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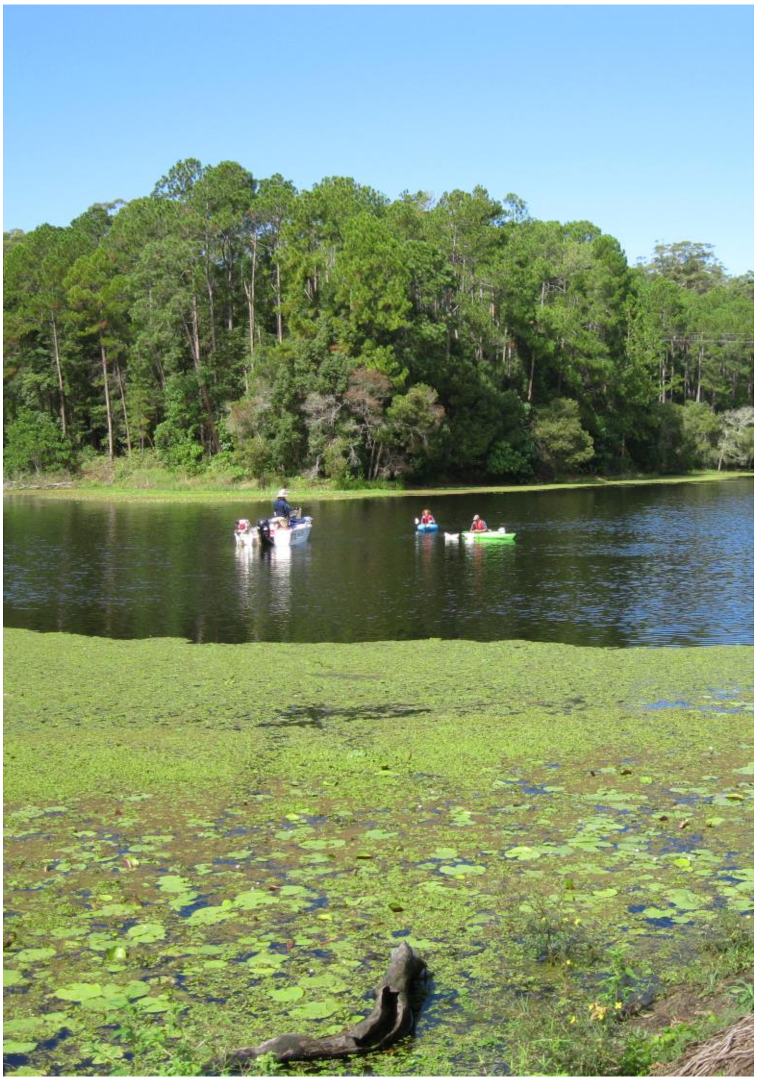

Catchment and Drinking Water Quality Micro Pollutant Monitoring Program – Passive Sampling

Report 9 – Winter 2018

Prepared for Seqwater
by Ruby Yu-Lu Yeh and
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Title

Catchment and Drinking Water Quality Micro Pollutant Monitoring program – Passive Sampling.
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Disclaimer

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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 August to December 2018 and represents the ninth 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), other pesticides, and polycyclic aromatic hydrocarbons (PAHs). In addition, the ninth sampling campaign includes data on per- and poly-fluoroalkyl substances (PFASs) from one drinking water reservoir as a follow up from the last report (Kaserzon *et al*, 2018). 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 72 different chemicals including 17 OCPs (and pesticides), 11 PAHs, 25 herbicides and insecticides and 12 PPCPs. In addition, polyethylene (PE) passive samplers were deployed at 3 sites in one reservoir with 7 PFASs detected, ranging in concentration between 24 – 37 ng L^{-1}. OCPs were detected at 97% of sites, with endosulfan sulfate, dacthal, op-DDD, and pp-DDD being the most prevalent between sites and chlorpyrifos showing the highest total concentration. Total ∑OCP water concentrations across sites ranged between 0.003 – 8 ng L^{-1}. PAHs were detected at 47% of sites, with phenanthrene followed by fluorene present at the highest concentrations across all sites. Chrysene was the most abundant, followed by benzo (e) pyrene. Total ∑PAH water concentrations across sites ranged between 0.002 – 3.4 ng L^{-1}. Herbicides/insecticides were detected at 81% of sites. Atrazine, simazine, and desisopropyl atrazine were present in high abundance. Total estimated ∑herbicide water concentrations across all sites ranged between 0.29 – 30 ng L^{-1} with atrazine and 2,4-D present at the highest concentration across all site. Fifteen PPCPs were detected at 28% of sites with carbamazepine found at the highest abundance, followed by paracetamol at 19%. Total estimated ∑PPCP water concentrations ranged between 0.13 - 90 ng L^{-1} across sites, with DEET and caffeine with the highest concentration. Australian Drinking Water Guidelines (ADWG) and guidelines for freshwater aquatic systems values are available for some of these chemicals for comparison (Table 7).

Introduction

As the bulk supplier of drinking water to South East Queensland, Seqwater has sustained 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 concentration and 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 the ability of monitoring chemical pollutants 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. In addition to the PDMS and ED passive samplers, this report includes the use of novel polyethylene (PE) passive samplers specifically designed for the monitoring of per- and poly-fluoroalkyl substances (PFAS).

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 applications, 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 data from the ninth monitoring campaign.

Methodology

Passive water samplers were deployed in 36 sites of SEQ reservoirs/waterways from July to August 2018 over a period of 28 - 30 days (Table 1). The deployment of samplers was conducted in alignment with "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, site SEQ15 (Lockyer Creek @ Lake Clarendon Way), SEQ16 (Lockyer Creek @ O'Reilly's Weir), SEQ21 (Lake Kurwongbah) and SEQ22 (North Pine River @ Petrie Offtake) were not deployed due to water level and logistical restrictions. In addition, randomly selected replicate samplers were deployed at six sites (highlighted in blue). Sites SEQ41 (Leslie Harrison Dam @ Stockyard Creek) and SEQ42 (Leslie Harrison Dam @ Tingalpa Wallaby Creek) represent new sites that were added to this campaign specifically for assessment of PFASs concentration using the deployment of PE passive samplers (highlighted in green) (Table 1).

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

Site#	Site code	Site Name	Date Deployed	Date Retrieved	Days Deployed	Flow velocity (cm/s)	Comments
SEQ1	MRS-SP012	MARY RIVER @ COLES CROSSING	19/07/2018	16/08/2018	28	2.20	ED and PDMS replicate site. Minimum flow of 3.4 cm/s used in calculations.
SEQ2	LMD-SP001	LAKE MACDONALD INTAKE	19/07/2018	16/08/2018	28	3.66	
SEQ3	BOD-SP001	BORUMBA DAM	16/07/2018	13/08/2018	28	7.09	ED and PDMS replicate site.
SEQ4	MRS-SP013	MARY RIVER @ KENILWORTH	19/07/2018	16/08/2018	28	7.88	
SEQ5	POD-SP001	POONA DAM	10/07/2018	9/08/2018	30	3.76	
SEQ6	SOR-SP001	SOUTH MAROOCHY INTAKE WEIR	10/07/2018	9/08/2018	30	2.33	Minimum flow of 3.4 cm/s used in calculations.
SEQ7	YAC-SP001	YABBA CREEK @ JIMNA WEIR	3/07/2018	31/07/2018	28	1.46	Minimum flow of 3.4 cm/s used in calculations.
SEQ8	BPD-SP001	BAROON POCKET DAM	5/07/2018	2/08/2018	28	3.71	
SEQ9	EMD-SP001	EWEN MADDOCK INTAKE	12/07/2018	9/08/2018	28	5.17	Minimum flow of 3.4 cm/s used in calculations.
SEQ10	SOD-SP010	KILCOY WTP OFFTAKE	11/07/2018	8/08/2018	28	3.29	Minimum flow of 3.4 cm/s used in calculations.
SEQ11	SOD-SP011	KIRKLEAGH	11/07/2018	8/08/2018	28	3.78	
SEQ12	SOD-SP001	SOMERSET DAM WALL	11/07/2018	8/08/2018	28	2.83	ED and PDMS replicate site. Minimum flow of 3.4 cm/s used in calculations.
SEQ13	WID-SP004	WIVENHOE DAM @ ESK PROFILER	9/07/2018	6/08/2018	28	4.24	
SEQ14	WID-SP001	WIVENHOE DAM WALL @ PROFILER	10/07/2018	7/08/2018	28	10.70	
SEQ15	LOC-SP034	LOCKYER CREEK @ LAKE CLARENDON WAY	n/a	n/a	n/a	n/a	Site not active.
SEQ16	LOC-SP031	LOCKYER CREEK @ O'REILLYS WEIR	n/a	n/a	n/a	n/a	Site not active.
SEQ17	MBR-SP016	LOWOOD INTAKE	18/07/2018	15/08/2018	28	3.91	ED and PDMS replicate site.
SEQ18	MBR-SP001	MID BRIS RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER	17/07/2018	14/08/2018	28	3.38	Minimum flow of 3.4 cm/s used in calculations.
SEQ19	NOD-SP091	NORTH PINE RIVER @ DAYBORO WELL	4/07/2018	1/08/2018	28	2.33	Minimum flow of 3.4 cm/s used in calculations.
SEQ20	NOD-SP001	NORTH PINE VPS	4/07/2018	1/08/2018	28	5.19	
SEQ21	LAK-SP001	LAKE KURWONGBAH	n/a	n/a	n/a	n/a	Site not active.
SEQ22	NOD-SP023	NORTH PINE RIVER @ PETRIE OFFTAKE	n/a	n/a	n/a	n/a	Site not active.
SEQ23	NSC-SP001	HERRING LAGOON	17/07/2018	14/08/2018	28	2.78	Minimum flow of 3.4 cm/s used in calculations.
SEQ24	LHD-SP005	LESLIE HARRISON DAM	3/07/2018	31/07/2018	28	3.66	PE samplers also deployed.
SEQ25	WYD-SP001	WYARALONG DAM WALL	4/07/2018	1/08/2018	28	4.02	

