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Catchment and Drinking Water Quality Micro Pollutant Monitoring Program – Passive Sampling

Report 10 – Summer 2019

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Executive Summary

The *Catchment and Drinking Water Quality Micro Pollutant Monitoring Program* was launched in mid-2014 with the aim of improving the characterisation and understanding of the micro-pollutant risk profile in source water reservoirs through annual summer and winter sampling campaigns. The monitoring program utilising passive samplers was continued in reservoirs in South East Queensland (SEQ) during January 2019 and represents the tenth of twelve sampling campaigns (targeting winter/summer from 2014 – 2020). Results presented provide a continued insight into the water quality of the target catchments and drinking water reservoirs.

A wide range of polar and non-polar organic contaminants of interest were monitored using passive samplers, including herbicides, insecticides, pharmaceuticals and personal care products (PPCPs), organochlorine pesticides (OCPs), and polycyclic aromatic hydrocarbons (PAHs). The extracts were analysed at Queensland Alliance for Environmental Health Sciences (QAEHS) by LC-QQQ MS/MS (polar compounds), LC-QToF MS/MS (polar compounds; suspect screening) and GC-HRMS (non-polar chemicals) using the latest analytical methods and established standard operating protocols (SOPs).

Chemical analyses of the passive sampler extracts detected 70 different chemicals including 14 OCPs (and pesticides), 11 PAHs, 30 herbicides and insecticides and 11 PPCPs. OCPs were detected at 88% of sampled sites (n=34), with endosulfan sulfate, pp-DDD, pp-DDE and dacthal being the most prevalent between sites, and chlorpyrifos showing the highest total concentration. Total ∑OCP water concentrations across sites ranged between 0.0004 – 4 ng L^{-1}. PAHs were detected at 91% of sites, with chrysene, fluoranthene, pyrene and benzo(a)anthracene at the highest concentrations across all sites. Chrysene was the most abundant, followed by benzo(a)anthracene and benzo(e)pyrene. Total ∑PAH water concentrations across sites ranged between 0.04 – 2.4 ng L^{-1}. Thirty herbicides/insecticides were detected at all sites (n=36). Desisopropyl atrazine, desethyl atrazine, metolachlor, simazine and atrazine were present in high abundance. Total estimated ∑herbicide water concentrations across all sites ranged between 0.5 – 154 ng L^{-1} with atrazine present at the highest concentration across all site. Twelve PPCPs were detected across sites with highest detection frequencies observed for carbamazepine (42%) and DEET (22%). Total estimated ∑PPCP water concentrations ranged between 0.08 - 68 ng L^{-1} across sites. Australian and New Zealand Guidelines for Drinking Water (ADWG) as well as Fresh and Marine Water Quality values are available for some of these chemicals (ANZECC & ANCANZ 2018) for comparison. No chemicals were present in concentrations that exceeded the ADWG values. Australia has set chlorpyrifos environmental water guideline values of 0.04 and 10 ng L^{-1} for 99% and 95% species protection, respectively. Fifteen sites exceeded the 99% species protection guideline level (ranging between 0.5 – 4.3 ng L^{-1}). No exceedance of the 95% species protection guideline values were observed.

Introduction

As the bulk supplier of drinking water to South East Queensland, Seqwater maintains a Catchment and Drinking Water Quality Micro Pollutant Monitoring Program to ensure safe and reliable supply of the region's drinking water source reservoirs. The aim of this program is to identify and understand the presence of micro-pollutants in the source water reservoirs as well as to recognise any spatial and temporal trends of micro-pollutants. An extension of this program has been introduced to include the use of passive sampling technologies in the monitoring of source water reservoirs over a six year period (2014 – 2020; summer and winter sampling campaigns), in order to accurately assess the risk from micro pollutants posed to drinking water quality. Additional passive samplers may be deployed at sites when required during high rainfall or event periods.

The typically low-level concentrations of micro-pollutants present in environmental waters makes sampling methods such as grab sampling challenging, as one litre grab samples often may not offer sufficient volume for detection of micro-pollutants and episodic contamination events may be missed when collecting single samples that provide a single point in time estimate of water quality. The use of passive sampling technologies have been introduced to complement and overcome some of these challenges, substantially improving chemical pollutant monitoring in liquid phases over the last 15 - 20 years. Some of the benefits of passive sampling tools can include: *in-situ* concentration of chemical pollutants, increased sensitivity and the provision of time-weighted average concentration estimates for chemicals over periods of ≥ 1 month, increased data resolution and risk profiling using a robust scientific methodology. Passive samplers designed to monitor non-polar (polydimethylsiloxane; PDMS) as well as polar (Empore™ Disk; ED) chemical pollutants have been chosen for deployment.

The list of target chemicals for inclusion in the monitoring campaign was identified via a review of the Australian Drinking Water Guideline (ADWG) and Australian and New Zealand Environmental Conservation Council (ANZECC) lists of chemicals and parameters. The list was refined based on an assessment of their possible application in the catchment areas investigated and assessment from Australian Pesticides and Veterinary Medicines Authority (AVMPA) registered products uses, as well as water solubility and guideline values. The target list is reviewed every six months to investigate the need for inclusion / exclusion of target analytes based on on-going risk assessment and detection frequency. This report presents monitoring data from the tenth monitoring campaign.

Methodology

Passive water samplers were deployed in 36 sites of SEQ reservoirs/waterways from December 2018 to February 2019 over a period of 28 - 29 days (Table 1). The deployment of samplers was conducted in alignment with the "Drinking and Catchment Water Quality Micro-pollutant Passive Sampling Procedure" (27 May 2014). Table 1 below lists the deployment site locations, site numbers, site codes, dates and lengths of deployment periods, as well as the water velocity (cm/s) estimated at each site. In this campaign, sites SEQ15 (Lockyer Creek @ Lake Clarendon Way) and SEQ16 (Lockyer Creek @ O'Reilly's Weir) were not sampled due to water level and logistical restrictions. Sites SEQ21 (Lake Kurwongbah) and SEQ22 (North Pine River @ Petrie Offtake) were not sampled as they are not currently connected to a water supply scheme with the decommissioning of the Petrie WTP. Due to a bushfire event, samplers for SEQ23 (Herring Lagoon) were deployed in duplicate approximately one month earlier than all other sites (Table 1). In addition to Herring Lagoon, replicate samplers were deployed at six randomly selected sites (Table 1, highlighted in blue).

Table 1. *Deployment locations, dates, lengths of deployment period and water velocity measured at each site. (*denotes replicate site)*

Site#	Site code	Site Name	Date Deployed	Date Retrieved	Days Deployed	Flow velocity (cm/s)	Comments
SEQ01	MRS-SP012	SEQ-MARY RIVER @ COLES CROSSING	9/01/2019	6/02/2019	28	3.45	
SEQ02	LMD-SP001	SEQ-LAKE MACDONALD INTAKE	22/01/2019	19/02/2019	28	8.52	
SEQ03	BOD-SP001	SEQ-BORUMBA DAM	22/01/2019	19/02/2019	28	7.53	
SEQ04	MRS-SP013	SEQ-MARY RIVER @ KENILWORTH	9/01/2019	6/02/2019	28	7.94	
SEQ05	POD-SP001	SEQ-POONA DAM	15/01/2019	12/02/2019	28	5.20	
SEQ06	SOR-SP001	SEQ-SOUTH MAROOCHY INTAKE WEIR	15/01/2019	12/02/2019	28	3.97	
SEQ07	YAC-SP001	SEQ-YABBA CREEK @ JIMNA WEIR	18/01/2019	15/02/2019	28	3.88	
SEQ08	BPD-SP001	SEQ-BAROON POCKET DAM	10/01/2019	7/02/2019	28	4.60	
SEQ09	EMD-SP001	SEQ-EWEN MADDOCK INTAKE	17/01/2019	14/02/2019	28	5.44	
SEQ10	SOD-SP010	SEQ-KILCOY WTP OFFTAKE	30/01/2019	27/02/2019	28	11.13	
SEQ11	SOD-SP011	SEQ-KIRKLEAGH	30/01/2019	27/02/2019	28	17.33	Both PFMs returned empty
SEQ12*	SOD-SP001*	SEQ-SOMERSET DAM WALL	24/01/2019	21/02/2019	28	7.54	ED and PDMS replicate site.
SEQ13*	WID-SP004*	SEQ-WIVENHOE DAM @ ESK PROFILER	31/01/2019	1/03/2019	29	6.95	ED and PDMS replicate site.
SEQ14	WID-SP001	SEQ-WIVENHOE DAM WALL @ PROFILER	31/01/2019	28/02/2019	28	13.39	
SEQ15	LOC-SP034	SEQ-LOCKYER CREEK @ LAKE CLARENDON WAY	n/a	n/a	n/a	n/a	Site not active.
SEQ16	LOC-SP031	SEQ-LOCKYER CREEK @ O'REILLYS WEIR	n/a	n/a	n/a	n/a	Site not active.
SEQ17	MBR-SP016	SEQ-LOWOOD INTAKE	23/01/2019	20/02/2019	28	5.01	
SEQ18	MBR-SP001	SEQ-MID BRIS RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER	23/01/2019	20/02/2019	28	12.28	
SEQ19	NOD-SP091	SEQ-NORTH PINE RIVER @ DAYBORO WELL	29/01/2019	26/02/2019	28	3.95	
SEQ20	NOD-SP001	SEQ-NORTH PINE VPS	11/01/2019	8/02/2019	28	5.82	
SEQ21	LAK-SP001	SEQ-LAKE KURWONGBAH	n/a	n/a	n/a	n/a	Site not active.
SEQ22	NOD-SP023	SEQ-NORTH PINE RIVER @ PETRIE OFFTAKE	n/a	n/a	n/a	n/a	Site not active.
SEQ23*	NSC-SP001*	SEQ-HERRING LAGOON	11/12/2018	8/01/2019	28	4.24	ED and PDMS replicate site.

