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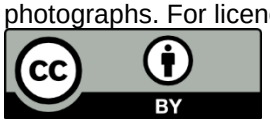

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Front cover photo: Empore™ Disk sampler and Passive Flux Metres deployed for inshore marine pesticide monitoring. ©TropWater/James Cook University.

The Great Barrier Reef Marine Park Authority acknowledges the continuing Sea Country management and custodianship of the Great Barrier Reef by Aboriginal and Torres Strait Island Traditional Owners whose rich cultures, heritage values, enduring connections and shared efforts protect the Reef for future generations.

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Acknowledgements

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Executive Summary

This report presents pesticide results from passive and grab samples collected during the 2023-24 wet season, as part of the Great Barrier Reef Marine Monitoring Program (MMP). The recent campaign aims to assess the risk from pesticides posed to the Great Barrier Reef as well as add to a longitudinal dataset to aid with catchment management.

Samples were collected from ten fixed monitoring sites located in three Natural Resource Management regions – the Wet Tropics (four sites at Low Isles, High Island, Dunk Island and Lucinda Jetty), Burdekin (Haughton River Mouth and Euri Creek), and Mackay Whitsundays (four sites at Whitsunday Channel, Repulse Bay, Flat Top, and Sarina Inlet). Sampling sites were chosen based on catchment information to address eReefs modelling input and validation needs, and include critical pesticide locations as well as control sites. Empore disk (ED) passive samplers (n = 52), polydimethylsiloxane (PDMS) passive samplers (n = 4) and grab samples for baseline site monitoring (n = 47) and flood site monitoring (n = 50) were collected successfully. Samples were analysed at the Queensland Alliance for Environmental Health Sciences (QAEHS), UQ by LC-QQQ MS/MS (25 polar chemicals; ED and grab samples), and GC-MS/MS (29 non-polar chemicals; PDMS samples) using the latest analytical methods and established standard operating protocols (SOPs).

Chemical analyses of the passive sampler extracts reported twenty-six pesticides detected with concentrations above the limit of reporting during the 2023-24 wet season. The most frequently detected pesticides across both passive samplers and grab samples were diuron, atrazine, hexazinone and imidacloprid. Concentrations ranged from 0.002 ng L^{-1} (HCB and cis-chlordane) to 145 ng L^{-1} (diuron). Total ∑polar pesticide concentrations ranged from 0.23 ng L^{-1} for Haughton River Mouth (in November 2023) to 584 ng L^{-1} for Sarina Inlet (January 2024).

Overall, number of pesticide detections across samples were typically higher in passive samplers compared with grab samples. Passive samplers were able to better reflect pesticide presence, observed via the higher detection frequencies reported compared with grab sampling data. However, the concentrations provided are averaged over time and therefore do not reflect potential acute exposure levels during flood events. Grab samples missed some instances of pesticides presence, especially at the lower end of the analytical reporting limits, but allowed for assessment of plume concentrations during the large flood event.

Monthly rainfall data for Queensland from the Bureau of Meteorology (BoM) over the duration of the sampling period (November 2023 – April 2024) revealed highest rainfall periods (January 2024 followed by December 2023) corresponded with the highest total pesticide concentrations observed for most fixed sites.

Flood events grab samples collected at different depth profiles (i.e. from near the surface and at depth) showed decreasing concentrations of pesticides (e.g., atrazine, diuron, metolachlor and hexazinone) were observed with increased salinity, suggesting pesticide concentrations are highest in the freshwater flood waters and during flood events. An exception was the pesticide imidacloprid where no such trend was observed at the Barron transect. This suggests that unlike the other pesticides, imidacloprid may already be present and or persistent in the marine waters.

Pesticide concentrations from grab and passive samplers were compared with Australia and New Zealand guidelines for Fresh and Marine Water Quality values where available. Metolachlor, metsulfuron methyl and tebuthiuron were often above the thresholds set for 99% species protection, however there were no chemicals detected above the 95% protection level. Calculation of the pesticide risk metric to assess mixture toxicity showed several exceedances of the 1% species affected target stipulated in the Reef 2050 Water Quality Improvement Plan (WQIP) in both the baseline and flood grab samples. Grab samples showed higher pesticide risk than the passive samplers, with Sarina Inlet (January 2024) and Flat Top (January 2024) having calculated PRMs of 6.09% and 5.65% species affected, respectively.

1 Introduction

The Great Barrier Reef Marine Park, encompassing the world's largest coral reef system, covers an area of 344,000 km^2, extending 2,300 kilometres along Queensland's coast (Great Barrier Reef Marine Park Authority, 2024). Thirty-five major rivers within a combined coastal catchment area of over 400,000 km^2 discharge into the Great Barrier Reef lagoon (Brodie *et al*., 2012), therefore it is imperative that water quality is closely monitored to ensure the Reef's long-term health. The Reef Authority runs an extensive Great Barrier Reef Marine Monitoring Program (MMP) to survey and report on the condition of inshore coral, seagrass and water quality annually, and has done so for 20 years. Data from the MMP is used to inform the Paddock to Reef Integrated Monitoring, Modelling and Reporting Program and evaluate progress towards the Reef 2050 Water Quality Improvement Plan (WQIP).

The aim of this current monitoring campaign was to support the MMP efforts by monitoring and understanding the presence of pesticides within the MMP inshore area as well as to recognise any spatial and temporal trends over the monitoring period. The current monitoring period covered the 2023-24 wet season (November 2023 to April 2024). The monitoring campaign used grab sample and passive sampling technologies for the monitoring of 25 polar pesticides and 29 non-polar pesticides and organochlorine compounds at ten fixed sites. In addition, flood events were monitored using grab samples to capture pesticides in flood waters entering near shore locations. The recent campaign aims to continue to assess the risk from pesticides posed to the GBR, as well as add to a longitudinal dataset to aid with catchment management.

The typically low concentrations of pesticides present in marine waters raise analytical challenges as well as challenges in obtaining representative samples. Grab samples collected at a single time point are extremely effective at capturing episodic contaminants events and can conveniently be taken at monitoring sites to measure acute exposure. However, they may not allow sufficient concentration of pesticides when concentrations are extremely low. Further, they may not reflect chronic exposure of contaminants as the timing of the sample collection (whether at a peak or low concentration event) would not be representative of chronic exposure over time. The use of passive sampling technologies has been introduced to complement and overcome some of these challenges, substantially furthering contaminant monitoring in liquid phases over the last 30 years. Benefits of passive sampling tools include in-situ concentration of chemical pollutants, increased sensitivity, the provision of time-weighted average concentration estimates for chemicals over periods of approximately one month, increased data resolution and risk profiling. Passive samplers designed to monitor polar chemical pollutants (Called Empore™ Disks; EDs) have been chosen for deployment in this program due to their effectiveness at capturing the target pesticides. Polydimethylsiloxane (PDMS) samplers have been used in previous monitoring campaigns to monitor non-polar pesticides. These were re-introduced for a single deployment during this campaign to trial their effectiveness for use in future monitoring.

The list of target chemicals for inclusion in the monitoring campaign was identified based on an assessment and review by the MMP and Department of Environment, Tourism Science and Innovation (DETSI), QLD. They include 25 pesticides that are of potential high use in the catchment areas and that may pose high risk based on marine species sensitivity indexes.

2 Methodology

2.1 Study Design

Ten fixed monitoring sites were sampled between November 2023 and April 2024 (Tables 1 and 2). Sampling sites were chosen based on catchment information to address eReefs modelling input and validation needs. The sites were located in three Natural Resource Management regions – the Wet Tropics (four sites at Low Isles, High Island, Dunk Island and Lucinda Jetty), Burdekin (Haughton River Mouth and Euri Creek), and Mackay Whitsundays (four sites at Whitsunday Channel, Repulse Bay, Flat Top, and Sarina Inlet) (Figure 1).

In this campaign two types of passives samplers were deployed, Empore disk (ED) passive samplers (n = 52) and polydimethylsiloxane (PDMS) passive samplers (n = 4) (Table 1, Figures 6 and 7). Grab samples (n = 47) were collected for assessing baseline chemical levels during the passive sampler deployment/retrieval periods at the same ten monitoring locations (Table 2, Figures 8 - 10). In addition, flood grab samples (n = 50) for assessing flood plume effects were collected from Cape York, Barron River, Russell Mulgrave River and Tully River in December 2023 and March 2024 (Table 2). Chemical analysis included 25 polar pesticide chemicals (ED passive samplers and grab samples), 29 non-polar pesticides and organochlorine compounds (PDMS passive samplers) (Tables 4 and 5) using the latest analytical methods and established standard operating protocols (SOPs).

In order to assess the risk form pesticides detected across sites and sampling periods, two methods were used. Maximum concentrations of pesticides detected from grab and passive samplers were compared with Australian freshwater and marine species protection guidelines (Tables 8 and 9). Additionally, the pesticide risk metric (PRM) that considers the combined mixture toxicity of 22 pesticides (Table 3) was investigated. The PRM approach allows for an estimation of instantaneous (acute) mixture toxicity at the time of collection of grab samples, as well as time weighted average mixture toxicity (acute) for the duration of deployment for passive samples. Results are presented as percentage of species affected by the mixtures and concentrations observed in the grab and passive samplers, respectively, and are useful for comparison against Reef 2050 (WQIP) target species protection values.

2.2 Passive samplers

A total of 52 ED passive water samplers (including six duplicates) and four PDMS passive samplers were successfully deployed and returned between November 2023 and May 2024 at ten fixed sites along the inshore region (Figure 1; Table 1). PDMS were deployed alongside EDs at all sites except for Euri Creek during March 2024. Four PDMS and six ED passive samplers were lost during deployment over the course of the sampling program (not shown). Duration of deployments varied between 12 and 51 days with variations due to retrieval marine conditions preventing access during some periods.

Table 1*. Passive sampler deployment locations (from North to South), Natural Resource Management (NRM) region, site name, dates, lengths of deployment period and water velocity measured at each site.*

Natural Resource Management (NRM) Region	Site Name	Deployment Date	Retrieval Date	Days Deployed	Flow Velocity (cm/s)	Comment
Wet Tropics	LOW ISLES	2024-01-23	2024-02-17	25	28.8	February deployment
	LOW ISLES	2024-02-17	2024-03-19	31	27	Jan sampler deployed in Feb
	LOW ISLES	2024-03-19	2024-04-13	25	30.7	ED replicate
Wet Tropics	HIGH ISLAND	2023-11-20	2023-12-02	12	37.9	PFM weight estimated -