SEQ26	MOD-SP027	REYNOLDS CREEK @ BOONAH	5/07/2018	2/08/2018	28	3.06	ED and PDMS replicate site. Minimum flow of 3.4 cm/s used in calculations.
SEQ27	MOD-SP002	MOOGERAH DAM @ OFFTAKE	5/07/2018	2/08/2018	28	7.40	
SEQ28	LRS-SP017	LOGAN RIVER @ KOORALBYN OFFTAKE	5/07/2018	2/08/2018	28	20.94	
SEQ29	MAD-SP004	MAROON DAM WALL @ OFFTAKE W2 BUOY	5/07/2018	2/08/2018	28	6.69	ED and PDMS replicate site.
SEQ30	LRS-SP013	LOGAN RIVER @ HELEN ST	5/07/2018	2/08/2018	28	13.37	
SEQ31	LRS-SP016	RATHDOWNEY WEIR	5/07/2018	2/08/2018	28	10.41	
SEQ32	CAC-SP001	CANUNGRA CREEK @ OFFTAKE	12/07/2018	9/08/2018	28	2.86	Minimum flow of 3.4 cm/s used in calculations.
SEQ33	LND-SP014	LITTLE NERANG DAM	11/07/2018	8/08/2018	28	5.52	
SEQ34	HID-SP001	HINZE DAM UPPER INTAKE	11/07/2018	8/08/2018	28	3.66	
SEQ35	HID-SP002	HINZE DAM LOWER INTAKE	11/07/2018	8/08/2018	28	5.29	
SEQ36	MBR-SP013	DOWNSTREAM OF FERNVALE STP @ SAVAGES CRC	17/07/2018	14/08/2018	28	7.45	
SEQ37	LRS-SP012	LOGAN RIVER @CEDAR GROVE	5/07/2018	2/08/2018	28	2.72	Minimum flow of 3.4 cm/s used in calculations.
SEQ38	WAD-SP001	WAPPA DAM	12/07/2018	9/08/2018	28	3.43	
SEQ39	COD-SP001	COOLOOLABIN DAM	10/07/2018	9/08/2018	30	4.79	
SEQ40	WID-SP061	WIVENHOE DAM @ LOGANS INLET PRW	9/07/2018	6/08/2018	28	7.79	
SEQ41	LHD-SP010	LESLIE HARRISON DAM @ STOCKYARD CREEK	3/07/2018	31/07/2018	28	5.15	PE samplers and PFMs only.
SEQ42	LHD-SP015	LESLIE HARRISON DAM @ TINGALPA WALLABY CREEK	3/07/2018	31/07/2018	28	3.45	PE samplers and PFMs only.

Passive sampler preparation and extraction

For this campaign, three 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, and 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). In addition to the PDMS and ED passive samplers, this campaign includes the use of novel polyethylene (PE) samplers to detect per- and poly-fluoroalkyl substances (PFAS). 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. PE passive samplers for detection of PFAS were prepared and extracted according to standard operation protocols (SOPs) developed at QAEHS (Table 2).

Figure 1. From left to right. Preparation of PDMS passive sampler in stainless steel cage, preparation and assembly of ED passive samplers and deployment setup for a PE passive sampler.

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 (75 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). PE extracts were analysed by LC-QQQ MS/MS for PFAS (24 chemicals).

The analytical methods for herbicides and PPCPs (LC-QQQ MS/MS), OCPs and PAHs (GC-HRMS) and non-target herbicide and PPCPs (LC-QToF MS/MS) have all been detailed in previous published reports (Kaserzon *et al.* 2017) and SOPs. The analytical methods for PFAS (24 chemicals) were developed at QAEHS (Table 2).

Data modelling and reporting of results

Passive sampling enables time-integrated estimates of water concentrations (C_w) of a wide range of organic pollutants calculated 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 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 as a means to assess site-specific effects of water flow on the sampling rates of chemicals and correct for the influence of flow (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, PDMS and PE). 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 average concentration of the blank samplers for it to be included in the 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 SEQ1 (Mary River @ Coles Crossing), SEQ3 (Borumba Dam), SEQ12 (Somerset Dam Wall), SEQ17 (Lowood Intake), SEQ26 (Reynolds Creek @ Boonah) and SEQ29 (Maroon Dam Wall @ Offtake W2 Buoy) (*Table 1*). Acceptable replicate values within coefficient of variation (CV) < 67 % were typically observed for passive sampler replicates deployed. OCPs, PAHs, herbicides/ insecticide and PPCPs were all within CV <67%, except for simazine (108%) and hexazinone (90%) at SEQ3 (Borumba Dam). PE samplers were deployed in duplicate at SEQ24 (Leslie Harrison Dam), SEQ41 (Leslie Harrison Dam @ Stockyard Creek) and SEQ42 (Leslie Harrison Dam @ Tingalpa Wallaby Creek) for PFAS; CV were <40% across all duplicates.

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 (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/MSMS-QQQ method for herbicide and PPCP analysis
NTX-P-001	Extraction of PDMS from water
NTX-P-002a	Preparation of PE (Polyethylene) Tubes for PFAS Passive Sampling
NTX-P-003a	Extraction of PE (Polyethylene) Tubes for PFAS Passive Sampling
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 SEQ4 (Mary River @ Kenilworth), SEQ12 (Somerset Dam Wall), SEQ33 (Little Nerang Dam), SEQ19 (North Pine River @ Dayboro Well) and SEQ30 (Logan River @ Helen St) with a >64% agreement (Figure 2). Average flow velocities estimated from PFMs over the deployment period ranged between 2.2 cm s^{-1} (SEQ1 Mary River @ Coles Crossing) – 21 cm s^{-1} (SEQ28 Logan River @ Kooralbyn Offtake). Low flow that falls below the linearity loss rate range of the PFM (i.e. < 3.4 cm s^{-1}; O'Brien *et al.* 2009) can be observed in some sites (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.

