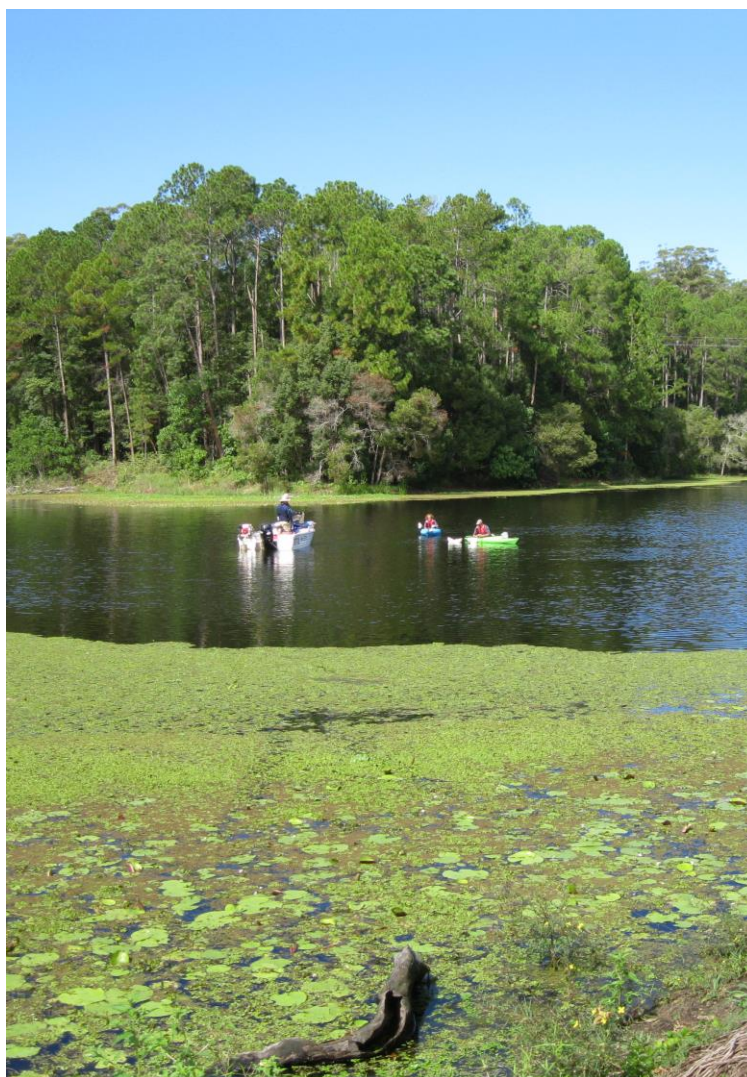




Queensland Alliance for  
Environmental Health Sciences



Prepared for Seqwater  
by Sarit Kaserzon and  
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# Catchment and Drinking Water Quality Micro Pollutant Monitoring Program – Passive Sampling

Report 8 – Summer 2018

**Title**

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

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## Executive Summary

The Catchment and Drinking Water Quality Micro Pollutant Monitoring Program 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 to July 2018 and represents the eighth 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 targeted, including herbicides, pharmaceuticals and personal care products (PPCPs), organochlorine pesticides (OCPs), other pesticides, and polycyclic aromatic hydrocarbons (PAHs), by deploying passive samplers. In addition, the eighth sampling campaign represents the first campaign to include results of glyphosate and its metabolite aminomethylphosphonic acid (AMPA) as well as per- and poly-fluoroalkyl substances (PFAS). 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-MS/MS (non-polar chemicals) using the latest analytical methods and established standard operating protocols (SOPs).

