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

Report 11 – Winter 2019

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Title

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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 July 2019 and represents the eleventh 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 15 OCPs (and pesticides), 12 PAHs, 29 herbicides and insecticides and 14 PPCPs. OCPs were detected at 29 out of 36 sampled sites (80%; n=36), with endosulfan sulfate, pp-DDD, heptachlor epoxide B and dacthal being the most prevalent between sites, and chlorpyrifos showing the highest total concentration. Total ∑OCP water concentrations across sites ranged between 0.002 – 2.8 ng L^{-1}. PAHs were detected at 24 out of 36 sampled sites (67%; n=36), with chrysene, benzo (bjk) fluoranthene and benzo(e)pyrene at the highest abundance across all sites. Total ∑PAH water concentrations across sites ranged between 0.002 – 2.6 ng L^{-1}. Twenty nine herbicides/insecticides were detected at all sites (n=36). Metsulfuron-methyl, MCPA and desisopropyl atrazine were present at the highest abundance. Total estimated ∑herbicide water concentrations across all sites ranged between 0.6 – 115 ng L^{-1} with MCPA present at the highest concentration across all sites. Fourteen PPCPs were detected across sites with highest detection frequencies observed for carbamazepine (25%) and cotinine (33%). Total estimated ∑PPCP water concentrations ranged between 0.05-16 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. Eleven sites exceeded the 99% species protection guideline level for chlorpyrifos of 0.04 ng L^{-1} (ranging between 0.4 – 2.5 ng L^{-1}). No exceedance of the 95% species protection guideline values were observed. In addition, 8 sites (ranging between 0.2 – 0.63 ng L^{-1}) exceed the 99% species protection guideline level of 0.03 ng L^{-1} for diazinon and no exceedance of the 95% species protection guideline value (of 10 ng L^{-1}) 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 (APVMA) 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 eleventh monitoring campaign.

Methodology

Passive water samplers were deployed in 36 sites of SEQ reservoirs/waterways from July 2019 to August 2019 over a period of 28 days (Table 1), with the exception of site SEQ30 (Logan River @ Helen St) where samplers were lost and therefore replacement samplers were deployed from August – September 2019. 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 human interference, samplers for SEQ30 (Logan River @ Helen St) were deployed again, with only the replacement data shown in this report (Table 1, highlighted in orange). Replicate samplers were deployed at six randomly selected sites (Table 1, highlighted in green).

Table 1. *Deployment locations, dates, lengths of deployment period and water velocity measured at each site. Flow velocity of 3.14 cm/s were used for calculation where the flow velocity falls below 3.14 cm/s. The symbol "r"denotes replicate (in green) and replacement site (in orange).*

Site#	Site code	Site Name	Date Deployed	Date Retrieved	Days Deployed	Flow velocity (cm/s)	Comments
SEQ01	MRS-SP012	SEQ-MARY RIVER @ COLES CROSSING	24/07/2019	21/08/2019	28	4.38	
SEQ02	LMD-SP001	SEQ-LAKE MACDONALD INTAKE	9/07/2019	6/08/2019	28	3.08	
SEQ03	BOD-SP001	SEQ-BORUMBA DAM	9/07/2019	6/08/2019	28	7.89	
SEQ04	MRS-SP013	SEQ-MARY RIVER @ KENILWORTH	24/07/2019	21/08/2019	28	12.44	
SEQ05	POD-SP001	SEQ-POONA DAM	10/07/2019	7/08/2019	28	2.94	
SEQ05r	POD-SP001	SEQ-POONA DAM	10/07/2019	7/08/2019	28	2.94	Replicate
SEQ06	SOR-SP001	SEQ-SOUTH MAROOCHY INTAKE WEIR	11/07/2019	8/08/2019	28	0.88	
SEQ07	YAC-SP001	SEQ-YABBA CREEK @ JIMNA WEIR	23/07/2019	20/08/2019	28	0.92	
SEQ08	BPD-SP001	SEQ-BAROON POCKET DAM	2/07/2019	30/07/2019	28	3.07	
SEQ09	EMD-SP001	SEQ-EWEN MADDOCK INTAKE	11/07/2019	8/08/2019	28	4.54	
SEQ10	SOD-SP010	SEQ-KILCOY WTP OFFTAKE	23/07/2019	20/08/2019	28	2.86	
SEQ10r	SOD-SP010	SEQ-KILCOY WTP OFFTAKE	23/07/2019	20/08/2019	28	2.86	Replicate
SEQ11	SOD-SP011	SEQ-KIRKLEAGH	23/07/2019	20/08/2019	28	3.69	
SEQ12	SOD-SP001	SEQ-SOMERSET DAM WALL	23/07/2019	20/08/2019	28	2.51	
SEQ13	WID-SP004	SEQ-WIVENHOE DAM @ ESK PROFILER	18/07/2019	15/08/2019	28	3.61	
SEQ14	WID-SP001	SEQ-WIVENHOE DAM WALL @ PROFILER	18/07/2019	15/08/2019	28	5.07	
SEQ15	LOC-SP034	SEQ-LOCKYER CREEK @ LAKE CLARENDON WAY	N/A	N/A	28	N/A	Site not active.
SEQ16	LOC-SP031	SEQ-LOCKYER CREEK @ O'REILLYS WEIR	N/A	N/A	28	N/A	Site not active.
SEQ17	MBR-SP016	SEQ-LOWOOD INTAKE	4/07/2019	1/08/2019	28	3.99	
SEQ17r	MBR-SP016	SEQ-LOWOOD INTAKE	4/07/2019	1/08/2019	28	3.99	Replicate
SEQ18	MBR-SP001	SEQ-MID BRIS RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER	4/07/2019	1/08/2019	28	5.91	
SEQ19	NOD-SP091	SEQ-NORTH PINE RIVER @ DAYBORO WELL	16/07/2019	13/08/2019	28	2.26	
SEQ20	NOD-SP001	SEQ-NORTH PINE VPS	3/07/2019	31/07/2019	28	4.67	