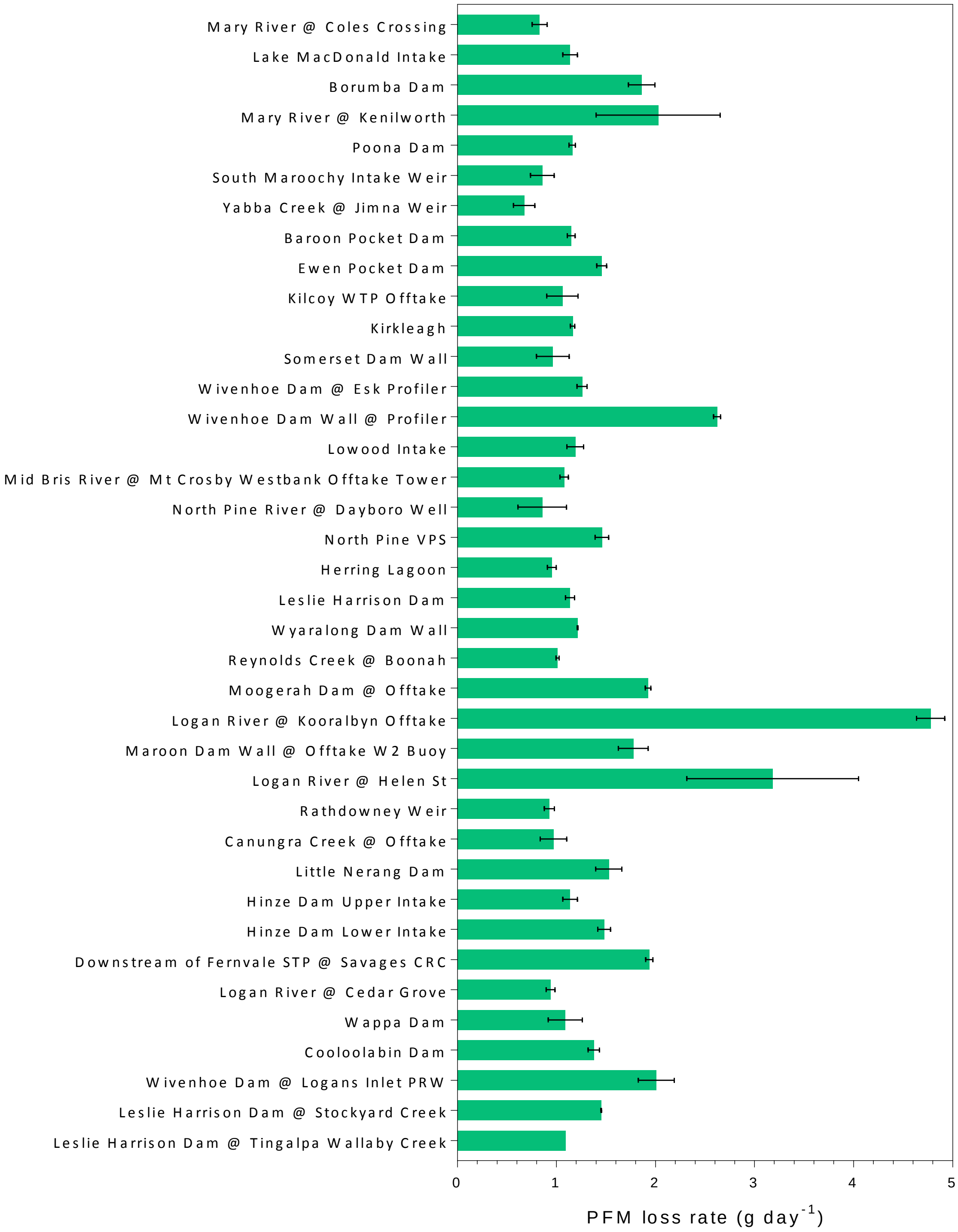

Figure 2. Passive flow monitors (PFMs) loss rate (g per day) of duplicate PFMs per site.

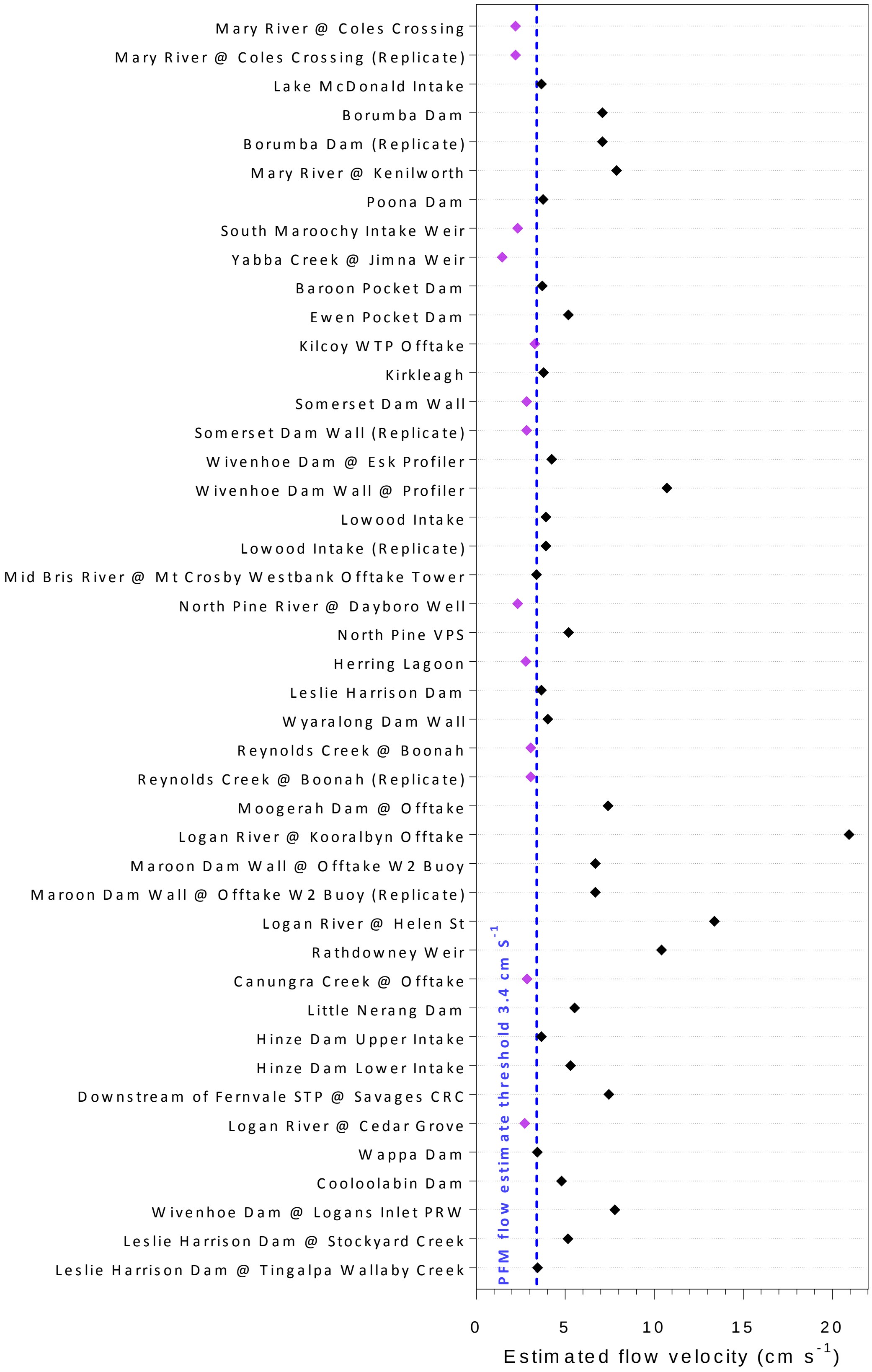

Figure 3. Passive flow monitor (PFM) based average water flow rate estimations at the deployment sites (n=38). A minimum flow velocity of 3.4 cm s^{-1} is used to assess flow velocity using Passive Flow Monitors (PFMs). The sites below minimum flow velocity are highlighted in purple.

Chemical analysis results

A summary of the number of chemicals detected at the sampling sites, the percent detection of each chemical and mass accumulation range (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 17 OCPs and 11 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% – 97% (for OCPs) and 6% – 47% (for PAHs). Table 4 summarises the polar chemicals detected with EDs (herbicides/ insecticides and PPCPs). A total of 25 herbicides/ insecticides and 12 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3% - 81% (for herbicides and insecticides) and 3% - 28% (for PPCPs).

Table 5 summarises the PFAS detected with PE samplers. Seven out of 12 PFAS were detected at the three deployment locations, all within Leslie Harrison Dam. The full data-reporting sheet listing individual masses and estimated water concentrations of all analytes for each site are provided in Appendix 1.

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 28-33 days (ng PDMS^{-1}).