						Cable tie snipped off. ED replicate
	HIGH ISLAND	2023-12-02	2024-01-05	34	29.8	
	HIGH ISLAND	2024-01-05	2024-02-06	32	31.8	PFMs empty
Wet Tropics	DUNK ISLAND	2023-11-21	2023-12-04	13	43.7	1 PFM lost. Result duplicated
	DUNK ISLAND	2023-12-04	2024-01-04	31	33	1 PFM lost. Result duplicated. ED replicate
	DUNK ISLAND	2024-01-04	2024-02-05	32	31.4	PFMs empty
	DUNK ISLAND	2024-02-05	2024-03-27	51	19	PFMs empty
	DUNK ISLAND	2024-03-27	2024-04-09	13	62.6	1 PFM empty
Wet Tropics	LUCINDA JETTY	2023-11-15	2023-12-20	35	17.6	
	LUCINDA JETTY	2023-12-20	2024-01-17	28	20.3	Original Dec samplers deployed in Jan, and Jan samplers deployed in Dec. Passive Input and labels updated.
	LUCINDA JETTY	2024-01-17	2024-02-14	28	18.8	
	LUCINDA JETTY	2024-02-14	2024-03-13	28	32.3	1 PFM empty. ED replicate
	LUCINDA JETTY	2024-03-26	2024-04-24	29	24.1	
Burdekin	HAUGHTON RIVER MOUTH	2023-11-01	2023-12-02	31	33	1 PFM lost, 1 empty. Lost PFM assumed empty
	HAUGHTON RIVER MOUTH	2024-01-09	2024-02-26	48	20.5	1 PFM lost, 1 empty. Single result duplicated.
	HAUGHTON RIVER MOUTH	2024-02-26	2024-03-25	28	36	PFM empty
	HAUGHTON RIVER MOUTH	2024-03-25	2024-05-04	40	24	PFMS lost (assumed empty)
Burdekin	EURI CREEK	2023-12-05	2024-01-18	44	22.9	PFMs empty
	EURI CREEK	2024-01-18	2024-02-27	40	25.4	
Mackay-Whitsunday	WHITSUNDAY CHANNEL	2023-11-08	2023-12-03	25	23.3	
	WHITSUNDAY CHANNEL	2023-12-13	2024-01-14	32	26.8	
	WHITSUNDAY CHANNEL	2024-01-14	2024-02-05	22	26.7	ED replicate
	WHITSUNDAY CHANNEL	2024-02-05	2024-03-03	27	27.1	
Mackay-Whitsunday	REPULSE BAY	2023-11-08	2023-12-03	25	26	
	REPULSE BAY	2023-12-13	2024-01-14	32	27.9	
	REPULSE BAY	2024-01-14	2024-02-05	22	27.5	
Mackay-Whitsunday	FLAT TOP	2023-11-05	2023-12-03	28	23.9	

	FLAT TOP	2023-12-13	2024-01-14	32	31.6	1 PFM empty
	FLAT TOP	2024-01-14	2024-02-05	22	30.4	
	FLAT TOP	2024-02-05	2024-03-04	28	29.5	
	FLAT TOP	2024-03-04	2024-04-03	30	26.5	
Mackay-Whitsunday	SARINA INLET	2023-11-05	2023-12-03	28	26.1	
	SARINA INLET	2023-12-13	2024-01-14	32	31.5	
	SARINA INLET	2024-01-14	2024-02-05	22	29.7	
	SARINA INLET	2024-02-05	2024-03-04	28	30.3	
	SARINA INLET	2024-03-04	2024-04-03	30	32.7	

Note:- *Flow velocity of 3.4 cm s^{-1} was used where the calculated flow velocity was smaller than 3.4 cm s^{-1}*

***Figure 1**. Map of Queensland, Australia coast indicating sampling locations.*

2.3 Grab samples

A total of 47 grab samples were collected from the ten fixed sampling sites between 1 November 2023 and 13 April 2024. Additionally, 48 flood monitoring grab samples were collected at Cape York and the Wet Tropics region between 14 December 2023 to 28

December 2023 (Table 2). Two flood event grabs were also collected in March 2024 from the Tully River. Grab samples included eight duplicate samples across all sites.

***Table 2**. Grab sample locations and dates.*

Natural Resource Management (NRM) Region	Site Name	Date of sample collection	Comment
Wet Tropics	LOW ISLES	2024-02-17	
	LOW ISLES	2024-03-19	
	LOW ISLES	2024-04-13	
	LOW ISLES	2024-07-08	
Wet Tropics	HIGH ISLAND	2023-11-20	
	HIGH ISLAND	2023-12-02	
	HIGH ISLAND	2024-01-05	
	HIGH ISLAND	2024-02-06	
Wet Tropics	DUNK ISLAND	2023-11-21	
	DUNK ISLAND	2023-11-21	Duplicate
	DUNK ISLAND	2023-12-04	
	DUNK ISLAND	2024-01-04	
	DUNK ISLAND	2024-02-05	
Wet Tropics	LUCINDA JETTY	2023-11-15	
	LUCINDA JETTY	2023-12-20	
	LUCINDA JETTY	2024-01-17	
	LUCINDA JETTY	2024-02-14	
	LUCINDA JETTY	2024-03-26	
Burdekin	HAUGHTON RIVER MOUTH	2023-11-01	
	HAUGHTON RIVER MOUTH	2023-12-02	
	HAUGHTON RIVER MOUTH	2023-12-02	Duplicate
	HAUGHTON RIVER MOUTH	2024-01-09	
	HAUGHTON RIVER MOUTH	2024-02-26	
	HAUGHTON RIVER MOUTH	2024-03-25	
Burdekin	EURI CREEK	2023-12-05	
	EURI CREEK	2024-01-18	
Mackay-Whitsunday	WHITSUNDAY CHANNEL	2023-11-09	
	WHITSUNDAY CHANNEL	2023-12-03	
	WHITSUNDAY CHANNEL	2024-01-14	
	WHITSUNDAY CHANNEL	2024-02-05	
	WHITSUNDAY CHANNEL	2024-03-03	
Mackay-Whitsunday	REPULSE BAY	2023-11-01	
	REPULSE BAY	2023-11-01	Duplicate
	REPULSE BAY	2023-12-03	
	REPULSE BAY	2024-01-14	
	REPULSE BAY	2024-02-05	
	REPULSE BAY	2024-03-04	
Mackay-Whitsunday	FLAT TOP	2023-11-05	
	FLAT TOP	2023-12-03	
	FLAT TOP	2024-01-14	

	FLAT TOP	2024-02-05	
	FLAT TOP	2024-03-14	
Mackay-Whitsunday	SARINA INLET	2023-11-05	
	SARINA INLET	2023-12-03	
	SARINA INLET	2024-01-14	
	SARINA INLET	2024-02-05	
	SARINA INLET	2024-03-04	
Flood Sites			
Cape York	Endeavour Estuary at Boat Ramp 14-DEC 08:25	2023-12-14	
	Endeavour River Mouth 14-DEC 12:20	2023-12-14	
	Endeavour River Mouth 14-DEC 15:40	2023-12-14	
	Endeavour River Boat Ramp 15-DEC 09:40	2023-12-15	
	Endeavour River Boat Ramp 15-DEC 14:40	2023-12-15	
	Endeavour River Boat Ramp 16-DEC 09:05	2023-12-16	
Barron River	JCF332_D0	2023-12-28	
	JCF332_D1	2023-12-28	Duplicate
	JCF331_D0	2023-12-28	
	JCF331_D1	2023-12-28	
	JCF333_D0	2023-12-28	
	JCF333_D1	2023-12-28	
	JCF335_D0	2023-12-28	
	JCF335_D1	2023-12-28	Duplicate
	JCF334_D0	2023-12-28	
	JCF334_D1	2023-12-28	
	JCF336_D0	2023-12-28	
	JCF336_D1	2023-12-28	
	JCF337_D0	2023-12-28	
	JCF337_D1	2023-12-28	
	JCF330_D0	2023-12-28	
	JCF330_D1	2023-12-28	
Russell Mulgrave River	JCF329_D0	2023-12-19	
	JCF314_D0	2023-12-19	
	JCF314_D1	2023-12-19	
	JCF300_D0	2023-12-19	
	JCF300_D1	2023-12-19	
	JCF305_D0	2023-12-19	
	JCF305_D1	2023-12-19	
	JCF301_D0	2023-12-19	Duplicate
	JCF301_D1	2023-12-19	
	JCF307_D0	2023-12-19	
	JCF307_D1	2023-12-19	Duplicate
	JCF313_D0	2023-12-19	
	JCF313_D1	2023-12-19	

2.4 Passive Flow Monitors (PFMs)

Passive flow monitors (in duplicate) were co-deployed with passive samplers and were used to estimate water velocity during the deployment period of the samplers (O'Brien *et al*. 2009,

2011a, 2011b; Figure 2). As the rate of diffusion of chemicals into a passive sampling device is a function of the turbulence or water velocity at the surface of the sampler, it is important to monitor this parameter to accurately estimate water concentrations of the target chemicals. PFMs provide a means of estimating water velocity based on the dissolution of calcium sulfate hemihydrate from the surface of the exposed PFM (13.85 cm^2) which is equal to that of the exposed surface of the membranes within the ED passive samplers.

The PFMs were prepared according to the method of O'Brien *et al*. (2009) by filling plastic specimen containers (150/75 mL volume, 42 mm Ø, 105/55 mm high) with a 1:2 plaster:water mix prepared using deionised water and dental plaster powder (Boral). Containers were capped once the plaster became firm (approximately 5 minutes) to prevent drying and were stored at room temperature. The mass of the PFMs was recorded both prior to and after deployment to determine the mass of plaster lost during deployment.

Figure 2. *PFMs prior to deployment (left) and after deployment (right).*

2.5 Passive sampler preparation and extraction

In this campaign Empore DiskTM (3M; ED) samplers were deployed to detect and quantify the presence of polar organic pollutants such as pesticides including herbicides (Figure 3). Polydimethylsiloxane (PDMS) strips in stainless steel cages were utilised for the March 2024 deployment period to quantify the presence of more hydrophobic organic pollutants (non-polar chemicals) such as certain organochlorine pesticides (OCPs) (Figure 4). ED and PDMS passive samplers were all prepared and extracted according to established SOPs and previously published procedures and methods described in Kaserzon *et al*. (2017).

2.6 Grab sample preparation and extraction

Grab samples (1 L) were collected at each passive sampler deployment and retrieval, and during flood monitoring events. Polyethylene bottles were used for sampling. Grab samples were prepared and extracted according to established SOPs and previously published procedures and methods described in Kaserzon *et al*. (2014). Briefly, samplers were extracted using hydrophilic-lipophilic balanced solid phase extraction (SPE) cartridges (Strata X, Phenomenex, Melbourne). Samples were concentrated 1,000 times to increase analytical limits of detection.

Figure 3. *Preparation of an Empore disk (ED) passive sampler.*

Figure 4*. Preparation of a Polydimethylsiloxane (PDMS) passive sampler.*

2.7 Analytical methods

Chemical analysis was performed at QAEHS using established standard operating procedures (SOPs). ED and grab extracts were analysed by LC-QQQ MS/MS for 25 polar pesticides. The analytical methods for pesticides (LC-QQQ MS/MS) are detailed in previously published reports (Kaserzon *et al*. 2018). Briefly, the analysis is performed by HPLC-MS/MS using an AB/Sciex API6500Q mass spectrometer (AB/Sciex, Concord, Ontario, Canada) equipped with an electrospray (TurboV) interface coupled to a Shimadzu Nexera HPLC system (Shimadzu Corp., Kyoto, Japan). Separation was achieved using a 2.6 micron, 50 x 2.0 mm Biphenyl column (Phenomenex, Torrance, CA) run at 45˚C, and a flow rate of 0.3 mL min^{-1} with a linear gradient starting at 5% B, ramped to 100% B in 5.2 minutes then held at 100% for 4.3 minutes followed by equilibration at 5% B for 3.5 minutes (where A = 1% methanol in HPLC grade water, B = 95% methanol in HPLC grade water, both containing 0.1%

acetic acid). The mass spectrometer was operated in both positive and negative ion multiple reaction-monitoring mode for different suites of analytes, using nitrogen as the collision gas monitoring two transitions for each analyte.