SEQ21	LAK-SP001	SEQ-LAKE KURWONGBAH	N/A	N/A	28	N/A	Site not active.
SEQ22	NOD-SP023	SEQ-NORTH PINE RIVER @ PETRIE OFFTAKE	N/A	N/A	28	N/A	Site not active.
SEQ23	NSC-SP001	SEQ-HERRING LAGOON	30/07/2019	27/08/2019	28	2.31	
SEQ24	LHD-SP005	SEQ-LESLIE HARRISON DAM	4/07/2019	1/08/2019	28	3.60	
SEQ25	WYD-SP001	SEQ-WYARALONG DAM WALL	18/07/2019	15/08/2019	28	4.26	
SEQ26	MOD-SP027	REYNOLDS CREEK @ BOONAH	16/07/2019	13/08/2019	28	4.74	
SEQ27	MOD-SP002	SEQ-MOOGERAH DAM @ OFFTAKE	16/07/2019	13/08/2019	28	12.57	PFM empty.
SEQ28	LRS-SP017	SEQ-LOGAN RIVER @ KOORALBYN OFFTAKE	16/07/2019	13/08/2019	28	8.94	
SEQ29	MAD-SP004	SEQ-MAROON DAM WALL @ OFFTAKE W2 BUOY	16/07/2019	13/08/2019	28	4.76	
SEQ29r	MAD-SP004	SEQ-MAROON DAM WALL @ OFFTAKE W2 BUOY	16/07/2019	13/08/2019	28	4.76	Replicate
SEQ30	LRS-SP013	SEQ-LOGAN RIVER @ HELEN ST	22/08/2019	19/09/2019	28	8.50	Replacement samplers as the original samplers had interference
SEQ31	LRS-SP016	SEQ-RATHDOWNEY WEIR	16/07/2019	13/08/2019	28	1.96	
SEQ32	CAC-SP001	SEQ-CANUNGRA CREEK @ OFFTAKE	10/07/2019	7/08/2019	28	1.99	
SEQ32r	CAC-SP001	SEQ-CANUNGRA CREEK @ OFFTAKE	10/07/2019	7/08/2019	28	1.99	Replicate
SEQ33	LND-SP014	SEQ-LITTLE NERANG DAM	11/07/2019	8/08/2019	28	2.06	
SEQ34	HID-SP001	SEQ-HINZE DAM UPPER INTAKE	10/07/2019	7/08/2019	28	2.97	
SEQ35	HID-SP002	SEQ-HINZE DAM LOWER INTAKE	10/07/2019	7/08/2019	28	4.91	
SEQ36	MBR-SP013	SEQ-DOWNSTREAM OF FERNVALE STP @ SAVAGES CRC	4/07/2019	1/08/2019	28	4.91	
SEQ37	LRS-SP012	SEQ-LOGAN RIVER @CEDAR GROVE	18/07/2019	15/08/2019	28	2.00	
SEQ38	WAD-SP001	SEQ-WAPPA DAM	11/07/2019	8/08/2019	28	2.05	
SEQ39	COD-SP001	SEQ-COOLOOLABIN DAM	10/07/2019	7/08/2019	28	3.99	
SEQ39r	COD-SP001	SEQ-COOLOOLABIN DAM			28	3.99	Replicate
SEQ40	WID-SP061	SEQ-WIVENHOE DAM @ LOGANS INLET PRW	18/07/2019	15/08/2019	28	7.32	

Passive sampler preparation and extraction

For this campaign, two types of passive samplers were deployed at each site. Empore Disk^{TM} (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 standard operating procedures (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 = 7 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 or exceed three times 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 SEQ05 (Poona Dam), SEQ10 (Kilcoy WTP Offtake), SEQ17 (Lowood Intake), SEQ29 (Maroon Dam Wall @ Offtake W2 Buoy), SEQ32 (Canungra Creek @ Offtake) and SEQ39 (Cooloolabin Dam) (

Table *1*). Acceptable replicate values within coefficient of variation (CV) < 30 % 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 passive flow monitors (PFMs) were deployed at each sampling site with good agreement observed between duplicate PFMs for most sites (>80%) except for SEQ07 (Yabba Creek @ Jimna Weir), SEQ28 (Logan River @ Kooralbyn Offtake), and SEQ30r (Logan River @ Helen St) with >75% agreement; SEQ04 (Mary River @ Kenilworth), and SEQ27 (Moogerah Dam @ Offtake) >45% agreement (Figure 2). Average flow velocities estimated from PFMs over the deployment period ranged between 0.88 cm s^{-1} (SEQ06; South Maroochy Intake Weir) to 13 cm s^{-1} (SEQ27; Moogerah Dam @ Offtake). Some sites were below 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.

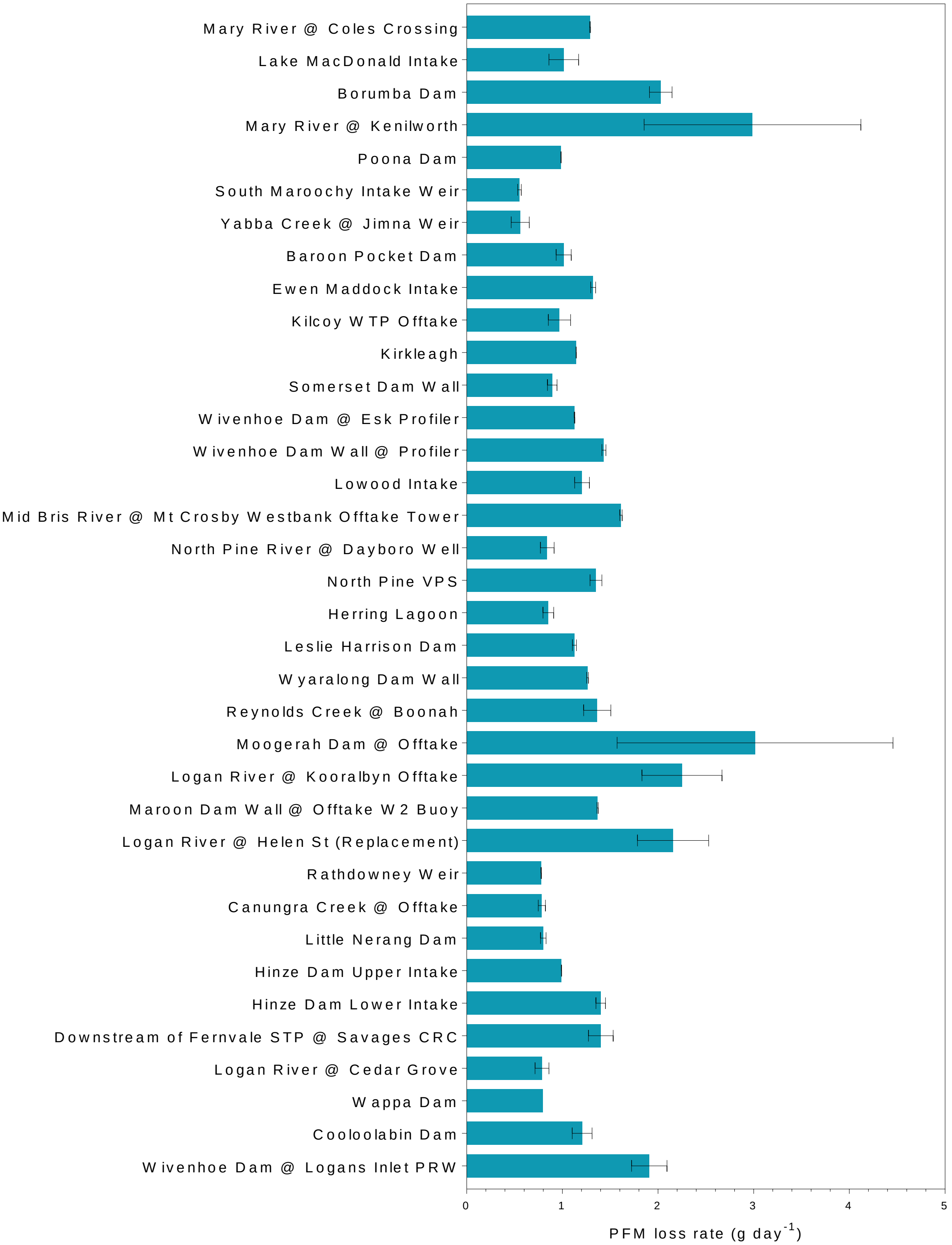

Figure 2. Passive flow monitors (PFMs) loss rate (g per day) of duplicate PFMs per site. Error bars are standard deviation derived from two co-deployed PFMs.

Figure 3. Passive flow monitor (PFM) based 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 4 below. Table 3 summarises the non-polar chemicals detected with PDMS (OCPs and PAHs). A total of 15 OCPs and 12 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% – 81% (for OCPs) and 3% – 67% (for PAHs). Table 4 summarises the polar chemicals detected with EDs (herbicides/ insecticides and PPCPs). A total of 29 herbicides/ insecticides and 14 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3% - 94% (for herbicides and insecticides) and 3% - 33% (for PPCPs).

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 days (ng PDMS^{-1}).