Chemical analyses of the passive sampler extracts detected 76 different chemicals including 23 OCPs (and pesticides), 11 PAHs, 35 herbicides and insecticides and 14 PPCPs. OCPs were detected at all sampling locations, with endosulfan sulfate, dacthal, heptachlor epoxide B, and pp-DDE being the most prevalent between sites and chlorpyrifos showing the highest total concentration. Total  $\Sigma$ OCP water concentrations across sites ranged between 0.085 to 27 ng L<sup>-1</sup>. PAHs were detected at 92% of sites with fluoranthene > pyrene > chrysene present at the highest concentrations. Fluoranthene was the most abundant, followed by pyrene. Total  $\Sigma$ PAH water concentrations across sites ranged between 0.001 – 2.8 ng L<sup>-1</sup>. Herbicides/insecticides were detected at all sampling locations. Atrazine, desethyl atrazine and desisopropyl atrazine were present in high abundance and/or concentration, as well as diuron, metolachlor and simazine. Total estimated  $\Sigma$ herbicide water concentrations across all sites ranged between 0.16 – 77 ng L<sup>-1</sup>. Fourteen PPCPs were detected at 13 out of 37 sites. Carbamazepine was present in the highest abundance at 35% of sites, followed by gabapentin at 27%. Total estimated  $\Sigma$ PPCP water concentrations ranged between 0.08 – 19 ng L<sup>-1</sup>. Australian Drinking Water Guidelines (ADWG) and guidelines for freshwater aquatic systems values are available for some of these chemicals for comparison.

## 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  $\geq 1$  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 for the monitoring of glyphosate and aminomethylphosphonic acid (AMPA) as well as per- and poly-fluoroalkyl substances (PFAS).

The list of target chemicals for inclusion in the monitoring campaign was identified by reviewing of Australian Drinking Water Guideline (ADWG) and Australian and New Zealand Environmental Conservation Council (ANZECC) listed parameters. The list was narrowed down based on an assessment of their possible application in the catchment areas and assessment from Australian Pesticides and Veterinary Medicines Authority (AVMPA) registered products applications, as well as water solubility and guideline values. A review of the target list is conducted every six months to investigate the need for inclusion / exclusion of target analytes from the list based on risk assessment and detection frequency. This report presents data from the eighth monitoring campaign.



