132), 2011–12 (n = 93) and 2012–13 (n = 31).

Pioneer River

Monitoring data were available for the Pioneer River from 2009 onwards (Figure 3.21). Detection frequencies increased over time for atrazine, diuron, and metolachlor. A decrease in detection frequency was observed for ametryn and simazine. There were no consistent temporal trends in detection frequency for bromacil or hexazinone. Fluometuron, tebuthiuron and terbutryn were only detected in one out of the four years so there is no clear trend apart from seldom being detected.

For the priority PSII herbicides, no consistent change in average annual concentration occurred over time. This was also true for the alternate pesticides, bromacil and metolachlor. A marked decrease in the simazine concentration occurred from 2009–10 to 2010–11, which then remained steady for the following years (although the last three years had a very low detection frequency). Fluometuron, tebuthiuron and terbutryn all had very low detection frequencies, and therefore it is difficult to judge concentration trends over time.

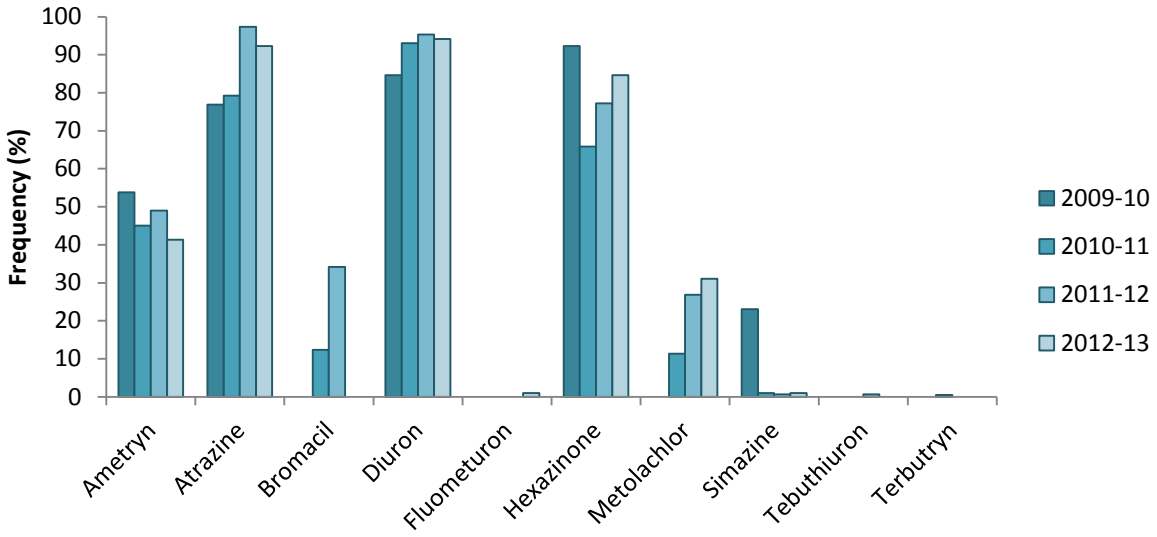

Figure 3.21: Temporal trends in the detection frequency of pesticides (greater than the limit of reporting) in the Pioneer River for the years 2009–10 (n = 13), 2010–11 (n = 202), 2011–12 (n = 149) and 2012–13 (n = 103).

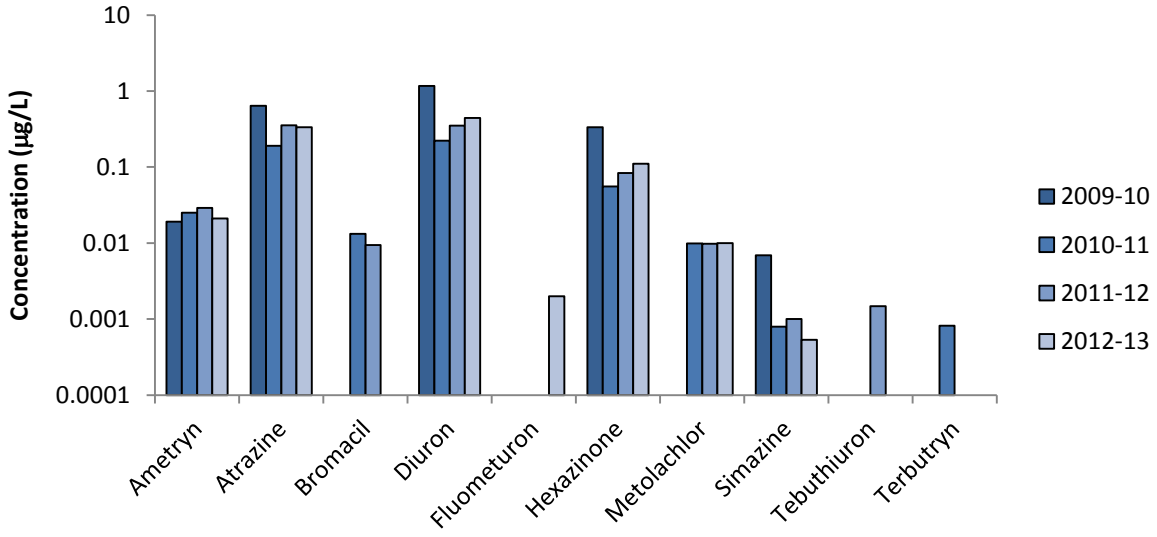

Figure 3.22: Temporal trends in the annual average concentration of pesticides (greater than the limit of reporting) in the Pioneer River for the years 2009–10 (n = 13), 2010–11 (n = 202), 2011–12 (n = 149) and 2012–13 (n = 103).

Sandy Creek

The changes in detection frequencies at Sandy Creek over a four year period are presented in Figure 3.23. For the majority of the priority PSII herbicides, atrazine, diuron, hexazinone and tebuthiuron, no temporal change in detection frequency was observed. There was a decreasing trend of detection frequency for ametryn. Of the alternate pesticides, only metolachlor indicated that there could be an increasing trend. For bromacil and terbutryn, there was a marked increase in detection frequency during 2011–12, but this did not continue in 2012–13, and prometryn was only detected in 2010–11. There was no trend for simazine in detection frequency.

The trends in changes of average annual pesticide concentrations over time were clearer than the corresponding trends for detection frequencies. A decrease in the average diuron concentration occurred from 2009–10 to 2010–11 and then remained fairly stable for the following years. In addition, a continual decrease in the hexazinone average concentration was observed over the four year period. A small increase was observed for atrazine, but there was no consistent trend for ametryn or tebuthiuron. Regarding the alternate pesticides, an increase was observed for metolachlor and a decrease in simazine. The first three years for bromacil indicated an increase however it was not detected at all in the last year. Prometryn and terbutryn were detected in only one year.

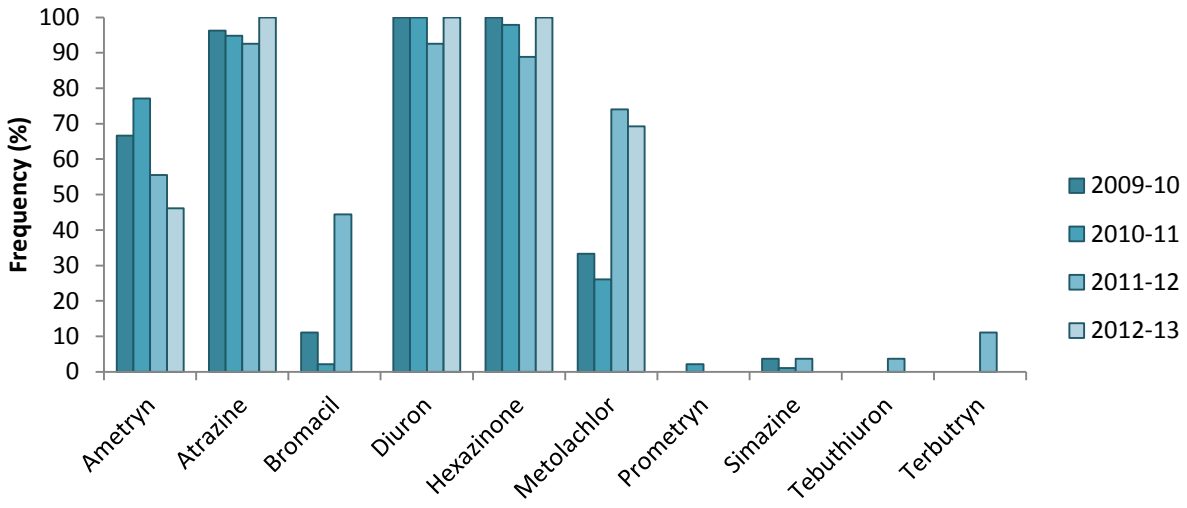

Figure 3.23: Temporal trends in the detection frequency of pesticides (greater than the limit of reporting) in Sandy Creek for the years 2009–10 (n = 27), 2010–11 (n = 96), 2011–12 (n = 27) and 2012–13 (n = 26).