Positive samples were confirmed by retention time and by comparing transition intensity ratios between the sample and an appropriate concentration standard from the same run. Samples were reported as positive if the two transitions were present: retention time was within 0.15 minutes of the standard and the relative intensity of the confirmation transition was within 20% of the expected value. The value reported was that for the quantitation transition. Using a 5 µL injection the limit of detection for this method was less than 0.2 µg L^{-1} or better, depending on sensitivity for a particular analyte. Response was linear to at least 100 µg L^{-1}.

PDMS extracts were analysed for 25 organochlorine pesticides (OCPs) and four other pesticides via GC-MS/MS. Analyses were conducted on a Thermo Scientific Q Exactive GC Orbitrap GC-MS/MS in splitless injection mode on a Restek Rxi-5Sil MS w/Integra-Guard column (30 m x 0.25 mm x 0.25 µm). Ions were generated via Electron Ionisation (EI) at 70 eV, acquired at 60,000 resolution in positive ion mode and analysed via 3-way multiplexed t-sim with windows spanning 3.5 m/z, corresponding to the retention times of the analytes of interest. The inlet, transfer line and source were held at 250°C, 280°C and 280°C respectively and the flow rate was maintained at 1.0 mL min^{-1}. The GC ramp rate was as follows (80°C for 2 minutes; increased to 180°C at 20°C min^{-1} and held for 0.5 min; increased to 300°C at 8°C min^{-1} and held for 10 minutes). The analytical methods for polar pesticides (LC-QQQ MS/MS), OCPs and other non-polar pesticides (GC-HRMS) have been detailed previously in Kaserzon *et al*. (2017).

2.8 Data modelling and reporting of results

Passive sampling enables estimation of time-integrated water concentrations (C_w) based on the amount of chemicals accumulated in the sampler within a given exposure period (Vrana *et al*. 2005). The uptake of these chemicals into the sampler is initially linear but eventually reaches steady state whereby equilibrium of the concentration in the sampler and the concentration in the water is reached. The size and polarity of the contaminant, and other environmental factors, such as water flow, turbulence, and temperature can affect the rate of uptake or sampling rate (R_s) which is measured as volume of water sampled per day (L day^{-1}). The duration of the deployment period is another critical factor determining whether time-integrated sampling or equilibrium phase sampling is occurring for a given analyte in a sampler. Equations 1 and 2 describe the estimation of water concentration based on linear or equilibrium phase sampling, respectively.

Equation 1. Estimation of water concentration based on linear phase sampling.

$$C_W = \frac{C_S \ x \ M_S}{R_S \ x \ t} = \frac{N_S}{R_S x \ t}$$

Equation 2. Estimation of water concentration based on equilibrium phase sampling.

$$C_W = \frac{C_S}{K_{SW}}$$

Where:

C_W = the concentration of the compound in water (ng L^{-1})
C_S = the concentration of the compound in the sampler (ng g^{-1})
M_S = the mass of the sampler (g)
N_S = the amount of compound accumulated by the sampler (ng)
R_S = the sampling rate (L day^{-1})
t = the time deployed (days)
K_{SW} = the sampler –water partition coefficient (L g^{-1})

Calibration data (such as sampling rates or sampler-water partition coefficients) obtained in laboratory or field studies were used to derive these concentration estimates. Together with the sampling rates derived from calibration data, deployment-specific PFM data are used to correct for site-specific effects of water flow velocity on the sampling rates of chemicals (O'Brien *et al*. 2009, 2011a, 2011b). For chemicals detected where no calibration data were available, results were either reported as ng sampler^{-1} or the data were reported via normalisation of sampling rate data with the sampling rate of a reference compound (i.e. Atrazine). Methodologies used to calculate site-specific sampling rates during the deployment periods are fully described in Kaserzon *et al*. (2018).

2.9 Pesticide Risk Metric Calculation

The pesticide risk metric (PRM) developed by Warne *et al.* (2020; 2023) considers the toxicity of 22 pesticides, with results expressed as estimated percentage of species affected. These pesticides were classified into three categories: PSII herbicides, 'other' herbicides and insecticides (Table 3). Seventeen of the twenty-two pesticides were analysed during this sampling campaign for the grab samples: ametryn, atrazine, diuron, hexazinone, metribuzin, prometryn, simazine, tebuthiuron, terbuthylazine, 2,4-D, fluroxypyr, haloxyfop, imazapic, MCPA, metsulfuron-methyl, metolachlor and imidacloprid. ED and PDMS results were combined to calculate the pesticide risk from passive samplers, with a total of nineteen pesticides (the seventeen listed above for the grab samples, as well as chlorpyrifos and pendimethalin).

The PRM method estimates the toxicity mixtures using species sensitivity distributions (SSDs), and the combining of mixture toxicity using the independent action (IA) model of joint action developed by Traas *et al.* (2002). The IA model of joint action can be described by equation 3.

Equation 3. Estimation of pesticide mixture toxicity.

$$Pesticide\ mixture\ toxicity = 1 - \prod_i (1 - PAF_i)$$

Where ∏ represents the product of a sequence of numbers, and PAFi is the potentially affected fraction of each pesticide active ingredient (PAI) calculated using SSDs. The resulting PAI mixture toxicity is expressed as the proportion of species affected (i.e., between 0 and 1), so this number is multiplied by 100 to achieve the percentage of species affected. Calculations were done using the R package *CatchThemAll.PRM* (Bezzina *et al.*, 2023).

The PAF estimates represent instantaneous mixture toxicity at the time of collection for grab samples, and time weighted average mixture toxicity for the duration of deployment for passive samples. Each PAF estimate is the percentage of species affected by the mixtures and concentrations of PAIs observed in the grab and passive samplers, respectively. The PRM method replaces values below the limits of reporting (<LOR) with a fraction of the batch-specific LOR that is standardised according to the toxicity of each PAI. This is done to minimise the introduction of toxicity through treatment of <LOR data that would occur with other, more popular treatment methods (e.g. by halving the LOR). Further information on the methods for PRM calculation, including treatment of <LOR data, is provided in Warne *et al*. (2023).

***Table 3**. The 22 pesticides included in the PRM calculation, and the pesticide group they are allocated to. Adapted from Warne et al. 2020.*

PSII Herbicide	Other Herbicide	Insecticide
Ametryn	2, 4-D	Chlorpyrifos
Atrazine	Fluroxypyr	Fipronil
Diuron	Haloxyfop	Imidacloprid
Hexazinone	Imazapic	
Metribuzin	Isoxaflutole (DKN)	
Prometryn	MCPA	
Simazine	Metsulfuron-methyl	
Tebuthiuron	Pendimethalin	
Terbuthylazine	Metolachlor	
	Triclopyr	

2.10 Quality control and assurance (QC/QA) procedures

QAEHS laboratory procedures are performed by fully trained staff in accordance with established Standard Operating Procedures (SOPs). Blank ED passive samplers were prepared, extracted and analysed in parallel with exposed samplers for each deployment period to ensure quality control and to prevent false positives. Laboratory blanks (n = 5) were prepared before each deployment and were retained at QAEHS for the duration of the deployment. These samplers were included with each batch to provide insight into any contamination arising in the laboratory from preparation or extraction. ED travel blanks (n = 5) were prepared in a similar manner, then were sent into the field and opened briefly before sealing and returned with the deployed samplers. Similarly blank grab water samples (containing MilliQ water) were extracted with each grab sample batch (n = 10). Duplicate passive samplers (n = 5) and grab samples (n = 8) were analysed to test replication of results. Where an analyte is detected in field or lab blanks above the Limit of Quantification (LOQ), the effective LOR is raised to the average blank value plus three times the standard deviation.

3 Results and discussion

3.1 Passive flow monitor (PFM) results

Results from the passive flow monitors (PFMs) used to estimate the in-situ flow velocities to which ED passive samplers were exposed ranged from 17.6 cm s^{-1} at Lucinda Jetty (for ED samplers deployed between November and December 2023) to 62.6 cm s^{-1} at Dunk Island (for ED samplers deployed between March and April 2024) (Table 1, Figure 5). Average PFM derived flow velocities across all sites was 28.9 ± 7.7 cm s^{-1} (Coefficient of variation (CV) = 27%) indicating relatively consistent water velocities observed across the deployment sites. Where PFMs were lost or empty, flow rates were estimated using the 100% gypsum loss rate (Table 1). While PFMs are not an indication of total flow velocities within the aquatic system, they provide an estimate of the turbulence to which a passive sampler is exposed and allow for the empirical correction of chemical uptake rates for more accurate water concentration estimates from ED passive samplers.

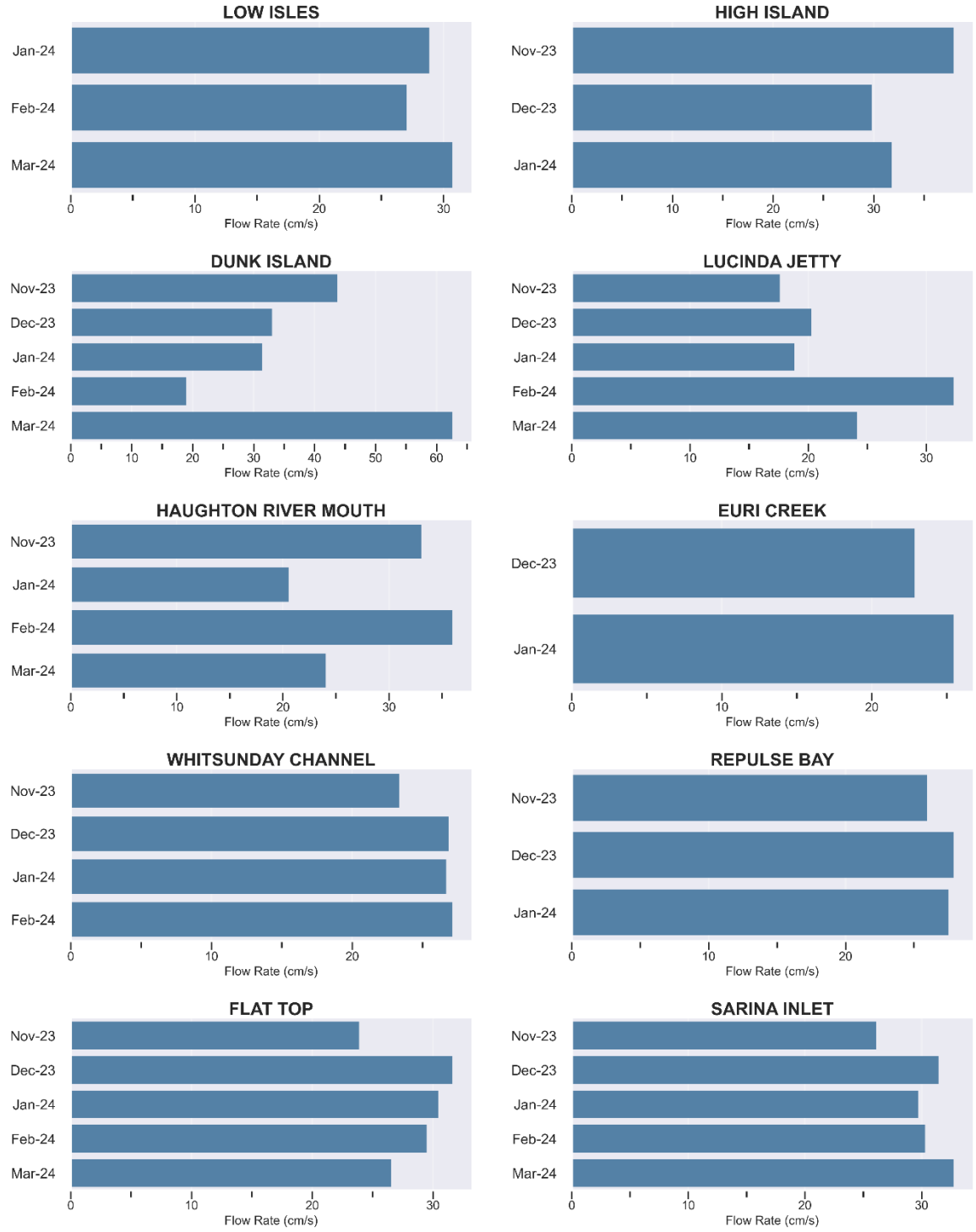

Figure 5. *Passive flow monitor (PFM) based water flow velocity estimations (cm s^{-1}) at the deployment sites.* ***Note:*** *A minimum flow velocity of 3.4 cm s^{-1} is used to assess flow velocity using Passive Flow Monitors (PFMs).*

3.2 Chemical analysis results - ED passive samplers

During the 2023-24 sampling period, a total of 15 different pesticides were detected in the Empore disk passive sampler extracts above the limits of reporting (LOR) (Table 4). A mixture of pesticides was detected in most samples, with only six samples containing a single detected pesticide above limits of reporting. PSII herbicides were most detected, with diuron the most frequently detected chemical (85% detection frequency), followed by hexazinone (79%) and atrazine (74%). The highest concentrations of diuron (34.9 ng L^{-1}) and hexazinone (17.2 ng L^{-1}) were both detected in the Flat Top January sample. This sample also contained the highest estimated concentrations of bromacil, metolachlor and metribuzin.

