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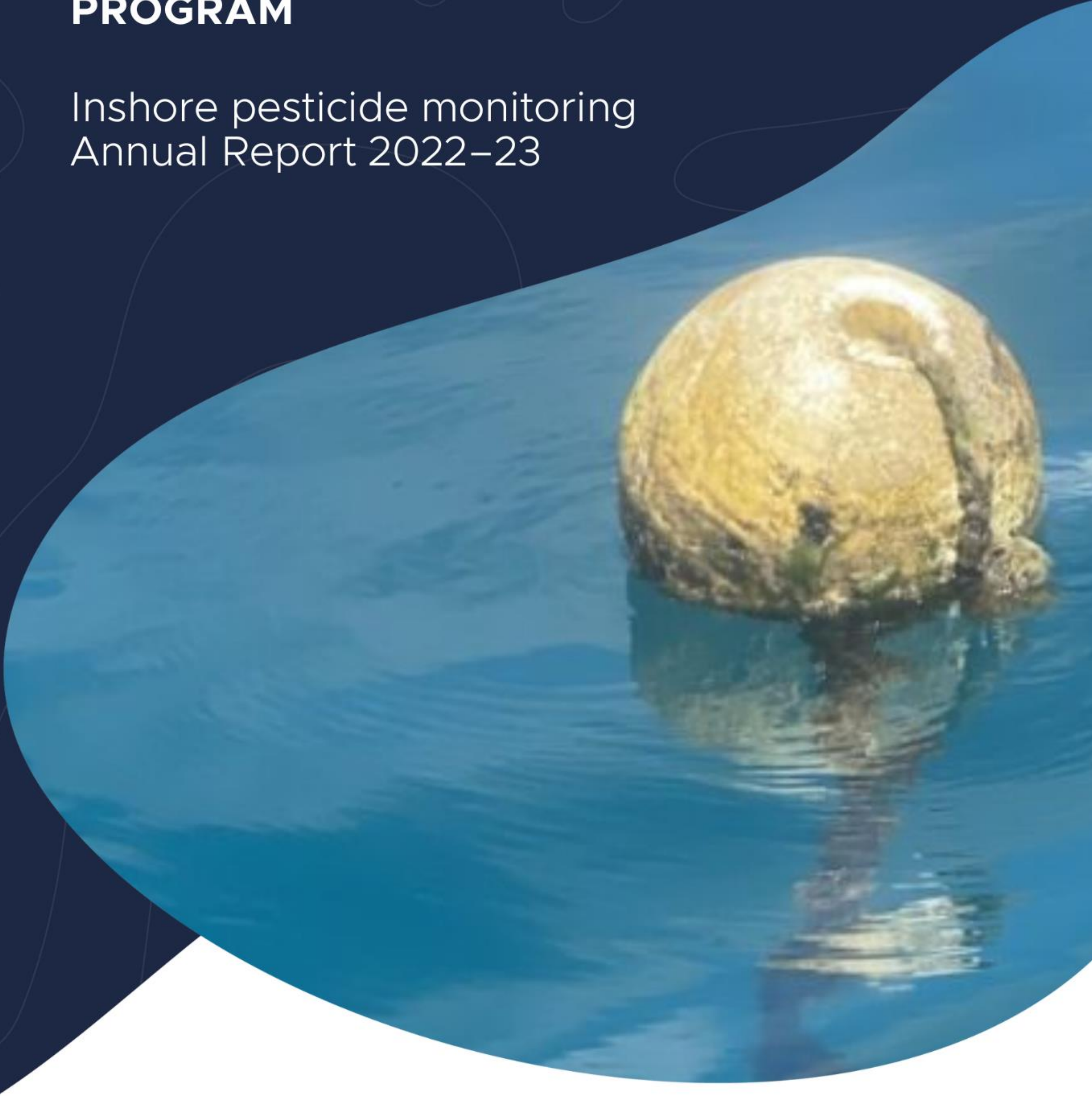
GREAT BARRIER REEF MARINE MONITORING PROGRAM

Inshore pesticide monitoring Annual Report 2022–23



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Front cover photo: Empore™ Disk sampler and Passive Flux Metres deployed for inshore marine pesticide monitoring at High Island, Wet Tropics. ©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.

DISCLAIMER

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Acknowledgements

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Executive Summary

The pesticide analysis for the inshore Great Barrier Reef Marine Monitoring Program (MMP) was re-instated to facilitate seasonal monitoring of pesticides including addressing polar herbicides in previously identified high risk catchments. Throughout the 2022-23 wet season, ten fixed locations were monitored via passive sampling techniques. Additional grab samples were collected at each of the fixed sites and during reactive flood monitoring. The aim of the project was to re-initiate pesticide monitoring in the inshore region of the Great Barrier Reef taking into consideration recent eReefs diuron modelling results and continue monitoring in previously identified high risk catchments. Specific objectives included:

- Determine herbicide concentrations and their spatial trends at 10 fixed monitoring sites from November 2022 to May 2023.
- Determine herbicide concentrations at additional flood monitoring sites.

The sampling approach included deployment of monthly Empore Disk (ED) passive samplers designed for the monitoring of polar pesticides at each site (deployed for ~4 weeks at a time). In addition, the collection of discrete grab samples was carried out during each deployment / retrieval of passive samplers at all locations. Additional flood monitoring grab samples were taken at inshore locations to investigate contaminants flush into the systems. Sites investigated included Low Isles, Dunk Island, High Island, Lucinda Jetty, Haughton River mouth, Euri Creek, Whitsundays Channel, Repulse Bay, Flat Top Island, and Sarina Inlet. Passive samplers (n = 57) and grab samples for baseline site monitoring (n = 56) and flood site monitoring (n = 26) were collected successfully, except for four passive samplers that were lost or compromised. Samples were analysed at the Queensland Alliance for Environmental Health Sciences (QAEHS), The University of Queensland by LC-QQQ MS/MS (polar compounds) using the latest analytical methods and established standard operating protocols (SOPs).

Nineteen of the twenty-five pesticides included in the monitoring campaign were detected across sites with concentrations above limits of detection varying from 0.078 ng L^{-1} (haloxyfop) to 543 ng L^{-1} (atrazine). The most frequently detected pesticides in both passive samplers and grab samples were atrazine, diuron, hexazinone and tebuthiuron. The total ∑herbicide concentrations observed at sites ranged from 0.183 ng L^{-1} for High Island (in November 2022) to 1448 ng L^{-1} for Sarina Inlet (January 2023). The overall number of herbicide detections across samples were typically higher in passive samplers compared with grab samples and baseline (i.e. non- flood plume event) concentrations were slightly higher in passive samplers for some pesticides. Grab samples revealed significantly higher concentrations when they were collected during a flood event and high river flow (i.e. during January 2023). Passive samplers provided time-weighted averaged water concentration estimates over the entire period of sampler deployment. Six of the nine sites with available temporal data over the wet season sampling campaign (from both grab and passive samplers), showed total herbicide concentrations in January 2023 were the highest (i.e., Flat Top, Lucinda Jetty, Repulse Bay, Sarina Inlet, and Whitsunday Channel), corresponding to rainfall data in the area.