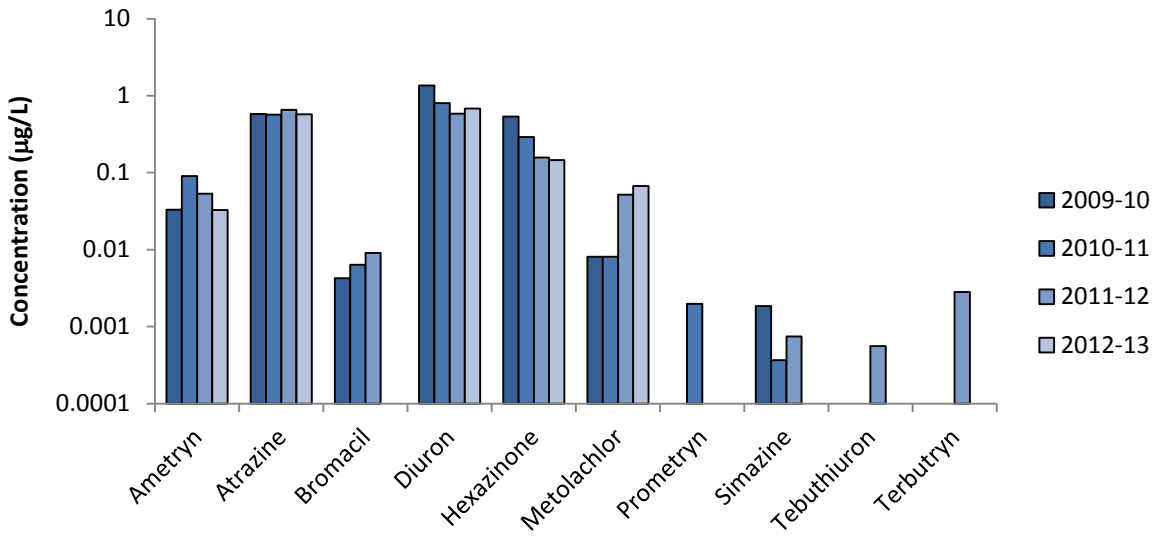

Figure 3.24: Temporal trends in the annual average concentration of pesticides (greater than the limit of reporting) in Sandy Creek for the years 2009–10 (n = 27), 2010–11 (n = 96), 2011–12 (n = 26) and 2012–13 (n = 26).

Metribuzin

Metribuzin has been monitored since 2009, but as it is analysed using GCMS and is an additional cost, only a small number of samples have been collected at each site between 2009 and 2012. In 2012–13 the number of samples analysed using GCMS was approximately equal to the number of samples analysed using LCMS. Therefore the temporal trends are likely to be impacted by the differences in the sampling regimes. Metribuzin was only detected at Barratta and Sandy creeks prior to 2012–13, but was detected in Tully River, Barratta Creek, Pioneer River and Sandy Creek in 2012–13 (Figure 3.25 and Figure 3.26). Metribuzin has not been detected in the North Johnstone or Herbert rivers. There was an increase in detection frequencies at all sites over time (Figure 3.25), a decrease in the annual average concentrations at Barratta Creek and an increase at Sandy Creek (Figure 3.26). However, as previously mentioned, these may be influenced by the different sampling regimes.

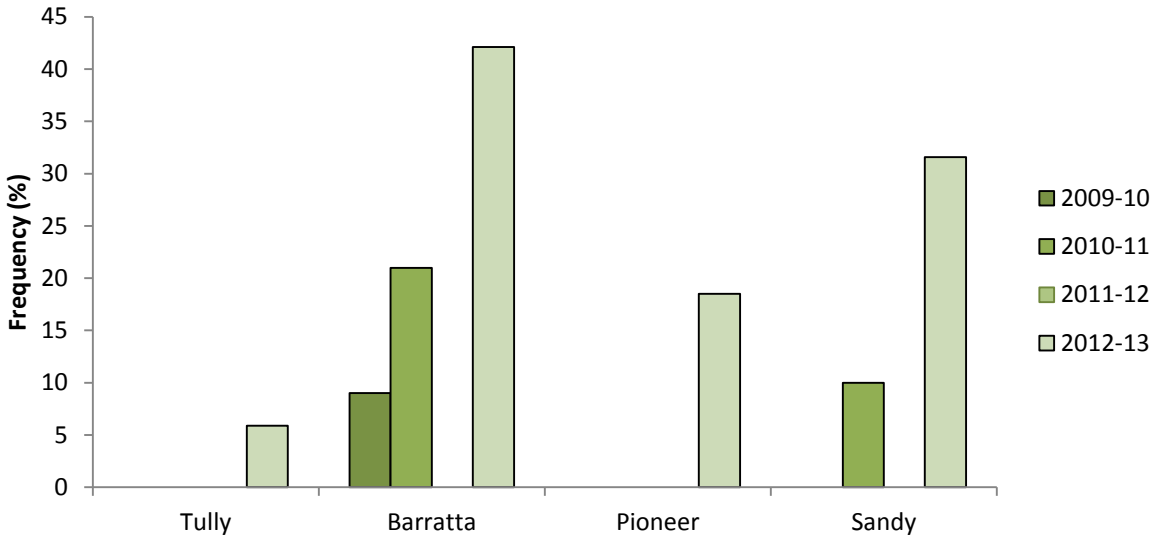

Figure 3.25: Temporal trends in the detection frequency of metribuzin (greater than the limit of reporting) in Tully River, Barratta Creek, Pioneer River and Sandy Creek between 2009 and 2013.

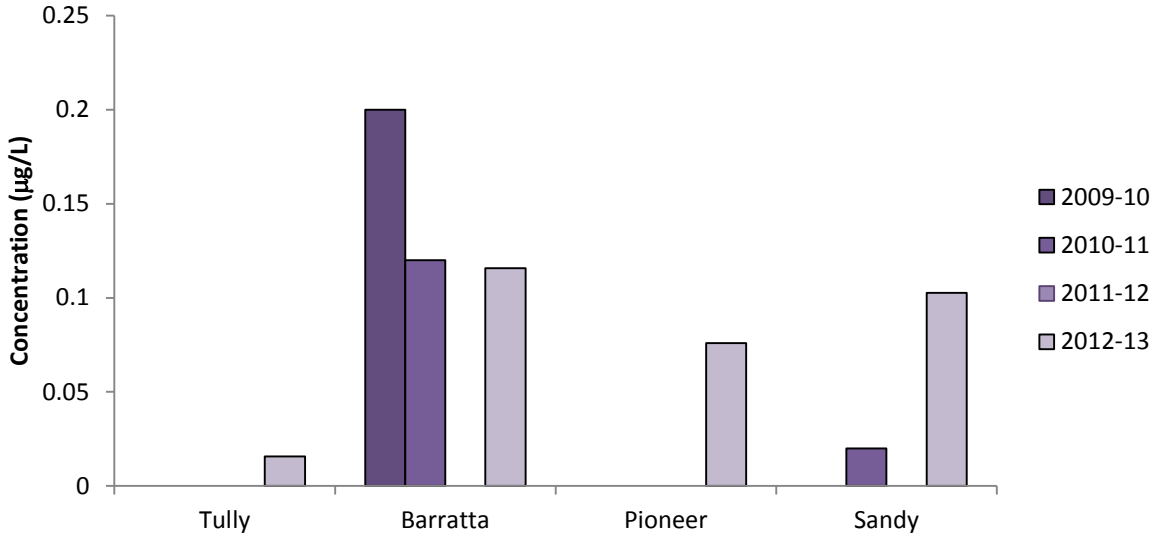

Figure 3.26: Temporal trends in the annual average concentration of metribuzin (greater than the limit of reporting) in Tully River, Barratta Creek, Pioneer River and Sandy Creek between 2009 and 2013.