Total ∑pesticides concentrations at sites ranged from 0.23 ng L^{-1} for Haughton River Mouth (in November 2023) to 70.1 ng L^{-1} for Flat Top (January 2024) (Figure 6). Eight out of the ten sites (High Island, Dunk Island, Lucinda Jetty, Haughton River Mouth, Euri Creek, Repulse Bay, Flat Top and Sarina Inlet) showed the highest pesticide loads were detected in January 2024, with Low Isles and Whitsunday Channel peaking in February 2024. Ten of the fifteen pesticides detected had highest concentrations in samples from January. Typically, lowest concentrations and numbers of pesticides detected were observed in samples taken during November 2023.

Table 4. *Summary of chemical analytes detected in ED passive samplers, number of detections across sites and deployment periods, percent (%) detection and minimum and maximum concentrations observed.*

Analyte	Number of Detects	% Detection	Min reported (ng/L)	Max reported (ng/L)
2,4-D	6	15	1.04	3.19
Ametryn	0	0	<LOR	<LOR
Atrazine	29	74	0.229	13.1
Atrazine desethyl	10	26	0.202	1.14
Atrazine desisopropyl	0	0	<LOR	<LOR
Bromacil	9	23	0.226	0.803
Diuron	33	85	0.327	34.9
Fluazifop	1	3	0.034	0.034
Fluometuron	0	0	<LOR	<LOR
Fluroxypyr	0	0	<LOR	<LOR
Haloxyfop	5	13	0.089	0.22
Hexazinone	31	79	0.228	17.2
Imazapic	0	0	<LOR	<LOR
Imidacloprid	21	54	0.308	5.03
MCPA	0	0	<LOR	<LOR
Metolachlor (S+R)	21	54	0.236	3.56
Metribuzin	7	18	0.198	0.893
Metsulfuron methyl	13	33	0.241	4.79
Prometryn	0	0	<LOR	<LOR
Propazine	0	0	<LOR	<LOR
Simazine	1	3	0.246	0.246
Tebuconazole	0	0	<LOR	<LOR
Tebuthiuron	13	33	0.243	6.71
Terbuthylazine	11	28	0.161	1.15
Terbutryn	0	0	<LOR	<LOR

Figure 6. *Total estimated water concentrations (ng L^{-1}) of ΣPesticides at each site/deployment period derived from ED passive samplers.*

3.3 Chemical analysis results - PDMS passive samplers

PDMS passive samplers were included during the March deployments as a trial, with successful deployments at four sites (Sarina Inlet, Flat Top, Dunk Island and Low Isles). A total of five pesticides were detected in the PDMS passive samplers (Table 5). HCB was detected at each of the four sites, and dieldrin was detected at three sites (75% detection frequency). Chlorpyrifos was detected at the highest concentration (0.096 ng L^{-1} at Low Isles). Total ∑pesticides concentrations at sites ranged from 0.012 ng L^{-1} for Sarina Inlet to 0.099 ng L^{-1} for Low Isles (Figure 7).

***Table 5**. Summary of chemical analytes detected in PDMS passive samplers, number of detections across sites and deployment periods, percent (%) detection and minimum and maximum concentrations observed.*

Analyte	Number of Detects	% Detection	Min reported (ng/L)	Max reported (ng/L)
Aldrin	0	0	<LOR	<LOR
Chlorpyrifos	1	25	0.096	0.096
Cypermethrin	0	0	<LOR	<LOR
Dacthal	0	0	<LOR	<LOR
Dieldrin	3	75	0.004	0.01
Endosulfan sulfate	0	0	<LOR	<LOR
Endrin	0	0	<LOR	<LOR
Endrin ketone	0	0	<LOR	<LOR
HCB	4	100	0.002	0.004
Heptachlor	0	0	<LOR	<LOR
Heptachlor epoxide a	0	0	<LOR	<LOR
Heptachlor epoxide b	0	0	<LOR	<LOR
Methoxychlor	0	0	<LOR	<LOR
Mirex	0	0	<LOR	<LOR
Pendimethalin	0	0	<LOR	<LOR
Permethrin	0	0	<LOR	<LOR
cis-Chlordane	1	25	0.002	0.002
o,p-DDD	0	0	<LOR	<LOR
o,p-DDE	0	0	<LOR	<LOR
o,p-DDT	0	0	<LOR	<LOR
p,p-DDD	0	0	<LOR	<LOR
p,p-DDE	0	0	<LOR	<LOR
p,p-DDT	0	0	<LOR	<LOR
trans-Chlordane	2	50	0.004	0.007
α-Endosulfan	0	0	<LOR	<LOR
α-HCH	0	0	<LOR	<LOR
β-HCH	0	0	<LOR	<LOR
β-endosulfan	0	0	<LOR	<LOR
γ-HCH (Lindane)	0	0	<LOR	<LOR

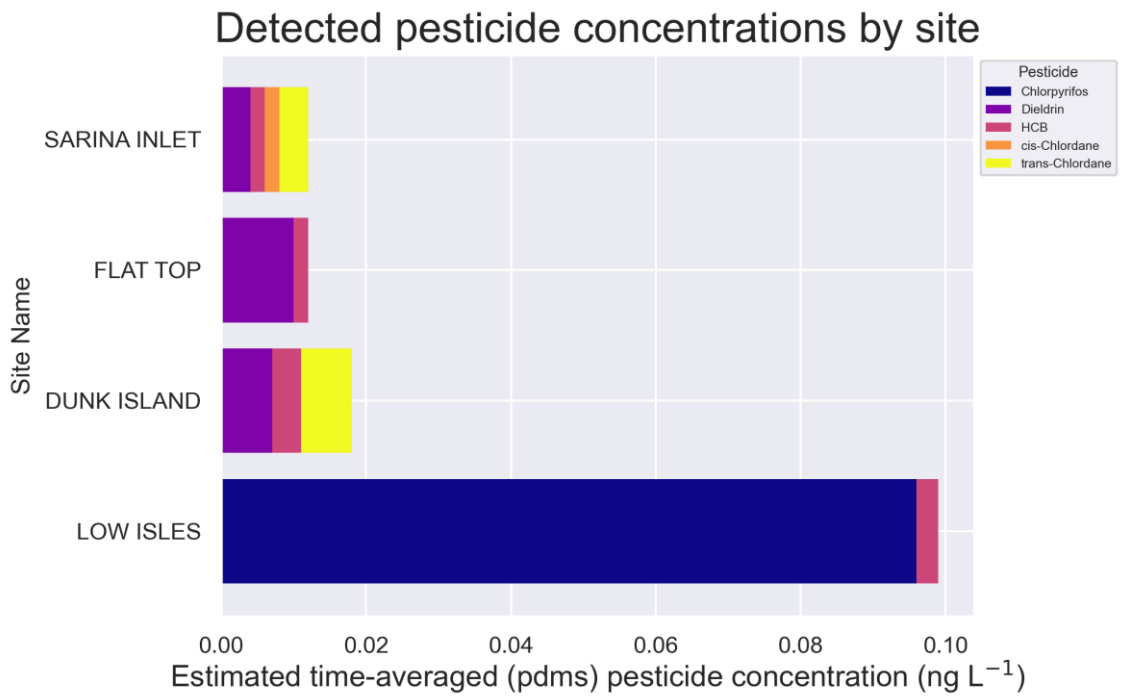

***Figure 7**. Total estimated water concentrations (ng L^{-1}) of ΣPesticides at each site derived from PDMS passive samplers.*

3.4 Chemical analysis results - Grab samples

Seventeen pesticides were detected across all grab samples taken from the routine monitoring sites (Table 6 and Figure 8). The most frequently detected pesticides across sites were atrazine and diuron (both with 48% detection frequency), followed by hexazinone (41%), 2,4-D and metolachlor (both 34%). Diuron and atrazine were also found at the highest concentrations, with maximum concentrations of 145 ng L^{-1} and 144 ng L^{-1}, respectively. The lowest reported concentration was ametryn (0.543 ng L^{-1}) at Haughton River Mouth. The total ∑pesticide concentrations at sites ranged from 1.02 ng L^{-1} for Whitsunday Channel (February 2024) to 584 ng L^{-1} for Sarina Inlet (January 2024) (Figure 8).

Three of the sites with available temporal data over the wet season showed highest total pesticide concentrations in January 2024 (i.e., Flat Top, Lucinda Jetty and Sarina Inlet). These observations are similar to those from ED passive samplers.