SEQ24	LHD-SP005	SEQ-LESLIE HARRISON DAM	10/01/2019	7/02/2019	28	7.58	
SEQ25*	WYD-SP001*	SEQ-WYARALONG DAM WALL	9/01/2019	6/02/2019	28	5.67	ED and PDMS replicate site.
SEQ26	MOD-SP027	REYNOLDS CREEK @ BOONAH	23/01/2019	20/02/2019	28	9.09	
SEQ27	MOD-SP002	SEQ-MOOGERAH DAM @ OFFTAKE	23/01/2019	20/02/2019	28	11.11	
SEQ28	LRS-SP017	SEQ-LOGAN RIVER @ KOORALBYN OFFTAKE	23/01/2019	20/02/2019	28	24.18	
SEQ29	MAD-SP004	SEQ-MAROON DAM WALL @ OFFTAKE W2 BUOY	7/01/2019	4/02/2019	28	9.29	
SEQ30*	LRS-SP013*	SEQ-LOGAN RIVER @ HELEN ST	23/01/2019	20/02/2019	28	15.54	ED and PDMS replicate site.
SEQ31	LRS-SP016	SEQ-RATHDOWNEY WEIR	23/01/2019	20/02/2019	28	5.00	
SEQ32	CAC-SP001	SEQ-CANUNGRA CREEK @ OFFTAKE	14/01/2019	11/02/2019	28	5.10	
SEQ33*	LND-SP014*	SEQ-LITTLE NERANG DAM	14/01/2019	11/02/2019	28	3.51	ED and PDMS replicate site.
SEQ34	HID-SP001	SEQ-HINZE DAM UPPER INTAKE	14/01/2019	11/02/2019	28	5.37	
SEQ35	HID-SP002	SEQ-HINZE DAM LOWER INTAKE	14/01/2019	11/02/2019	28	7.18	
SEQ36	MBR-SP013	SEQ-DOWNSTREAM OF FERNVALE STP @ SAVAGES CRC	23/01/2019	20/02/2019	28	15.55	PDMS lost. Only ED.
SEQ37	LRS-SP012	LOGAN RIVER @CEDAR GROVE	23/01/2019	20/02/2019	28	3.41	PDMS lost. Only ED.
SEQ38*	WAD-SP001*	WAPPA DAM	16/01/2019	13/02/2019	28	4.17	ED and PDMS replicate site.
SEQ39	COD-SP001	COOLOOLABIN DAM	15/01/2019	12/02/2019	28	5.98	1 PFM lost. Estimated based on 1 PFM.
SEQ40	WID-SP061	WIVENHOE DAM @ LOGANS INLET PRW	31/01/2019	28/02/2019	28	17.21	Both PFMs returned empty

Passive sampler preparation and extraction

For this campaign, two types of passive samplers were deployed at each site. Empore Disk™ (EDs) samplers were deployed to detect the presence of polar organic pollutants such as herbicides, pharmaceuticals and personal care products (PPCPs). Polydimethylsiloxane (PDMS) strips in stainless steel cages were deployed to detect the presence of more hydrophobic organic pollutants (non-polar chemicals) such as certain organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs). 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 and PDMS passive samplers were all prepared and extracted according to previously published procedures and methods described in Kaserzon *et al.* (2017).

Figure 1. Preparation of a PDMS passive sampler in a stainless steel cage.

Analytical methods

Chemical analysis was performed at QAEHS using established SOPs. ED extracts were analysed by LC-QQQ MS/MS for polar herbicides and PPCPs (77 chemicals) as well as on LC-QToF MS/MS with detect/non-detect screening conducted for an additional 45 chemicals. PDMS extracts were analysed for non-polar chemicals comprising of 29 OCPs and 16 PAHs via GC-HRMS (Appendix 1). The analytical methods for herbicides and PPCPs (LC-QQQ MS/MS), OCPs and PAHs (GC-HRMS) and suspect screening of herbicides and PPCPs (LC-QToF MS/MS) have all been detailed in previously published reports (Kaserzon *et al.* 2017) and SOPs.

Data modelling and reporting of results

Passive sampling enables estimation of time-integrated water concentrations (C_w) based on the amounts of chemicals accumulated in the sampler within a given exposure period (Vrana *et al.* 2005; Kot *et al.* 2000). 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 (typically sampling rates or sampler-water coefficients) obtained in laboratory or field studies were used to derive these concentration estimates. Together with the sampling rates calibration data, deployment-specific PFM data are used to correct for site-specific effects of water flow on the sampling rates of chemicals (O'Brien *et al.* 2009). For chemicals detected where no calibration data was available, results were reported as ng sampler^{-1}. Methodologies used to calculate site-specific sampling rates during the deployment periods are fully described in Kaserzon *et al.* (2017).

Quality control and assurance (QC/QA) procedures

QAEHS laboratory procedures are performed by fully trained staff in accordance to established Standard Operating Procedures (SOPs) (Table 2). QAEHS use internal SOPs for the preparation, extraction and analysis of samplers.

In order to ensure quality control and to identify any instances of laboratory contamination, blank passive samplers were prepared, extracted and analysed in parallel with exposed samplers for each deployment period (n = 3 for each sampler type; ED, and PDMS). Laboratory blanks were prepared before each deployment but were not exposed to air or water for the duration of the deployment. These samplers were included in each batch of samples that were extracted and analysed. In cases where chemicals were detected in blanks as well as exposed samples, the concentration in the exposed sample had to exceed three times the standard deviation of the blanks plus the average sum of the blanks in order for the values to be included in the reported data. Results were not subtracted for detections in blank samples. Any blank levels are reported in Appendix 1.

Replicate ED and PDMS passive sampler sites were randomly chosen and deployed in SEQ12 (Somerset Dam Wall), SEQ13 (Wivenhoe Dam @ Esk Profiler), SEQ25 (Wyaralong Dam Wall), SEQ30 (Reynolds Creek @ Boonah), SEQ33 (Little Nerang Dam) and SEQ38 (Wappa Dam) (Table 1). Apart from the six replicates, SEQ23 (Herring Lagoon) was deployed in duplicate one month earlier than the rest of the sites, due to an unforeseen bushfire. Acceptable replicate values within coefficient of variation (CV) < 40 % were observed for passive sampler replicates deployed (i.e. OCPs, PAHs, herbicides/ insecticide and PPCPs).

Recovery of chemicals was verified by spiking blank and exposed samplers with various surrogates prior to extraction and internal standards prior to analysis. Non-extracted side spikes (NESS; solvent blanks spiked with surrogates and recovery standards) were prepared in parallel to spiking and extracting exposed samples. These represent 100% recoveries and are essential in recovery correction calculations.

Table 2. List of established standard operating procedures (SOPs) used in relation to this campaign.

Code	Description
NTX-A-003	GC-HRMS Method for Pesticide and PAH Analysis
NTX-A-004	Target and Non-target Polar Herbicides and PPCP Analysis by LC-ESI-QTOF-MS/MS
NTX-A-005	LC-MS/MS/QQQ method for herbicide and PPCP analysis
NTX-P-001	Extraction of PDMS from water
NTX-P-004	Preparation of Empore Disks (EDs)
NTX-P-005	Extraction of EDs
NTX-P-008	Pre-cleaning and preparation of PDMS samplers
NTX-P-009	Preparation of Flow Monitoring Devices (PFMs) for use with Water Passive Samplers
NTX-S-001	Deployment and Retrieval of Passive Samplers-Empore Disks, Sampling Cages, Passive Flow Monitors

Results and Discussion

PFM results

Two PFMs were deployed at each sampling site with good agreement observed between duplicate PFMs for most sites (>80%) except for SEQ1 (Mary River @ Coles Crossing), SEQ7 (Yabba Creek @ Jimna Weir), SEQ27 (Moogerah Dam @ Offtake), SEQ28 (Logan River @ Kooralbyn Offtake),and SEQ38 (Wappa Dam) with >70% agreement; SEQ4 (Mary River @ Kenilworth), and SEQ37 (Logan River @ Cedar Grove with >40% agreement (Figure 2). Average flow velocities estimated from PFMs over the deployment period ranged between 3.4 cm s^{-1} (SEQ37 Logan River @ Cedar Grove) to 24 cm s^{-1} (SEQ28 Logan River @ Kooralbyn Offtake). All sites were above the linearity loss rate range of the PFM (i.e. < 3.4 cm s^{-1}; O'Brien *et al.* 2009) (Table 1 and Figure 3).

Under stagnant to very low flow conditions there is little difference in the mass lost from the PFM and therefore the PFM cannot provide an accurate prediction for the effect of flow on sampling rate (R_s) (i.e. below a threshold flow of 3.4 cm s^{-1} or PFM loss rate equal to 0.58 g d^{-1}; O'Brien *et al.* 2009; 2011b). When correlating PFM mass loss rate with chemical sampling rates in passive samplers, both the PFM and R_s require minimum flow or turbulence before any effects of flow begin to influence loss rate and chemical accumulation, respectively (i.e. via linear loss rate in PFMs and linear chemical accumulation in passive sampling) (Kaserzon *et al.* 2014; O'Brien *et al.* 2011b). Therefore, in order to remain within the accurate mathematical modelling range for PFM-based flow velocity prediction, we applied a minimum flow rate of 3.4 cm s^{-1} for the sites showing flow below this threshold and the minimum atrazine equivalence R_s. This may result in a slight over-estimation of R_s and under-estimation of water concentration estimates (C_w), though we do not expect this to be significant.