	Number of sites detected (n = 36)	**% detection**	**Min detect (ng PDMS^{-1})**	**Max detect (ng PDMS^{-1})**
Organochlorine pesticides (OCPs)				
a-HCH	3	8	0.19	0.49
chlorpyrifos	11	31	30	180
cis-chlordane (a)	4	11	0.65	0.90
dacthal	26	72	1.1	36
dieldrin	5	14	4.9	11
endosulfan sulfate	29	81	0.06	2.16
endrin aldehyde	1	3	0.29	0.29
endrin ketone	3	8	0.03	0.10
heptachlor epoxide B	24	67	0.19	1.25
op-DDE	4	11	0.02	0.11
PeCB	1	3	1.2	1.2
pp-DDD	26	72	0.12	3.5
pp-DDE	13	36	0.69	7.9
pp-DDT	2	6	0.75	1.4
trans-chlordane (r)	6	17	1.1	2.0
Polycyclic aromatic hydrocarbons (PAHs)				
Acenaphthylene	1	3	19	19
Phenanthrene	1	3	202	202
Anthracene	1	3	16	16
Fluoranthene	7	19	24	51
Pyrene	2	6	30	36
Benzo (a) anthrancene	12	33	1.1	5.0
Chrysene	24	67	2.2	6.8
Benzo (bjk) fluoranthene	20	56	0.5	1.8
Benzo (e) pyrene	16	44	0.7	1.9
Benzo (a) pyrene	6	17	0.7	0.9
Indeno (1,2,3-cd) pyrene	16	44	0.3	0.9
Benzo (g,h,i) perylene	11	31	0.5	1.6

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 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	0.30	7.4
245T	3	8	1.39	2.9
3,4 Dichloro Aniline	7	19	0.19	0.97
Ametryn	7	19	0.13	0.49
Atrazine	21	58	0.21	19
Bromacil	2	6	1.81	1.9
Desethyl Atrazine	22	61	0.11	6.8
Desisopropyl Atrazine	23	64	0.16	5.0
Diazinon	6	17	0.13	0.26
Diuron	10	28	0.36	10
Fluroxypyr	3	8	1.04	1.7
Haloxyfop	8	22	0.13	1.1
Hexazinone	17	47	0.10	8.9
Imidacloprid	8	22	0.10	2.6
MCPA	23	64	0.25	147
Metalaxyl	6	17	0.12	0.68
Metsulfuron-Methyl	34	94	0.46	11
Metolachlor	18	50	0.10	25
Prometryn	4	11	0.16	0.42
Propazine	3	8	0.15	0.22
Propiconazole	1	3	0.60	0.60
Propoxur	1	3	0.31	0.31
Pyrimethanil	1	3	0.11	0.11
Simazine	16	44	0.19	14
Tebuconazole	1	3	0.17	0.17
Tebuthiuron	19	53	0.11	2.1
Terbuthylazine	1	3	2.28	2.3
Terbuthylazine des ethyl	2	6	0.26	1.1
Triclopyr	16	44	0.72	16
Pharmaceuticals and personal care products (PPCPs)				
Caffeine	5	14	17	27
Atorvastatin	1	3	1.18	1.2
Carbamazepine	9	25	0.1	18
Cotinine	12	33	2.1	5.5
Fluoxetine	3	8	0.7	5.2
Gabapentin	4	11	0.3	4.5
Iopromide	2	6	25	194
Naproxen	3	8	0.4	0.5
Nicotine	1	3	57	57
Hydroxycotinine	7	19	0.76	2.3
Paracetamol	2	6	0.5	1.1

Paraxanthine	1	3	19	19
Triclosan	1	3	2.8	2.8
Hydrochlorothiazide	1	3	15	15

Organochlorine pesticides (OCPs)

In total, 15 OCPs and pesticides were accumulated in PDMS samplers over the 28 day deployment period (Table 3, Figure 4, Appendix 1), with the amount of ∑OCPs accumulated ranging between 0.06 – 195 ng PDMS^{-1} for sites SEQ07 (Yabba Creek @ Jimna Weir) and SEQ26 (Reynolds Creek @ Boonah), respectively. The highest frequency of detection was observed for endosulfan sulfate (81%) followed by pp-DDD (76%), dacthal (76%) and heptachlor epoxide B (71%).

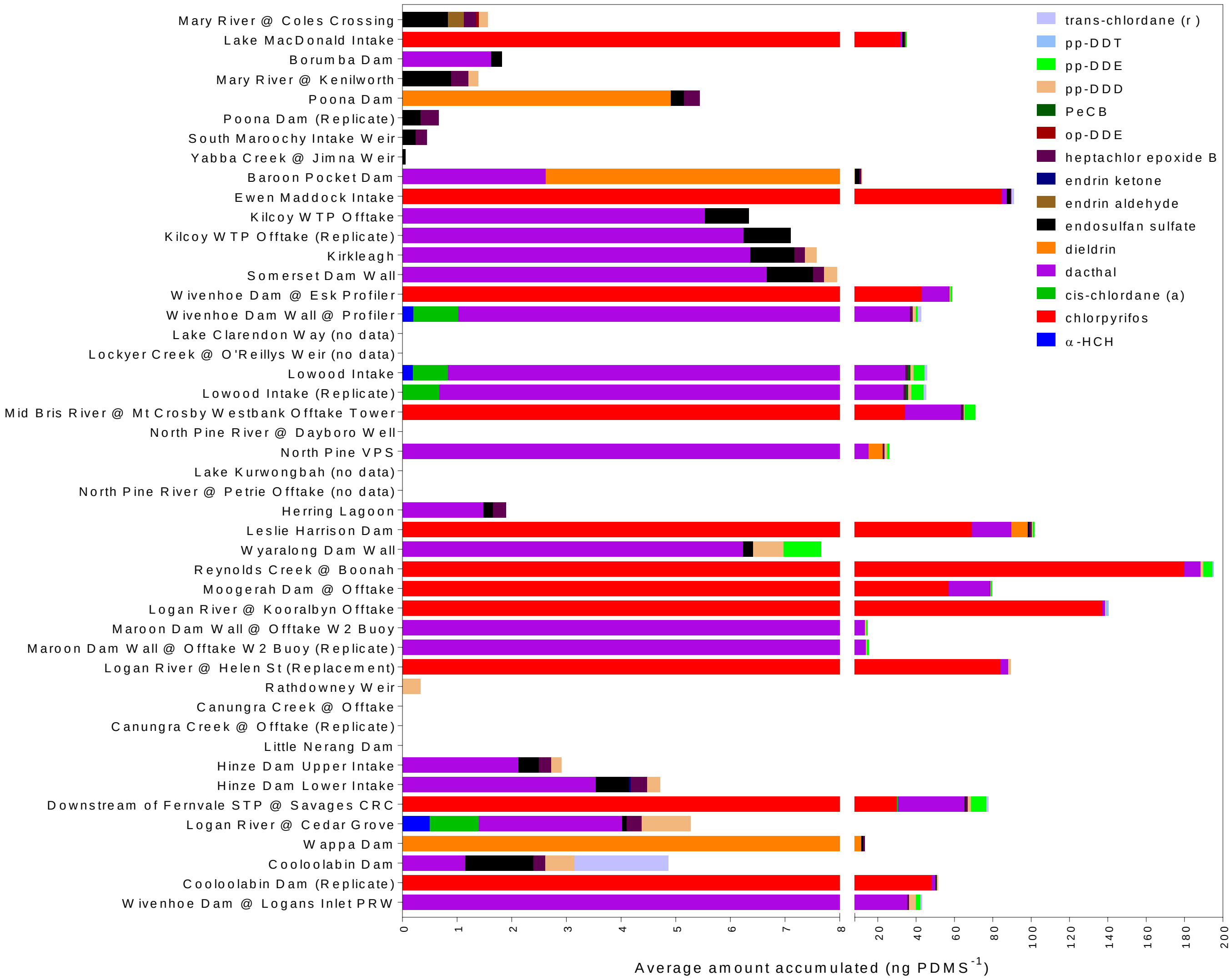

Figure 4. Total amounts (mass) of 15 ΣOCPs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

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 0.002 – 2.8 ng L^{-1} for sites SEQ31 (Rathdowney Weir) and SEQ26 (Reynolds Creek @ Boonah), respectively. (Figure 5).