Maximum concentrations from grab and passive samplers were compared with Australian freshwater species protection guidelines since no guidelines are currently available for marine environments. The maximum concentrations of metolachlor and metsulfuron-methyl observed in some samples exceeded the 99% freshwater species protection guidelines, but not the 95% guideline. Diuron has no current guidelines except for a default toxicant guideline. One grab sample (Sarina Inlet, January 2023) reported diuron at a concentration 1.56 times above the default toxicant guideline (i.e. 200 ng L^{-1}).

This report summarises observations from the 2022-2023 wet season. In order to continue to assess the new eReef herbicide modelling and identify high risk catchment locations, continued monitoring of sites is recommended to provide insight into the water quality of the reef catchments and inform spatial and temporal trends. Monitoring during a dry season period is advised to better assess baseline concentrations and to enable time-trend modelling.

1 Introduction

The Great Barrier Reef Marine Park Authority runs an extensive marine monitoring program (MMP) to survey and report on the condition of inshore coral, seagrass and water quality annually, and has done so for over 15 years. The MMP was established to support the resilience of the Great Barrier Reef ecosystem. The aim of this current monitoring campaign was to support the MMP efforts by monitoring and understanding the presence of pesticides within the MMP catchment areas as well as to recognise any spatial and temporal trends. The current monitoring period covered the 2022-23 wet season (November 2022 to May 2023). The monitoring campaign has been introduced to extend the use of grab sample and passive sampling technologies for the monitoring of 25 pesticides at 10 fixed sites. In addition, the monitoring of flood events using grab samples was introduced in order 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 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. Single point in time grab samples 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 1 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.

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 and Sciences (DES), QLD. They include 25 pesticides and 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 Passive samplers

A total of 57 passive water samplers (including 5 duplicates) were deployed between November 2022 and May 2023 at 10 fixed sites along the inshore region (Figure 1; Table 1). Three passive samplers were lost during deployment and one sampler was unable to be analysed due to a fault. Duration of deployments varied between 20 and 54 days.

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	2022-11-18	2022-12-19	31	32.9	PFMS EMPTY
	LOW ISLES	2022-12-19	2023-01-18	30	29.6	ED STAINED
	LOW ISLES	2023-01-18	2023-02-09	22	41.5	
	LOW ISLES	2023-02-09	2023-03-16	35	29.5	NO ED OR MEMBRANE IN HOUSING
	LOW ISLES	2023-03-16	2023-05-04	49	20.3	
	LOW ISLES	2023-03-16	2023-05-04	49	20.3	Duplicate
Wet Tropics	HIGH ISLAND	2022-11-11	2022-12-07	26	33.3	
	HIGH ISLAND	2022-11-11	2022-12-07	26	33.3	Duplicate
	HIGH ISLAND	2022-12-07	2023-01-12	36	28.2	1 PFM EMPTY
	HIGH ISLAND	2023-01-12	2023-02-09	28	31.7	
	HIGH ISLAND	2023-02-09	2023-03-13	32	30.1	ED STAINED
	HIGH ISLAND	2023-02-09	2023-03-13	32	30.1	Duplicate. ED STAINED
	HIGH ISLAND	2023-03-13	2023-04-04	22	30.3	ED STAINED
Wet Tropics	DUNK ISLAND	2022-11-10	2022-12-08	28	33.4	ED CONTAINED SEDIMENT
	DUNK ISLAND	2022-12-08	2023-01-11	34	29.9	ED CONTAINED SEDIMENT, ONE PFM MISSING, REMAINING EMPTY
	DUNK ISLAND	2022-12-08	2023-01-11	34	29.9	Duplicate
	DUNK ISLAND	2023-01-11	2023-02-08	28	34.3	
	DUNK ISLAND	2023-02-08	2023-03-14	34	30.1	ED STAINED AND SLIGHTLY CRUMPLED
	DUNK ISLAND	2023-03-14	2023-04-03	20	35.6	
Wet Tropics	LUCINDA JETTY	2022-11-16	2022-12-16	30	21.2	ED STAINED
	LUCINDA JETTY	2022-12-16	2023-01-11	26	22.3	ED STAINED
	LUCINDA JETTY	2023-01-11	2023-02-08	28	22.4	ED STAINED
	LUCINDA JETTY	2023-02-08	2023-03-08	28	24.6	

	LUCINDA JETTY	2023-03-08	2023-04-04	27	22.9	ED STAINED
Burdekin	HAUGHTON RIVER MOUTH	2022-11-03	2022-12-01	28	34.9	PFMS EMPTY
	HAUGHTON RIVER MOUTH	2022-12-01	2023-01-05	35	28.7	
	HAUGHTON RIVER MOUTH	2023-01-05	2023-02-08	34	30	ED STAINED, PFMS EMPTY
	HAUGHTON RIVER MOUTH	2023-02-08	2023-03-10	30	3.4	ALL LOST
	HAUGHTON RIVER MOUTH	2023-03-10	2023-04-17	38	26.8	
Burdekin	EURI CREEK	2022-12-06	2023-01-06	31	32.9	ED STAINED
	EURI CREEK	2023-02-16	2023-04-09	52	19.2	ED LOST, PFMS EMPTY
Mackay-Whitsunday	WHITSUNDAY CHANNEL	2022-11-15	2022-12-11	26	31.5	1 PFM LOST. REMAINING PFM USED FOR FLOW
	WHITSUNDAY CHANNEL	2022-12-11	2023-01-21	41	24	ED STAINED (RED), PFMS EMPTY
	WHITSUNDAY CHANNEL	2023-01-24	2023-03-10	45	22.2	ED STAINED, PFMS EMPTY
	WHITSUNDAY CHANNEL	2023-01-24	2023-03-10	45	22.2	Duplicate. ED STAINED, PFMS EMPTY
	WHITSUNDAY CHANNEL	2023-03-10	2023-04-06	27	30.5	ED STAINED, CONTAINED SEDIMENT
	WHITSUNDAY CHANNEL	2023-04-06	2023-05-01	25	30.8	
Mackay-Whitsunday	REPULSE BAY	2022-11-13	2022-12-12	29	35	
	REPULSE BAY	2022-12-12	2023-01-24	43	22.9	ED LOST. REMAINING PFM USED FOR FLOW. PFM EMPTY
	REPULSE BAY	2023-01-24	2023-03-10	45	22.6	
	REPULSE BAY	2023-03-10	2023-04-06	27	31.7	
	REPULSE BAY	2023-04-06	2023-05-01	25	29.2	ED CONTAINED SEDIMENT
Mackay-Whitsunday	FLAT TOP	2022-11-14	2022-12-13	29	34.8	ED RED STAIN. 1 PFM LOST. REMAINING PFM USED FOR FLOW
	FLAT TOP	2022-12-13	2023-01-12	30	33.9	ED CRUMPLED, STAINED, CONTAINED SEDIMENT; PFMS EMPTY
	FLAT TOP	2023-01-12	2023-03-07	54	18.1	ED STAINED, PFMS EMPTY
	FLAT TOP	2023-03-07	2023-04-05	29	32.1	