	Number of sites detected (n = 36)	**% detection**	**Min detect (ng PDMS^{-1})**	**Max detect (ng PDMS^{-1})**
	Organochlorine pesticides (OCPs)			
α-HCH	5	14	0.16	4.2
aldrin	4	11	16	20
β-HCH	4	11	0.14	0.24
chlorpyrifos	17	47	15	550
dacthal	28	78	1	88
dieldrin	9	25	6.9	29
endosulfan sulfate	35	97	0.03	2.1
endrin	1	3	0.32	0.32
HCB	1	3	12	12
heptachlor	1	3	1.9	1.9
heptachlor epoxide B	8	22	0.2	1.9
mirex	1	3	0.07	0.066
op-DDD	26	72	0.04	0.83
op-DDT	1	3	0.48	0.48
pp-DDD	26	72	0.14	4.8
pp-DDE	15	42	0.52	6.1
pp-DDT	2	6	0.59	0.76
	Polycyclic aromatic hydrocarbons (PAHs)			
Acenaphthylene	2	6	26	35
Fluorene	4	11	57	68
Phenanthrene	2	6	240	250
Pyrene	2	6	62	77
Benzo (a) anthrancene	11	31	2.1	9.8
Chrysene	17	47	4.1	14
Benzo (bjk) fluoranthene	12	33	0.86	4.5
Benzo (e) pyrene	14	39	1.3	6.6
Benzo (a) pyrene	7	19	0.74	4.1
Indeno (1,2,3-cd) pyrene	8	22	0.71	1.6
Benzo (g,h,i) perylene	9	25	0.89	4.3

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 28-30 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	18	50	0.90	24
3,4 Dichloro Aniline	12	33	0.11	0.26
Ametryn	1	3	0.27	0.27
Ametryn hydroxy	11	31	0.24	1.3
Atrazine	29	81	0.08	15
Bromacil	6	17	0.15	0.97
Chlorpyrifos	2	6	0.13	0.13
Desethyl Atrazine	23	64	0.13	4.5
Desisopropyl Atrazine	27	75	0.12	2.7
Diuron	17	47	0.46	8.6
Fluroxypyr	1	3	1.3	1.3
Haloxyfop	10	28	0.15	1.7
Hexazinone	22	61	0.19	10
Imidacloprid	3	8	0.66	2.3
MCPA	6	17	0.65	4.99
Metalaxyl	6	17	0.13	1.9
Metolachlor	20	56	0.10	3.9
Metsulfuron-Methyl	27	75	0.31	5.9
Picloram	1	3	0.34	0.34
Simazine	29	81	0.13	3.8
Simazine hydroxy	1	3	0.24	0.24
Tebuconazole	3	8	0.12	0.13
Tebuthiuron	17	47	0.29	10
Terbuthylazine des ethyl	11	31	0.11	0.81
Triclopyr	1	3	0.72	0.72
Pharmaceuticals and personal care products (PPCPs)				
Atenolol	1	3	4.1	4.1
Caffeine	3	8	8.1	28
Carbamazepine	10	28	0.27	5.8
Codeine	1	3	7.4	7.4
DEET	2	6	17	27
Desmethyldiazepam	1	3	0.18	0.18
Gabapentin	3	8	0.32	3.4
Hydrochlorothiazide	1	3	3.7	3.7
Ibuprofen	1	3	7.1	7.1
Iopromide	4	11	0.13	1.8
Naproxen	1	3	1.6	1.6
Paracetamol	7	19	0.10	0.32
Paraxanthine	2	6	5.9	8.1
Temazepam	1	3	1.8	1.8
Venlafaxine	1	3	16	16

Table 5. Per- and poly-fluoroalkyl substances (PFAS) accumulated in PE passive samplers across Leslie Harrison Dam (SEQ24, SEQ41 and SEQ42) and the range of mass accumulated over 28-30 days (ng L^{-1}).

Per- and poly-fluoroalkyl substances (PFAS)	Abbreviation	Detection	Min detect (ng L^{-1})	Max detect (ng L^{-1})
Perfluoro-n-butanoic acid	PFBA	Yes	7.8	14
Perfluoro-n-pentanoic acid	PFPeA	No	n/a	n/a
Perfluoro-n-hexanoic acid	PFHxA	Yes	2.5	4.4
Perfluoro-n-heptanoic acid	PFHpA	Yes	1.2	2.5
Perfluoro-n-octanoic acid	PFOA	Yes	2.9	4.6
Perfluoro-n-nonanoic acid	PFNA	No	n/a	n/a
Perfluoro-n-decanoic acid	PFDA	No	n/a	n/a
Perfluorobutane sulfonate	PFBS	Yes	1	2.2
Perfluorohexane sulfonate	PFHxS	Yes	2.5	4.6
Perfluorooctane sulfonate	PFOS	Yes	3.4	5.9
Perfluoro-1-decanesulfonate	PFDS	No	n/a	n/a
1H, 1H, 2H, 2H-perfluorooctane sulfonate	6:2 FTS	No	n/a	n/a

Organochlorine pesticides (OCPs)

In total, 17 OCPs and pesticides were accumulated in PDMS samplers over the 28 – 30 day deployment period (Table 3, Figure 4, Appendix 1), with the amount of ∑OCPs accumulated ranging between 0.03 – 560 ng PDMS^{-1} for sites SEQ7 (Yabba Creek @ Jimna Weir) and SEQ26 (Reynolds Creek @ Boonah), respectively.

The highest frequency of detection was observed for endosulfan sulfate (97%) followed by dacthal (78%), op-DDD, and pp-DDD at 72% detection each. Highest accumulation was observed for chlorpyrifos at 530 ng PDMS^{-1} followed by dacthal at 88 ng PDMS^{-1} from site SEQ26 (Reynolds Creek @ Boonah) and SEQ14 (Wivenhoe Dam Wall @ Profiler), respectively.

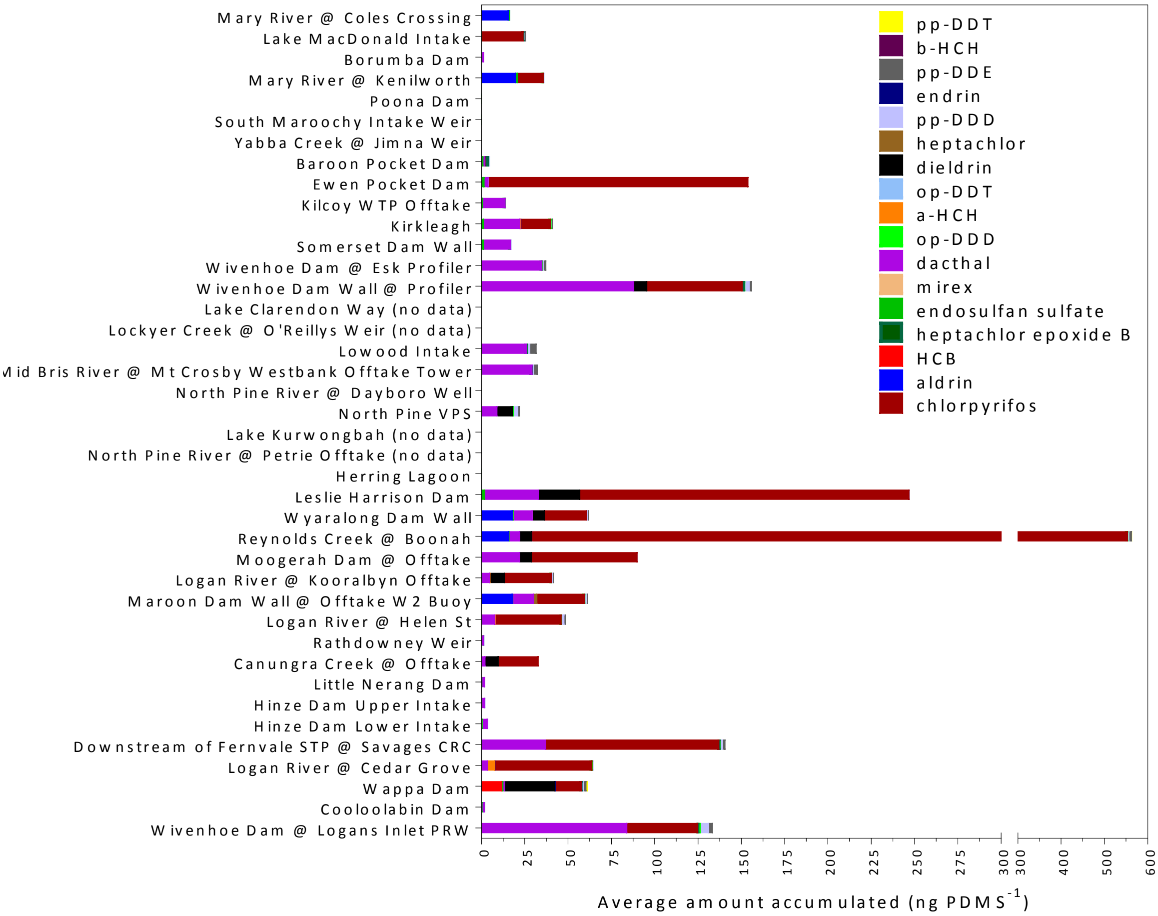

Figure 4. Total amounts (mass) of 17 ΣOCPs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

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 0.003 – 8 ng L^{-1} for sites SEQ7 (Yabba Creek @ Jimna Weir) and SEQ26 (Reynolds Creek @ Boonah), respectively (Figure 5). SEQ24 (Leslie Harrison Dam) had the next highest concentration of ∑OCPs of 3.8 ng L^{-1}.