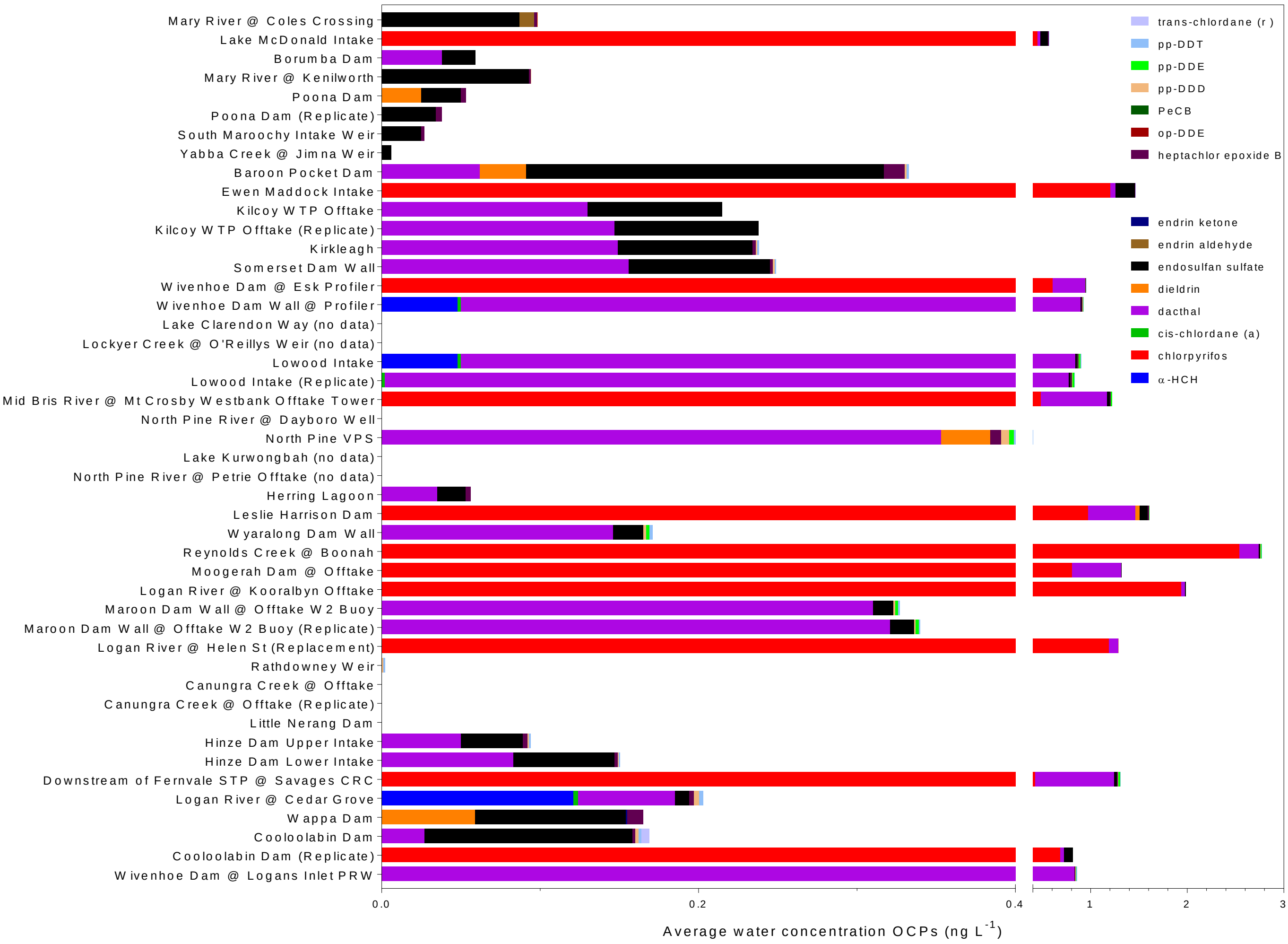

Figure 5. Total estimated water concentrations (ng L^{-1}) of 15 ΣOCPs at each site derived from PDMS passive samplers.

Polycyclic aromatic hydrocarbons (PAHs)

In total, 12 PAHs were accumulated in PDMS samplers with an average amount of ∑PAHs accumulated ranging between 0.5– 318 ng PDMS^{-1} for sites SEQ32 (Canungra Creek @ Offtake) and SEQ24 (Leslie Harrison Dam), respectively (Table 3, Figure 6, Appendix 1). The highest frequency of detection was observed for chrysene (67%) followed by benzo (bjk) fluoranthene (56%).