	FLAT TOP	2023-04-05	2023-04-30	25	33.5	
Mackay-Whitsunday	SARINA INLET	2022-11-14	2022-12-13	29	35.6	1 PFM LOST. REMAINING PFM USED FOR FLOW
	SARINA INLET	2022-12-13	2023-01-12	30	34.4	ED STAINED. 1 PFM EMPTY
	SARINA INLET	2023-01-12	2023-03-07	54	18.3	ED STAINED, PFMS EMPTY
	SARINA INLET	2023-03-07	2023-04-05	29	35.9	ED STAINED, 1 PFM EMPTY
	SARINA INLET	2023-04-05	2023-04-30	25	38	

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.*

2.2 Grab samples

A total of 56 grab samples were collected from the 10 fixed sampling sites between 1 December 2022 and 9 April 2023. Additionally, 26 flood monitoring grab samples were collected at additional sites between 24 December 2022 to 22 January 2023 (Table 2). 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	2022-11-18	
	LOW ISLES	2022-12-19	
	LOW ISLES	2023-01-24	
	LOW ISLES	2023-02-09	
	LOW ISLES	2023-03-16	
Wet Tropics	HIGH ISLAND	2022-12-07	
	HIGH ISLAND	2023-01-06	
	HIGH ISLAND	2023-02-09	
	HIGH ISLAND	2023-03-01	
	HIGH ISLAND	2023-04-04	
	HIGH ISLAND	NaT	
Wet Tropics	DUNK ISLAND	2022-12-08	
	DUNK ISLAND	2022-12-08	Duplicate
	DUNK ISLAND	2023-01-11	
	DUNK ISLAND	2023-02-08	
	DUNK ISLAND	2023-03-09	
	DUNK ISLAND	2023-04-03	
	DUNK ISLAND	NaT	
Wet Tropics	LUCINDA JETTY	2022-12-16	
	LUCINDA JETTY	2023-01-11	
	LUCINDA JETTY	2023-01-11	Duplicate
	LUCINDA JETTY	2023-02-08	
	LUCINDA JETTY	2023-03-08	
	LUCINDA JETTY	2023-04-04	
Burdekin	HAUGHTON RIVER MOUTH	2022-12-01	
	HAUGHTON RIVER MOUTH	2023-01-05	
	HAUGHTON RIVER MOUTH	2023-01-23	
	HAUGHTON RIVER MOUTH	2023-02-06	
	HAUGHTON RIVER MOUTH	2023-03-10	
	HAUGHTON RIVER MOUTH	2023-04-17	
Burdekin	EURI CREEK	2022-12-06	
	EURI CREEK	2023-02-16	
	EURI CREEK	2023-04-09	
Mackay-Whitsunday	WHITSUNDAY CHANNEL	2022-11-15	
	WHITSUNDAY CHANNEL	2022-12-11	
	WHITSUNDAY CHANNEL	2023-01-24	
	WHITSUNDAY CHANNEL	2023-03-10	
	WHITSUNDAY CHANNEL	2023-04-06	
	WHITSUNDAY CHANNEL	2023-04-06	Duplicate
Mackay-Whitsunday	REPULSE BAY	2022-11-13	

	REPULSE BAY	2022-12-12	
	REPULSE BAY	2023-01-24	
	REPULSE BAY	2023-01-24	Duplicate. Sample Not Reported
	REPULSE BAY	2023-03-10	
	REPULSE BAY	2023-04-06	
Mackay-Whitsunday	FLAT TOP	2022-11-14	
	FLAT TOP	2022-12-13	
	FLAT TOP	2023-01-12	
	FLAT TOP	2023-03-07	
	FLAT TOP	2023-04-05	
Mackay-Whitsunday	SARINA INLET	2022-11-11	
	SARINA INLET	2022-12-13	
	SARINA INLET	2023-01-12	
	SARINA INLET	2023-03-07	
	SARINA INLET	2023-03-07	Duplicate
	SARINA INLET	2023-04-05	
Flood Sites			
	Endeavour River Ramp	2022-12-24	
	Endeavour River Ramp	2022-12-24	Duplicate
	Endeavour River Ramp	2023-01-11	Outgoing tide
	Endeavour River Ramp	2023-01-19	
	JCF Flood	2023-01-21	
	JCF Flood	2023-01-21	
	JCF Flood	2023-01-21	Duplicate
	JCF Flood	2023-01-21	
	JCF Flood	2023-01-21	
	JCF Flood	2023-01-21	
	JCF Flood	2023-01-21	
	JCF Flood	2023-01-21	Duplicate
	JCF Flood	2023-01-21	
	JCF Flood	2023-01-21	
	JCF Flood	2023-01-21	
	JCF Flood	2023-01-21	
	JCF Flood	2023-01-22	
	JCF Flood	2023-01-22	Outgoing tide
	JCF Flood	2023-01-22	
	JCF Flood	2023-01-22	
	JCF Flood	2023-01-22	
	JCF Flood	2023-01-22	
	JCF Flood	2023-01-22	
	JCF Flood	2023-01-22	
	JCF Flood	2023-01-22	
	McIvor Gauge	2023-01-18	

2.3 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).*

2.4 Passive sampler preparation and extraction

In this campaign Empore Disk^{TM} (3M; ED) samplers were deployed to detect and quantify the presence of polar organic pollutants such as pesticides including herbicides. Passive flow monitors (PFMs) were co-deployed in duplicate with the passive samplers at each site to estimate the water flow conditions during the deployment period. ED passive samplers were all prepared and extracted according to established SOPs and previously published procedures and methods described in Kaserzon et al. (2018) (Figure 3).

2.5 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.*

2.6 Analytical methods

Chemical analysis was performed at QAEHS using established standard operating procedures (SOPs). ED extracts were analysed by LC-QQQ MS/MS for polar pesticides, in a total of 25 chemicals. 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 2.0mm 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. (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 typically 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}.

2.7 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).

2.8 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 = 10) 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. 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. No herbicide detection was observed in passive sampler or grab sample blanks.

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 18.3 cm s^{-1} at Sarina Inlet (for ED samplers deployed between January and March 2023) to 41.5 cm s^{-1} at Low Isle (for ED samplers deployed between January and February 2023) (Table 1, Figure 4). Average PFM derived flow velocities across all sites was 29.2 ± 5.6 cm s^{-1} (Coefficient of variation (CV) = 19%) 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.