3.3 Pesticide Loads

Annual loads could not be calculated for the North Johnstone River due to the limited number of samples collected. Therefore, the following analysis of pesticide loads only discusses the loads calculated for the Herbert, Pioneer and Tully rivers and Barratta and Sandy creeks.

3.3.1 Comparison of alternate pesticide loads to the priority PSII pesticide loads

The pesticide loads were calculated using the average load (linear interpolation of concentration) for Herbert River, Barratta Creek, and Pioneer River (Figure 3.27 a-c), and the Beale ratio method for Tully River and Sandy Creek (Figure 3.27d-e). All pesticides detected in the five sites were included in the figures to provide a comparative assessment of the loads across all sites.

Generally the loads for each catchment reflected the results of the 2012–13 detection frequencies and average annual concentrations (Section 3.2.1). At all five sites, atrazine and diuron had the largest loads. At the Tully River, Herbert River, and Pioneer River the hexazinone loads were also larger than the loads of any of the alternate pesticides. The largest load of an alternate pesticide was for 2,4-D at all sites, except at Pioneer River where the metribuzin load was marginally higher. The metribuzin load at Sandy Creek was also very close to the 2,4-D load. Isoxaflutole, metolachlor and MCPA had the next largest loads, while bromacil, fluometuron, fluroxypyr, haloxyfop, metsulfuron-methyl, prometryn, propazine-2-hydroxy, simazine and triclopyr all had small loads.

The largest loads of ametryn (28 kg), diuron (444 kg), hexazinone (93 kg), 2,4-D (61 kg), metribuzin (62 kg) and fluometuron (4 kg) were all recorded at the Pioneer River. Whereas the largest load of atrazine (444 kg), isoxaflutole (21 kg), simazine (1 kg) were recorded at Barratta Creek, along with tebuthiuron, bromacil, fluroxypyr, haloxyfop, prometryn and propazin-2-hydroxy which were only detected at Barratta Creek. The largest loads of metsulfuron-methyl (7 kg) and triclopyr (1 kg) were recorded at the Herbert River. The largest loads of metolachlor and MCPA were recorded at Sandy Creek.

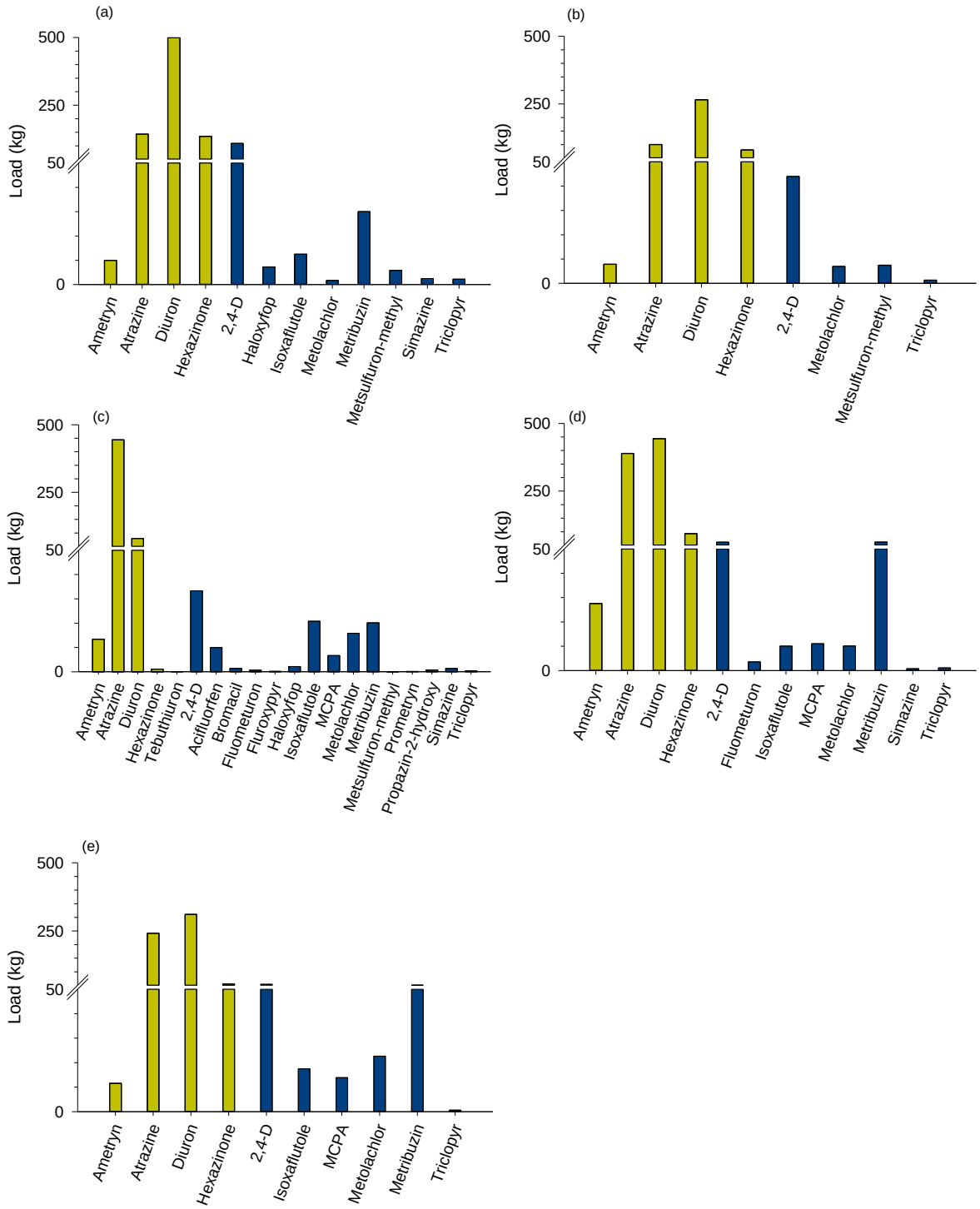

Figure 3.27: Annual pesticide loads (2012–2013) for (a) Tully River, (b) Herbert River, (c) Barratta Creek, (d) Pioneer River and (e) Sandy Creek. Yellow bars denote the priority photosystem II inhibiting herbicide loads, blue bars denote the alternate pesticide loads.

3.3.2 Contribution of the alternate pesticide loads to the total pesticide load

The total pesticide load was calculated for each catchment by summing the loads of each pesticide detected in the catchment. The contribution of the priority PSII herbicides and the alternate pesticides (individually and as a whole) to the total pesticide load were determined and will be discussed for each catchment below.

Tully River

The total pesticide load in the Tully River was 1033 kg, of which the priority PSII herbicides contributed 83% (Figure 3.28). Diuron on its own contributed more than half (56%) of the total pesticide load. Atrazine and hexazinone contributed another 14 and 13%, respectively and ametryn made up only 1% of the total load. The alternate pesticides contributed the remaining 17% (171 kg) of the total load. Of the alternate pesticides, 2,4-D had the largest load (11% of the total pesticide load) followed by metribuzin (3%). The remaining alternate pesticides, haloxyfop, isoxaflutole, metolachlor, metsulfuron-methyl, simazine and triclopyr, each contributed ≤ 1% of the total pesticide load.