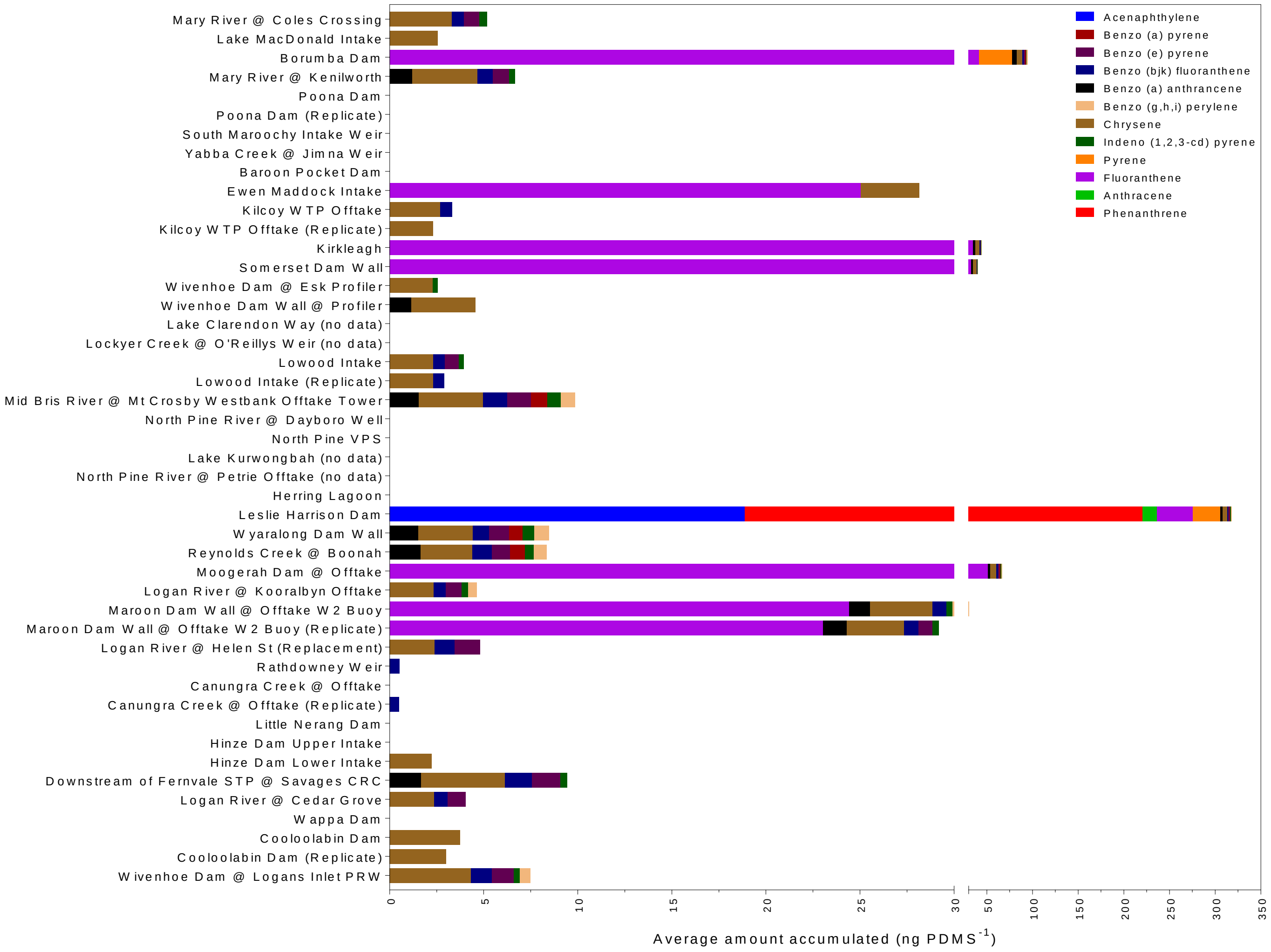

Figure 6. Total amounts (mass) of 12 ΣPAHs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

When converting the masses of accumulated PAHs in passive samplers to average water concentrations over the deployment period, concentrations of ∑PAHs ranged between 0.002 – 2.6 ng L^{-1} (Figure 7) for SEQ32 (Canungra Creek @ Offtake) and SEQ24 (Leslie Harrison Dam), respectively.

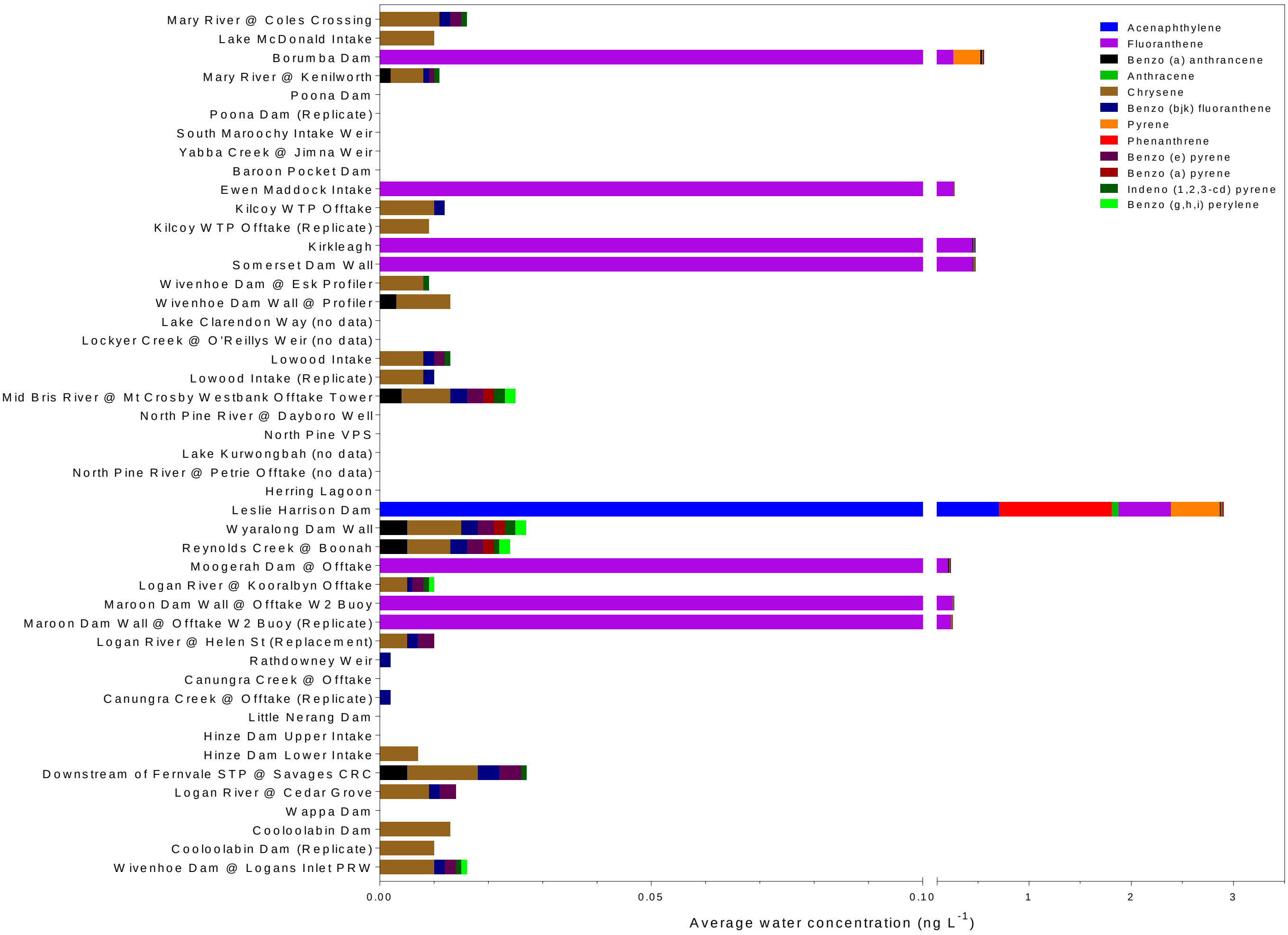

Figure 7. Total estimated water concentrations (ng L^{-1}) of 12 ΣPAHs at each site derived from PDMS passive samplers.

Herbicides and insecticides

Over the 28 day deployment period, 29 herbicides and insecticides accumulated in ED passive samplers (Table 4, Figure 8, Appendix 1). The average amount of ∑herbicides and insecticides accumulated ranged between 0.46 – 176 ng ED^{-1} for sites SEQ 33 (Little Nerang Dam) and SEQ38 (Wappa Dam), respectively. The highest frequency of detection was observed for metsulfuron-methyl (94%), MCPA (64%) and desisopropyl atrazine (61%).