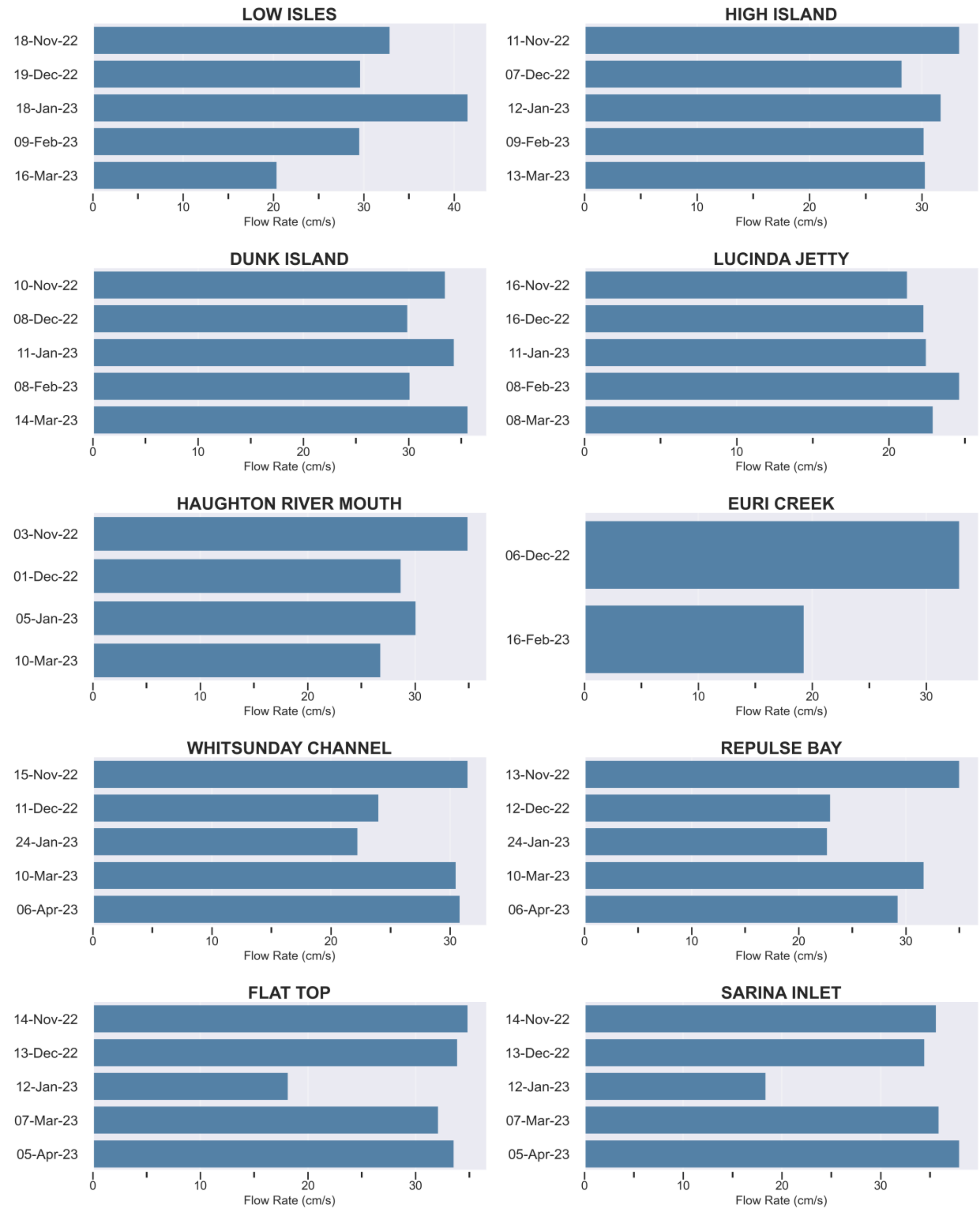

Figure 4. *Passive flow monitor (PFM) based water flow velocity estimations (cm s^{-1}) at the deployment sites.* ***Note:*** *A minimum flow velocity of 3.4 cm s^{-1} is used to assess flow velocity using Passive Flow Monitors (PFMs).*

3.2 Chemical analysis results - ED passive samplers

Of the 25 pesticides monitored during the 2022-23 wet season, 16 were detected in ED passive samplers above the limits of detection (Tables 1 and 3). The most frequently detected pesticides across sites were diuron (with a detection frequency of 98%), the triazine herbicide atrazine (91%) and hexazinone (79%), followed by metolachlor (72%) and tebuthiuron (63%). Reported concentrations ranged from 0.078 ng L^{-1} (haloxyfop) to 64.2 ng L^{-1} (diuron). Total ∑pesticides concentrations at sites ranged from 0.183 ng L^{-1} for High Island (in November 2022) to 153 ng L^{-1} for Flat Top (January 2023) (Figure 5). Six of the 9 sites with available temporal data over the wet season showed the highest total herbicide concentrations in January 2023 (i.e. Flat Top, Haughton River Mouth, Lucinda Jetty, Repulse Bay, Sarina Inlet and the Whitsunday Channel). The highest total herbicide concentrations at Low Isles were observed in March 2023. At Dunk Is and High Is the highest concentrations were observed in December 2022 and February 2023, respectively.

Relatively elevated concentrations of imidacloprid (15.3 ng L^{-1}) and metolachlor (17.1 ng L^{-1}) at Flat Top (January 2023) as well as metsulfuron-methyl at 2.47 ng L^{-1} detected at Whitsunday Channel (November 2022). The single sampling point at Euri Creek showed low concentrations of tebuthiuron > atrazine > and diuron.

Table 3. *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	1	2	0.817	0.817
Ametryn	0	0	0	0
Atrazine	39	91	0.239	18.3
Atrazine desethyl	15	35	0.291	1.26
Atrazine desisopropyl	0	0	0	0
Bromacil	19	44	0.155	0.837
Diuron	42	98	0.156	64.2
Fluazifop	0	0	0	0
Fluometuron	0	0	0	0
Fluroxypyr	2	5	0.338	0.52
Haloxyfop	6	14	0.078	0.327
Hexazinone	34	79	0.194	36.7
Imazapic	0	0	0	0
Imidacloprid	17	40	0.258	15.3
MCPA	0	0	0	0
Metolachlor (S+R)	31	72	0.245	17.1
Metribuzin	4	9	0.28	1.03
Metsulfuron methyl	16	37	0.165	2.47
Prometryn	0	0	0	0
Propazine	1	2	0.204	0.204
Simazine	2	5	0.133	0.253
Tebuconazole	0	0	0	0
Tebuthiuron	27	63	0.141	7.15
Terbuthylazine	11	26	0.231	1.73
Terbutryn	0	0	0	0

Figure 5. *Total estimated water concentrations (ng L^{-1}) of ΣPesticides at each site/deployment period derived from ED passive samplers.*

3.3 Chemical analysis results - Grab samples

Nineteen pesticides were detected at sampling sites above the limits of detection in grab samples from the baseline sites (Tables 2 and 4). The most frequently detected pesticides across sites were tebuthiuron (detection frequency 67%), atrazine (65%), diuron (57%) and hexazinone (43%), in agreement with passive sampling results. Reported concentrations ranged from 0.224 ng L^{-1} for tebuthiuron to 543 ng L^{-1} for atrazine (Table 4). The total ∑herbicide concentrations at sites ranged from 0.633 ng L^{-1} for Euri Creek (December 2022) to 1448 ng L^{-1} for Sarina Inlet (January 2023) (Figure 6).

It was noted that the reported concentrations and the number of compounds detected are highly influenced by the results observed in one grab sample collected from Sarina Inlet in January 2023. While the four most frequently detected pesticides remain unchanged, when excluding the Sarina Inlet grab sample, the concentration range and maximum concentrations observed for some pesticides (i.e., 2,4 D, atrazine, and diuron) are significantly lower (≥ x5 times) (Table 5).