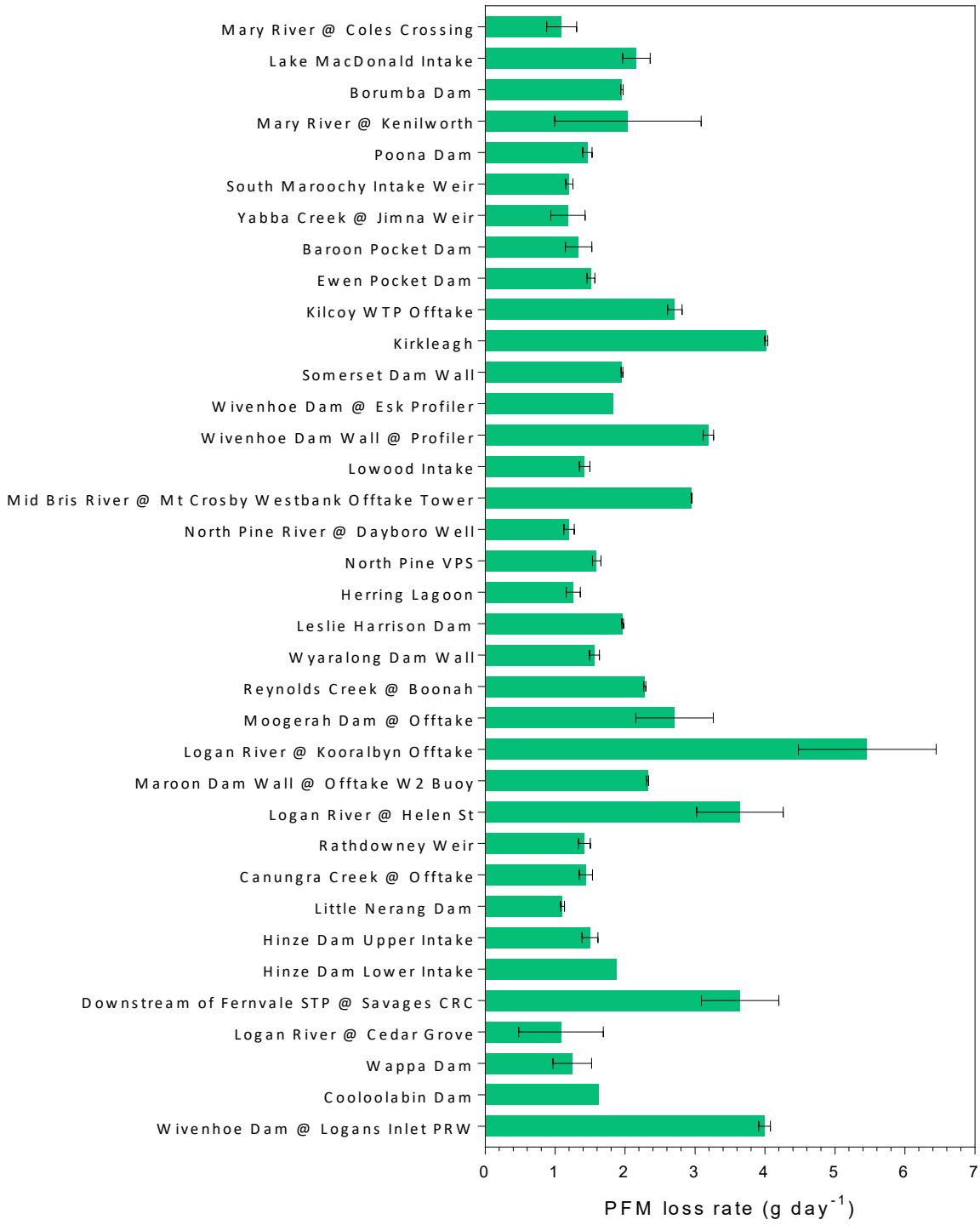

Figure 2. Passive flow monitors (PFMs) loss rate (g per day) of duplicate PFMs per site. Error bars are standard deviation derived from two co-deployed PFMs. It should be noted that Cooloolabin Dam lost one PFM during sampling.

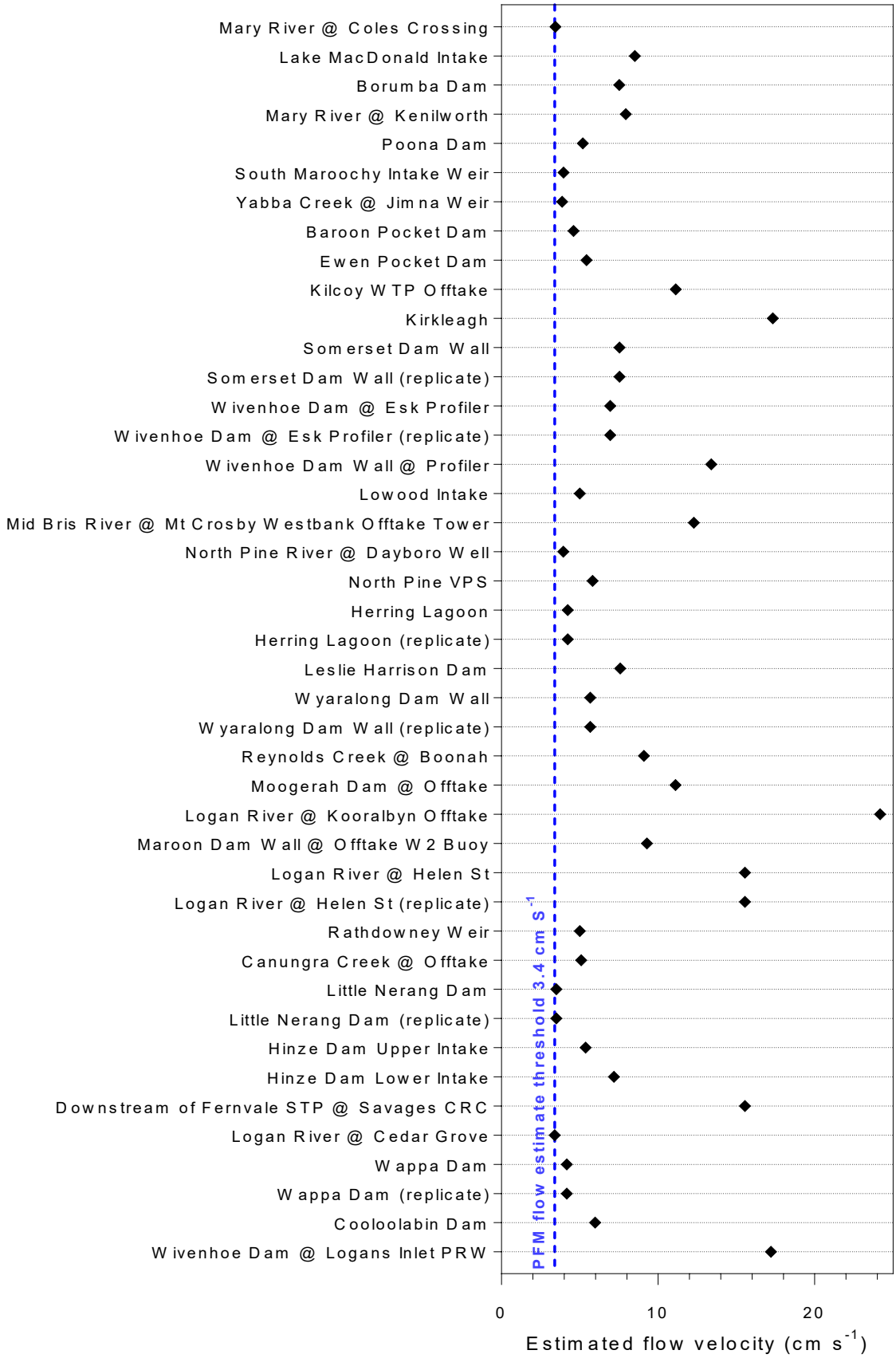

Figure 3. Passive flow monitor (PFM) based average water flow rate estimations at the deployment sites (n=36). A minimum flow velocity of 3.4 cm s^{-1} is used to assess flow velocity using Passive Flow Monitors (PFMs).

Chemical analysis results

A summary of the number of chemicals detected at the sampling sites, the percent detection of each chemical and mass accumulation (ng sampler^{-1}) is presented in Table 3 to Table 6 below. Table 3 summarises the non-polar chemicals detected with PDMS (OCPs and PAHs). A total of 14 OCPs and 11 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% – 88% (for OCPs) and 3% – 91% (for PAHs). Table 4 summarises the polar chemicals detected with EDs (herbicides/ insecticides and PPCPs). A total of 30 herbicides/ insecticides and 12 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3% - 97% (for herbicides and insecticides) and 3% - 42% (for PPCPs). It should be noted that due to instrumental matrix interferences, naphthalene, acenaphthylene, acenaphthene and fluorene at site SEQ14 (Lockyer Creek @ Lake Clarendon Way) were not reported.

Table 3. Summary of the number of chemicals accumulated in PDMS passive samplers, percentage of detection at the sites and the range of mass accumulated over 28-29 days (ng PDMS^{-1}).