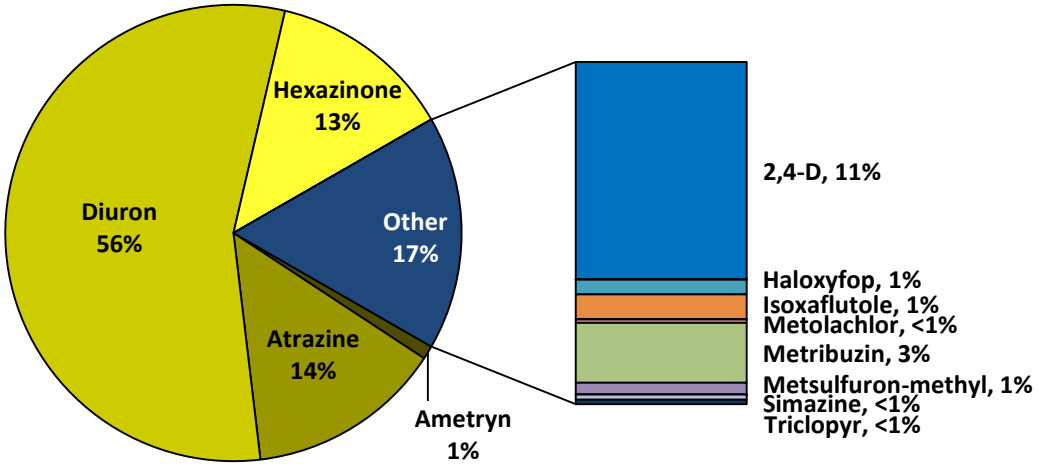

Figure 3.28: Contribution of priority photosystem II inhibiting herbicides (green/yellow pie segments) and the alternate pesticides (blue pie segment) to the total pesticide load in the Tully River.

Herbert River

The total pesticide load in the Herbert River was 514 kg, of which the priority PSII herbicides contributed 88% (Figure 3.29). As was the case with the Tully River, diuron contributed more than half of the total pesticide load (52%). Atrazine and hexazinone contributed another 20 and 16%, respectively and ametryn made up only 2% of the total load. The remaining 12% (60 kg) consisted of alternate pesticides, of which the majority was 2,4-D comprising 9% of the total pesticide load. The remaining alternate pesticides, metolachlor, metsulfuron-methyl and triclopyr, combined contributed only 3% of the total pesticide load.

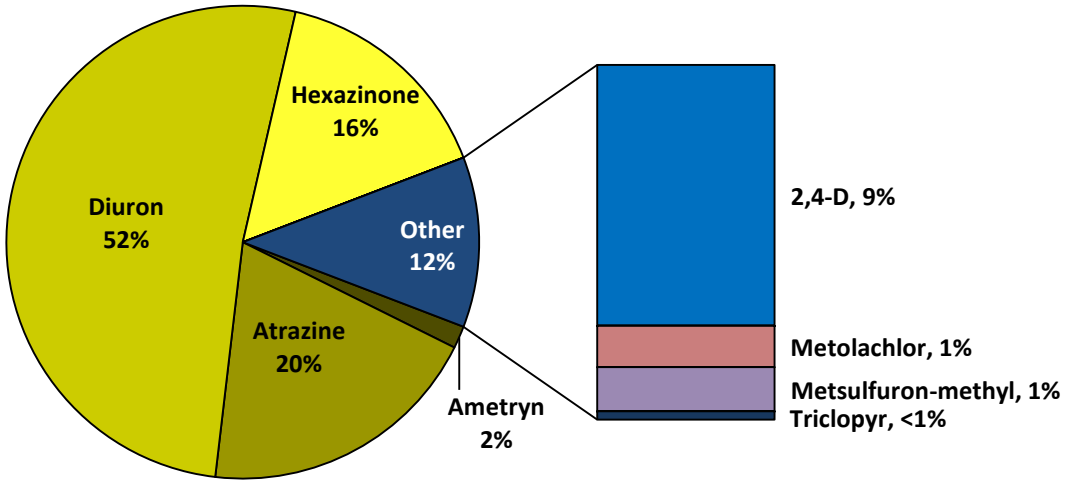

Figure 3.29: Contribution of priority photosystem II inhibiting herbicides (green/yellow pie segments) and the alternate pesticides (blue pie segment) to the total pesticide load in the Herbert River.

Barratta Creek

The calculated total pesticide load at Barratta Creek was 643 kg which, despite the difference in catchment sizes (Table 2.1), was greater than the total pesticide load of the Herbert River. Similar to the Tully and Herbert rivers, the priority PSII herbicides made up the majority of the total load (approximately 83%), however the greatest contributor was atrazine (68%) rather than diuron. Diuron only made up 12% of the total load, ametryn only 2% and hexazinone and tebuthiuron less than 1% each. Fifteen alternate pesticides contributed 17% of the total pesticide load (Figure 3.27). 2,4-D was again the greatest contributor of the alternates (5%), followed by isoxaflutole and metribuzin (both 3%), acifluorfen and metolachlor (both 2%) and MCPA (1%). The nine remaining

alternate pesticides each contributed less than 1% each of the total load, and when combined contributed only 2%.

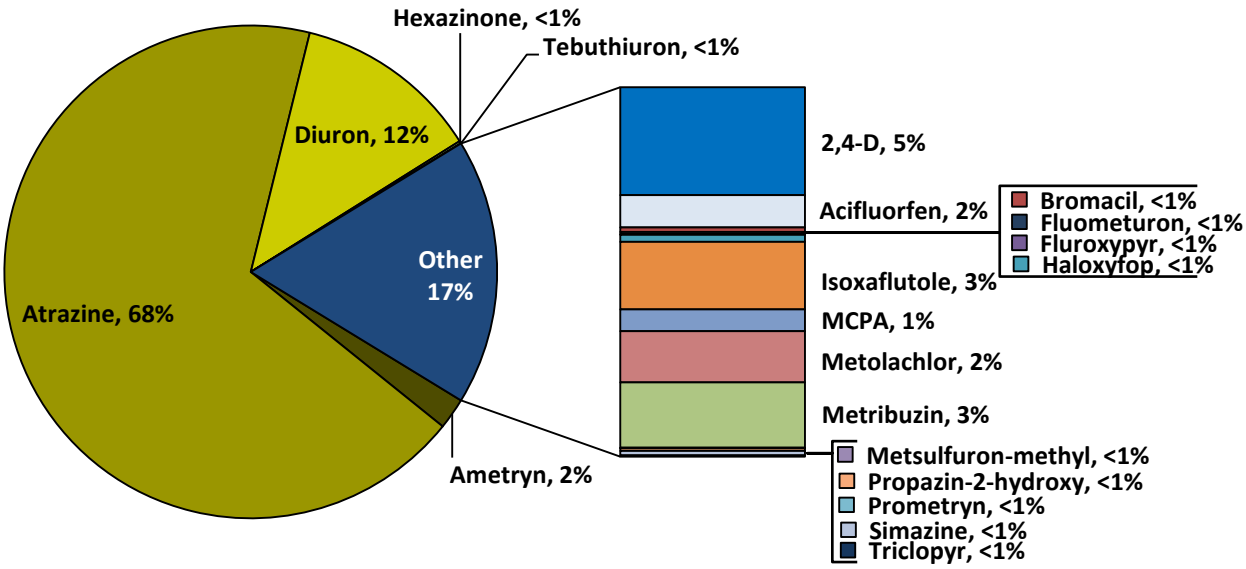

Figure 3.30: Contribution of the priority photosystem II inhibiting herbicide loads (green/yellow pie segments) and the alternate pesticide load (blue pie segment) to the total pesticide load at Barratta Creek.

Pioneer River

The Pioneer had the largest total pesticide load (1114 kg) of the five catchments. As with the other catchments, the priority PSII herbicides made up the majority (85%) of the total load (Figure 3.31). Atrazine and diuron had similar contributions, 35 and 40%, respectively while hexazinone contributed 8%, and ametryn contributed 2% of the total load. The alternate pesticide contribution to the total pesticide load was also in a similar range to the other catchments, contributing 15% of the total pesticide load. Metribuzin and 2,4-D both contributed 6% of the total pesticide load.

Isoxaflutole, MCPA and metolachlor each contributed 1% to the load while fluometuron, simazine and triclopyr each contributed less than 1%.