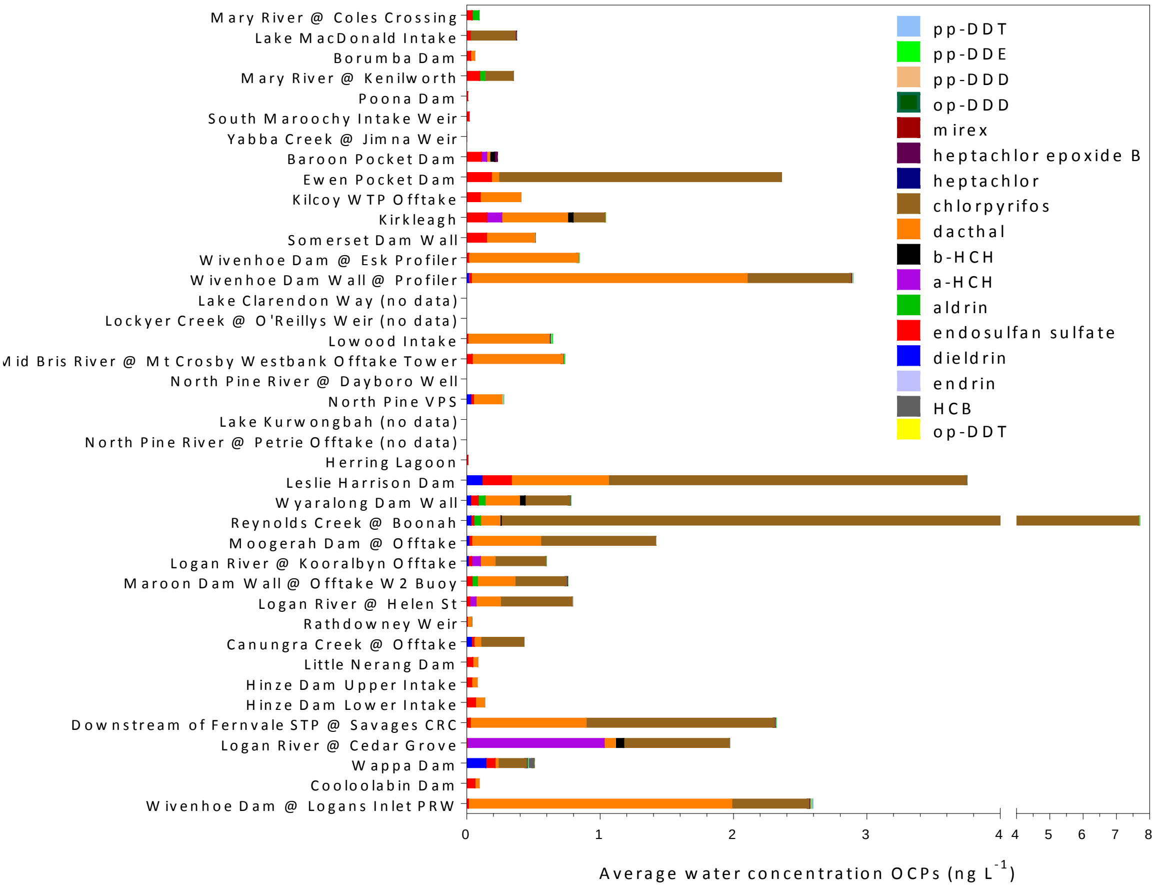

Figure 5. Total estimated water concentrations (ng L^{-1}) of 17 ΣOCPs at each site derived from PDMS passive samplers.

Polycyclic aromatic hydrocarbons (PAHs)

In total, 11 PAHs were accumulated in PDMS samplers with an average amount of ∑PAHs accumulated ranging between 0.9 – 390 ng PDMS^{-1} for sites SEQ31 (Rathdowney Weir) and SEQ38 (Wappa Dam), respectively (Table 3, Figure 6, Appendix 1). The highest frequency of detection was observed for chrysene with 47% detection, followed by benzo(e)pyrene with 39% detection and benzo(bjk)fluoranthene at 33% detection frequency.

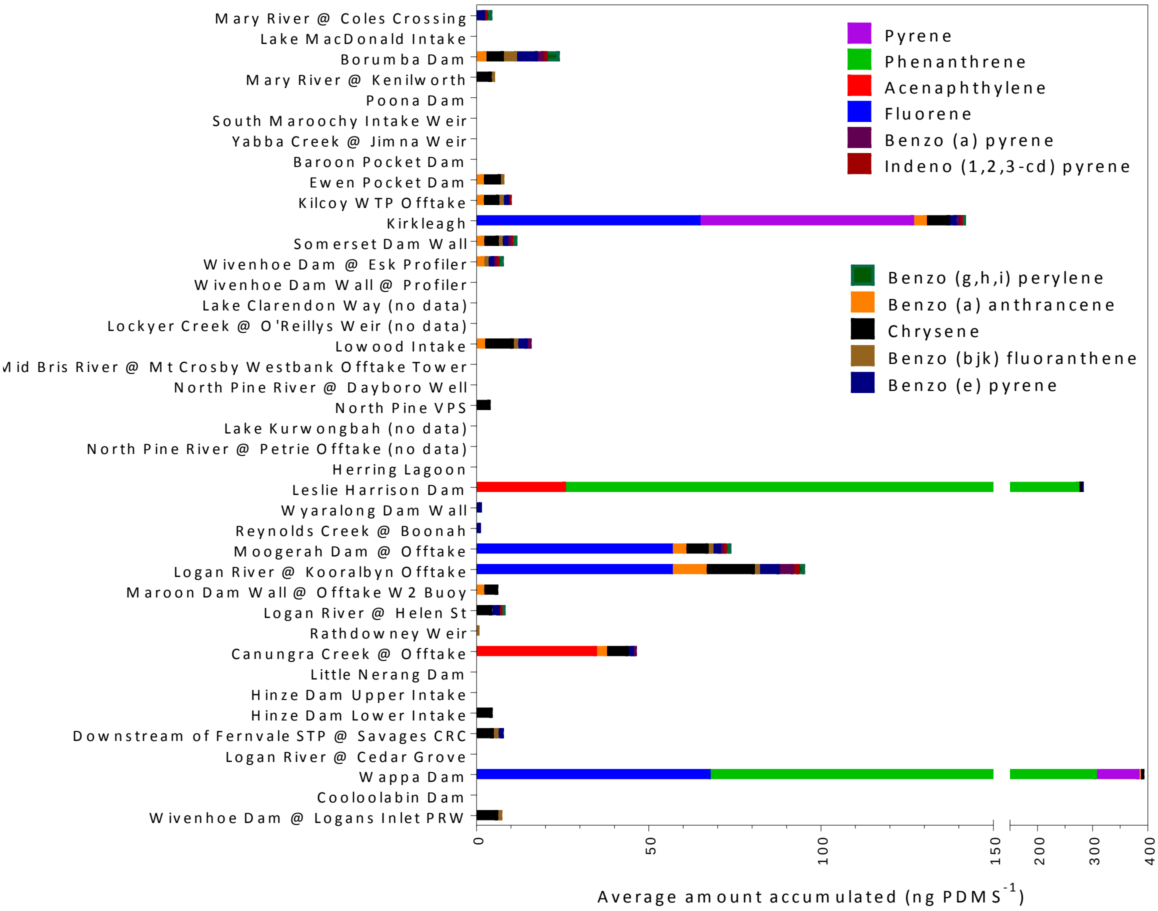

Figure 6. Total amounts (mass) of 11 ΣPAHs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

When converting the masses of accumulated PAHs in passive samplers to average water concentrations over the deployment period, concentrations of ∑PAHs ranged between 0.002 – 3.4 ng L^{-1} (Figure 7) for SEQ31 (Rathdowney Weir) and SEQ38 (Wappa Dam), respectively. Twenty-six sites had reportable water concentrations of PAHs (Appendix A).