	Number of sites detected (n = 34)	% detection	Min detect (ng PDMS^{-1})	Max detect (ng PDMS^{-1})
Organochlorine pesticides (OCPs)				
b-endosulfan	1	3%	0.6	0.6
chlorpyrifos	14	41%	38	294
dacthal	23	68%	1.1	30
dieldrin	6	18%	15	34
endosulfan sulfate	30	88%	0.1	1.6
endrin	9	26%	0.2	0.3
heptachlor epoxide A	2	6%	0.4	0.6
heptachlor epoxide B	11	32%	0.5	2.0
op-DDD	6	18%	0.2	0.9
op-DDE	3	9%	0.1	0.4
op-DDT	4	12%	0.03	0.2
pp-DDD	28	82%	0.1	17
pp-DDE	24	71%	0.2	11
pp-DDT	7	21%	0.3	1.7
Polycyclic aromatic hydrocarbons (PAHs)				
Acenaphthene	1	3%	18	18
Anthracene	2	6%	14	18
Fluoranthene	11	32%	25	274
Pyrene	9	26%	23	129
Benzo (a) anthracene	25	74%	1.0	15
Chrysene	31	91%	1.6	21
Benzo (bjk) fluoranthene	6	18%	2.1	6.3
Benzo (e) pyrene	23	68%	0.7	6.2
Benzo (a) pyrene	13	38%	0.5	2.6
Indeno (1,2,3-cd) pyrene	13	38%	0.5	3.6
Benzo (g,h,i) perylene	15	44%	0.7	5.2

Table 4. Summary of the number of chemicals accumulated in ED passive samplers, percentage of detection at the sites and the range of mass accumulated over 28-29 days (ng ED^{-1}).

	Numbers of site detected (n = 36)	% detection	Min detect (ng ED^{-1})	Max detect (ng ED^{-1})
Herbicides and Insecticides				
2,4-D	28	78%	0.10	9
3,4 Dichloro Aniline	1	3%	0.59	0.59
Ametryn	4	11%	0.05	1.29
Ametryn hydroxy	13	36%	0.09	3.38
Atrazine	32	89%	0.79	79
Bromacil	2	6%	2.9	6.2

DCPMU	2	6%	0.07	1.1
Desisopropyl Atrazine	35	97%	0.12	5
Desethyl Atrazine	35	97%	0.11	9
Diazinon	18	50%	0.15	1.1
Diketonitrile	10	28%	0.07	0.13
Diuron	25	69%	0.89	25
Haloxyfop	11	31%	0.14	2.8
Hexazinone	26	72%	0.15	20
Imidacloprid	5	14%	1.0	2.9
MCPA	25	69%	0.11	2.9
Metolachlor	33	92%	0.17	89
Metalaxyl	17	47%	0.06	3.3
Metsulfuron-Methyl	31	86%	0.73	28
Picloram	2	6%	0.53	1.0
Prometryn	2	6%	0.17	5
Propazine	14	39%	0.17	1.5
Propiconazole	28	78%	0.11	1.26
Propoxur	5	14%	0.28	9
Simazine	33	92%	0.16	21
Simazine hydroxy	8	22%	0.08	3.1
Tebuconazole	20	56%	0.10	0.83
Tebuthiuron	27	75%	0.07	22
Terbuthylazine des ethyl	15	42%	0.12	1.0
Triclopyr	10	28%	0.11	4.3
Pharmaceuticals and personal care products (PPCPs)				
Atenolol	2	6%	0.46	3.9
Acesulfame	1	3%	0.38	0.38
Caffeine	1	3%	79	79
Carbamazepine	15	42%	0.18	26
DEET	8	22%	36	133
Desmethyldiazepam	1	3%	0.45	0.45
Gabapentin	2	6%	0.13	0.5
Hydrochlorothiazide	5	14%	0.37	3.1
Iopromide	2	6%	14	58
Naproxen	2	6%	0.27	0.5
Paracetamol	4	11%	0.13	0.3
Temazepam	3	8%	0.70	6.8

Organochlorine pesticides (OCPs)

In total, 14 OCPs and pesticides were accumulated in PDMS samplers over the 28 – 29 day deployment period (Table 3, Figure 4, Appendix 1), with the amount of ∑OCPs accumulated ranging between 0.07 – 310 ng $PDMS^{-1}$ for sites SEQ19 (North Pine River @ Dayboro Well) and SEQ30 (Logan River @ Helen St), respectively. The highest frequency of detection was observed for endosulfan sulfate (88%) followed by pp-DDD (78%), and pp-DDE (67%). Highest accumulation across sites was observed for chlorpyrifos at 1400 ng $PDMS^{-1}$ followed by dacthal at 180 ng $PDMS^{-1}$.

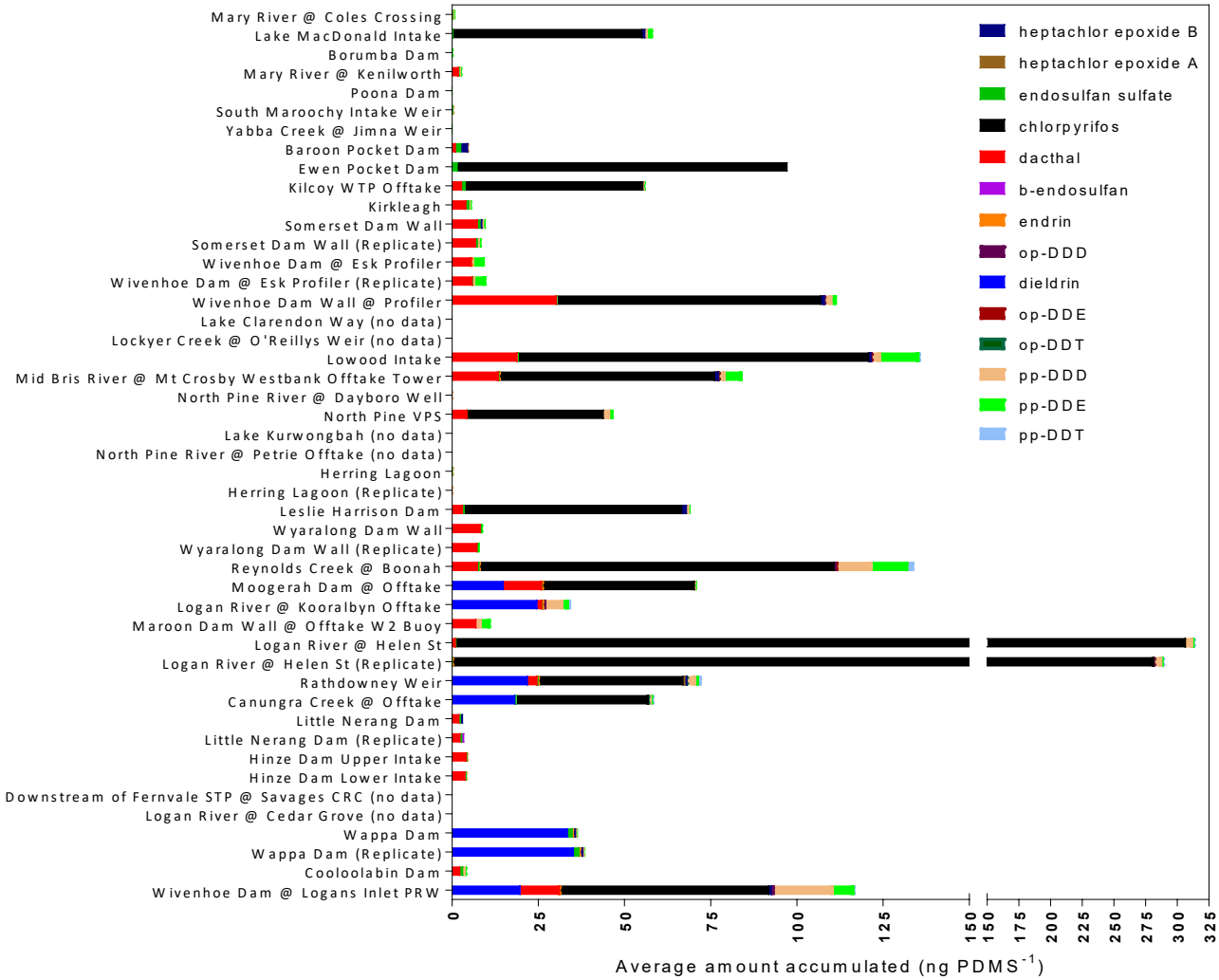

Figure 4. Total amounts (mass) of 14 ΣOCPs (ng $PDMS^{-1}$) accumulated in PDMS passive samplers at each site.

The conversion of OCP masses accumulated in passive samplers to average water concentrations over the deployment period revealed an estimated water concentration range of ∑OCPs between 0.0004 – 4.3 ng L^{-1} for sites SEQ19 (North Pine River @ Dayboro Well) and SEQ30 (Logan River @ Helen St), respectively. (Figure 5). SEQ17 (Lowood Intake) had the next highest concentration of ∑OCPs of 1.9 ng L^{-1}.