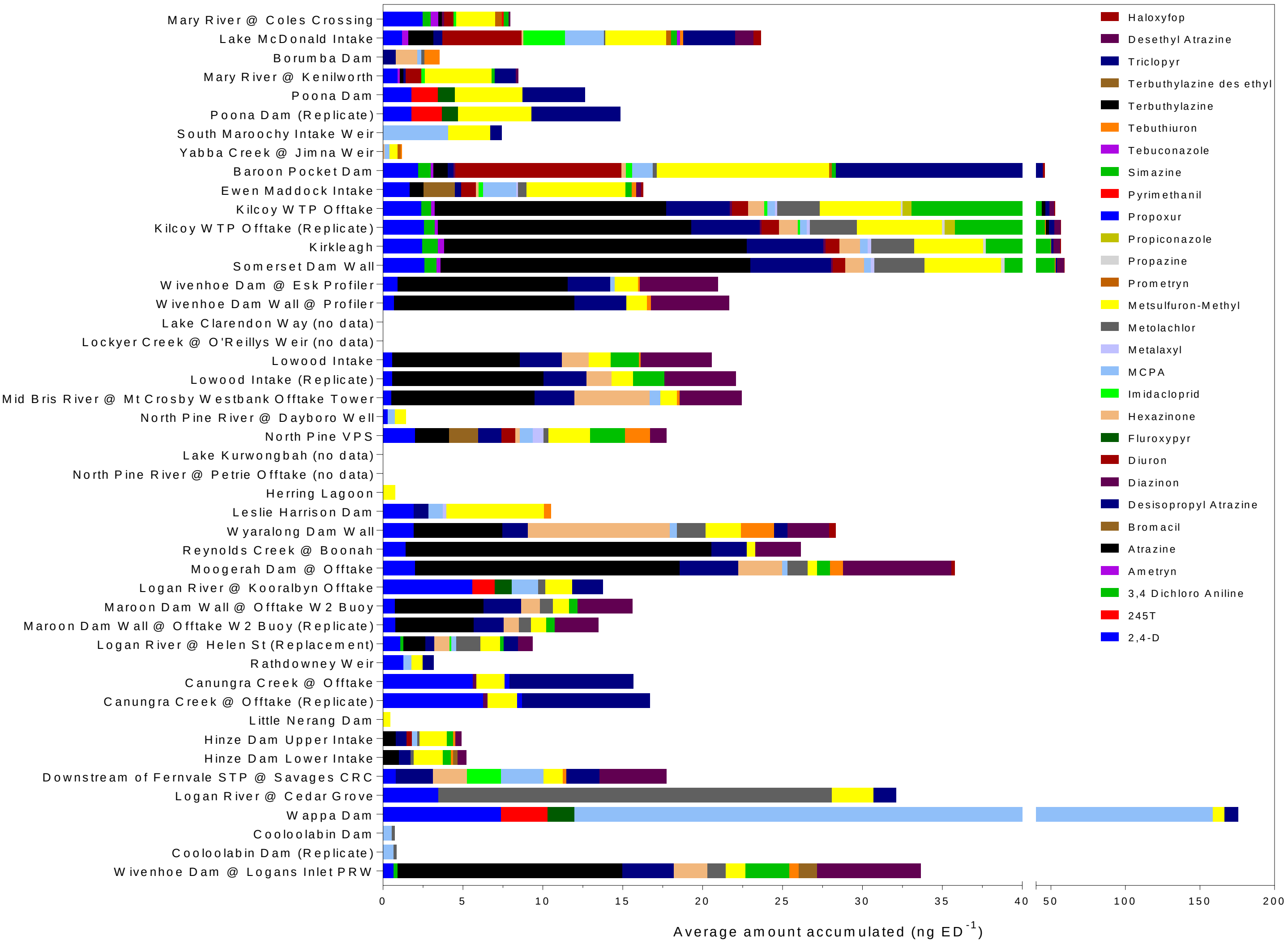

Figure 8. Total amounts (mass) of 29 Σherbicides and insecticides (ng ED^{-1}) accumulated in ED passive samplers at each site.

Water concentrations were estimated for 18 herbicides and insecticides with average ∑concentrations ranging between 0.6 – 115 ng L^{-1} for sites SEQ19 (North Pine River @ Dayboro Well) and SEQ38 (Wappa Dam), respectively (Figure 9).

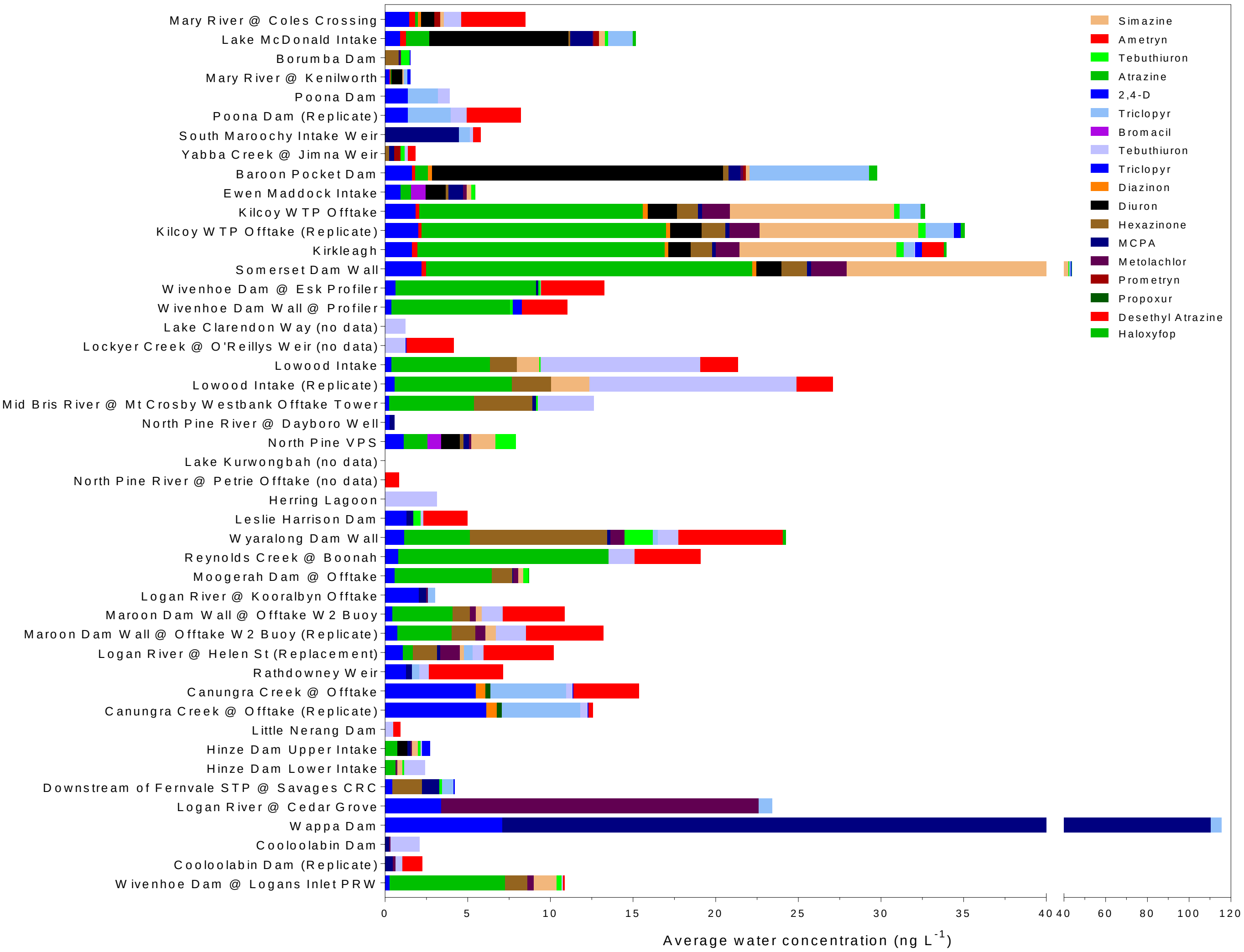

Figure 9. Total estimated water concentrations (ng L^{-1}) of 18 Σherbicides and insecticides at each site derived from ED passive samplers.

Pharmaceuticals and personal care products (PPCPs)

Fourteen PPCPs were detected with the average amount of ΣPPCPs accumulated ranging between 0.24 - 260 ng ED^{-1} at sites SEQ09 (Ewen Maddock Intake) and SEQ36 (Downstream of Fernvale STP @ Savages CRC), respectively (Figure 10) (Appendix 1). Unsurprisingly, the widest variety of PPCPs were detected downstream from the Fernvale water treatment facility. The highest frequency of detection was observed for cotinine (33%), carbamazepine (25%) and hydroxycotinine (19%).