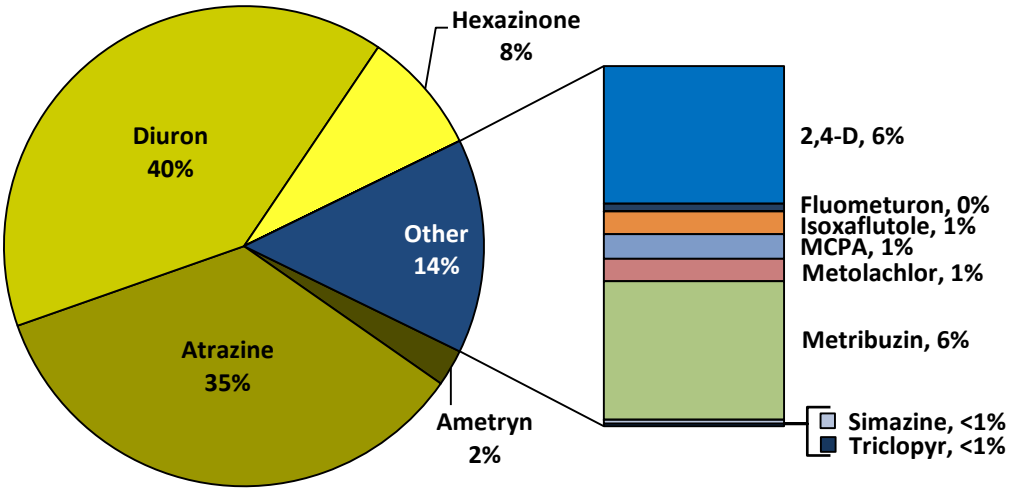

Figure 3.31: Contribution of the priority photosystem II inhibiting herbicide loads (green/yellow pie segments) and the alternate pesticide load (blue pie segment) to the total pesticide load at Pioneer River.

Sandy Creek

The total pesticide load calculated from Sandy Creek was 779 kg. The priority PSII herbicides still made up the majority of the total pesticide load (79%), although the contribution from the alternate pesticides was larger (21%) in Sandy Creek compared to the other catchments (Figure 3.32). As with the Pioneer River, the contributions of atrazine and diuron to the total pesticide load were comparable, being 31 and 40%, respectively. The proportions of hexazinone and ametryn were also similar to the Pioneer River results, contributing 7 and 1%, respectively of the total pesticide load. The alternate pesticides contribution was made up of equal proportions of 2,4-D and metribuzin (7% each). Metolachlor (3%), isoxaflutole (2%), MCPA (2%) and triclopyr (<1%) made up the remainder of the total pesticide load.

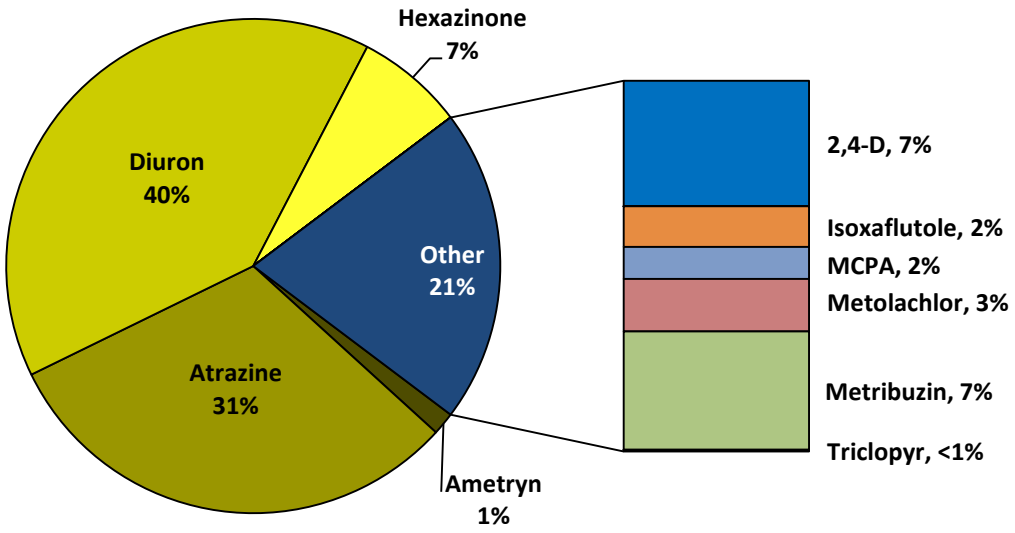

Figure 3.32: Contribution of the priority photosystem II inhibiting herbicide loads (green/yellow pie segments) and the alternate pesticide load (blue pie segment) to the total pesticide load at Sandy Creek.

3.4 Spatial trends

There were consistencies in the prevalence of the alternate pesticides across catchments monitored in this study. The priority PSII herbicides, in particular atrazine and diuron, were generally more prevalent, had higher concentrations and larger loads than the alternate pesticides. 2,4-D was the main alternate pesticide detected, being detected at every site, having a high detection frequency and a larger load than the other alternate pesticides. Metolachlor and triclopyr were common to all sites except North Johnstone. Triclopyr was always detected at a low frequency and low concentrations, whereas metolachlor was detected more frequently and at higher concentrations, particularly at Barratta Creek, Pioneer River and Sandy Creek. Metribuzin was not detected at all sites or as frequently, but it did have higher concentrations relative to other alternate pesticides. These results are likely to be due to its high LOR (0.1 µg/L). Isoxaflutole and MCPA were also common to a number of sites, had moderate detection frequencies and concentrations.

The proportions of the total pesticide load were fairly consistent across the sites where loads were calculated; i.e. the Tully, Herbert and Pioneer rivers and Barratta and Sandy creeks. Across the five catchments, the priority PSII herbicides made up 79–88% of the total load, and of this, ametryn consistently made up the least with only 1–2%. While the contribution of the total PSII herbicide load did not vary much between catchments, the contributions of atrazine and diuron did, ranging from 22–82% and 15–59%, respectively. The greatest contributor to the alternate pesticide loads was 2,4-D, except when metribuzin had equal weighting (at Pioneer River and Sandy Creek). In addition, the contribution of 2,4-D to the total pesticide load only varied from 5–11% between catchments. Except at the Herbert River, the next main contributors, in descending order, for the alternate pesticides were metribuzin, isoxaflutole, MCPA and metolachlor. Metolachlor was also a main contributor at the Herbert River along with metsulfuron-methyl to the alternate pesticide loads.

3.5 Ecotoxicity assessment of the alternate pesticides

The Australian and New Zealand water quality guideline trigger values (TVs) for the default level of protection of freshwater ecosystems (i.e. the concentration that should theoretically protect 95% of species –PC95) (ANZECC and ARMCANZ 2000) and recently derived Ecotoxicity Threshold Values (ETVs) (Smith et al. in prep) are reported in

Table 3.2 for the priority PSII herbicides and, where available, the alternate pesticides. A trigger value and/or an ETV are only available for the priority PSII herbicides and five of the alternate pesticides, of which four are a low reliability value. The ETVs are based only on phototrophic species as the species sensitivity distributions were found to be bimodal with phototrophic species being the most sensitive, due to the herbicides exerting their toxicity on photosynthesis. The TVs are generally based on both plant and animal species where data were available.

The 95th percentile of measured pesticide concentrations were compared to TVs and ETVs where available. The diuron TV and ETV was exceeded at all sites apart from North Johnstone. The highest exceedence occurred at Sandy Creek in which the 95th percentile concentration was 14 times greater than the diuron TV (10 times greater than the ETV). The metolachlor TV was exceeded at Pioneer River and Barratta and Sandy creeks, with the greatest exceedence recorded at Barratta Creek in which the 95th percentile was 115 times the TV. It should be noted that the metolachlor TV is a low reliability value (ANZECC and ARMCANZ 2000). The ametryn ETV was exceeded at two sites, Barratta and Sandy Creek, with the greatest exceedence being 12 times the ETV at Barratta Creek. The only other exceedence was of the atrazine ETV at Barratta Creek; where the 95th percentile concentration was twice the ETV.