## Methodology

Passive water samplers were deployed in 37 sites of SEQ reservoirs/waterways from February to April 2018 over a period of 28 - 33 days. For instances where the deployment exceeded the desired deployment period, replacement samplers were re-deployed (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. For this campaign, site SEQ15 (Lockyer Creek @ Lake Clarendon Way) and SEQ16 (Lockyer Creek @ O’Reilly’s Weir) were inactive whereas site SEQ28 (Logan River @ Kooralbyn Offtake) was not deployed due to weather conditions. In addition, replicate samplers were selected randomly and deployed at six sites (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	SEQ-MARY RIVER @ COLES CROSSING	15/02/2018	15/03/2018	28	16.96	ED and PDMS
SEQ2	LMD-SP001	SEQ-LAKE MACDONALD INTAKE	13/02/2018	13/03/2018	28	5.88	ED and PDMS
SEQ3	BOD-SP001	SEQ-BORUMBA DAM	15/02/2018	15/03/2018	28	7.30	ED and PDMS
SEQ4	MRS-SP013	SEQ-MARY RIVER @ KENILWORTH	15/02/2018	4/04/2018	48	9.58	PDMS only. Over deployed, ED/PFM redeployed.
SEQ4**	MRS-SP013	SEQ-MARY RIVER @ KENILWORTH	4/04/2018	2/05/2018	28	20.83	ED only. Replacement result.
SEQ4*	MRS-SP013	SEQ-MARY RIVER @ KENILWORTH	4/04/2018	2/05/2018	28	20.83	ED only. Replacement result. Replicate.
SEQ5	POD-SP001	SEQ-POONA DAM	20/02/2018	20/03/2018	28	8.42	ED and PDMS
SEQ6	SOR-SP001	SEQ-SOUTH MAROOCHY INTAKE WEIR	20/02/2018	20/03/2018	28	4.58	ED and PDMS
SEQ7	YAC-SP001	SEQ-YABBA CREEK @ JIMNA WEIR	21/02/2018	22/03/2018	29	3.72	ED and PDMS
SEQ8	BPD-SP001	SEQ-BAROON POCKET DAM	8/02/2018	8/03/2018	28	4.93	ED and PDMS
SEQ9	EMD-SP001	SEQ-EWEN MADDOCK INTAKE	22/02/2018	22/03/2018	28	8.54	ED and PDMS
SEQ10	SOD-SP010	SEQ-KILCOY WTP OFFTAKE	14/02/2018	14/03/2018	28	5.78	ED and PDMS
SEQ11	SOD-SP011	SEQ-KIRKLEAGH	14/02/2018	14/03/2018	28	7.77	ED and PDMS
SEQ12	SOD-SP001	SEQ-SOMERSET DAM WALL	14/02/2018	14/03/2018	28	6.18	ED and PDMS
SEQ13	WID-SP004	SEQ-WIVENHOE DAM @ ESK PROFILER	12/02/2018	12/03/2018	28	8.50	ED and PDMS
SEQ14	WID-SP001	SEQ-WIVENHOE DAM WALL @ PROFILER	15/02/2018	15/03/2018	28	11.22	ED and PDMS
SEQ15	LOC-SP034	SEQ-LOCKYER CREEK @ LAKE CLARENDON WAY	n/a	n/a	n/a	n/a	Site not active due to low water levels
SEQ16	LOC-SP031	SEQ-LOCKYER CREEK @ O'REILLYS WEIR	n/a	n/a	n/a	n/a	Site not active due to low water levels
SEQ17	MBR-SP016	SEQ-LOWOOD INTAKE	27/03/2018	24/04/2018	28	6.84	ED and PDMS. Deployed late.
SEQ18	MBR-SP001	SEQ-MID BRIS RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER	19/02/2018	21/03/2018	30	6.30	ED and PDMS.
SEQ18*	MBR-SP001	SEQ-MID BRIS RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER	19/02/2018	21/03/2018	30	6.30	ED and PDMS. Replicate.
SEQ19	NOD-SP091	SEQ-NORTH PINE RIVER @ DAYBORO WELL	6/02/2018	29/03/2018	51	8.63	PDMS only. Over deployed, ED/PFM redeployed.
SEQ19**	NOD-SP091	SEQ-NORTH PINE RIVER @ DAYBORO WELL	29/03/2018	1/05/2018	33	6.59	ED only. Replacement result.
SEQ20	NOD-SP001	SEQ-NORTH PINE VPS	6/02/2018	6/03/2018	28	6.12	ED and PDMS
SEQ21	LAK-SP001	SEQ-LAKE KURWONGBAH	6/02/2018	6/03/2018	28	4.30	ED and PDMS
SEQ22	NOD-SP023	SEQ-NORTH PINE RIVER @ PETRIE OFFTAKE	7/02/2018	14/03/2018	35	4.41	PDMS only. Over deployed, ED/PFM redeployed.
SEQ22**	NOD-SP023	SEQ-NORTH PINE RIVER @ PETRIE OFFTAKE	29/03/2018	1/05/2018	33	4.78	ED only. Replacement result.