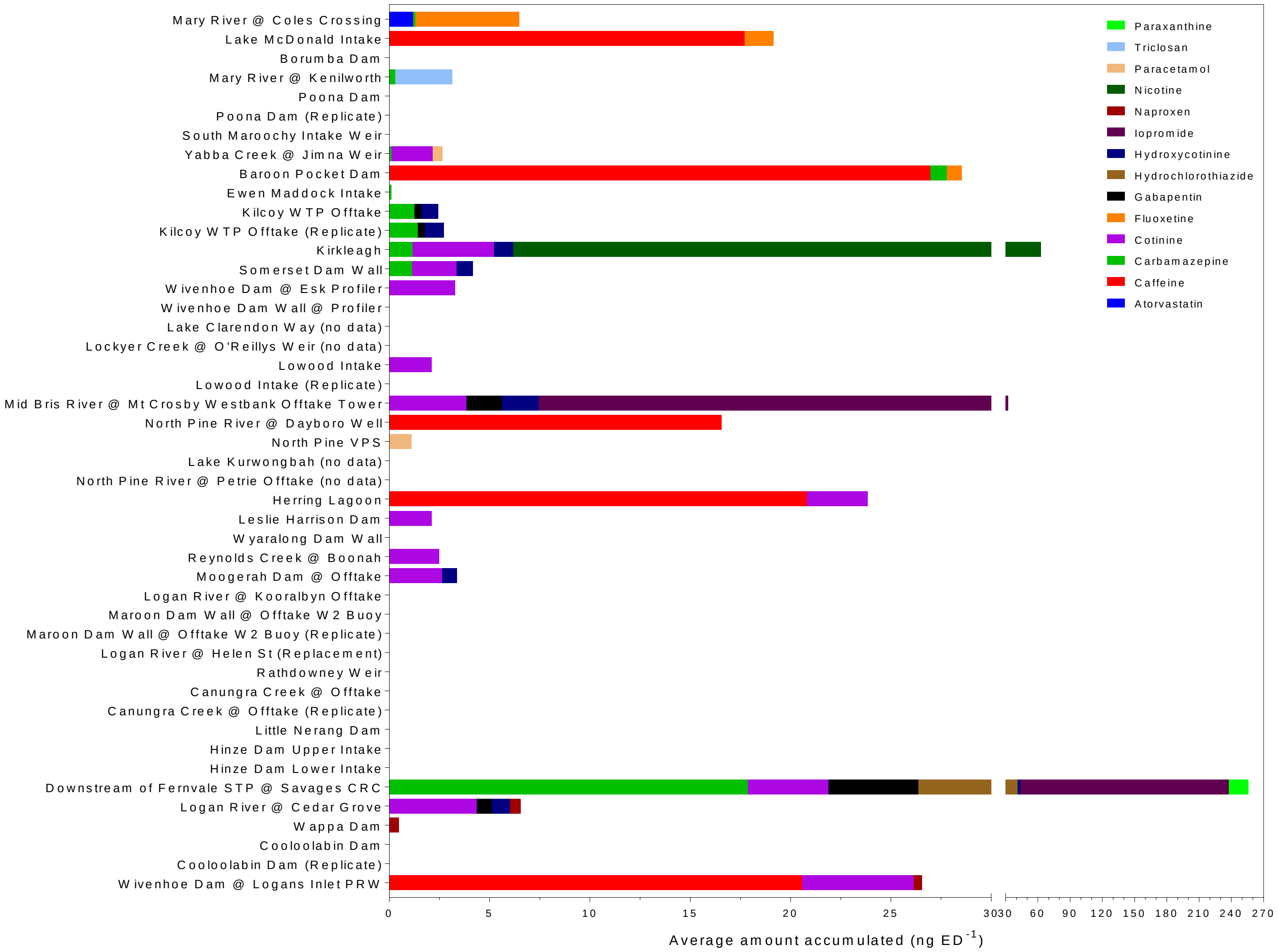

Figure 10. Total amounts (mass) of 14 ΣPPCPs (ng ED^{-1}) accumulated in ED passive samplers at each site.

When converting the masses of accumulated PPCPs in EDs to average water concentrations over the deployment period only caffeine, carbamazepine and hydrochlorothiazide can be quantified. For these PPCPs, average ∑PPCP water concentrations ranged between 0.05 – 16 ng L^{-1} for site SEQ01 (Mary River @ Coles Crossing) and site SEQ36 (Downstream of Fernvale STP @ Savages CRC), respectively (Figure 11).

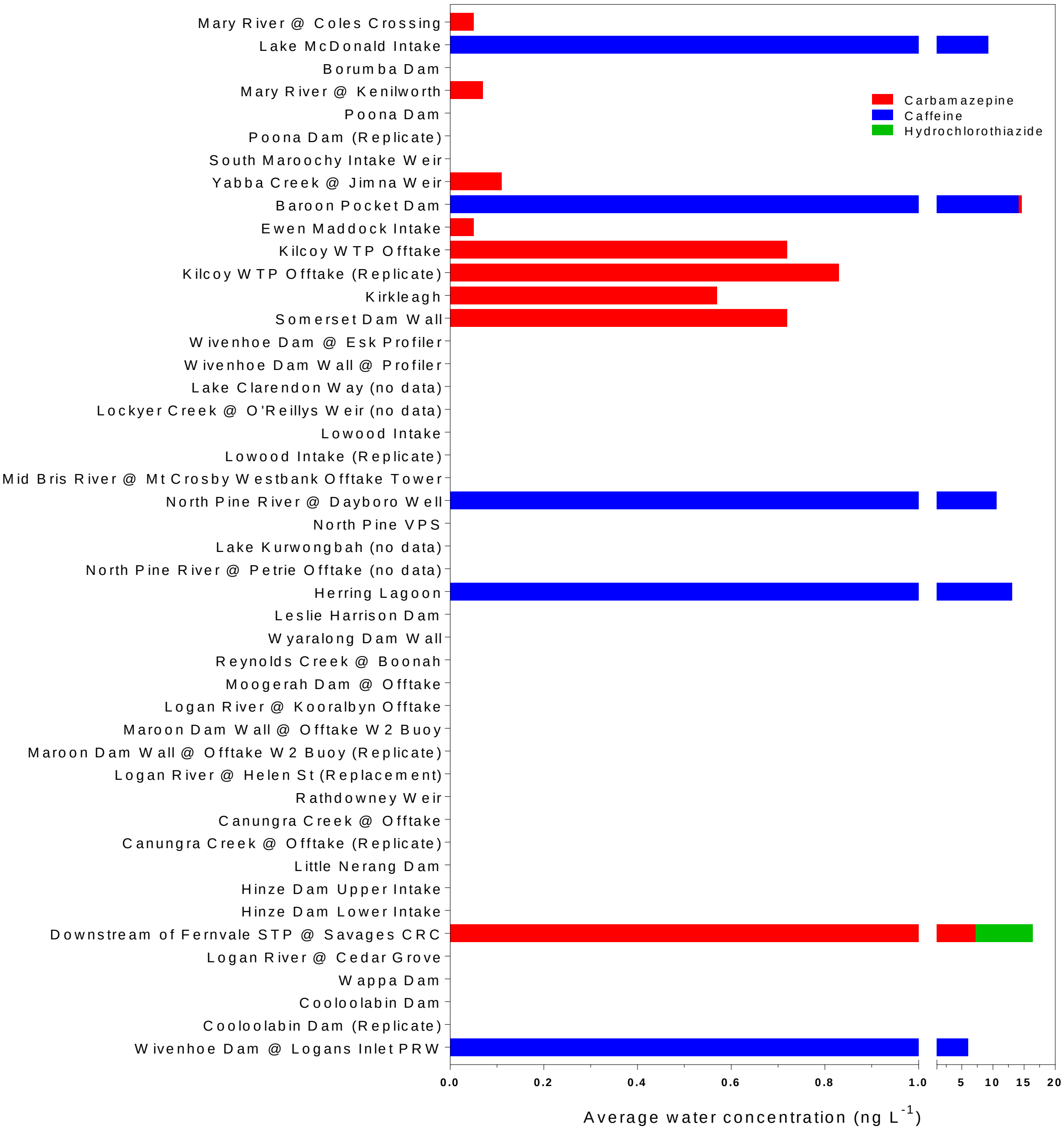

Figure 11. Total estimated water concentrations (ng L^{-1}) of 3 ΣPPCPs.