Table 3.2: Australian and New Zealand trigger values (PC95) and ecotoxicity threshold values (PC95) for the five priority photosystem II inhibiting herbicides and alternate pesticides.

Pesticide	Water Quality Guideline trigger value[1] (µg/L)	Ecotoxicity Threshold Value[2] (µg/L)
Ametryn	nv	0.1
Atrazine	13	6.0
Diuron	0.2*	0.3
Hexazinone	75*	0.7
Tebuthiuron	2.2	8.8*
2,4-D	280*	nv
Bromacil	180*	nv
MCPA	1.4*	nv
Metolachlor	0.02*	nv
Simazine	3.2	nv

1. ANZECC and ARMCANZ (2000), 2. Smith et al (in prep), *Low reliability, nv = No value.

The toxicity ranges (the minimum NOEC - maximum NOEC) of the priority herbicides and alternate pesticides to phototrophic species were compared (Figure 3.33). A range lying at the lower end (i.e. to the left) of the x-axis indicates a pesticide with a high toxicity, as it means that a very low concentration of the pesticide is required to cause an impact, compared to a pesticide which lies at the higher (right hand side) end of the x-axis. Thus, based on the minimum NOECs from Figure 3.33, ametryn has the highest toxicity of the priority PSII herbicides followed by diuron, hexazinone, atrazine and tebuthiuron. Metsulfuron-methyl has a marginally higher toxicity than ametryn, making it the most toxic pesticide to phototrophic species detected in this study. Prometryn has a similar toxicity to diuron. Isoxaflutole and metolachlor have a similar minimum NOEC to hexazinone, however they have a high maximum NOEC indicating a large variation in their toxicities between species. Bromacil and simazine have a similar toxicity range, and they lie between hexazinone and atrazine. Metribuzin and propazine are similar to atrazine, whereas the minimum NOEC of 2,4-D, and triclopyr are closer to the toxicity of tebuthiuron. 2,4-D and triclopyr also have a large range between the minimum and maximum NOECs. Aciflurofen, fluometuron, fluroxypyr, MCPA and haloxyfop had the lowest toxicities. However, there were results for only one phototrophic species for haloxyfop, so its range of toxicity is unknown.

Based on these toxicity rankings, we can make an overall assessment of the risk of each pesticide to phototrophic species in these catchments. The HU (Equation 5) of each pesticide (from each catchment) was plotted against the corresponding frequency of detection and are presented in Figure 3.34. A HU ≥ 1 indicates pesticides are present at a concentration high enough to potentially cause an impact to phototrophic species. Figure 3.34 is divided into four sections with the x-axis divided at HU=1 and the y-axis divided at 50% detection frequency. Pesticides with a high HU and high detection frequency would pose the highest risk, therefore, pesticides lying in the top right hand section pose the highest risk. Pesticides in the bottom right hand corner have high HUs and therefore pose a potential threat to phototrophic species, however they are detected infrequently and therefore pose a lower risk. Pesticides in the top left hand section have a high frequency of detection but their concentrations are low relative to their toxicity and so they pose a low risk. Lastly, the pesticides in the bottom left hand section pose a very low risk as they have low HU values and are infrequently detected.

Diuron was found to be a high risk pesticide, with five sites sitting in the top right-hand section of Figure 3.34. Fifty per cent of the time ametryn had high HUs (≥ 1), but in only one case, at Barratta Creek, was the high HU coupled with a high detection frequency. If the detection frequency of ametryn was to increase in the future it would pose a much greater risk to phototrophic species, particularly because of its high toxicity. Atrazine had a high detection frequency (always above 48%), but HUs less than 1, except at Barratta Creek where it poses a high risk. Metolachlor also fell in the high risk section of the graph at Barratta Creek, but for the remainder of the sites it was in the left-hand side of Figure 3.33 indicating it posed a low risk. These results support rainfall trials which also found that ametryn, diuron, metolachlor and atrazine were the highest risk pesticides based on their runoff potential and toxicity (Lewis et al. 2013).

Hexazinone, 2,4-D, MCPA and isoxaflutole generally were located in the top left-hand section of Figure 3.34 indicating high detection frequencies but low concentrations relative to their toxicity to phototrophs. Pesticides in this portion of the figure may not be a risk to organisms on their own, but due to their prevalence are likely to make a substantial contribution to the combined risk of pesticide mixtures. The majority of the alternate pesticides were considered a low risk, i.e. low HU and low detection frequency, at all sites where they were detected. The low risk alternate pesticides included acifluorfen, fluometuron, fluroxypyr, haloxyfop, metribuzin, metsulfuron-methyl, prometryn, simazine and triclopyr. But it should be noted that this assessment is based on the current concentration and frequency of detection. If these changed so would the risk. Of the priority PSII herbicides, tebuthiuron was also considered a low risk herbicide, whereas hexazinone and ametryn were only low risk at some of the sites where they were detected.

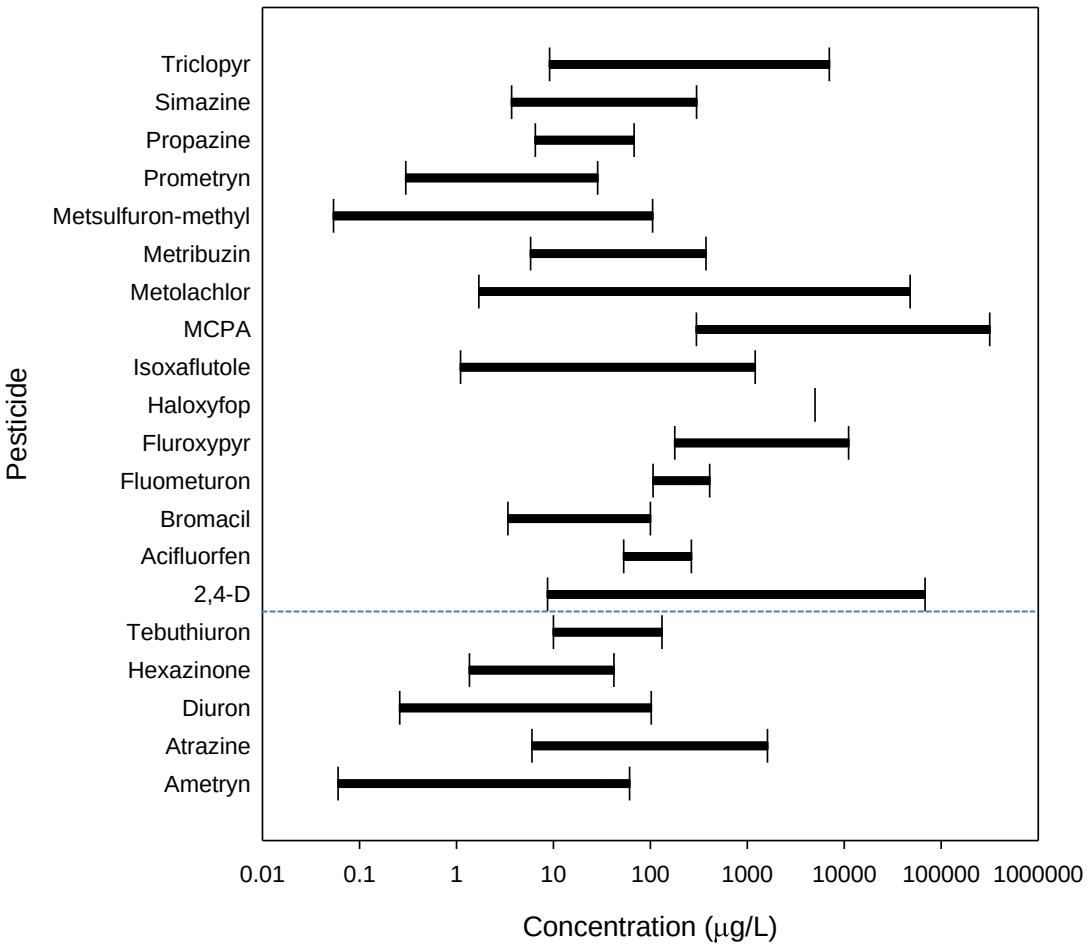

Figure 3.33: Horizontal boxplots of the minimum and maximum concentrations of pesticides at which toxic effects on phototrophic species have commenced. Ranges for alternate pesticides are above the dotted line while those for the priority photosystem II inhibiting herbicides are below the dotted line.