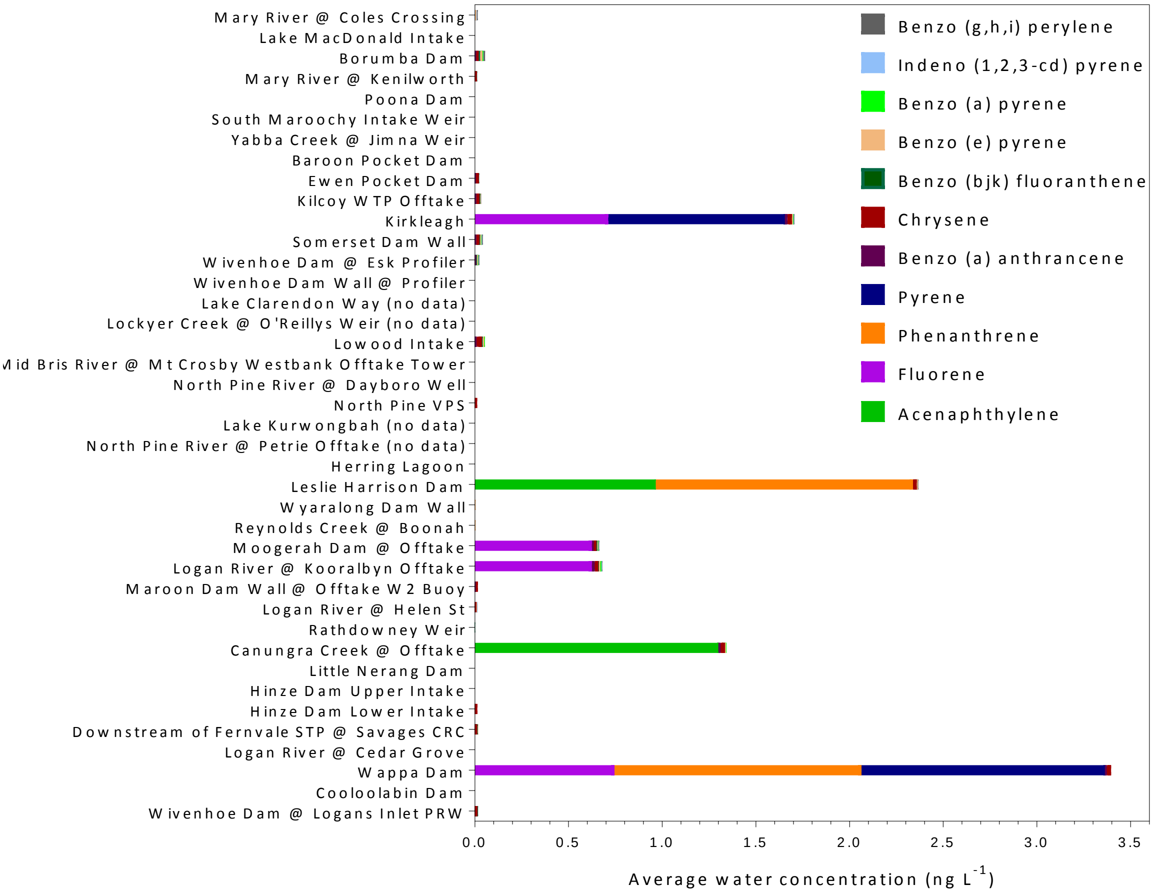

Figure 7. Total estimated water concentrations (ng L^{-1}) of 11 ΣPAHs at each site derived from PDMS passive samplers.

Herbicides and insecticides

Over the 28-30 day deployment period, 25 herbicides and insecticides accumulated in ED passive samplers (Table 3, Figure 8, Appendix 1). The average amount of ∑herbicides and insecticides accumulated ranged between 0.4 – 42 ng ED^{-1} for sites SEQ7 (Yabba Creek @ Jimna Weir) and SEQ25 (Wyaralong Dam Wall), respectively. Out of the 28 priority herbicides and pesticides, 11 were found among sites. The most frequently detected herbicides were atrazine (81%) and simazine (81%), followed by desisopropyl atrazine (75%), metsulfuron-methyl (75%) and desethyl atrazine (64%).

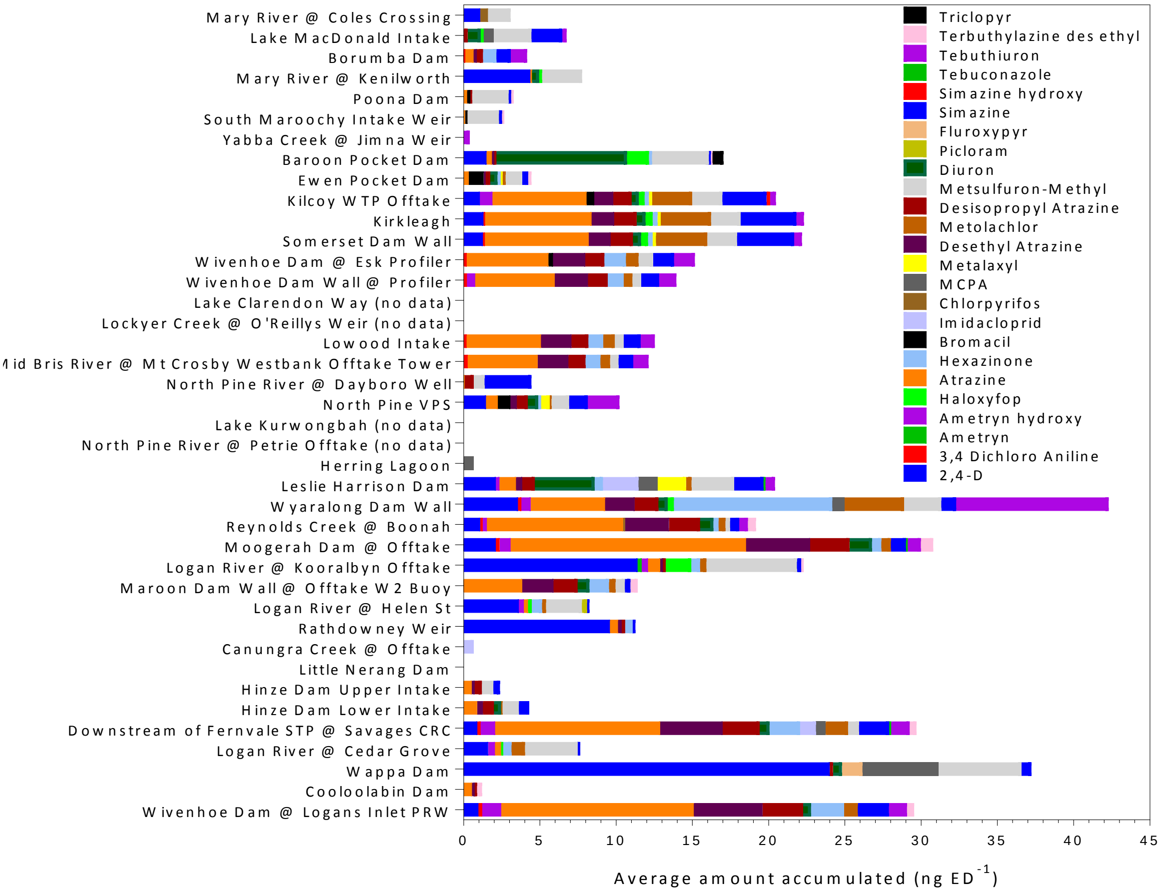

Figure 8. Total amounts (mass) of 25 Σherbicides and insecticides (ng ED^{-1}) accumulated in ED passive samplers at each site.

Water concentrations were estimated for 12 herbicides and insecticides with average ∑concentrations ranging between 0.29 – 30 ng L^{-1} for sites SEQ5 (Poona Dam) and SEQ25 (Wyaralong Dam Wall), respectively (Figure 9). Atrazine was detected in 81% of sites and had the highest total ∑concentration across all sites (68 ng L^{-1}).