SEQ23***	NSC-SP001	SEQ-HERRING LAGOON	13/02/2018	13/03/2018	28	2.85	ED and PDMS
SEQ24	LHD-SP005	SEQ-LESLIE HARRISON DAM	7/02/2018	7/03/2018	28	6.21	ED and PDMS
SEQ25	WYD-SP001	SEQ-WYARALONG DAM WALL	7/02/2018	7/03/2018	28	7.17	ED and PDMS
SEQ26	MOD-SP027	REYNOLDS CREEK @ BOONAH	9/02/2018	9/03/2018	28	4.03	ED and PDMS
SEQ27	MOD-SP002	SEQ-MOOGERAH DAM @ OFFTAKE	9/02/2018	9/03/2018	28	5.14	ED and PDMS
SEQ28	LRS-SP017	SEQ-LOGAN RIVER @ KOORALBYN OFFTAKE	n/a	n/a	n/a	n/a	Deployment not possible due to weather conditions
SEQ29	MAD-SP004	SEQ-MAROON DAM WALL @ OFFTAKE W2 BUOY	9/02/2018	9/03/2018	28	7.53	ED and PDMS
SEQ30	LRS-SP013	SEQ-LOGAN RIVER @ HELEN ST	8/02/2018	28/03/2018	48	10.41	PDMS only. Over deployed, ED/PFM redeployed.
SEQ30**	LRS-SP013	SEQ-LOGAN RIVER @ HELEN ST	28/03/2018	26/04/2018	29	20.11	ED only. Replacement result.
SEQ31	LRS-SP016	SEQ-RATHDOWNEY WEIR	8/02/2018	28/03/2018	48	7.67	PDMS only. Over deployed, ED/PFM redeployed.
SEQ31**	LRS-SP016	SEQ-RATHDOWNEY WEIR	28/03/2018	26/04/2018	29	4.74	ED only. Replacement result.
SEQ32	CAC-SP001	SEQ-CANUNGRA CREEK @ OFFTAKE	12/02/2018	12/03/2018	28	3.86	ED and PDMS
SEQ33	LND-SP014	SEQ-LITTLE NERANG DAM	28/02/2018	28/03/2018	28	4.09	ED and PDMS
SEQ34	HID-SP001	SEQ-HINZE DAM UPPER INTAKE	12/02/2018	12/03/2018	28	5.97	ED and PDMS
SEQ35	HID-SP002	SEQ-HINZE DAM LOWER INTAKE	12/02/2018	12/03/2018	28	9.83	ED and PDMS
SEQ36	MBR-SP013	SEQ-DOWNSTREAM OF FERVALE STP @ SAVAGES CRC	19/02/2018	21/03/2018	30	8.62	ED and PDMS
SEQ37	LRS_SP012	SEQ-CEDAR GROVE WEIR	8/02/2018	8/03/2018	28	9.61	ED and PDMS
SEQ37*	LRS_SP012	SEQ-CEDAR GROVE WEIR	8/02/2018	8/03/2018	28	9.61	ED and PDMS. Replicate.
SEQ38	WAD-SP001	SEQ-WAPPA DAM	22/02/2018	22/03/2018	28	4.45	ED and PDMS
SEQ38*	WAD-SP001	SEQ-WAPPA DAM	22/02/2018	22/03/2018	28	4.45	ED and PDMS. Replicate.
SEQ39	COD-SP001	SEQ-COOLLOOLABIN DAM	20/02/2018	20/03/2018	28	5.87	ED and PDMS
SEQ39*	COD-SP001	SEQ-COOLLOOLABIN DAM	20/02/2018	20/03/2018	28	5.87	ED and PDMS. Replicate.
SEQ40	WID-SP061	SEQ-WIVENHOE DAM @ LOGANS INLET PRW	15/02/2018	15/03/2018	28	9.08	ED and PDMS
SEQ40*	WID-SP061	SEQ- WIVENHOE DAM @ LOGANS INLET PRW	15/02/2018	15/03/2018	28	9.08	ED and PDMS. Replicate.



### Passive sampler preparation and extraction

For this campaign, four 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 hydrophilic 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) passive samplers filled with titanium dioxide and agarose gel to detect the presence of glyphosate and its metabolite aminomethylphosphonic acid (AMPA) as well as novel PE samplers filled with Strata X-AW anion exchange sorbent 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. Novel PE passive samplers for detection of glyphosate/AMPA and PFAS were prepared and extracted according to standard operation procedures (SOP) developed at QAEHS (Table 2).



Figure 1. From left to right. Preparation of PDMS strip in stainless steel cage, preparation and assembly of ED samplers and deployment setup for a PE 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) and separately for glyphosate/ AMPA.

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) and glyphosate/ AMPA 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.*

$$C_w = \frac{C_s \times M_s}{R_s \times t} = \frac{N_s}{R_s \times t}$$

*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 concentration in the blank sampler for it to be included in the data. Results were not subtracted for detections in blank samples. Results for all blank samples are reported in the Appendix 1.