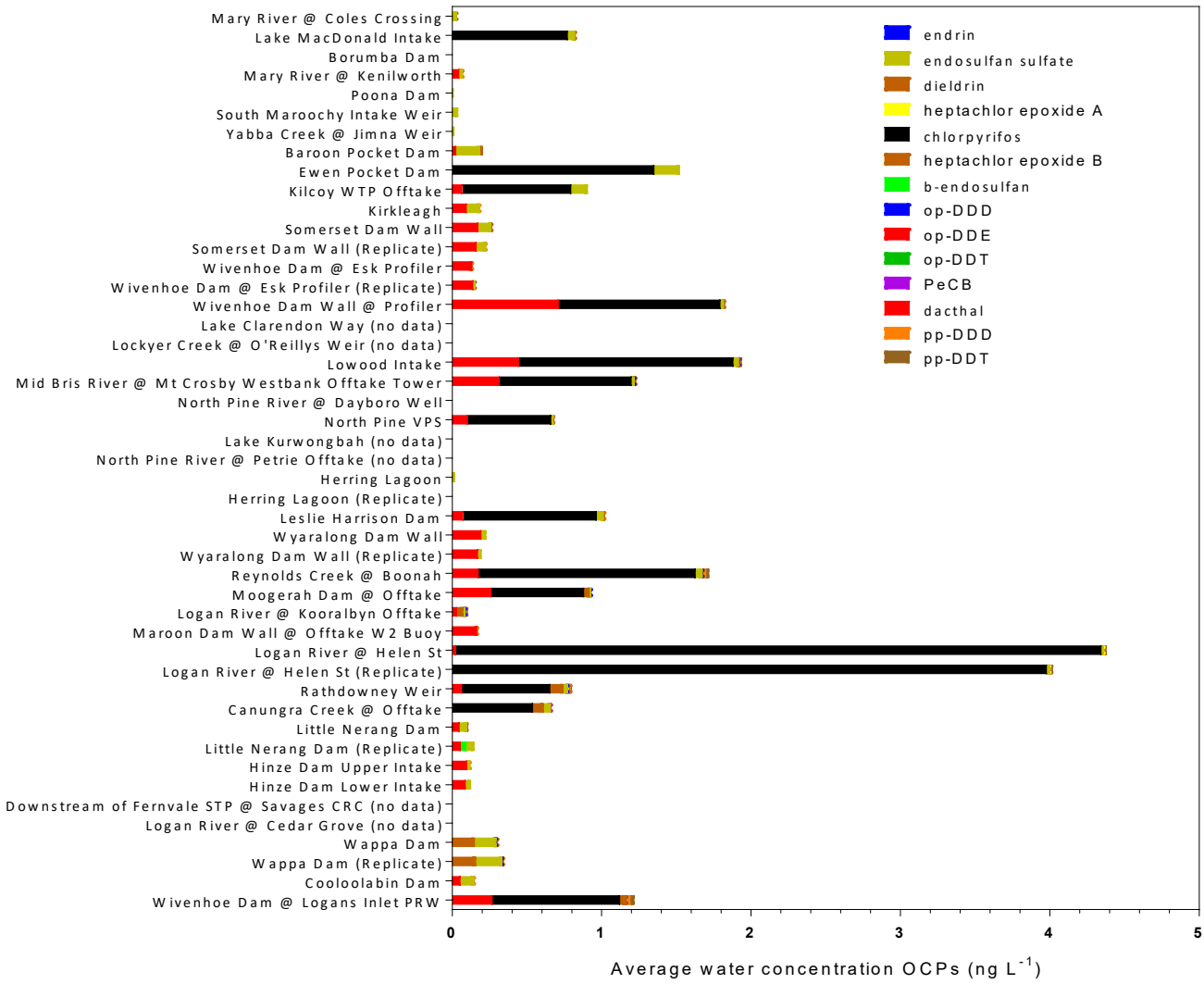

Figure 5. Total estimated water concentrations (ng L^{-1}) of 14 ΣOCPs at each site derived from PDMS passive samplers.

Polycyclic aromatic hydrocarbons (PAHs)

In total, 11 PAHs were accumulated in PDMS samplers with an average amount of ∑PAHs accumulated ranging between 1.5 – 460 ng PDMS^{-1} for sites SEQ6 (South Maroochy Intake Weir) and SEQ29 (Maroon Dam Wall @ Offtake W2 Buoy), respectively (Table 3, Figure 6, Appendix 1). The highest frequency of detection was observed for chrysene with 91% detection, followed by Benzo (a) anthracene with 74% detection and benzo(e)pyrene at 62% detection frequency.

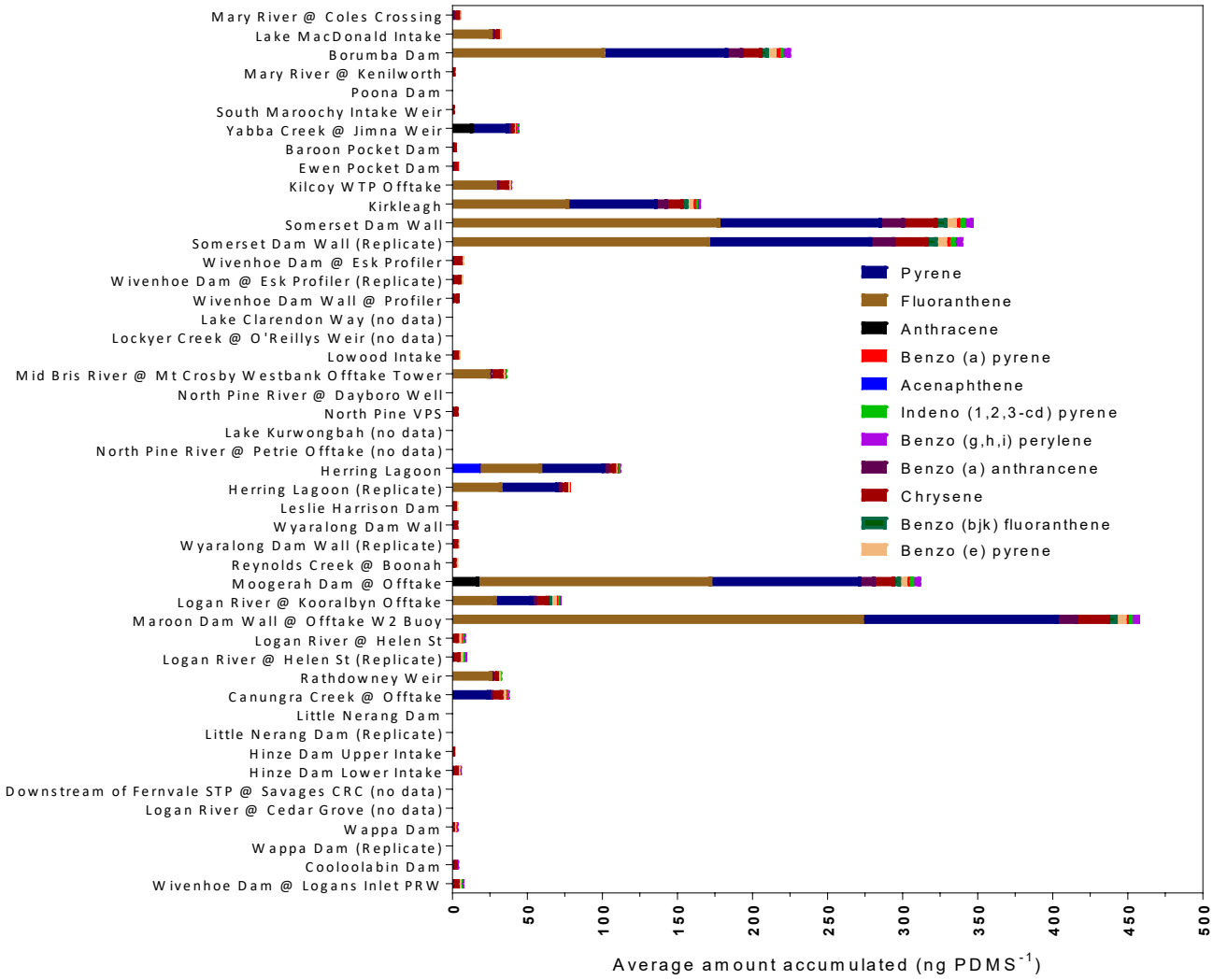

Figure 6. Total amounts (mass) of 11 ΣPAHs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

When converting the masses of accumulated PAHs in passive samplers to average water concentrations over the deployment period, concentrations of ∑PAHs ranged between 0.005 – 2.4 ng L^{-1} (Figure 7) for SEQ34 (Hinze Dam Upper Intake) and SEQ29 (Maroon Dam Wall), respectively.