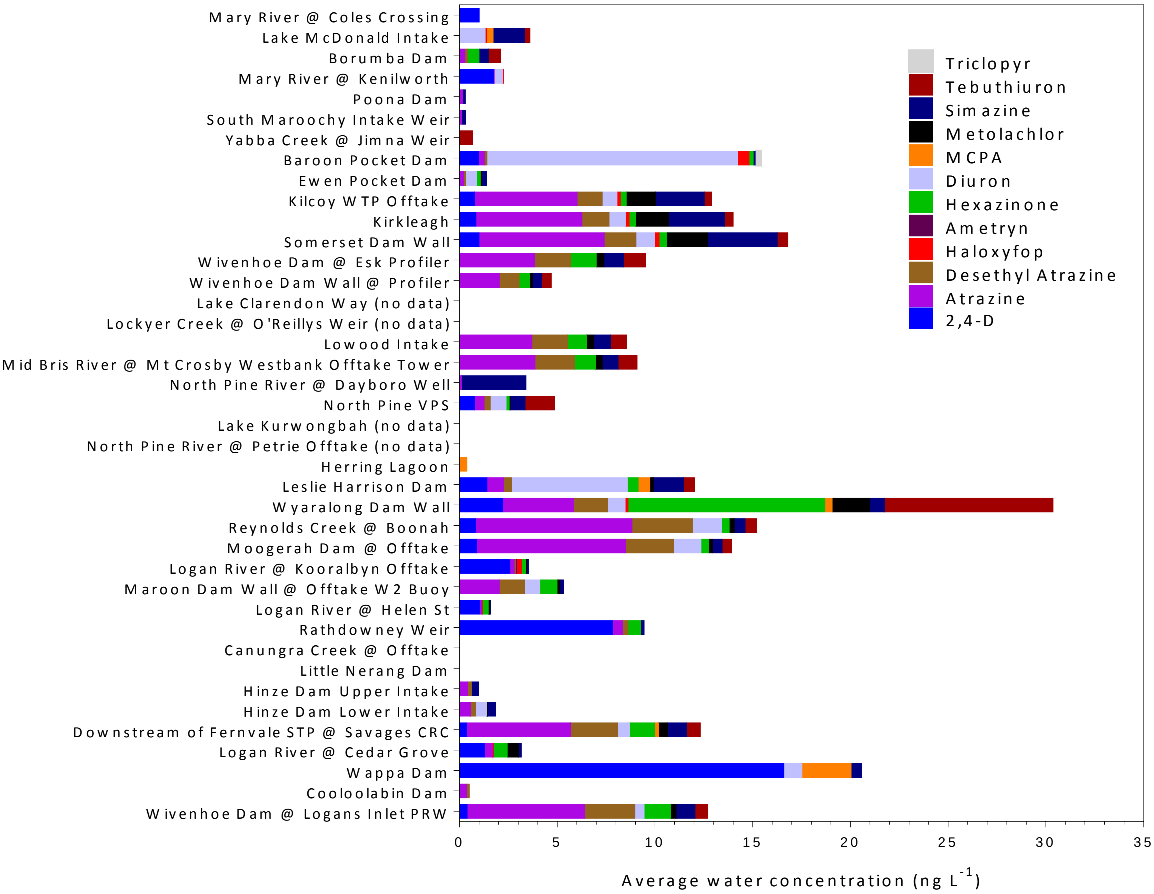

Figure 9. Total estimated water concentrations (ng L^{-1}) of 12 Σherbicides and insecticides at each site derived from ED passive samplers.

Pharmaceuticals and personal care products (PPCPs)

Fifteen PPCPs were detected with the average amount of ΣPPCPs accumulated ranging between 0.13 - 90 ng ED^{-1} at sites SEQ23 (Herring Lagoon) 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 (28 ng ED^{-1}), ibuprofen (7 ng ED^{-1}), codeine (7.4 ng ED^{-1}) and carbamazepine (5.8 ng ED^{-1}). Most frequently detected were carbamazepine with a detection frequency of 28% at low concentration (0.3 – 5.8 ng ED^{-1}), followed by paracetamol at 19% (0.1 – 0.3 ng ED^{-1}).

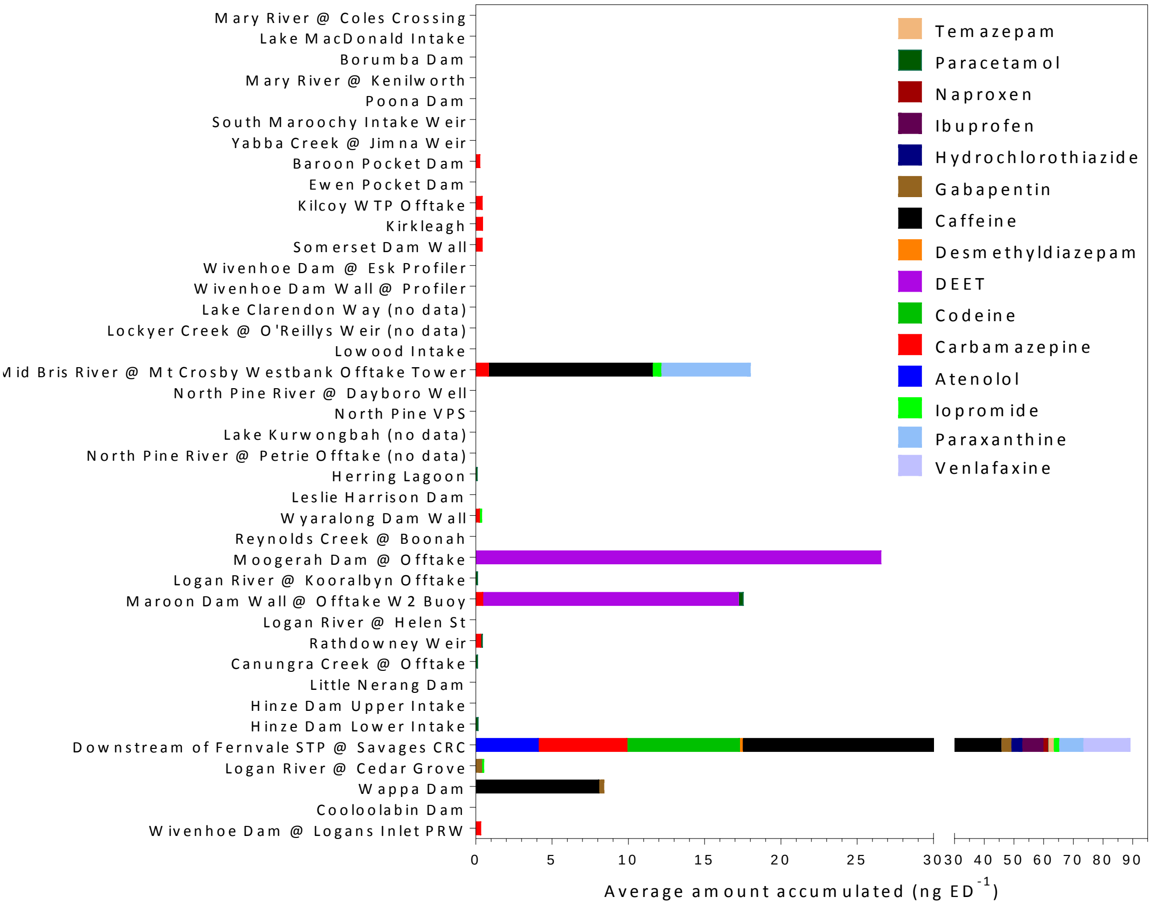

Figure 10. Total amounts (mass) of 15 ΣPPCPs (ng ED^{-1}) accumulated in ED passive samplers at each site.

When converting the masses of accumulated PPCPs in EDs to average water concentrations over the deployment period only caffeine, carbamazepine, codeine, DEET and hydrochlorothiazide can be quantified. For these PPCPs, average ∑PPCP water concentrations ranged between 0.10 – 16 ng L^{-1} for site SEQ40 (Wivenhoe Dam @ Logans Inlet PRW) and SEQ36 (Downstream of Fernvale STP @ Savages CRC), respectively (Figure 11).

Figure 11. Total estimated water concentrations (ng L^{-1}) of 5 ΣPPCPs.

Per- and poly-fluoroalkyl substances (PFASs)

Leslie Harrison Dam was the only site in this campaign to be sampled for PFASs at three location. In addition to the routine on-going passive sampling site (i.e. SEQ24 – Leslie Harrison Dam), the sites; SEQ41 – Leslie Harrison Dam @ Stockyard Creek and SEQ42 – Leslie Harrison Dam @ Tingalpa Wallaby Creek were added. Water concentrations were estimated for seven PFAS (Figure 12, Appendix 1) with total ΣPFASs concentrations ranging between 24 - 37 ng L^{-1} across sites. Each site had duplicate samplers. The total accumulated PFASs with regulatory values that is PFOS, PFHxS and PFOA, are plotted in Figure 13. The current Australian Drinking Water Guidelines 6 (2011) values for PFOS/ PFHxS combined is 70 ng L^{-1} and for PFOA 560 ng L^{-1} (Table 7).

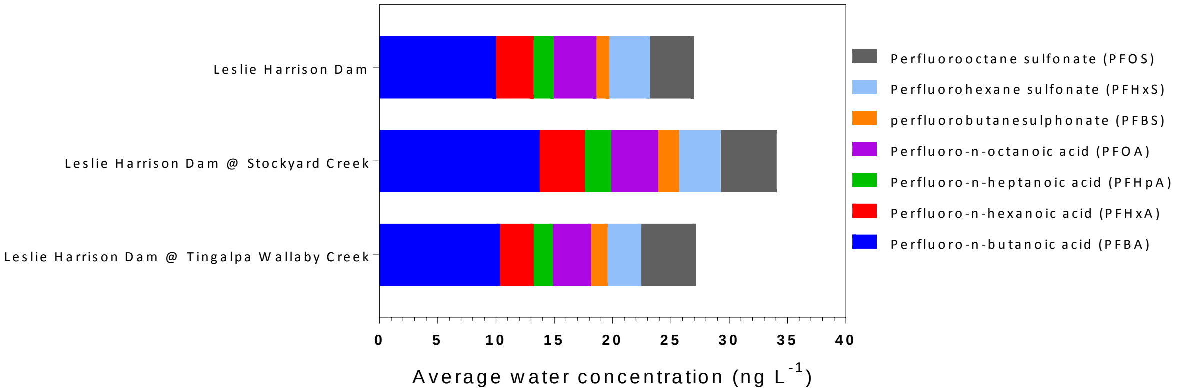

Figure 12. Total average estimated water concentrations (ng L^{-1}) of 7 PFASs detected across 3 sites within Leslie Harrison Dam.