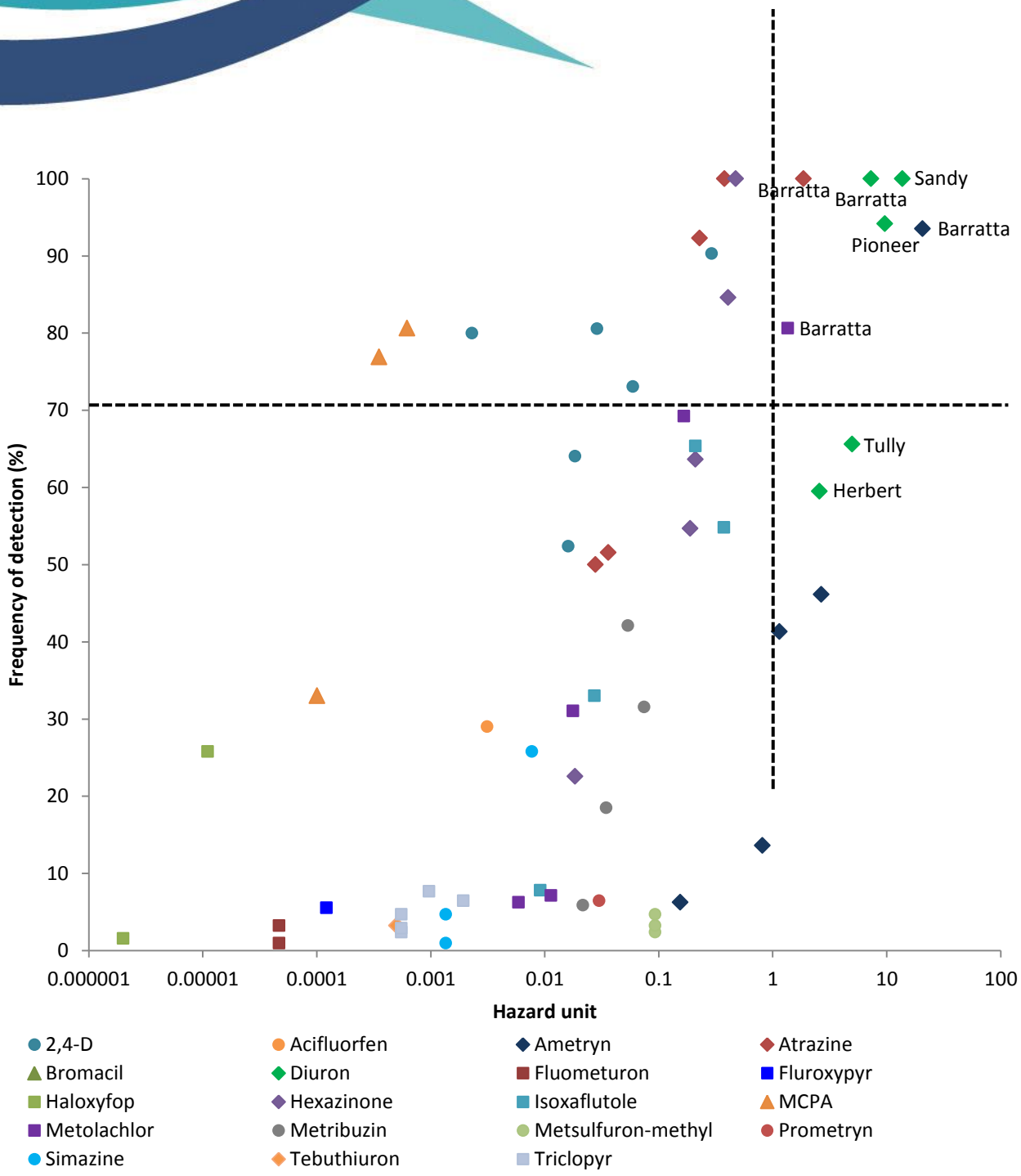

Figure 3.34: Risk of pesticides based on their hazard units and detection frequency recorded at North Johnstone, Tully, Herbert and Pioneer rivers and Barratta and Sandy Creeks. Replicate symbols represent sites the pesticide was detected. Dotted horizontal line indicates high (above the dotted line) and low (below the line) detection frequency. Vertical dotted line indicates high (right side) and low (left side) hazard units. A pesticide not in the figure is due to a 95th percentile concentration of 0 µg/L.

3.6 Implications for policy and farming best management practice

By monitoring the alternate pesticides as well as the priority PSII herbicides, we are able to calculate a more comprehensive estimate of the total pesticide load. This study indicated that alternate pesticides currently make up 12–21% of the total pesticide load, depending on the catchment. However, from 2016 onwards the pesticide reduction targets for Reef Plan 2013 will be based on the total toxic load of pesticides (i.e. a load weighted based on the toxicities of the pesticides). Therefore, as an extension to the results presented here, the toxic loads of the alternate pesticides need to be determined to assess the contribution of the alternate pesticides to the total toxic load. In doing so, we will be able to evaluate the contribution of the alternate pesticides in relation to the pesticide reduction targets. It is envisioned that the contribution of alternate pesticides will increase with the decrease in the use of the priority PSII herbicides. Ideally this change will reduce the total toxic load of pesticides being transported to the GBR and therefore move towards reaching the 60% reduction targets. However, it was shown that some of the alternate pesticides have toxicities equal to or greater than the priority PSII herbicides. A switch to these pesticides could thwart efforts to achieve the reduction targets.

Based on the toxicity rankings in Figure 3.33, there are a number of alternate pesticides which would pose a lower risk to water quality compared to the priority PSII herbicides. Acifluorfen, fluometuron, fluroxypyr and haloxyfop all have low toxicities and were also detected in low frequencies and concentrations. There were also a number of other alternates which had high toxicities but presented a low risk (e.g. metsulfuron-methyl). The next step would be to determine why some of the alternate products were present at low concentrations and low detection frequencies, i.e. to determine whether it was due to few applications in the monitored catchment, low application rates and/or low runoff potentials. The weed control implications of changing pesticide usage profiles would also need to be considered.

There were a number of alternate pesticides that were expected to be detected but were not (i.e. imazapic, imazethapyr, trifloxysulfuron-Na, trifluralin, and pendimethalin). If they were in fact being applied during the study period, then it may indicate that these pesticides have a low runoff potential and therefore would pose a lower risk to water quality, alternately it could be that these pesticides were scarcely used and/or used at low rates. A rainfall simulation study (Lewis et al, 2013) found that pendimethalin had a low runoff potential which, assuming it is being applied in sufficient amounts, is consistent with the no detections (above the LOR) of pendimethalin found in this study. Lewis et al (2013) also found that fluroxypyr had a relatively low runoff potential compared to the priority PSII herbicides, which is also consistent with the low concentrations and detection frequencies found in this study. In the same study (Lewis et al 2013), imazapic was found to have a high runoff potential in terms of the percent that was applied, however the application rate of imazapic is relatively low compared to other pesticides. In this study imazapic was not detected at all above the LOR. This may in part be due to the low application rates, but also likely to be due to the high LOR of imazapic (0.5 µg/L).

Currently the alternate pesticides seem to pose a much lower risk to aquatic ecosystems than the PSII herbicides. However, if future use of the alternate pesticides increases the risk would certainly increase, particularly for those with high toxicities, e.g. metsulfuron-methyl, prometryn, isoxaflutole and metolachlor. Therefore it is important to discern which alternate pesticides have high toxicities and high runoff potentials to inform farmers and extension officers of those pesticides that need to be used with caution. Conversely, those with low toxicities or with a low runoff potential need also to be determined to inform farmers about the products which pose least threat to water quality entering the Great Barrier Reef. It should be noted here, the assessment of toxicity in this study was based just on phototrophic species. A more thorough assessment needs to be conducted to also assess the toxicity of these pesticides to non-phototrophic aquatic species.