***Table 6**. Summary of chemical analytes detected in grab samples, number of detections across sites and deployment periods, percent (%) detection and minimum and maximum concentrations observed.*

Analyte	Number of Detects	% Detection	Min reported (ng/L)	Max reported (ng/L)
2,4-D	15	34	1.98	78
Ametryn	3	7	0.543	4.77
Atrazine	21	48	1.02	144
Atrazine desethyl	10	23	1.09	13.4
Atrazine desisopropyl	7	16	1.22	7.34
Bromacil	4	9	1.27	6.85
Diuron	21	48	0.847	145
Fluazifop	0	0	<LOR	<LOR
Fluometuron	0	0	<LOR	<LOR
Fluroxypyr	3	7	2.85	6.57

Haloxyfop	0	0	<LOR	<LOR
Hexazinone	18	41	2.41	109
Imazapic	0	0	<LOR	<LOR
Imidacloprid	11	25	1.17	30.2
MCPA	9	20	1.45	10.2
Metolachlor (S+R)	15	34	0.695	19.8
Metribuzin	1	2	19.2	19.2
Metsulfuron methyl	2	5	1.82	3.08
Prometryn	0	0	<LOR	<LOR
Propazine	1	2	1.19	1.19
Simazine	0	0	<LOR	<LOR
Tebuconazole	0	0	<LOR	<LOR
Tebuthiuron	8	18	0.867	98.3
Terbuthylazine	5	11	2.82	12.4
Terbutryn	0	0	<LOR	<LOR

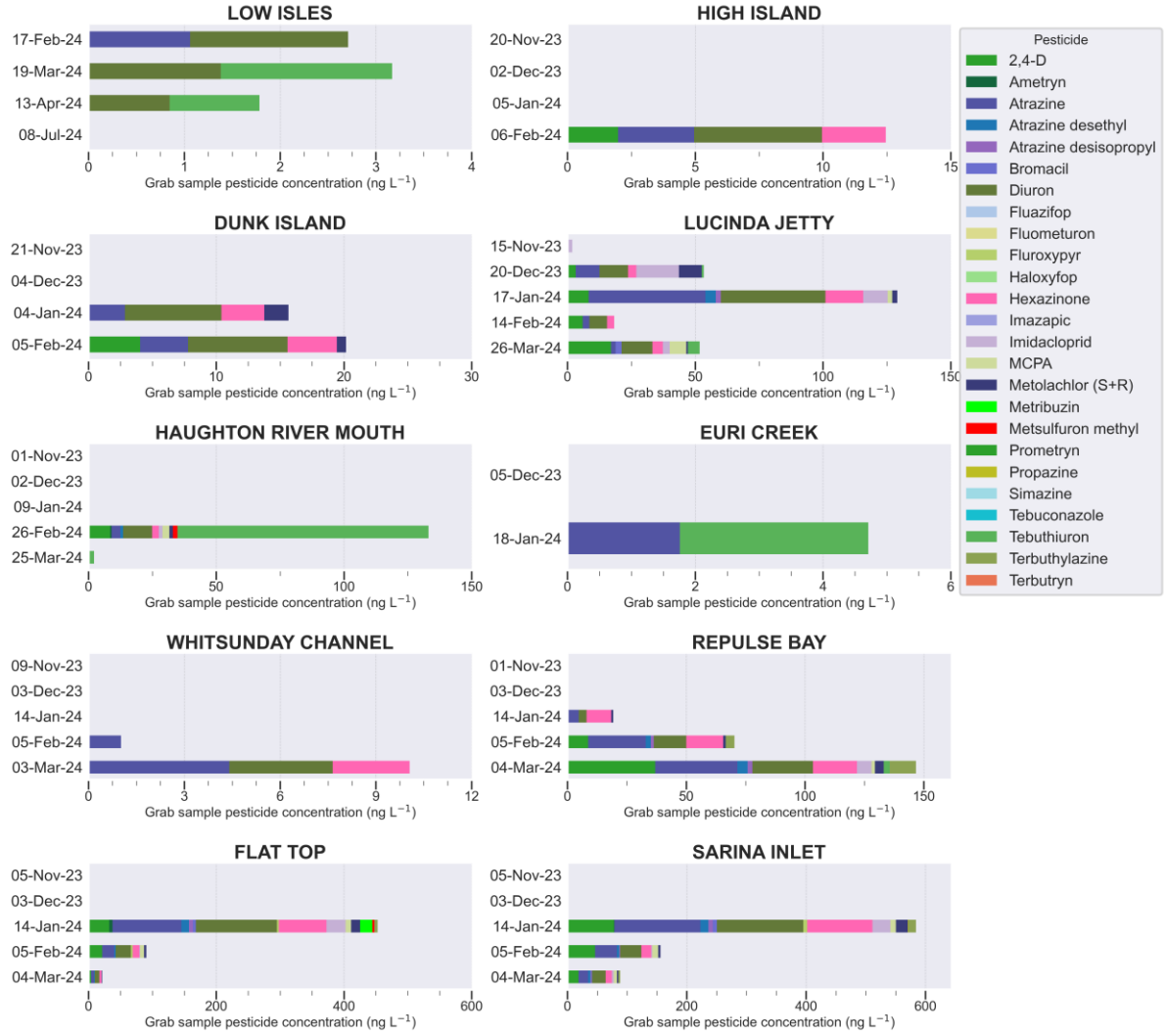

Figure 8. *Water concentrations (ng L^{-1}) of ΣPesticides at each site derived from grab samples.*

3.5 Flood monitoring grab sample results

Grab samples were collected during flood events in December 2023 sampled by the Great Barrier Reef Marine Monitoring Program (MMP) from the Cape York region, in the Wet Tropics region around the Barron River, and further south around the Russell River and Tully River mouths (Figure 9). A further two event samples were collected from the Tully River area in March 2024.

A total of 13 pesticides were detected at levels above limits of detection across all sampling sites (Table 7). Imidacloprid was the most frequently detected pesticide (69%), followed by diuron (53%), atrazine (47%) and metolachlor (47%). Reported concentrations ranged from 0.659 ng L^{-1} to 103 ng L^{-1} for tebuthiuron and diuron, respectively (Table 7; Figure 10).

Samples from the Cape York flood event showed typically lower concentrations than the surface samples from the Wet Tropics region. 2,4-D, hexazinone and tebuthiuron were detected in samples from the Endeavour River Boat Ramp, ranging in concentration from 0.664 ng L^{-1} (hexazinone) to 2.02 ng L^{-1} (tebuthiuron).

In the Tully area, the total ∑pesticide concentrations at sites ranged from 0.827 ng L^{-1} for site JCF320 to 242 ng L^{-1} for site JCF326, despite these samples being collected on the same day. Overall pesticide levels were lower in the Barron region compared to the Tully region, with total ∑pesticide concentrations at sites ranging from 1.64 ng L^{-1} for site JCF335 (D1) to 35.6 ng L^{-1} for site JCF337. Samples taken from the Russell transect showed ∑pesticide concentrations at sites ranged from 1.22 ng L^{-1} for site JCF301 (D1) to 120 ng L^{-1} for site JCF313.

Differences in pesticide concentrations were observed when comparing the samples taken from the surface (denoted with D0) with those taken from deeper water (marked as D1). Imidacloprid was the most frequently detected pesticide in the depth samples, found in 67% of the samples. The other pesticides detected in the depth samples were diuron (20% detection frequency), atrazine and metolachlor (both 13%). JCF334_D1 and JCF337_D1 were the only depth samples to contain a mixture of pesticides, with total ∑pesticide concentrations of 11.98 ng L^{-1} and 9.5 ng L^{-1}, respectively.

When concentrations of atrazine, diuron, metolachlor and hexazinone were plotted against salinity of the samples, a decreasing trend was observed as salinity increases (Figure 11), suggesting pesticide run-off with flood waters. However, no clear trends were observed for imidacloprid in the Barron transect (Figure 12). This suggests that unlike the other pesticides, imidacloprid may already be present in the marine waters and has not been carried with the flood plume.

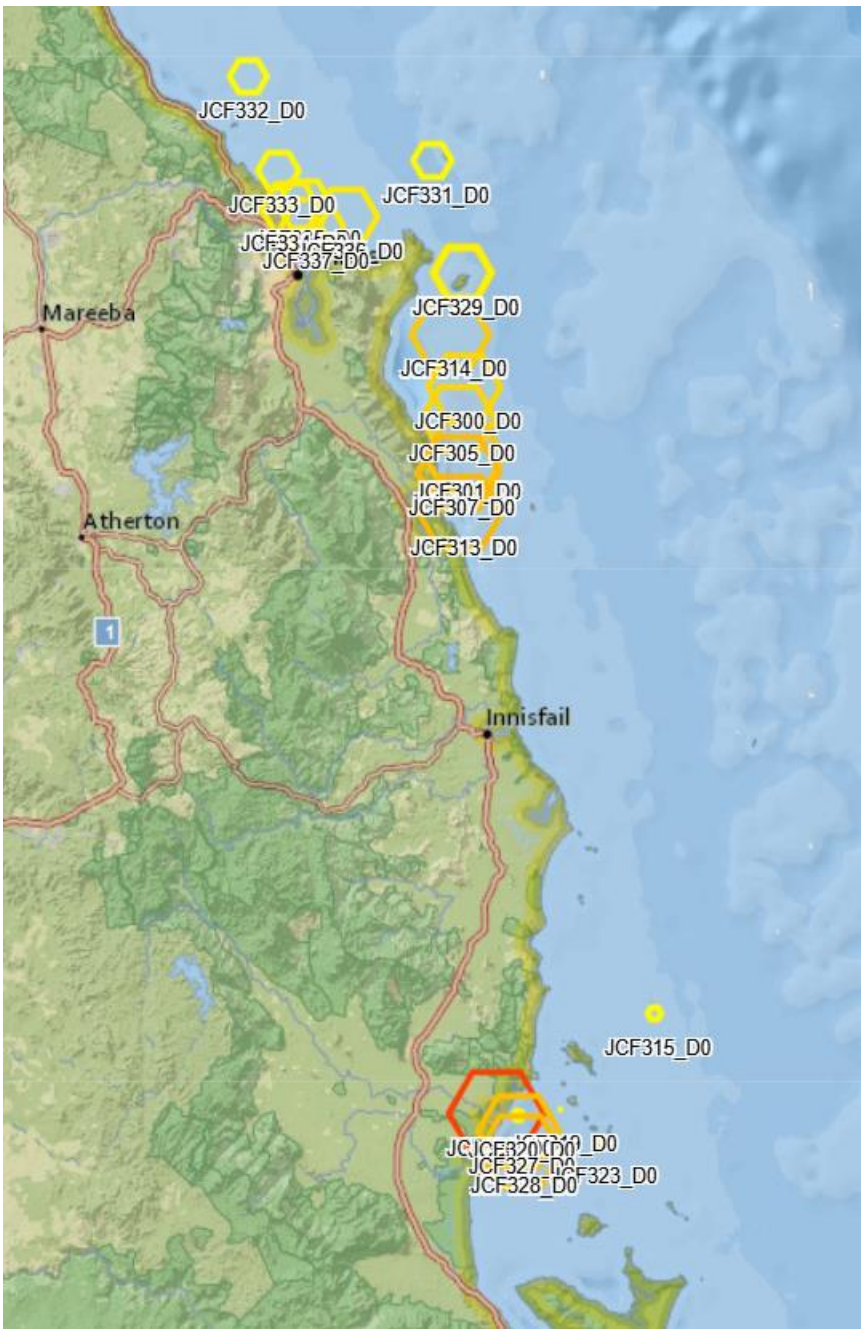

Figure 9. *Map representing GPS locations of grab samples collected during the flood sampling investigations in the Wet Tropics Region. Hexagon size and colour correspond to total ∑pesticide concentrations*

Table 7. *Summary of chemical analytes detected in flood monitoring grab samplers, number of detections across sites and deployment periods, percent (%) detection and minimum and maximum concentrations observed.*

Analyte	Number of Detects	% Detection	Min reported (ng/L)	Max reported (ng/L)
2,4-D	18	40	1.71	8.61
Ametryn	0	0	<LOR	<LOR
Atrazine	21	47	1.55	15.3
Atrazine desethyl	10	22	1.15	4.08
Atrazine desisopropyl	1	2	2.02	2.02

Bromacil	0	0	<LOR	<LOR
Diuron	24	53	0.827	103
Fluazifop	0	0	<LOR	<LOR
Fluometuron	0	0	<LOR	<LOR
Fluroxypyr	0	0	<LOR	<LOR
Haloxyfop	2	4	3.37	6.88
Hexazinone	19	42	1.21	30.9
Imazapic	0	0	<LOR	<LOR
Imidacloprid	31	69	1.11	60.8
MCPA	0	0	<LOR	<LOR
Metolachlor (S+R)	21	47	0.679	31.7
Metribuzin	3	7	1.85	3.79
Metsulfuron methyl	0	0	<LOR	<LOR
Prometryn	0	0	<LOR	<LOR
Propazine	0	0	<LOR	<LOR
Simazine	5	11	0.806	2.44
Tebuconazole	3	7	0.91	1.13
Tebuthiuron	4	9	0.659	4.22
Terbuthylazine	0	0	<LOR	<LOR
Terbutryn	0	0	<LOR	<LOR