Replicate ED and PDMS passive sampler sites were randomly chosen and deployed in site SEQ4 (Mary River @ Kenilworth), SEQ18 (Mid Bris River @ Mt Crosby Westbank Offtake Tower), SEQ37 (Cedar Grove Weir), SEQ38 (Wappa Dam), SEQ39 (Cooloolabin Dam) and SEQ40 (Wivenhoe Dam @ Logans Inlet PRW) (Table 1). Acceptable replicate values (within < 67 %) were typically observed for passive sampler replicates deployed, except for metolachlor, atrazine, imidacloprid, hexazinone, desisopropyl atrazin, desethyl Atrazine, and ametryn hydroxy at SEQ30 (<135%) and 2,4-D at SEQ4 (100%). Only values that were significantly above blank background levels (> x3 blk level) are reported. PE samplers were deployed in duplicate at all sites for glyphosate and PFAS. Replicate values were within 20% CV and 6% CV for glyphosate and AMPA, respectively. For PFAS coefficient of variation of replicate samplers were between 2 - 67% (with the exception of one site at 115% (i.e. PFOS at SEQ40 Wivenhoe Dam @ Logans Inlet PRW).

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 SOPs by QAEHS 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-A-010	Analysis of Glyphosate/AMPA in Water Extracts
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-P-016a	Preparation of PE (Polyethylene) Tubes for Glyphosate and AMPA Passive Sampling
NTX-P-016b	Extraction of Glyphosate and AMPA from PE (Polyethylene) 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 SEQ18 (Mid Bris River @ Mt Crosby Westbank offtake tower), SEQ30 (Logan River @ Helen St), SEQ21 (Lake Kurwongbah) and SEQ4 (Mary River @ Kenilworth) with a >60% agreement. Average flow velocities estimated from PFMs over the deployment period ranged between  $2.85 \text{ cm s}^{-1}$  (SEQ23 Herring Lagoon) –  $20.83 \text{ cm s}^{-1}$  (SEQ4 MRS-SP013 Mary River @ Kenilworth). Low flow that falls below the linearity loss rate range of the PFM (i.e.  $< 3.4 \text{ cm s}^{-1}$ ; O'Brien *et al.* 2009) was observed at site SEQ23 NSC-SP001 Herring Lagoon (Table 1 and Figure 1).

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  $3.4 \text{ cm s}^{-1}$  or PFM loss rate equal to  $0.58 \text{ g d}^{-1}$ ; 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  $3.4 \text{ cm s}^{-1}$  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.