It has been shown that while some herbicide concentrations increased during a flood event at Barratta Creek, other herbicide concentrations decreased (Novic et al. 2017). Therefore, it is possible that herbicide concentrations had not quite reached their peak when the grab samples were taken, or that the peak had just passed. It is also noted that a grab sample collected during a plume event is likely more representative of concentrations entering the system via the plume, but less representative of the concentrations in the marine environment once mixing and dilution has occurred. Correlating the data with the salinity of samples collected and the salinity gradient from upstream to locations where the system is well mixed could help better reflect the information extracted from the grab samples.

Six of the nine sites with available temporal data over the wet season showed highest total pesticide concentrations in January 2023 (i.e., Flat Top, Lucinda Jetty, Repulse Bay, Sarina Inlet, and Whitsunday Channel)[1]. These observations are similar to those from ED passive samplers. Similarly, observations with ED passive sampler results, metsulfuron-methyl was highlighted at Whitsunday Channel (November 0222) with reported grab sample concentration of 202 ng L^{-1}.

***Table 4**. 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	17	35	1	208
Ametryn	4	8	0.386	0.616
Atrazine	32	65	0.872	543
Atrazine desethyl	8	16	1.3	32.2
Atrazine desisopropyl	2	4	1.15	16.4
Bromacil	1	2	2.73	2.73
Diuron	28	57	0.747	312
Fluazifop	0	0	0	0
Fluometuron	0	0	0	0
Fluroxypyr	2	4	7.63	9.08
Haloxyfop	1	2	1.76	1.76
Hexazinone	21	43	1.12	210
Imazapic	0	0	0	0
Imidacloprid	6	12	1.44	25.7
MCPA	2	4	11.1	28.6
Metolachlor (S+R)	10	20	1.07	47.6

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[1] The highest total concentrations of pesticides in January 2023 for those sites is true only when the unusually high detection of metsulfuron-methyl is regarded as an outlier.

Metribuzin	2	4	2.17	8.04
Metsulfuron methyl[1]	4	8	2.19	202
Prometryn	0	0	0	0
Propazine	1	2	5.53	5.53
Simazine	1	2	1.33	1.33
Tebuconazole	0	0	0	0
Tebuthiuron	33	67	0.224	9.94
Terbuthylazine	2	4	2.11	15.6
Terbutryn	0	0	0	0

Table 5. *Summary of chemical analytes detected in grab samples, number of detections across sites and deployment periods, percent (%) detection and minimum and maximum concentrations observed – when Sarina Inlet sample (12 Jan 2023) was removed.*

Analyte	Number of Detects	% Detection	Min reported (ng/L)	Max reported (ng/L)
2,4-D	16	33	1	13.7
Ametryn	4	8	0.386	0.616
Atrazine	31	65	0.872	49.3
Atrazine desethyl	7	15	1.3	2.89
Atrazine desisopropyl	1	2	1.15	1.15
Bromacil	1	2	2.73	2.73
Diuron	27	56	0.747	56.7
Fluazifop	0	0	0	0
Fluometuron	0	0	0	0
Fluroxypyr	1	2	7.63	7.63
Haloxyfop	1	2	1.76	1.76
Hexazinone	20	42	1.12	65.1
Imazapic	0	0	0	0
Imidacloprid	5	10	1.44	17.6
MCPA	1	2	11.1	11.1
Metolachlor (S+R)	9	19	1.07	13.3
Metribuzin	1	2	2.17	2.17
Metsulfuron methyl	4	8	2.19	202
Prometryn	0	0	0	0
Propazine	0	0	0	0
Simazine	0	0	0	0
Tebuconazole	0	0	0	0
Tebuthiuron	32	67	0.232	9.94
Terbuthylazine	2	4	2.11	15.6
Terbutryn	0	0	0	0

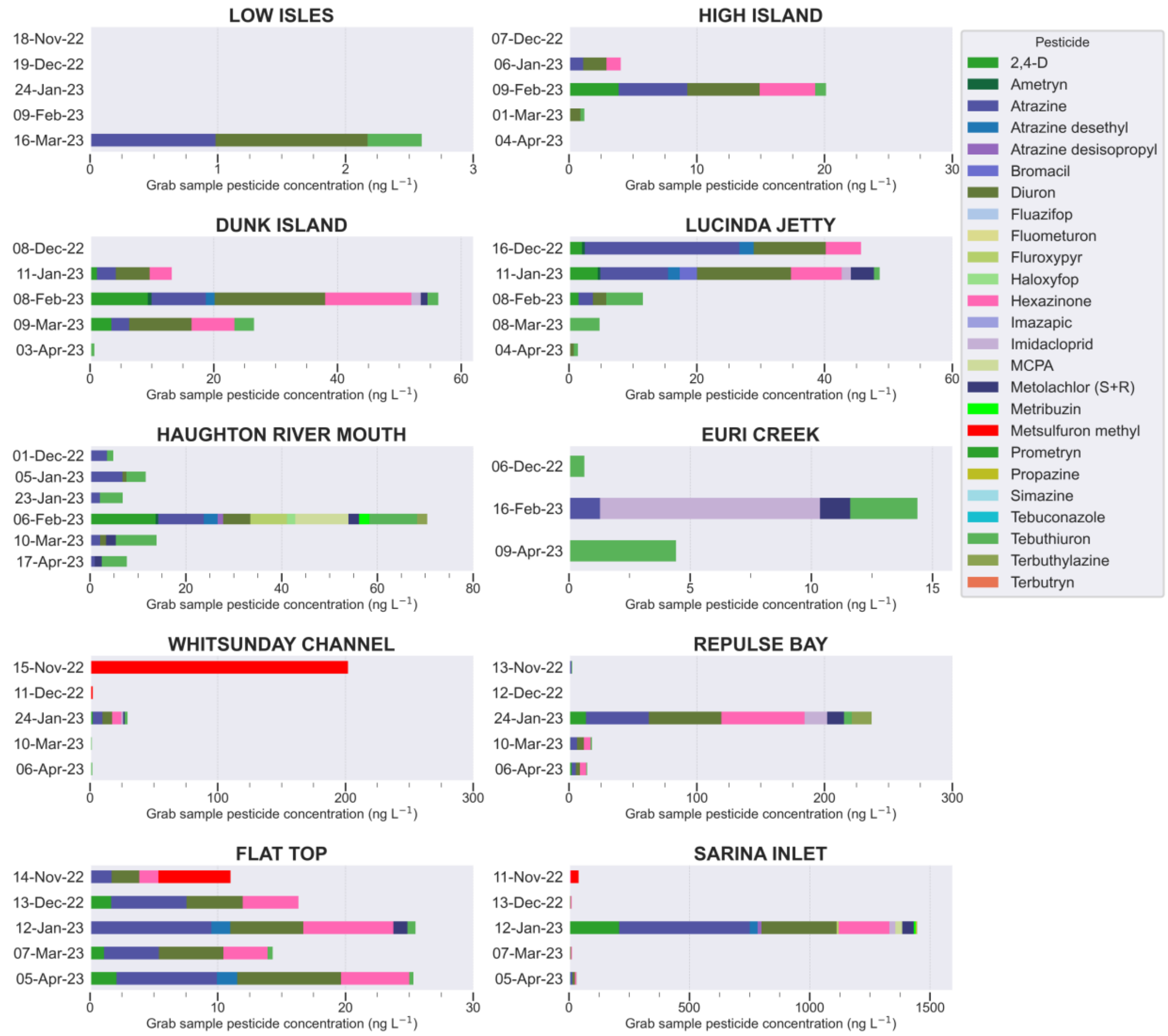

Figure 6. *Water concentrations (ng L^{-1}) of ΣPesticides at each site derived from grab samples.*

It should be noted that single point in time grab samples and passive sampler data represent very different sampling scenarios and consequently different acquisition of information and therefore comparisons of concentrations between the two methods are not of statistical relevance. Grab samples represent a point in time concentration estimate whereas passive samplers represent a time-integrated average water concentration over the deployment period. Therefore, the two methods are representing very different data sets.