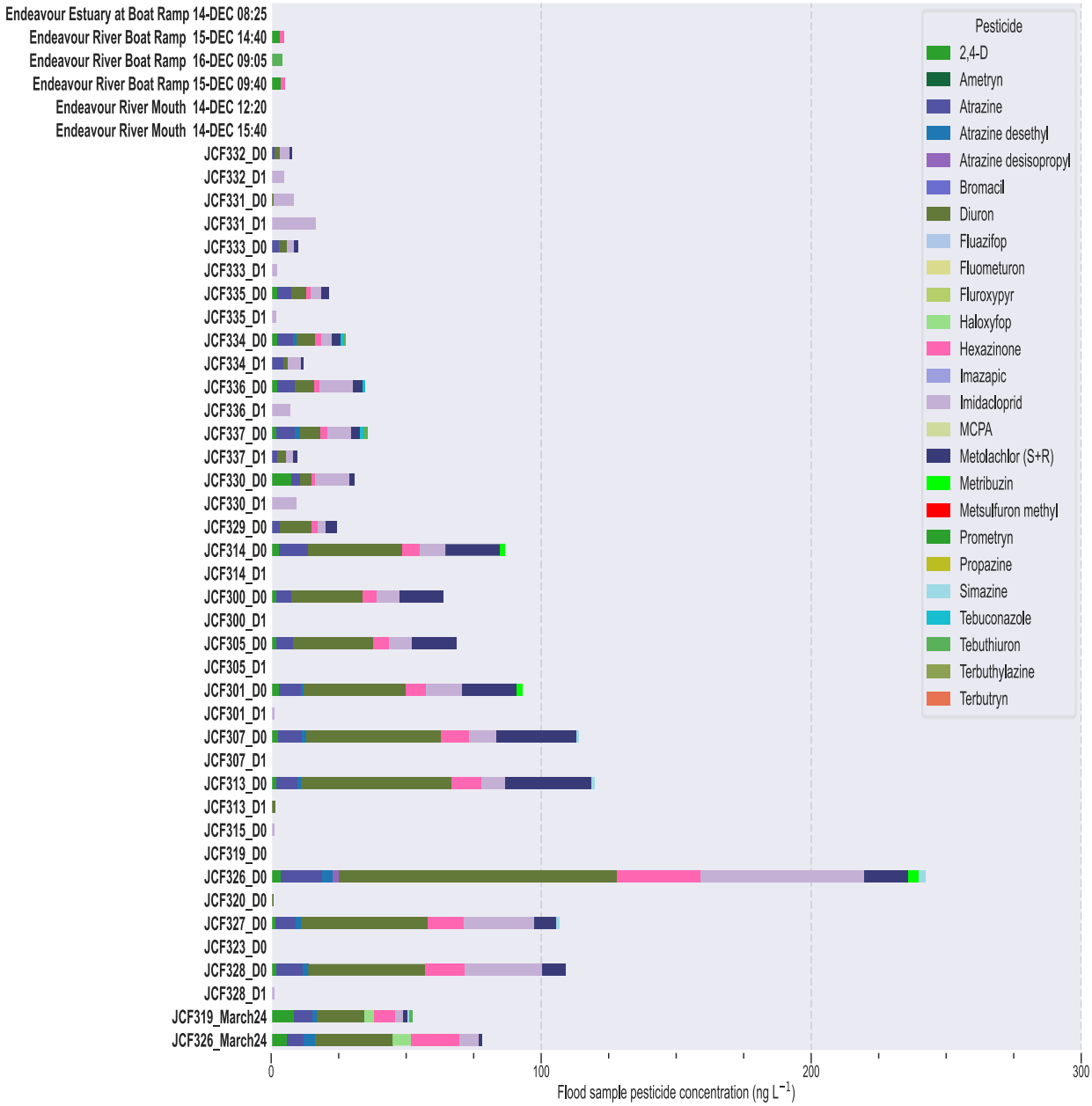

***Figure 10**. Water concentrations (ng L^{-1}) of ΣPesticides at each site derived from grab samples.*

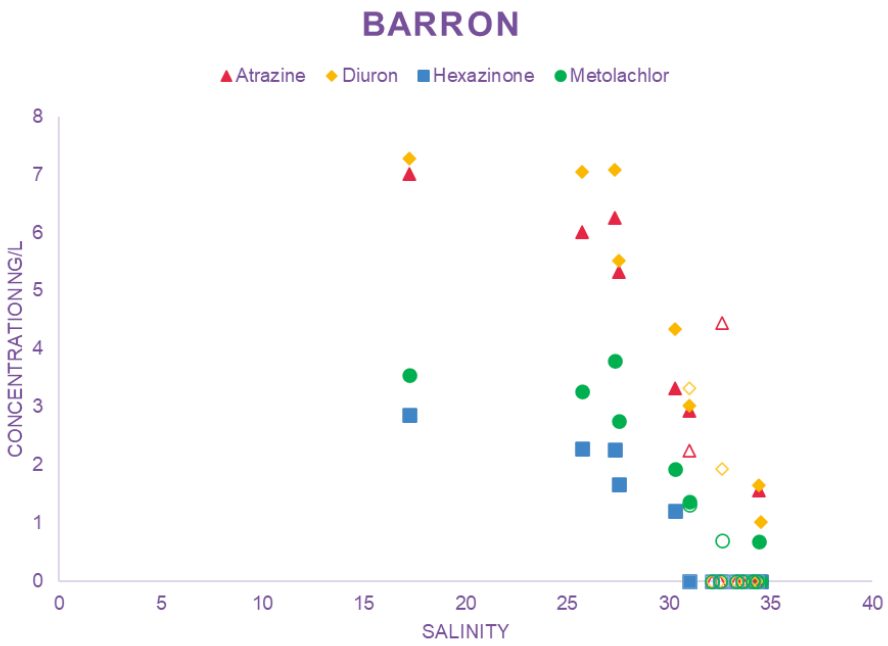

***Figure 11**. Pesticide concentration vs salinity in Barron transect flood grab samples for selected pesticides. Closed shapes denote surface samples, and open shapes correspond to depth samples.*

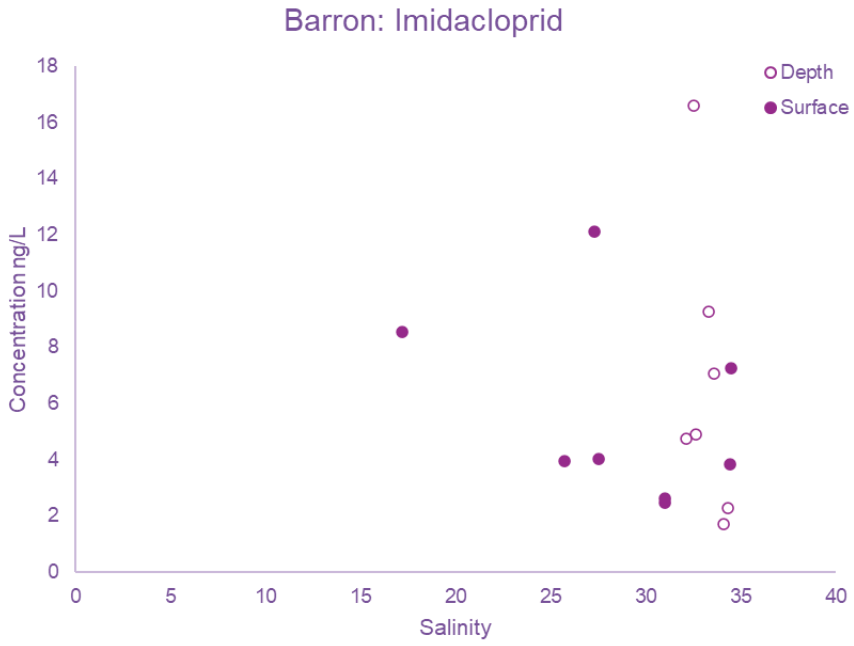

***Figure 12**. Imidacloprid concentration vs salinity in Barron transect flood grab samples. Closed shapes correspond to surface samples, and open shapes correspond to depth samples.*

3.6 Rainfall data

Monthly rainfall data for Queensland from the Bureau of Meteorology (BoM) over the duration of the sampling period (November 2023 – April 2024) is shown below (Figure 13). The highest rainfall along the coastal regions was observed in January 2024 followed by December 2023. These periods of higher rainfall correspond with highest total pesticide concentrations observed for most fixed sites (Figure 6 and Figure 8). Elevated rainfall is associated with

increased transport of nutrients and pesticides into the reef catchment areas (Brodie *et al*. 2012).

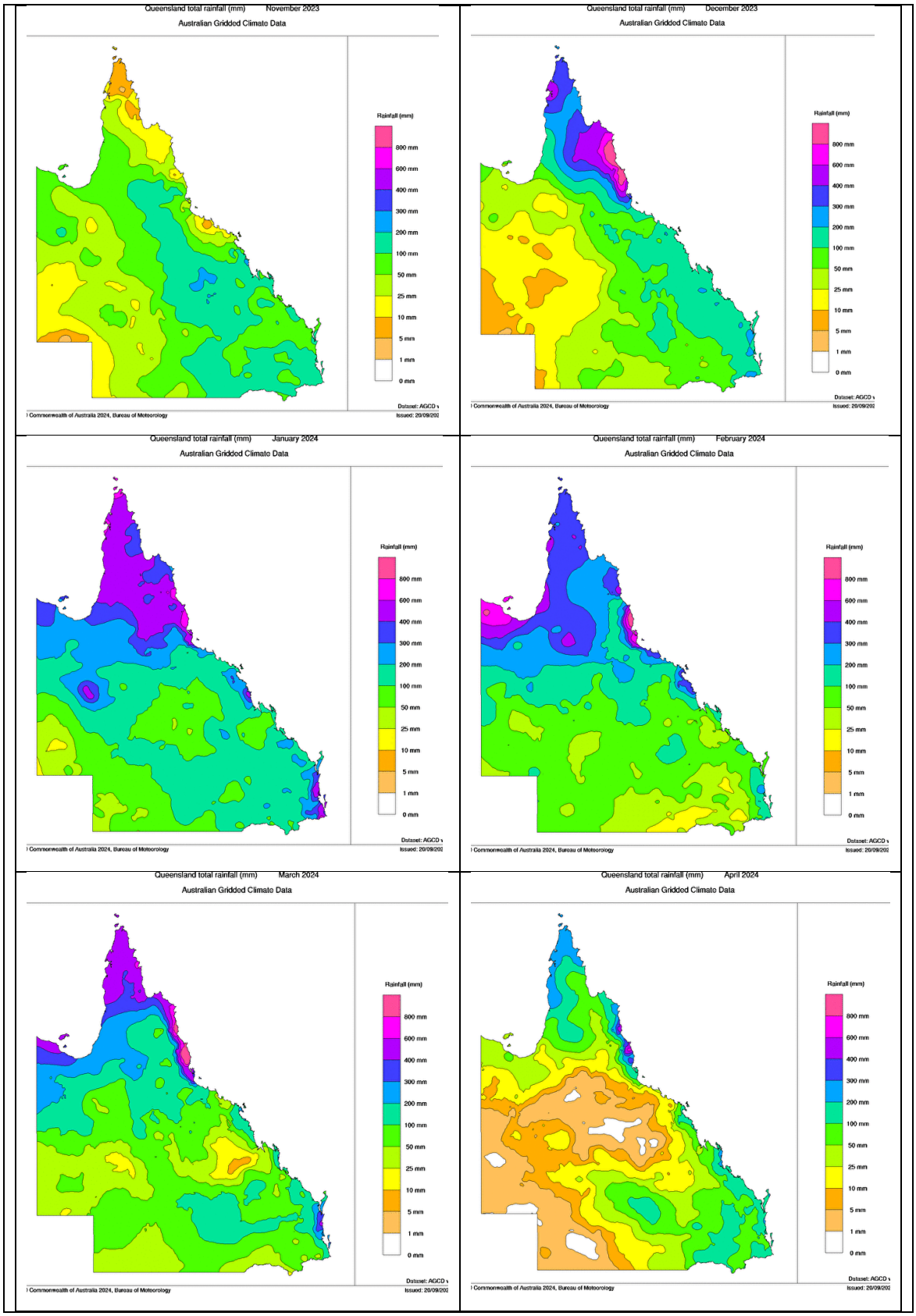

Figure 13. *Monthly rainfall totals for November (2023), top left to April 2024, bottom right (BOM, Climate Data Online - Map search – [bom.gov.au](bom.gov.au)).*

3.7 Comparison with species protection guideline values

Maximum concentrations from grab and passive samplers were compared with Australian freshwater and marine species protection guidelines (ANZECC 2000; Table 8 and Table 9). Guidelines are very limited for marine environments. Only chlorpyrifos and HCB had 99% and 95% marine species protection guideline values available. For other chemicals, comparisons were made with freshwater guidelines or toxicant values where possible.