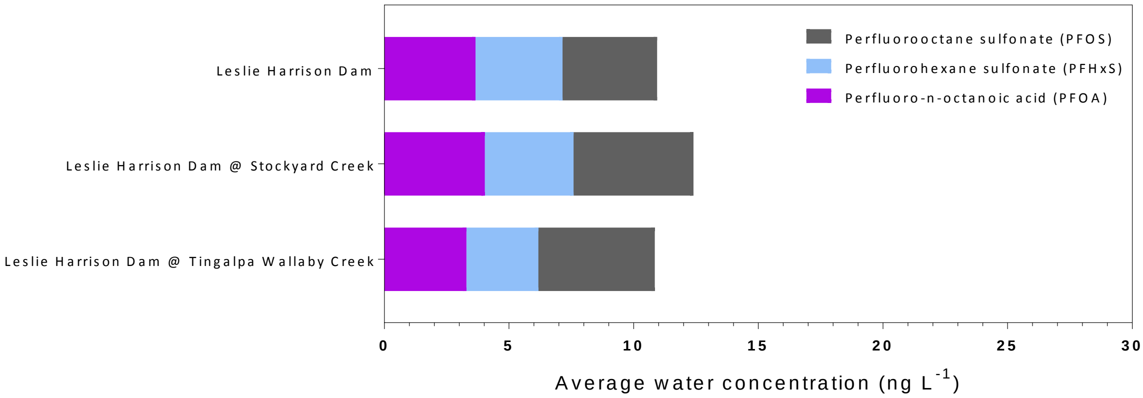

Figure 13. Total estimated water concentrations (ng L^{-1}) of PFOS, PFHxS and PFAS detected across 3 sites within Leslie Harrison Dam.

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Analysis of non-target polar chemicals

Along with the target list of 75 polar chemicals identified for investigation, 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, five non-target chemicals were detected. The suspect search tentatively identified a number of insecticides, herbicides, fungicides and antibiotics (Table 6). Any new chemicals tentatively identified here will be added to the suspect screening library list for investigation in future sampling campaigns. Performing full non-target screening on all samples is an extremely time-consuming process and will only be conducted if/when time permits. It is possible that further investigations will be carried out on specific sites and/or samples of concern if/when time permits.

Table 6. List of tentatively identified non-target chemicals in EDs, and the sites in which they were detected.

Chemical Name	Description	Sites with Tentative detects
Carbendazim	fungicide	SEQ11 (Kirkleagh)
Carbofuran	pesticides	SEQ30 (Logan River @ Helen St)
Prothiofos	insecticide	SEQ17 (Lowood Intake)
Sulphadiazine	antibiotic	SEQ28 (Logan River @ Kooralbyn Offtake), SEQ30 (Logan River @ Helen St)
Sulphamethoxazole	antibiotic	SEQ36 (Downstream of Fernvale STP @ Savages CRC)

Comparison to water quality guideline values

A comparison with a selection of available water guideline values and species protection values are provided in Table 7. No herbicides/insecticides with an available ADWG value were detected at concentrations that exceeded their drinking water guideline value. Chlorpyrifos exceeded the 99% species protection value of 0.04 ng L^{-1} at all sites but does not exceed the 95% species protection value of 10 ng L^{-1} with the lowest detected at 0.2 ng L^{-1} and the highest detected at 7.8 ng L^{-1}.

Although globally and in Australia, bans and restrictions have been applied on some PFASs (i.e. PFOS and PFOA) due to their possible toxicity, it is estimated that thousands of formulations and precursor products are in existence and that their persistence in the environment is predicted to remain a problem for decades to come (Wang *et al.* 2017). Therefore, the monitoring of these chemicals in water systems (predominantly drinking and recreational systems) is of the utmost importance. The highest concentrations detected of PFOA, and PFOS/ PFHxS (for which regulatory guidelines are available, Table 7) across monitoring sites at Leslie Harrison Dam are 120, and 6 times below the current regulatory guidelines in Australia, respectively.

Table 7. Threshold chemical guidelines for Australian Drinking Water and Freshwater Aquatic Ecosystems.

ANZECC & ANCANZ (2000) Trigger values for freshwater			
	Australian Drinking Water Guidelines 6 (2011) (ng L^{-1})	**99% species protection (ng L^{-1})**	**95% species protection (ng L^{-1})**
Herbicides & Insecticides			
Atrazine	20000	700	13000
Bromacil	400000	N/A	N/A
Diazinon	4000	0.03	10
Diuron	20000	N/A	N/A
Haloxyfop	1000	N/A	N/A
Hexazinone	400000	N/A	N/A
Metolachlor	300000	N/A	N/A
Metsulfuron methyl	40000	N/A	N/A
Simazine	20000	200	3200
Tebuthiuron	N/A	20	2200
Triclopyr	20000	N/A	N/A
2,4-D	30000	140000	280000
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
PFAS			
PFBA	N/A	N/A	N/A
PFPeA	N/A	N/A	N/A
PFHxA	N/A	N/A	N/A
PFHpA	N/A	N/A	N/A
PFOA	560	N/A	N/A
PFNA	N/A	N/A	N/A
PFDA	N/A	N/A	N/A
PFBS	N/A	N/A	N/A
PFHxS/ PFOS	70	N/A	N/A
PFDS	N/A	N/A	N/A

6:2 FTS	N/A	N/A	N/A

Conclusion

A wide range of organic micro-pollutants were detected at all thirty-six sampling locations during the winter 2018 deployment period. In summary, 17 OCPs were detected at all monitoring sites; the majority of chemicals were present at very low levels (< 8 ng L^{-1} ΣOCPs per sites) which may indicate residue background levels because of years of persistent use and subsequent deregulation. Most site profiles are dominated by endosulfan sulfate, dacthal, op-DDD, pp-DDD 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. Chlorpyrifos across all sites falls between the 99% and 95% species protection value, with the lowest detected at 0.2 ng L^{-1} and the highest detected at 7.8 ng L^{-1}.

PAHs were detected at 18 sites with profiles dominated by chrysene, benzo(e)pyrene, benzo(bjk)fluoranthene and benzo(a)anthracene (Table 3). Maximum ΣPAHs were below 3.4 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).

Herbicides and insecticides were detected at 29 (81%) of sites with 10 out of 25 detected falling within the priority category. The highest total Σherbicides and insecticides detected was 30 ng L^{-1} (SEQ25 Wyaralong Dam Wall). Triazine class herbicides were the most commonly detected with frequencies of detection of 81%, 75% for atrazine and desisopropyl Atrazine and 81% for simazine, followed by metsulfuron-methyl with a frequency of detection at 75%. 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 2000).

PPCPs were found at 15 out of 38 sites with site SEQ36 (Downstream of Fernvale STP @ Savages CRC) containing the highest PPCPs with total concentrations of 16 ng L^{-1}. The predominant PPCP was carbamazepine at 28% detection, 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.

Passive (PE) samplers were deployed in duplicate for Leslie Harrison Dam with three monitoring sites (SEQ24, SEQ41 and SEQ42) to detect levels of per- and poly-fluoroalkyl substances (PFAS). This is a follow up from last report as the highest total ΣPFAS concentrations were observed at site SEQ24 (Leslie Harrison Dam) from report 8, the summer 2018 campaign (Kaserzon *et al*, 2018). The total ΣPFAS concentrations in this sampling season ranged from 24 to 37 ng L^{-1}. Extensive historic use of per- and polyfluoroalkyl substances (PFAS) as key ingredients in numerous domestic, industrial and commercial applications including in aqueous film forming foams (AFFF) has led to widespread environmental contamination. The moderate water solubility of these compounds means they are often found in aquatic environments, and transport via waterways appears to be a major distribution pathway both locally and globally (Giesy & Kannan 2002).

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.
- The addition of PFAS samplers has revealed the presence of these pollutants in water systems and it is therefore recommended to continue sampling for these chemicals to better understand occurrences, distributions and trend.
- 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.

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Appendix 1

See enclosed excel file ‘SEQW results_Summer2018.xls’

Reporting sheet listing all micro-pollutants investigated, levels accumulated in PDMS, ED and PE passive samplers (ng sampler^{-1}) and estimated average water concentrations over the deployment periods (ng L^{-1}) (28-30 days).