It should also be considered that the timeframes of grab and passive sampler collections do not overlap, as grab samples were collected when passive samplers were deployed. This point is highlighted when considering Sarina Inlet as an example (Table 6). A comparison of herbicide concentrations obtained from Sarina Inlet ED passive samplers deployed between early March and early April, and grab samples collected in early March reveal concentrations within the grab to passive sampler concentration ratios of 0.24-0.67 for diuron and tebuthiuron, respectively, with concentrations slightly higher in ED passive samplers. It is also noted that ten pesticides are detected in ED samplers versus only four in grab samples.

When considering ED samplers deployed between early January and early March, concentrations in grab samples are significantly higher than those reported with EDs (i.e., within the grab to passive sampler concentration ratios of 0.2-120 for tebuthiuron and atrazine, respectively). Here, 14 pesticides are detected in grab samples, with 10 detected in ED passive samplers.

Explanations for this could be that in the first case, grab samples were collected during a baseline event (i.e., representing background levels), which may by chance have represented closely time-weighted average concentrations over the 54-day period. In the second case, grab samples may have been collected during a large flood event. Passive samplers would not reflect a 'peak' event during a plume, as they remained in the system for an additional 54 days and would therefore have integrated the average concentrations over that timeframe. While the single collection of a grab sample during a flood event does not guarantee the sample represents the peak of the concentrations during the flood event but is a measurement of the in-situ herbicide levels at a particular point in time. The information gained by these methods are exclusive but complement one another in relation to interpreting the results, and particularly in the case of specific flood events or higher levels of discharge.

What can be examined is the different information provided by each method. When considering overall detection frequencies of pesticides during the sampling campaign, these varied between the passive and grab sampling methods. Except for tebuthiuron, where detection frequencies were similar between grabs and EDs, and 2,4-D where detection frequencies were much higher in grab samples, the remaining pesticides showed significantly higher frequency of detection in ED samplers. For example, diuron was detected in 41 ED passive sampler (95%) vs 27 detects in grab samples (56%), while bromacil was detected in 19 ED passive samplers (44%) vs one detect (2%) in grab samples. This could be attributed to the ability of passive samplers to extract higher volumes of water (~ 2 L during a 30-day deployment period), which can reduce detection limits for certain chemicals.

When examining herbicide concentration ranges, maximum reported time-weighted average concentrations for ED samplers were typically between 0.7 - 16 times lower than those reported from grab samples, with minimum concentrations reported in ED samplers between 1.2 - 22 times of those detected in grab samples.

These results may be related to the averaging out of *in-situ* concentrations by ED passive samplers. Finally, when considering the suite of pesticides detected by each method, ametryn, atrazine desisopropyl, and MCPA were not detected by ED passive samplers, while propazine and simazine were not detected by grab samples. However, in these cases the frequency of detection of these chemicals were low and close to reporting limits.

Table 6. *Summary of chemical concentrations detected in grab samples vs passive samplers at Sarina Inlet for samples collected or deployed, respectively, during early January. Ratios represent the concentration in grab samples / concentration in passive sampler.*

Sample type	**Grab sample concentrations (ng L^{-1})**	**ED sampler concentrations (ng L^{-1})**	**Ratio Grab / ED concentrations**	**Grab sample concentrations (ng L^{-1}, (Ave ± SD of duplicate samples)**		**ED sampler concentrations (ng L^{-1})**	**Ratio Grab / ED concentrations**
Sample Date	**12/01/2023**	**12/01/2023 - 07/03/2023**		**7/03/2023**		**7/03/2023 - 05/04/2023**	
Analyte							
2,4-D	208	<0.628		<0.833		<0.915	
Atrazine	543	4.53	*120*	3.42	0.03	12.8	*0.27*
Atrazine desethyl	32.2	<0.179		<0.992		1.1	
Atrazine desisopropyl	16.4	<0.149		<1.07		<0.217	
Bromacil	<1.27	0.214		<1.23		0.2	
Diuron	312	21.9	*14.2*	4.8	0.05	19.9	*0.24*
Fluroxypyr	9.08	<0.149		<1.98		<0.217	

Hexazinone	210	12.2	*17.2*	3.47	0.025	9.2	*0.38*
Imidacloprid	25.7	4.61	*5.6*	<1.11		0.6	
MCPA	28.6	<0.455		<1.09		<0.662	
Metolachlor (S+R)	47.6	6.52	*7.3*	<0.913		1.8	
Metribuzin	8.04	0.302	*26.6*	<1.21		<0.217	
Metsulfuron methyl	<1.71	0.373		<1.67		0.4	
Propazine	5.53	<0.149		<1.11		<0.217	
Simazine	1.33	<0.101		<1.07		<0.148	
Tebuthiuron	0.224	1.16	*0.2*	0.32	0.051	0.5	*0.67*
Terbuthylazine	<1.04	0.489		<1.01		0.59	
Total ∑pesticides	1448	52.3		12.0		47.1	

< - Values indicate below Limit of Reporting (LOR)

Only analytes with reportable values in grab and/or ED samples were included in this table

3.4 Flood monitoring grab sample results

Grab samples were collected during two main flood events sampled by the Great Barrier Reef Marine Monitoring Program (MMP): at Cape York region in December 2022/January 2023; and Mackay-Whitsunday region in January 2023. A total of 13 pesticides were detected across all sampling sites above the limits of detection (Figures 7 and 8; Table 7). The most commonly detected pesticides were diuron, atrazine, and tebuthiuron, which showed detections of 86%, followed by hexazinone, 2,4-D and imidacloprid (all with detections of 81%). Reported concentrations ranged from 0.257 ng L^{-1} – 118 ng L^{-1} for tebuthiuron and hexazinone, respectively (Table 7).

In the Mackay-Whitsunday region, the total ∑herbicide concentrations at sites ranged from 2.78 ng L^{-1} for site JCF213 to 494 ng L^{-1} for site JCF223, despite these samples being collected two days apart on January 21st and 22nd 2023, respectively. The highest observed total herbicide concentrations were observed at near shore sites JCF203 and JCF223.

No pesticides were observed in Cape York flood events, except for one single detection of 2,4-D at 3.28 ng L^{-1} from the Endeavour River collect on the 11th January 2023. Flood river samples from the McIvor Gauge showed no presence of pesticides.