Metolachlor (in baseline and flood event grabs), metsulfuron methyl (in Sarina Nov 2023 ED) and tebuthiuron (in Haughton River Mouth grab, taken 26 Feb 2024) all had instances that exceeded the 99% species protection guideline value (Table 8, highlighted in pink). Metolachlor's 99% species protection value was exceeded multiple times, at the fixed sites Lucinda Jetty (December), Flat Top (January) and Sarina Inlet (January), as well as in flood grabs from the Tully Region (JCF326 and JCF328) and in all surface samples taken from the Russell-Mulgrave region except for JCF329.

No chemicals detected in the PDMS samples exceeded the guidelines (Table 9). However, the freshwater 99% species protection guideline for chlorpyrifos (0.04 ng L^{-1}) was exceeded at Low Isles in PDMS.

Table 8. *Summary of maximum herbicide concentrations detected at sites in passive and grab samples and how these compare to species protection guidelines (ANZECC 2000), where values were available.*

	Grab samples	ED passive samplers	Flood monitoring grab samples	ANZECC & ARMCANZ Guidelines (updated 2023) (ng/L)		
Analyte	Max reported (ng/L)	Max reported (ng/L)	Max reported (ng/L)	99% Species Protection (Freshwater)	95% Species Protection (Freshwater)	Default Toxicant guideline
2,4-D	78	3.19	8.61	140000	280000	
Ametryn	4.77	0	0			
Atrazine	144	13.1	15.3	700	13000	
Atrazine desethyl	13.4	1.14	4.08			
Atrazine desisopropyl	7.34	0	2.02			
Bromacil	6.85	0.803	0			
Diuron	145	34.9	103			200
Fluazifop	0	0.034	0			
Fluometuron	0	0	0			
Fluroxypyr	6.57	0	0			
Haloxyfop	0	0.22	6.88			
Hexazinone	109	17.2	30.9			
Imazapic	0	0	0			
Imidacloprid	30.2	5.03	60.8			
MCPA	10.2	0	0	3000	7700	
Metolachlor (S+R)	**19.8**	3.56	**31.7**	8.4	460	
Metribuzin	19.2	0.893	3.79			
Metsulfuron methyl	3.08	**4.79**	0	3.7	18	
Prometryn	0	0	0			
Propazine	1.19	0	0			
Simazine	0	0.246	2.44	200	3200	
Tebuconazole	0	0	1.13			
Tebuthiuron	**98.3**	6.71	1.5	20	2200	
Terbuthylazine	12.4	1.15	0			
Terbutryn	0	0	0			

***Table 9**. Summary of maximum pesticide concentrations detected at sites in PDMS samples and how these compare to species protection guidelines (ANZECC 2000), where values were available.*

Analyte	PDMS samples	ANZECC & ARMCANZ Guidelines (updated 2023) (ng/L)		
	Max reported (ng/L)	99% Species Protection (^Marine/*Fresh water)	95% Species Protection (^Marine/*Fresh water)	Default Toxicant guideline
Chlordane	0.007	30*	80*	1^
Chlorpyrifos	0.096	0.5^	9^	
Dieldrin	0.01			10*
HCB	0.004	50^	100^	

3.8 Pesticide Risk Metric

A limitation of solely comparing water concentration estimates with guideline values, is that this method only considers individual pesticide risk. However, both grab and passive samplers show that pesticides are more commonly found in mixtures. The Reef 2050 WQIP has moved away from a target to reduce end-of-catchment pesticide loads, to a new target of protecting at least 99% of aquatic species at the end-of-catchments by 2025. To that end, mixture toxicity must be assessed to improve risk measurement accuracy.

Overall, passive sampler risk was low, with a maximum of 0.99% species affected (Flat Top, January 2024; Figure 14). 'Other' herbicides were mostly influencing the PRM results for the passive samplers, with small input from PSII herbicides, and no influence from insecticides. Samplers from Whitsunday Channel had the lowest percentage of species affected, with 0.01% species affected in samples from November 2023, December 2023 and February 2024. Since passive samplers represent average concentrations over time, these results indicate low level chronic exposure to pesticides.

From the same sites grab samples showed higher pesticide risk than the passive samplers, with Sarina Inlet (January 2024) and Flat Top (January 2024) having calculated PRMs of 6.09% and 5.65% species affected, respectively (Figure 15). There were ten instances across five sites (Lucinda Jetty, Haughton River Mouth, Repulse Bay, Sarina Inlet and Flat Top) where the PRM exceeded 1% species affected, which is equivalent to an exceedance of 99% of species protected.

When investigating the grab samples from the flood monitoring, there were nine flood monitoring samples that had an estimated pesticide risk of more than 1% of species affected: three sites from the Tully transect, and six out of the seven surface samples taken from the Russell transect (Figure 16). Sample JCF326_D0 from the Tully transect showed the highest PRM, with an estimated 4.28% of species affected.