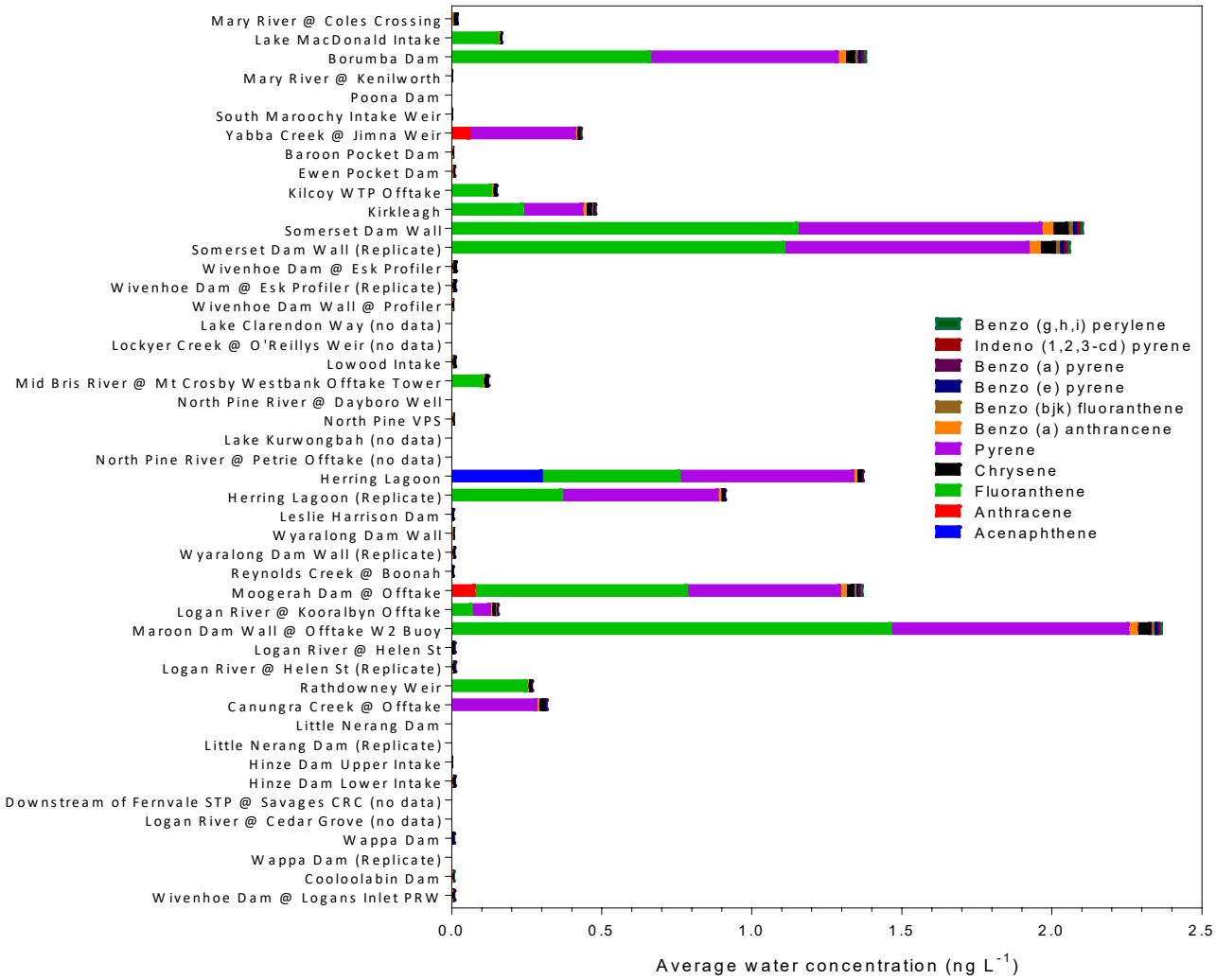

Figure 7. Total estimated water concentrations (ng L^{-1}) of 11 ΣPAHs at each site derived from PDMS passive samplers.

Herbicides and insecticides

Over the 28-29 day deployment period, 30 herbicides and insecticides accumulated in ED passive samplers (Table 3, Figure 8, Appendix 1). The average amount of ∑herbicides and insecticides accumulated ranged between 2.3 – 210 ng ED^{-1} for sites SEQ 33 (Little Nerang Dam) and SEQ37 (Logan River @ Cedar Grove), respectively. Out of the 28 priority herbicides and pesticides monitored, 12 were found among sites. The most frequently detected herbicides were desisopropyl atrazine (97%), metolachlor and simazine (92%), followed by atrazine (89%), metsulfuron-methyl (86%) and propiconazole / 2,4-D (78%). Triazine herbicides can remain in soils for several months and can migrate from soil to groundwater or transport to waterways via runoff and flooding events. Atrazine and simazine have been widely used in Australia and are registered for 1600 uses including weed control in orchards and various crops (APVMA 2011a; ANZECC & ARMCANZ 2018).

Figure 8. Total amounts (mass) of 30∑herbicides and insecticides (ng ED^{-1}) accumulated in ED passive samplers at each site.

Water concentrations were estimated for 16 herbicides and insecticides with average ∑concentrations ranging between 0.5 – 152 ng L^{-1} for sites SEQ33 (Little Nerang Dam) and SEQ37 (Logan River @ Cedar Grove), respectively (Figure 9). Atrazine had the highest total ∑concentration across all sites, with SEQ37 (Logan River @ Cedar Grove) showing the highest concentration at 66 ng L^{-1}.

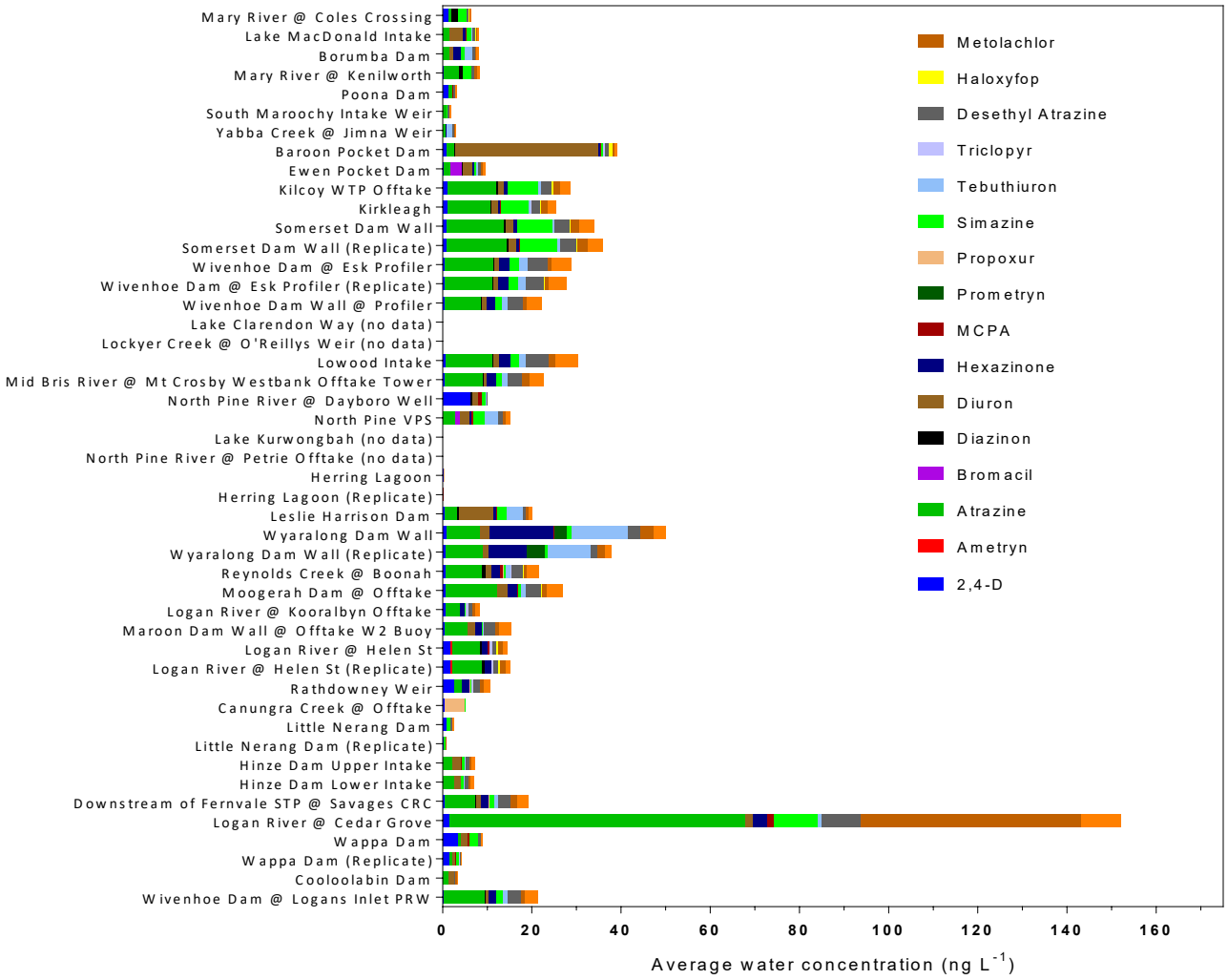

Figure 9. Total estimated water concentrations (ng L^{-1}) of 16 Σherbicides and insecticides at each site derived from ED passive samplers.

Pharmaceuticals and personal care products (PPCPs)

Twelve PPCPs were detected with the average amount of ΣPPCPs accumulated ranging between 0.11 - 220 ng ED^{-1} at sites SEQ19 (North Pine River @ Dayboro Well) and SEQ36 (Downstream of Fernvale STP @ Savages CRC), respectively (Appendix 1). Unsurprisingly, the widest variety of PPCPs were detected downstream from the Fernvale water treatment facility. Dominating this site on a mass basis were caffeine (78 ng ED^{-1}), iopromide (58 ng ED^{-1}), DEET (39 ng ED^{-1}) and carbamazepine (26 ng ED^{-1}). Appreciable levels of DEET were detected in replicate samplers from site SEQ23 (Herring Lagoon), However, there are likely attributed to background contamination during sampling.