Overall total herbicide concentrations in the flood monitoring sites were higher than those observed from grab samples at the baseline monitoring sites (during Jan-Feb 2023), however the flood event grab samples did not detect ametryn, haloxyfop, metribuzin and metsulfuron-methyl at any location, while grab samples from the baseline sites report low detection frequencies of these pesticides at some sites.

Figure 7. *Map representing GPS locations of grab samples collected during the flood sampling investigations.*

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	17	81	1.47	38.6
Ametryn	0	0	0	0
Atrazine	18	86	1.08	58.6
Atrazine desethyl	16	76	1.12	8.63
Atrazine desisopropyl	8	38	1.15	4.4
Bromacil	2	10	2.38	3.01
Diuron	18	86	1.45	113
Fluazifop	0	0	0	0
Fluometuron	0	0	0	0
Fluroxypyr	2	10	2.59	2.75
Haloxyfop	0	0	0	0
Hexazinone	17	81	4.89	118
Imazapic	0	0	0	0
Imidacloprid	17	81	1.63	79.5
MCPA	12	57	1.11	7.29
Metolachlor (S+R)	16	76	2.37	22.5
Metribuzin	0	0	0	0
Metsulfuron methyl	0	0	0	0
Prometryn	0	0	0	0
Propazine	0	0	0	0
Simazine	0	0	0	0

Tebuconazole	0	0	0	0
Tebuthiuron	18	86	0.257	16.7
Terbuthylazine	14	67	1.09	21.8
Terbutryn	0	0	0	0

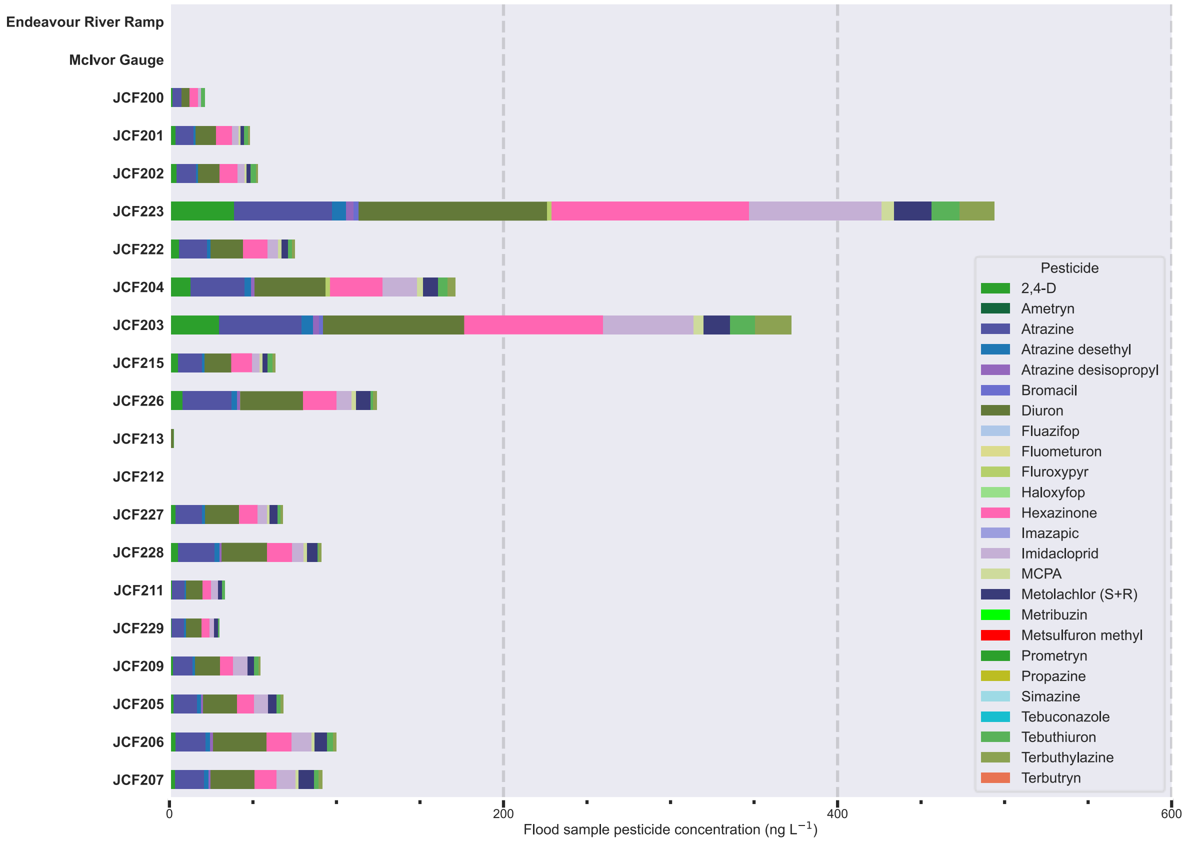

*Figure **8**. Water concentrations (ng L-1) of ΣPesticides at each site derived from grab samples.*

3.5 Rainfall data

Monthly rainfall data from the Bureau of Meteorology (BoM) was extracted for the sampling period (November 2022 – April 2023) (Figure 9) as an indicative estimation of rainfall during the monitoring period. The highest rainfall was observed in January followed by February 2023. The rainfall data corresponds with highest total herbicide concentrations observed for most fixed sites (Figures 5 and 6). Elevated rainfall is associated with increased transport of nutrients and pesticides into the reef catchment areas (Brodie et al. 2012).