This study has provided a baseline data set for future assessment of changes in pesticides being transported to the GBR associated with changes in land management practices. In particular, greater changes are expected in 2014–15 as the final stage of the APVMA's move to new label restrictions for diuron only finished in November 2013. As shown from the results in this study, diuron was one of the most prevalent pesticides detected, had higher loads, higher concentrations and higher detection frequencies than the majority of the other pesticides detected. Furthermore it has a high toxicity. The APVMA's enforced restrictions may mean that farmers replace diuron with other pesticides; at this stage it is unknown what these will be and if it will be consistent amongst farmers and regions. Some of the alternate pesticides were found to have a higher toxicity than diuron. If farmers were to switch to these pesticides, or others with an equal toxicity, then the risk posed by pesticides to the GBR will not improve or could potentially worsen.

In addition, this study has demonstrated that a diverse range of pesticides are co-occurring in the monitored catchments; i.e. up to 20 different pesticides were detected in each catchment. Large numbers of pesticides present together most likely will have additive effects particularly to organisms in which a direct impact occurs, i.e. herbicides have a direct impact on phototrophic species. So while the concentrations of individual pesticides might be below toxicity levels, the combined toxicity of the mixture could present a risk. Consequently, it is important to determine the risk of the mixture of pesticides as well as the risk of the individual pesticides. To do so would involve a more thorough assessment of the literature to collate all available toxicity data for each pesticide, quality check the information and derive species sensitivity distributions based on the methods of Batley et al. (in review) and Warne et al. (in review). To date, this has been completed for the priority PSII herbicides (Smith et al, in prep) and allows the calculation of toxic loads, ETVs and the toxicity of mixtures.

4 References

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5 Appendix 1

Table 5.1: Pesticides detected in the LCMS suite of the Organics Laboratory, Queensland Health Forensic and Scientific Service

Pesticide	Limit of Reporting (µg/L)
Ametryn	0.01
Atrazine	0.01
Bromacil	0.01
Desethyl Atrazine	0.01
Desisopropyl Atrazine	0.01
Diuron	0.01
Fluometuron	0.01
Hexazinone	0.01
Imidacloprid	0.01
Metolachlor	0.01
Prometryn	0.01
Simazine	0.01
Tebuthiuron	0.01
Terbutryn	0.01

Table 5.2: Pesticides detected in the GCMS suite of the Organics Laboratory, Queensland Health Forensic and Scientific Service

Pesticide	Limit of Reporting (µg/L)
Ametryn	0.1
Amitraz	0.1
Atrazine	0.1
Bromacil	0.1
Desethyl Atrazine	0.1
Desisopropyl Atrazine	0.1
Diclofop-methyl	0.1
Fluazifop-butyl	0.1
Fluometuron	0.1
Haloxyfop-2-etotyl	0.1
Haloxyfop-methyl	0.1
Hexazinone	0.1
Metolachlor	0.1
Metribuzin	0.1
Molinate	0.1
Oxyfluorfen	0.1
Pendimethalin	0.1
Prometryn	0.1
Propanil	0.1
Propazine	0.1
Simazine	0.1
Tebuthiuron	0.1
Terbuthylazine	0.1
Terbutryn	0.1
Triallate	0.1
Trifluralin	0.1
Aldrin	0.1
Chlordane cis	0.1
Total Chlordane	0.2
Chlordane trans	0.1
Chlordene	0.1
Chlordene epoxide	0.1
Chlordene-1-hydroxy	0.1
Chlordene-1-hydroxy-2,3-epoxide	0.1
Dicofol	1.5
Dieldrin	0.1
α-Endosulfan	0.2
β-Endosulfan	0.2
Endosulfan ether	0.1
Endosulfan lactone	0.5
Endosulfan sulfate	0.2
Endrin	0.1
Endrin aldehyde	0.1
HCB	0.2
α-HCH	0.1

Pesticide	Limit of Reporting (µg/L)
β-HCH	0.1
δ-HCH	0.1
Heptachlor	0.1
Heptachlor epoxide	0.1
Lindane (γ-HCH)	0.1
Methoxychlor	0.1
Nonachlor cis	0.1
Nonachlor trans	0.1
DDD (op)	0.1
DDE (op)	0.1
DDT (op)	0.1
Oxychlordane	0.1
DDD (pp)	0.1
DDE (pp)	0.1
DDT (pp)	0.1
Total Aldrin & Dieldrin	0.2
Total DDT	0.4
Total Endosulfan	0.6
Total Heptachlor	0.2
Azinphos-ethyl	0.1
Azinphos-methyl	0.1
Bromophos-ethyl	0.1
Cadusafos	0.1
Carbophenothion	0.1
Chlorfenvinphos	0.1
Chlorpyrifos	0.1
Chlorpyrifos oxon	0.1
Chlorpyrifos-methyl	0.1
Coumaphos	0.1
Demeton-S	0.1
Demeton-S-methyl	0.1
Diazinon	0.1
Dichlorvos	0.1
Dimethoate	0.1
Dioxathion	0.1
Disulfoton	0.1
Ethion	0.1
Ethoprophos	0.1
Etrimphos	0.1
Famphur	0.1
Fenamiphos	0.1
Fenchlorphos	0.1
Fenitrothion	0.1
Fenthion (methyl)	0.1
Fenthion-ethyl	0.1
Isofenphos	0.1
Malathion (Maldison)	0.1
Methidathion	0.1
Mevinphos	0.1

Pesticide	Limit of Reporting (µg/L)
Monocrotophos	0.5
Omethoate	0.5
Oxydemeton-methyl	0.1
Parathion (ethyl)	0.2
Parathion-methyl	0.1
Phorate	0.1
Phosmet	0.2
Phosphamidon	0.1
Pirimiphos-methyl	0.1
Profenofos	0.1
Prothiofos	0.1
Pyrazophos	0.1
Sulprofos	0.1
Temephos	0.1
Terbufos	0.1
Tetrachlorvinphos	0.1
Total Dimethoate	0.6
Benalaxyl	0.1
Bendiocarb	0.1
Bitertanol	0.1
Captan	0.2
Carbaryl	0.1
DEET	0.1
Dimethomorph	0.2
Fipronil	0.1
Furalaxyl	0.1
Metalaxyl	0.1
Methoprene	0.1
Oxadiazon	0.1
Piperonyl butoxide	0.1
Pirimicarb	0.2
Procymidone	0.1
Propargite	0.2
Propiconazole	0.1
Propoxur	0.1
Rotenone	0.1
Tebuconazole	0.1
Tetradifon	0.1
Thiabendazole	0.2
Total Triadimefon	0.4
Triadimefon	0.3
Triadimenol	0.1
Vinclozolin	0.2
Bifenthrin	0.1
Bioresmethrin	0.1
Cyfluthrin	0.7
Cyhalothrin	0.2
Cypermethrin	0.5
Deltamethrin	1

Pesticide	Limit of Reporting (µg/L)
Fenvalerate	0.5
Fluvalinate	0.5
Permethrin	0.2
Phenothrin	0.1
Tetramethrin	0.2
Transfluthrin	0.1

Table 5.3: Pesticides detected in the extended LCMS suite of the Organics Laboratory of Queensland Health Forensic and Scientific Services

Pesticide	Limit of Reporting (µg/L)
2,4-D	0.01
2,4-DB	0.01
Acifluorfen	0.01
Clomazone	0.01
Cyanazine	0.01
Ethametsulfuron methyl	0.01
Fluroxypyr	0.03
Flusilazole	0.01
Haloxyfop (acid)	0.01
Imazethapyr	0.01
Isoxaflutole	0.01
MCPA	0.01
MCPB	0.01
Mecoprop	0.01
Mesosulfuron methyl	0.01
Metsulfuron methyl	0.01
Napropamide	0.01
Propachlor	0.01
Propazin-2-hydroxy	0.01
Sethoxydim (including Clethodim)	0.08
Sulfosulfuron	0.01
Terbuthylazine	0.01
Terbuthylazine desethyl	0.01
Total Imazapic	0.5
Triclopyr	0.01
Trifloxysulfuron	0.01