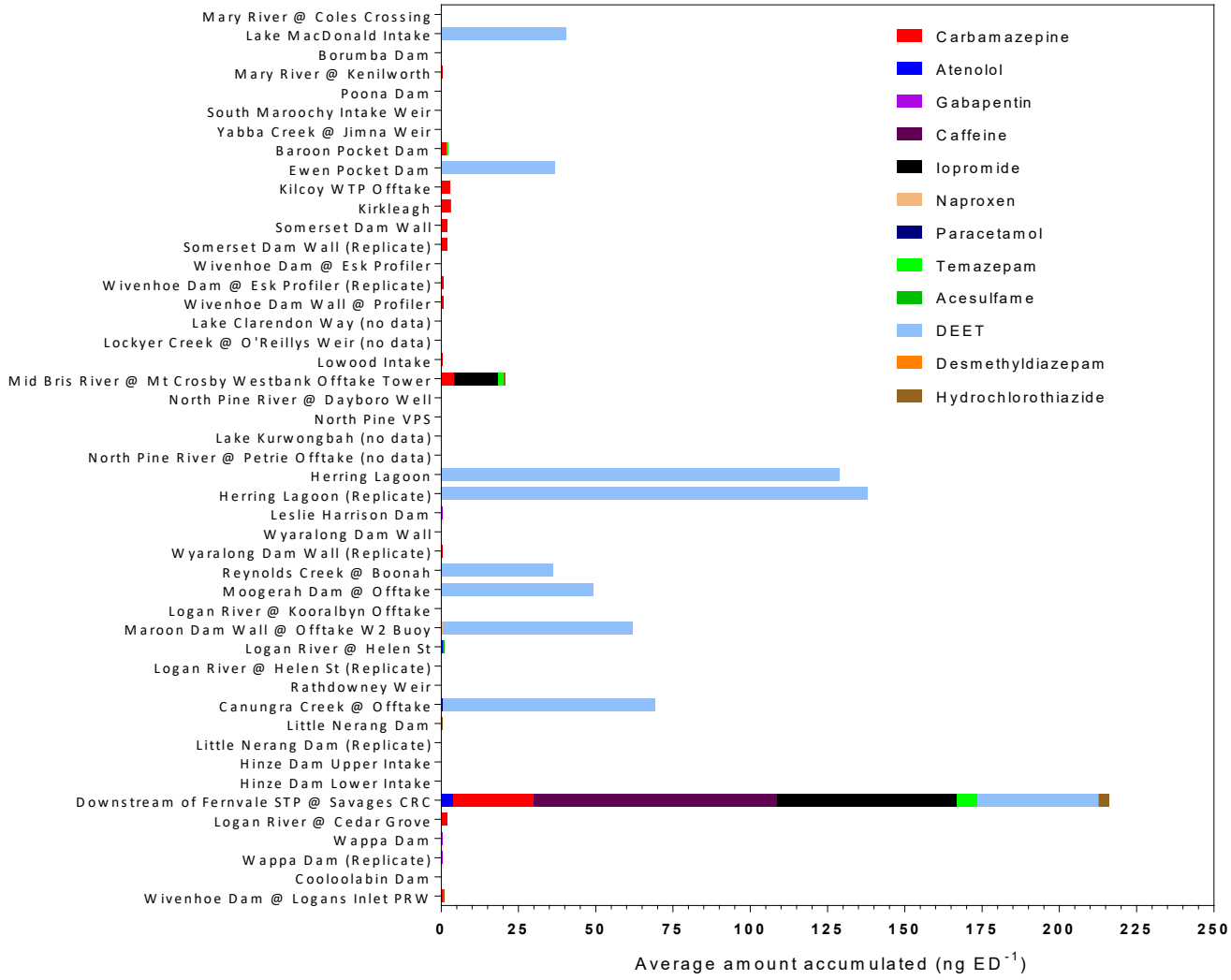

Figure 10. Total amounts (mass) of 12 ΣPPCPs (ng ED^{-1}) accumulated in ED passive samplers at each site.

When converting the masses of accumulated PPCPs in EDs to average water concentrations over the deployment period, only 4 PPCPs can be quantified. For these PPCPs, average ∑PPCP water concentrations ranged between 0.08 – 68 ng L^{-1} for site SEQ24 (Leslie Harrison Dam) and site SEQ23 (Herring Lagoon), respectively (Figure 11).

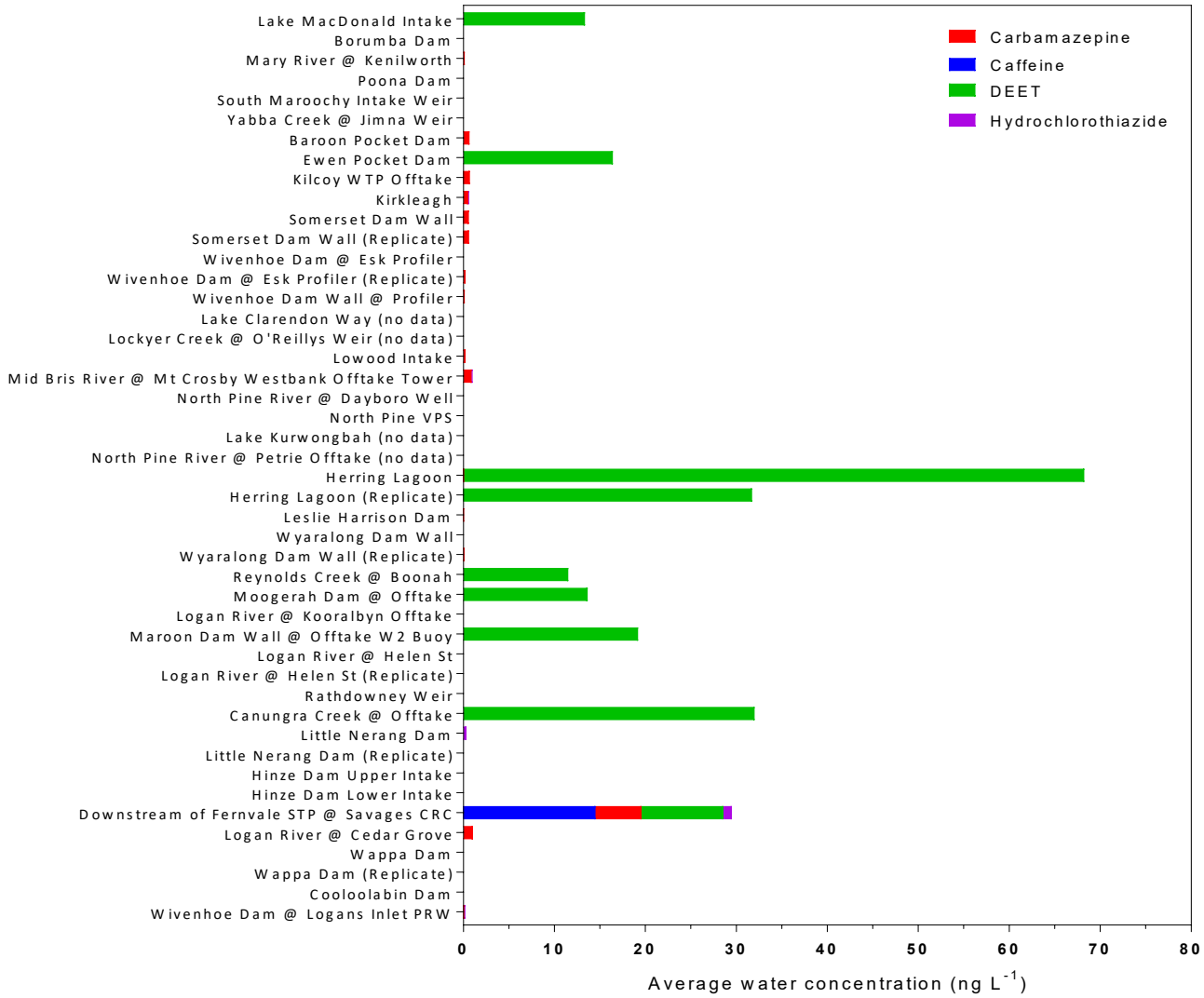

Figure 11. Total estimated water concentrations (ng L^{-1}) of 4 ΣPPCPs.

Analysis of non-target polar chemicals

Along with the target list of polar chemicals identified for investigation, the screening for an additional 45 herbicides and PPCP chemicals that have the potential to transport to waterways has been performed to investigate their presence in the water systems. During this sampling season, three non-target chemicals were potentially detected, including two fungicides and an antibiotic (Table 5). The suspect screening provides tentative identification of the presence / absence of these chemicals. We note that in order to fully confirm the identification and quantification of these analytes, the use of appropriate chemical standards would be necessary.

Table 5. List of tentatively identified non-target chemicals in EDs, and the sites in which they were detected.

Chemical Name	Description	Sites with Tentative detects
Lincomycin	**antibiotic**	SEQ10 (Kilcoy WTO Offtake)
Pencycuron	**fungicide**	SEQ2 (Lake Macdonald Intake); SEQ5 (Poona Dam); SEQ8 (Baroon Pocket Dam); SEQ26 (Reynolds Creek @ Boonah); SEQ28 (Logan River @ Kooralbyn Offtake); SEQ31 (Rathdowney Weir); SEQ34 (Hinze Dam Upper Intake); SEQ35 (Hinze Dam Lower Intake); SEQ38 (Wappa Dam)
Trifloxystrobin	**fungicide**	SEQ23 (Herring Lagoon)

Comparison to water quality guideline values

A selection of available water guideline values and species protection values are provided in Table 6. No herbicides/insecticides, PPCPs, OCPs and PAHs with an available ADWG value were detected at concentrations that exceeded their drinking water or freshwater guideline value.