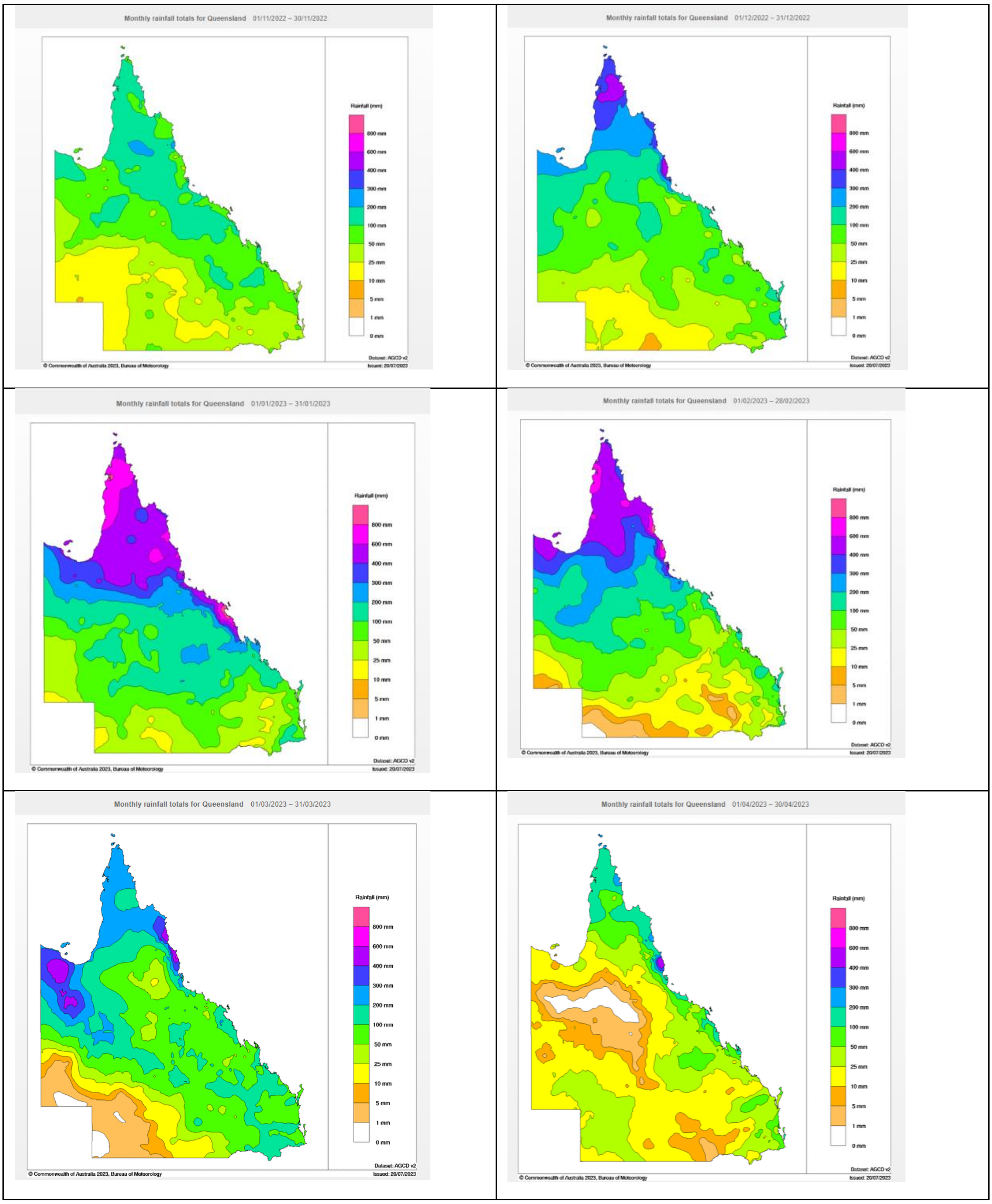

Figure 9. *Monthly rainfall totals for November (2022), top left to April 2023, bottom right (BOM, Climate Data Online - Map search – bom.gov.au).*

3.6 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). No guidelines are currently available for marine environments, so comparisons were made with freshwater guidelines or toxicant values, if available. Metolachlor exceeded the 99% freshwater species protection guideline value with all sampling methods, but not the 95% freshwater species protection guideline value (Table 8). Similarly, metsulfuron-methyl was detected above the 99% species protection guideline value, but not above the 95% species protection guideline value, in grab samples collected from baseline sites. But no exceedances for this compound were observed in passive sampling data or flood monitoring grab samples. Diuron has no current guidelines except for a default toxicant guideline. Only the Sarina Inlet grab sample reported diuron at a concentration 1.56 times above the default toxicant guideline.

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 (excluding Sarina Inlet, Jan 2023)	Grab samples (with Sarina Inlet, Jan 2023)	ED passive samplers	Flood monitoring grab samples	ANZECC 2000 Fresh & Marine guidelines		
Analyte	**Max reported (ng/L)**	**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	13.7	208	0.817	38.6	140000	280000	
Ametryn	0.616	0.616	0	0			
Atrazine	49.3	543	18.3	58.6	700	13000	
Atrazine desethyl	2.89	32.2	1.26	8.63			
Atrazine desisopropyl	1.15	16.4	0	4.4			
Bromacil	2.73	2.73	0.837	3.01			
Diuron	56.7	**312**	64.2	113			200
Fluazifop	0	0	0	0			
Fluometuron	0	0	0	0			
Fluroxypyr	7.63	9.08	0.52	2.75			
Haloxyfop	1.76	1.76	0.327	0			
Hexazinone	65.1	210	36.7	118			
Imazapic	0	0	0	0			
Imidacloprid	17.6	25.7	15.3	79.5			
MCPA	11.1	28.6	0	7.29			1400
Metolachlor (S+R)	**13.3**	**47.6**	**17.1**	**22.5**	8.4	460	
Metribuzin	2.17	8.04	1.03	0			
Metsulfuron methyl	**202**	**202**	2.47	0	20	2200	
Prometryn	0	0	0	0			
Propazine	0	5.53	0.204	0			
Simazine	0	1.33	0.253	0	200	3200	
Tebuconazole	0	0	0	0			
Tebuthiuron	9.94	9.94	7.15	16.7	20	2200	
Terbuthylazine	15.6	15.6	1.73	21.8			
Terbutryn	0	0	0	0			

4 Conclusions and future recommendations

Up to nineteen pesticides were detected in the marine monitoring sites during the 2022-23 wet season between November 2022 and May 2023. Concentrations ranged from 0.078 ng L^{-1} (haloxyfop) to 543 ng L^{-1} (atrazine). The most frequently detected pesticides in both passive samplers and grab samples were atrazine, diuron, hexazinone and tebuthiuron. The total ∑herbicide concentrations observed at sites ranged from 0.183 ng L^{-1} for High Island (November 2022) to 1448 ng L^{-1} for Sarina Inlet (January 2023). The overall number of herbicide detections across samples were typically higher in passive samplers compared with grab samples. Grab samples enabled reporting of a flood concentration during a flush event in January 2023, 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. Six of the nine sites with available temporal data over the wet season (from both grab and passive samplers) showed total herbicide concentrations in January 2023 were the highest (i.e., Flat Top, Lucinda Jetty, Repulse Bay, Sarina Inlet, and Whitsunday Channel), corresponding to rainfall data in the area.

The information provided by grab and passive samplers reflect the advantages and limitations of both methods. Passive samplers were able to better reflect herbicide presence, observed via the higher detection frequencies reported compared with grab sampling data. However, the concentrations provided are averaged over time. Grab samples missed some instances of pesticides presence (especially at the lower end of the analytical reporting limits), but grab samples allowed for assessment of plume concentrations during a large flood event. These could be beneficial especially when considering herbicide species protection and risk values to better understand exposure during a flood event. It should be noted that when the actual peak concentration occurs would be difficult to ascertain from a single point in time grab sample. The peak concentration of an herbicide could also be highly dependent on the river system and herbicide of question. Regardless of the method used, both sampling methods identified similar patterns in terms of total herbicide 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 herbicide when considering longer term changes (i.e., on scales of >10 – 20 years; Taucare et al. 2022).

The flood sampling sites in the new monitoring region of Cape York provided a snapshot during the wet season. It was evident that higher concentrations were observed closest to shore, however as mentioned above, whether the peak concentrations for these sites were captured remains unknown. Total herbicide concentrations observed from flood samples, where detected, were generally higher than those observed from the baseline sites investigated.

4.1 Future recommendations

- The information gained from the sampling period revealed herbicide patterns can vary on a spatial and temporal scale. The correlation with rainfall in particular has been observed. In order to better model herbicide 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 in order 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 herbicide concentrations. It may further inform longer term persistence of pesticides at the sites investigated.
- Sampling locations further upstream, especially during wet season, and/or correlating with existing data from upstream sampling, for example from DES monitoring programs, may help elucidate the more dominant concentration inputs to the system.

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