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, four non-target chemicals were tentatively detected, including an acaricide commonly used for mites and ticks, a veterinary antibiotic, an anti-inflammatory and an opioid (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
Chlordimeform	**acaricide**	SEQ37 (Logan River @Cedar Grove)
Danofloxacin	**veterinary antibiotic**	SEQ9 (Ewen Maddock Intake) SEQ12 (Somerset Dam Wall) SEQ20 (North Pine VPS) SEQ28 (Logan River @ Kooralbyn Offtake) SEQ30 (Logan River @ Helen St) SEQ31 (Rathdowney Weir) SEQ34 (Hinze Dam Upper Intake) SEQ35 (Hinze Dam Lower Intake)
Nalbuphine	**opioid pain relief**	SEQ24 (Leslie Harrison Dam) SEQ38 (Wappa Dam)
Phenazone	**nonsteroidal anti-inflammatory drug**	SEQ30 (Logan River @ Helen St) SEQ37 (Logan River @ Cedar Grove)

- Tentative identifications are considered when spectral library match scores exceed >80%.

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. Australia has set chlorpyrifos environmental water guideline values of 0.04 and 10 ng L^{-1} for 99% and 95% species protection, respectively. 11 sites (ranging between 0.4 – 2.5 ng L^{-1}) exceeded the 99% species protection guideline. No exceedance of the 95% species protection guideline values were observed. In addition, 8 sites (ranging between 0.2 – 0.6 ng L^{-1}) exceed the 99% species protection guideline level of 0.03 ng L^{-1} for diazinon and no exceedance of the 95% species protection guideline values were observed.

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**		**This campaign**
		99% species protection value (ng L^{-1})	**95% species protection value (ng L^{-1})**	**Highest Detected Value (ng L^{-1})**
Herbicides & Insecticides				
Atrazine	20000	700	13000	20
Ametryn	70000	N/A	N/A	0.4
Bromacil	400000	N/A	N/A	0.91
Carbaryl	30000	N/A	N/A	N/A
Carbendazim	90000	N/A	N/A	N/A
Carbofuran	10000	60	1200	N/A
Diazinon	4000	0.03	10	0.63
Dicamba	100000	N/A	N/A	N/A
Dichlorvos	5000	N/A	N/A	N/A
Diuron	20000	N/A	N/A	18
Fenamiphos	500	N/A	N/A	N/A
Fluometuron	70000	N/A	N/A	N/A
Haloxyfop	1000	N/A	N/A	0.5
Hexazinone	400000	N/A	N/A	8.3
MCPA	40000	N/A	N/A	103
Methiocarb	7000	N/A	N/A	N/A
Malathion	700000	2	50	N/A
Mathomyl	20000	N/A	N/A	N/A
Metolachlor	300000	N/A	N/A	19
Metsulfuron methyl	40000	N/A	N/A	N/A
Pendimethalin	400000	N/A	N/A	N/A
Picloram	300000	N/A	N/A	N/A
Propazine	50000	N/A	N/A	N/A
Propiconazole	100000	N/A	N/A	N/A
Simazine	20000	200	3200	14
Tebuthiuron	N/A	20	2200	1.7
Terbuthylazine	10000	N/A	N/A	N/A
Terbutryn	400000	N/A	N/A	N/A
Triclopyr	20000	N/A	N/A	7.2
2,4-D	30000	140000	280000	7.1
2,4,5-T	100000	3000	36000	N/A
3,4-Dichloroaniline	N/A	1300	3000	N/A
OCPs				
Chlordane	2000	30	800	N/A
Chlorpyrifos	10000	0.04	10	2.5
DDT	9000	6	10	0.008
Dieldrin and Aldrin	300	N/A	N/A	0.06

Endosulfan	20000	30	200	N/A
Endrin	N/A	10	20	N/A
Heptachlor	300	10	90	N/A
r-HCH (lindane)	10000	70	200	N/A
PAHs				
Benzo(a)pyrene	10	N/A	N/A	0.003
Naphthalene	10	2500	16000	N/A

Summary

OCPs were first introduced into Australia in the mid-1940s and were applied in many commercial products in different forms (such as powders and liquids). At one time up to 150 commercial products containing OCPs may have been registered in Australia. This followed a period of widespread use until the 1970s when recognition of risks related to OCPs resulted in reduced use and their ultimate ban in the 1980s. Since then human biomonitoring studies in blood and breastmilk have showed the substantial decline of these chemicals from the early 1980s to the 1990s after which levels appear to plateau (Toms *et al.* 2012). Although a number of OCPs were detected at almost all monitoring sites, the majority of chemicals were present at very low levels (< 2.8 ng L^{-1}) which may indicate residual background levels as a result of years of persistent use and subsequent regulation. Most site profiles were dominated by endosulfan sulfate, pp-DDD, heptachlor epoxide B and dacthal, with chlorpyrifos and dacthal showing the highest water concentration values. Dacthal is currently permitted for the use of controlling stinging nettle in lettuce crops (APVMA 2016) and may be in use close to these sites. The insecticide chlorpyrifos was introduced in 1965 and has been included in a large number of products and formulations aimed at agricultural, urban, commercial and residential uses. Although regulation measures have been put in place in Australia (APVMA 2011b) the chemical has not been strictly banned. A continued review of both dacthal and chlorpyrifos is warranted to estimate any future risk.

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). A number of PAHs have been included as chemicals of concern under the Stockholm Convention on Persistent Organic Pollutants (2011) due to their toxic and carcinogenic properties. They enter aquatic systems via storm water runoff from urban and industrial areas, roads and spills as well as via recreational activities such as boating. PAHs can undergo long-range atmospheric transport and deposition and are distributed in waterways during intense rainfall and flooding (Nguyen *et al.* 2014). The hydrophobic nature of PAHs typically results in low concentrations in water as they generally associate with particles and sediment. Twenty four sites showed reportable concentrations of PAHs including chrysene, benzo (bjk) fluoranthene, benzo (e) pyrene and indeno (1,2,3-cd) pyrene, at low levels (< 2.6 ng L^{-1}).

Herbicides were detected at every sampling site with total concentrations of ∑herbicides < 115 ng L^{-1}. Metsulfuron-methyl, MCPA and desisopropyl atrazine were present at the highest abundance. The triazine class herbicides and their degradation products were highly detected with frequencies of detection of 64% (desisopropyl atrazine), 61% (desethyl atrazine), 58% (atrazine) and 44% (simazine) among sites. 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).

Pharmaceuticals and personal care products have emerged as a major group of environmental contaminants over the past decade. Widespread contamination from these chemicals in waterways is attributed to widespread use and subsequent discharge into waterways. Some polar organic chemicals persist through wastewater treatment processes resulting in their continuous release into the aquatic environment (Kaserzon *et al.* 2014). PPCPs that could be converted to water concentrations were found at 33% of sites with total concentrations < 16 ng L^{-1}. The most frequently detected PPCP was cotinine. 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, the low levels and isolated number of chemicals reported here do not indicate such contributions to the water systems.

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.

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Appendix 1

See enclosed excel file ‘SEQW results_Winter2019.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 days).