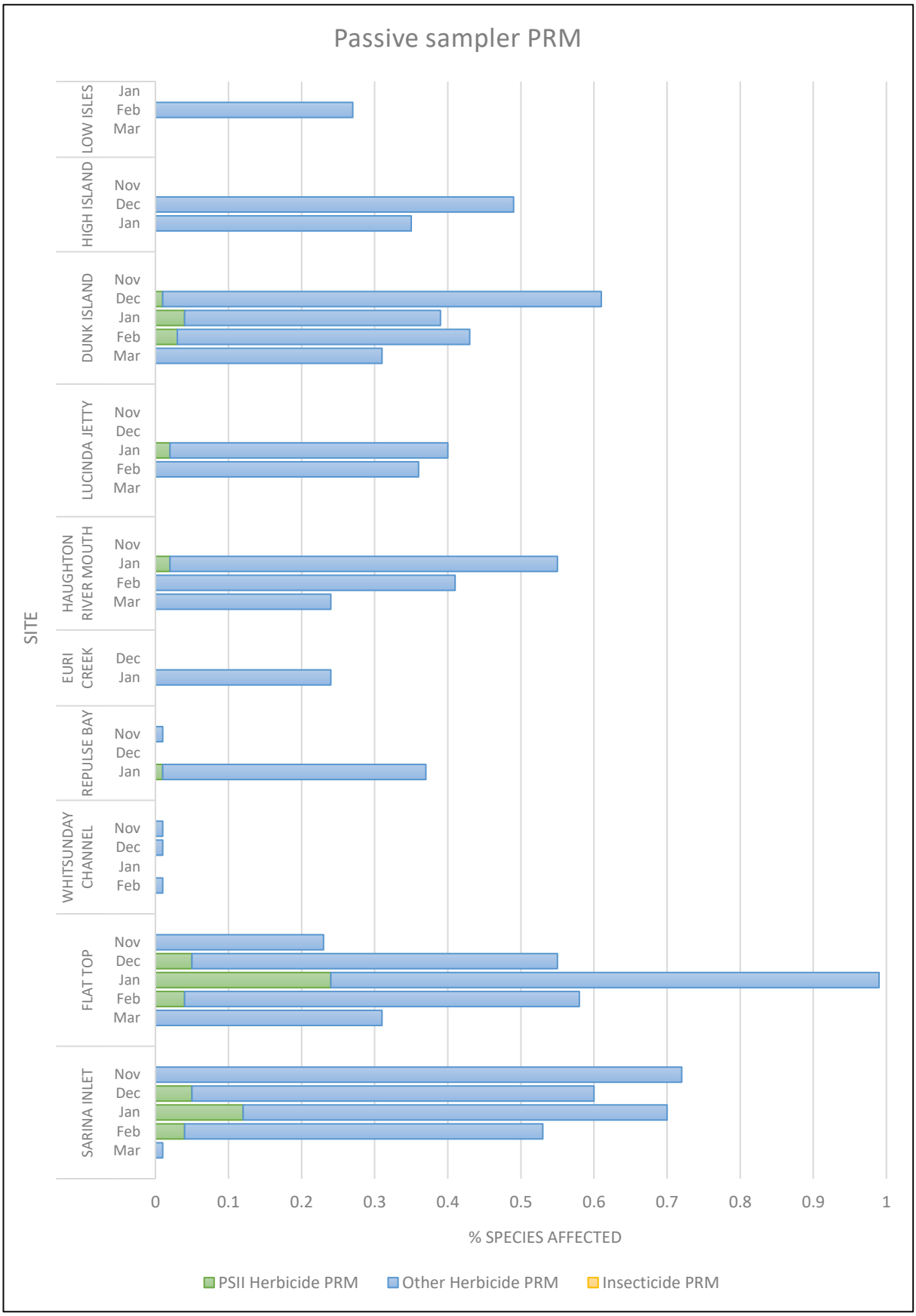

***Figure 14**. Pesticide risk metric for passive samplers (ED and PDMS combined).*

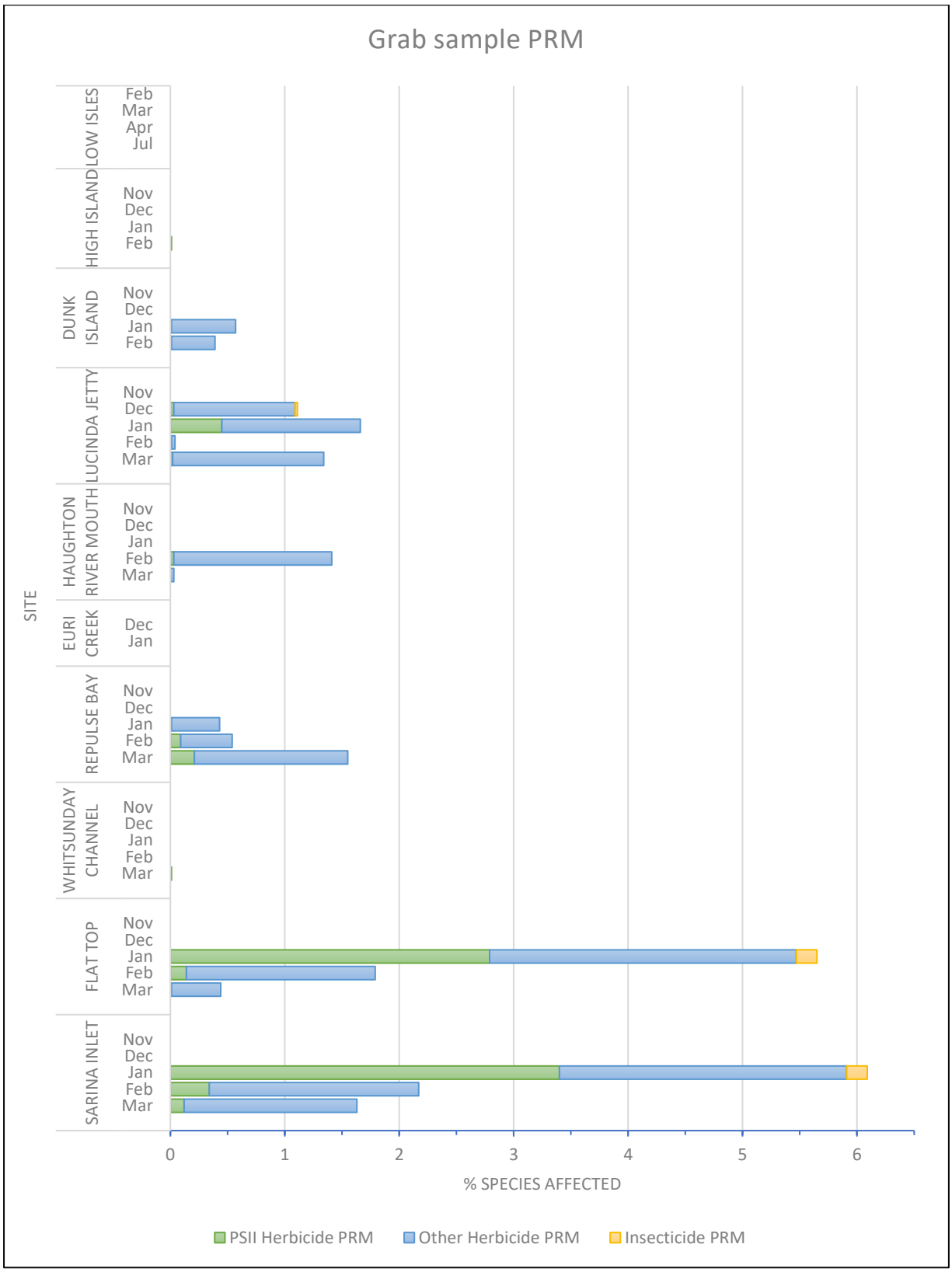

***Figure 15**. Pesticide risk metric for grab samples at routine monitoring sites.*

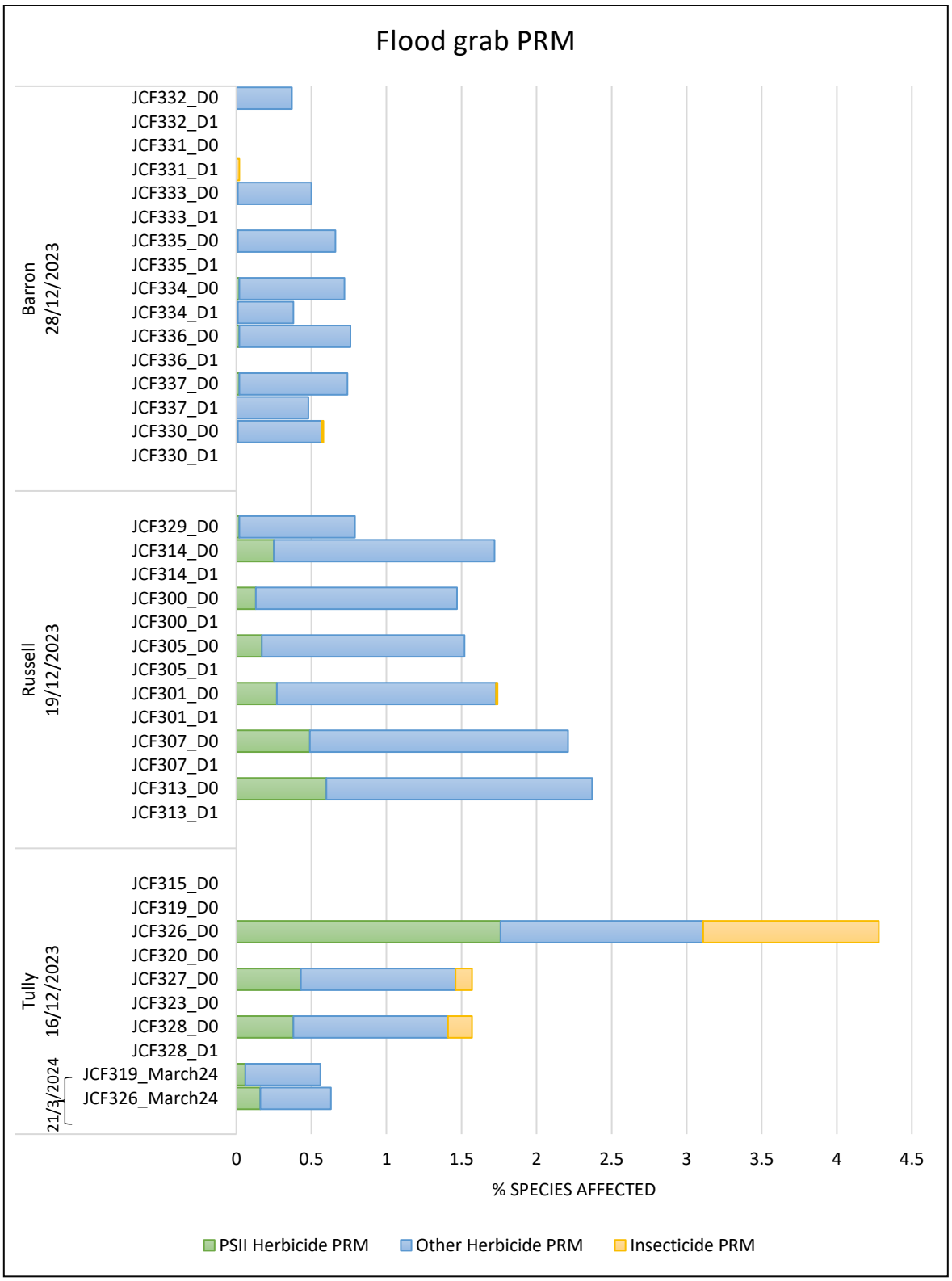

***Figure 16**. Pesticide risk metric for grab samples at Wet Tropics flood monitoring sites.*

4 Conclusions and future recommendations

Up to twenty-six pesticides were detected in the marine monitoring sites during the 2023-24 wet season between November 2023 and April 2024. Concentrations ranged from 0.034 ng L^{-1} (fluazifop) to 145 ng L^{-1} (diuron). The most frequently detected pesticides across both

passive samplers and grab samples were diuron, atrazine, hexazinone and imidacloprid. The total ∑pesticide concentrations observed at sites ranged from 0.23 ng L^{-1} for Haughton River Mouth (in November 2023) to 584 ng L^{-1} for Sarina Inlet (January 2024). The overall number of pesticide detections across samples were typically higher in passive samplers compared with grab samples. Grab samples enabled reporting of water concentrations during flush events in the Cape York region, and transects extending from the Barron River, Russell River and Tully River mouths in January 2024, which was higher than those observed in passive samplers. Passive samplers provided time-weighted averaged water concentrations estimates over the entire period of sampler deployment. It should be noted that single point in time grab samples and passive sampler data represent very different sampling scenarios and are therefore not directly comparable. Grab samples represent a point in time concentration estimate whereas passive samplers represent a time-integrated average water concentration over the deployment period which is more representative of longer-term chronic exposure. Therefore, the two methods are representing very different data sets.

Eight of the ten sites showed passive sampler estimated total pesticide concentrations were the highest in January 2024 (i.e., Haughton River Mouth, Euri Creek, High Island, Dunk Island, Flat Top, Lucinda Jetty, Repulse Bay, and Sarina Inlet), corresponding to the highest rainfall data in the area during the period of sampling.

The information provided by grab and passive samplers reflects the complementary nature of both methods. Passive samplers were able to better reflect pesticide presence, observed via the higher detection frequencies reported compared with grab sampling data. However, the concentrations provided are averaged over time and therefore do not reflect potential acute exposure levels during flood events. Grab samples missed some instances of pesticides presence (especially at the lower end of the analytical reporting limits), but allowed for assessment of plume concentrations during a large flood event. Grab samples could be beneficial especially when considering pesticide species protection and risk values to better understand exposure during a flood event. However, it's important to note that determining the actual peak concentration from a single grab sample is difficult. The peak concentration of a pesticide could also be highly dependent on the river system and pesticide of question. Regardless of the method used, both sampling methods identified similar patterns in terms of total pesticide loads across the sampling months and across the sites investigated. Choosing a consistent long-term sampling approach will increase confidence in the reporting and trend analysis of pesticides when considering longer term changes (i.e., on scales of >10 – 20 years; Taucare *et al*. 2022).

Water quality guideline values are currently limited, especially those specifically for the marine environment and species. Guideline values are based on toxicity of single chemicals, and do not consider the cumulative effects these may have. Given that most of the samples taken showed pesticide mixtures, it is imperative that toxicity is assessed for the entire mixture rather than single pesticides. Calculation of the pesticide risk metric to assess mixture toxicity showed several exceedances of the 1% species affected target stipulated in the Reef 2050 WQIP in both the baseline and flood grab samples. Two grab samples taken from baseline monitoring sites (Flat Top and Sarina Inlet) had estimated risk of more than 5% species affected, equivalent to less than 95% species protected. This highlights the importance of considering the entire pesticide mixture, since no single chemicals were found to exceed the 95% species protection freshwater guideline values.

Future recommendations:

- The information gained from the sampling period revealed pesticide patterns can vary on a spatial and temporal scale. The correlation with rainfall has been observed. To better model pesticide occurrences and identify the high-risk locations and timeframes, continued monitoring is advised. Data can then inform priority sites and timeframes for continued investigation, where appropriate.
- Passive samplers can be effective in allowing for temporal assessments of time-weighted average water concentrations as the information provided is an integration of the sampling period. Grab samples can be effective in providing rough estimates of plume concentrations, with the caveat that knowledge of when the peak of the plume occurs is limited from one grab sample.
- A structured sampling regime is needed with consistent sites monitored over time to reduce potential bias introduced in the sampling and analysis (Taucare *et al*. 2022).
- Monitoring during a dry season would provide further assessment of baseline concentrations of pesticides when not influenced by the wet season allowing for a more comparable temporal assessment of pesticide concentrations. It may further inform longer term persistence of pesticides at the sites investigated.
- Sampling locations further upstream, especially during the wet season, and/or correlating with existing data from upstream sampling (e.g., DETSI monitoring programs), may help elucidate the more dominant concentration inputs to the system.
- In future reporting, continuing to assess data using the PRM approach would be more representative of chemical mixtures present in the catchment and provide a more robust benchmark against the target stipulated in the Reef 2050 WQIP.
- Inclusion of additional pesticides and chemicals of concern (above the 25 currently included in the program) would better represent mixture toxicity effects, especially when considering the PRM approach.

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