Table 6. Threshold chemical guidelines for Australian Drinking Water and Freshwater Aquatic Ecosystems

Australian Drinking Water Guidelines 6 (2011) Version 3.5 Updated August 2018 (ng L^{-1})		**ANZECC & ANCANZ (2018) Trigger values for freshwater**	
		99% species protection value (ng L^{-1})	**95% species protection value (ng L^{-1})**
Herbicides & Insecticides			
Atrazine	20000	700	13000
Ametryn	70000	N/A	N/A
Bromacil	400000	N/A	N/A
Carbaryl	30000	N/A	N/A
Carbendazim	90000	N/A	N/A
Carbofuran	10000	60	1200
Diazinon	4000	0.03	10
Dicamba	100000	N/A	N/A
Dichlorvos	5000	N/A	N/A
Diuron	20000	N/A	N/A
Fenamiphos	500	N/A	N/A
Fluometuron	70000	N/A	N/A
Haloxyfop	1000	N/A	N/A
Hexazinone	400000	N/A	N/A
MCPA	40000	N/A	N/A
Methiocarb	7000	N/A	N/A
Malathion	700000	2	50
Mathomyl	20000	N/A	N/A
Metolachlor	300000	N/A	N/A
Metsulfuron methyl	40000	N/A	N/A
Pendimethalin	400000	N/A	N/A
Picloram	300000	N/A	N/A
Propazine	50000	N/A	N/A
Propiconazole	100000	N/A	N/A
Simazine	20000	200	3200
Tebuthiuron	N/A	20	2200
Terbuthylazine	10000	N/A	N/A
Terbutryn	400000	N/A	N/A
Triclopyr	20000	N/A	N/A
2,4-D	30000	140000	280000
2,4,5-T	100000	3000	36000
3,4-Dichloroaniline	N/A	1300	3000
OCPs			
Chlordane	2000	30	800
Chlorpyrifos	10000	0.04	10
DDT	9000	6	10
Dieldrin and Aldrin	300	N/A	N/A
Endosulfan	20000	30	200
Endrin	N/A	10	20
Heptachlor	300	10	90
r-HCH (lindane)	10000	70	200
PAHs			
Benzo(a)pyrene	10	N/A	N/A
Naphthalene	10	2500	16000

Summary

A wide range of organic micro-pollutants were detected at all 36 sampling locations during the summer 2019 deployment period. In summary, 14 OCPs were detected at all monitoring sites; the majority of chemicals were present at very low levels (< 4.4 ng L^{-1} ΣOCPs per sites) which may indicate residual background levels because of years of persistent use and subsequent deregulation. Most site profiles are dominated by endosulfan sulfate, pp-DDD, PP-DDE, dacthal and chlorpyrifos. Australia has set chlorpyrifos environmental water guideline values of 0.04 and 10 ng L^{-1} for 99% and 95% species protection, respectively. Fifteen sites exceeded the 99% species protection guideline level (ranging between 0.5 – 4.3 ng L^{-1}). No exceedance of the 95% species protection guideline value were observed.

Eleven PAHs were detected across all sites with maximum ΣPAHs below 2.4 ng L^{-1}, indicating low background levels. PAHs are ubiquitous in the environment and are introduced via anthropogenic sources primarily as a result of incomplete combustion as well as via natural sources (i.e. forest fires and the transformation of biogenic precursors) (Nguyen *et al*. 2014). The hydrophobic nature of PAHs typically results in low concentrations in water as they generally associate with particles and sediment (Nguyen *et al.* 2014). In this sampling campaign elevated levels of PAHs were observed at site 23 (Herring Lagoon) located on Stradbroke Island (with total PAH Σ140 ng sampler or Σ1.4 ng L^{-1}). On a mass basis, these levels were 28 times higher then what was observed over the last eight summer/winter sampling campaigns at this location. This is attributed to the fire occurrence adjacent to this site during early December 2018 and the deployment of the passive samplers close to the event (i.e. 11/12/2018).

Herbicides and insecticides were detected at most sites with 12 out of 30 detected falling within the priority category. The highest total Σherbicides and insecticides detected was 85 ng L^{-1} (SEQ37 Logan River @ Cedar Grove) with the triazine class of herbicides being the most commonly detected.

PPCPs were found at 15 out of 36 sites with site SEQ37 (Logan River @ Cedar Grove) containing the highest PPCPs with total concentrations of 68 ng L^{-1}. The predominant PPCP was carbamazepine at 42%, likely due to its persistence in the environment. The contribution of pharmaceuticals and personal care products would generally be an indicator of systems which are used for human recreational activities or which receive some degree of treated effluent, however a number of PPCPs may be ubiquitous in many environments.

Future recommendations

Several recommendations for future work are suggested to build upon the preliminary findings in the current report.

- Continue temporal and seasonal comparisons to assess if any new trends emerge between sites and seasons.

- Sampling devices should be placed strategically at high rainfall sites to better measure and account for any higher water flow velocities and increased runoff activity.

- The screening for non-target chemicals will continue over the next sampling campaign, followed by a re-assessment of the need to continue with non-target screenings. This perhaps could be done at a reduced capacity for a handful of sites that have been identified to contain increased inputs of micro-pollutants.

References

ANZECC & ARMCANZ (2018). Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Volume 1 The Guidelines. National Water Quality Management Strategy No. 4., Australian & New Zealand Environment & Conservation Council and the Agriculture & Resource Management Council of Australia & New Zealand.

NHMRC, NRMMC (2011) Australian Drinking Water Guidelines Paper 6. Version 3.5; Updated *AUGUST 2018*. National Water Quality Management Strategy. National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia, Canberra.

APVMA (2010). Endosulfan Chemical Review - 9. Implementation review process workflow, Australian Pesticides and Veterinary Medicines Authority, Australian Government.

APVMA (2011a). Atrazine. Environmental Assessment, Australian Pesticides and Veterinary Medicines Authority, Australian Government.

APVMA (2011b). Chlorpyrifos. Environmental Assessment, Australian Pesticides and Veterinary Medicines Authority, Australian Government.

APVMA (2016). Permit to allow minor use of an agvet chemical product for the control of stinging nettle in lettuce crops. Australian Pesticides and Veterinary Medicines Authority, Australian Government.

Beeton R, Buckley K, Jones G, Morgan D, Reichelt R, Trewin D. (2006). Australian State of the Environment Committee 2006. Independent report to the Australian Government Minister for the Environment and Heritage. Department of the Environment and Heritage.

Benbrook, C.M. (2016). Trends in glyphosate herbicide use in the United States and globally. Environ. Sci. Eur. 28.

Fauvelle V, Montero N, Mueller JF, Banks A, Mazzella N and Kaserzon SL. (2017). Glyphosate and AMPA passive sampling in freshwater using a microporous polyethylene diffusion sampler. Chemosphere 188: 241-248.

Ghassemi M, Fargo L, Painter P, Quinlivan S, Scofield R and Takata A. (1981). Environmental fates and impacts of major forest use pesticides. p. A-149-168. U.S. EPA. Office of Pesticides and Toxic Substances. Washington D.C.

Giesy, J. P., Kannan, K. (2002). Perfluorochemical surfactants in the environment. Environ. Sci. Technol 36 (7): 146−152.

Hughes, S.R., Kay, P., Brown, L.E., (2013). Global Synthesis and Critical Evaluation of Pharmaceutical Data Sets collected from River Systems. Environmental Science & Technology 47: 661-667

Kaserzon, S., O'Malley, E., Thompson, K., Paxman, C., Elisei, G., Eaglesham, G., Gallen, M. and Mueller, J. (2017). Catchment and Drinking Water Quality Micro Pollutant Monitoring Program – Passive Sampling Report 6 – Summer 2017 and summary report, prepared for Seqwater, 11 August 2017.

Kaserzon, S.L., Hawker, D.W., Kennedy, K., Bartkow, M., Carter, S., Booij, K., Mueller, J.M.,(2014). Characterisation and comparison of the uptake of ionizable and polar pesticides, pharmaceuticals and personal care products by POCIS and Chemcatchers. Environ. Sci.: Processes Impacts 16: 2517–2526

Kot, A., Zabiegala, B., Namiesnik, J. (2000). Passive sampling for long-term monitoring of organic pollutants in water. Trends in Analytical Chemistry 19 (7):446-459

Nguyen, T.C., Loganathan, P., Nguyen, T.V., Vigneswaran, S., Kandasamy, J., Slee, D., Stevenson, G., Naidu, R. (2014). Polycyclic aromatic hydrocarbons in road-deposited sediments, water sediments,

and soils in Sydney, Australia: Comparisons of concentration distribution, sources and potential toxicity. Ecotoxicology and Environmental Safety 104:339–348

O'Brien, D., Chiswell, B., Mueller, J. F. (2009). A novel method for the in situ calibration of flow effects on a phosphate passive sampler. Journal of Environmental Monitoring 11: 201-219

O'Brien, D., Booij, K., Hawker, D., Mueller, J.F. (2011a). Method for the in Situ Calibration of a Passive Phosphate Sampler in Estuarine and Marine Waters. Environmental Science & Technology 45 (7): 2871-2877

O'Brien, D., Bartkow, M., Mueller, J.F. (2011b). Determination of deployment specific chemical uptake rates for SDB-RPS EmporeTM disk using a passive flow monitor. Chemosphere 83 (9): 1290-1295

Vrana, B., Greenwood, R., Mills, G., Dominiak, E., Svensson, K., Knutsson, J., Morrison, G. (2005). Passive sampling techniques for monitoring pollutants in water. Trends in Analytical Chemistry 10: 845-868

Wang, Z., DeWitt, J., Higgins, C., Cousins, IT. (2017). A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? Environ. Sci. Technol 51 (5): 2508-2518.

Kaserzon, S., Yeh, R., Thompson, K., Paxman, C., Gallen, C., Elisei, G., Prasad, P., Schacht, V., Van Niekerk, S., Verhagen, R., Vijayasarathy, S., Gallen, G., Reeks, T., Jiang, H., Eaglesham, G. and Mueller, J. (2018). Catchment and Drinking Water Quality Micro Pollutant Monitoring Program – Passive Sampling Report 8 – Summer 2018 and summary report, prepared for Seqwater, August 2018.

Appendix 1

See enclosed excel file 'SEQW results_Summer2019.xls'

Reporting sheet listing all micro-pollutants investigated, levels accumulated in PDMS, and ED passive samplers (ng sampler^{-1}) and estimated average water concentrations over the deployment periods (ng L^{-1}) (28-29 days).