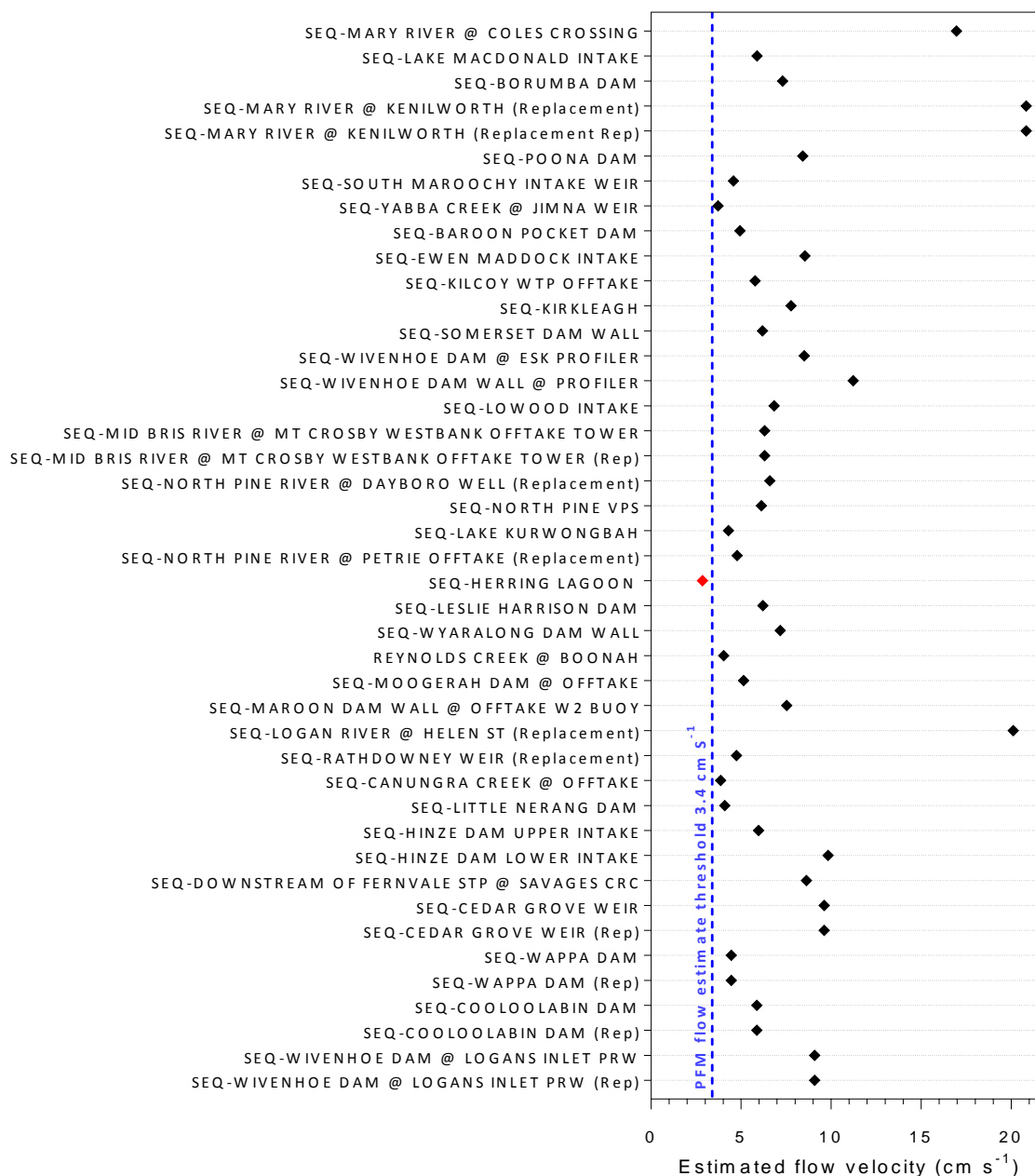


Figure 2. Passive flow monitor (PFM) based average water flow rate estimations at the deployment sites ( $n=37$ ). A minimum flow velocity of  $3.4 \text{ cm s}^{-1}$  is required in order to assess flow velocity using Passive Flow Monitors (PFMs). SEQ-HERRING LAGOON was the only site during this campaign to fall below the minimum flow velocity.

### 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<sup>-1</sup>) is presented in Table 3 to Table 6 below. Table 3 summarises the non-polar chemicals detected with PDMS (OCPs, pesticides and PAHs). A total of 23 OCPs and pesticides and 11 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% – 100% (for OCPs) and 3% – 92% (for PAHs). Table 4 summarises the polar chemicals detected with EDs (herbicides, insecticides and PPCPs). A total of 35 herbicides/ insecticides and 14 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3%-100% (for herbicides and insecticides) and 3% - 35% (for PPCPs). Table 5 summarises the glyphosate/ AMPA detected with PE samplers. The glyphosate/ AMPA accumulated in the PE samplers with percent detection at sampling sites ranging from 11% to 30%. Table 6 summarises the PFAS detected with PE samplers. The PFAS accumulated in the PE samplers with percent detection at sampling sites ranging from 3% to 76%. 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, percentage of detection at the sites and the range of mass accumulated over 28-33 days (ng PDMS<sup>-1</sup>).

	Numbers of site detected (n = 37)	% detection	Min detect (ng PDMS <sup>-1</sup> )	Max detect (ng PDMS <sup>-1</sup> )
<b>Organochlorine pesticides (OCPs)</b>				
α-endosulfan	22	59	0.33	1.0
α-HCH	25	68	0.03	6.9
aldrin	14	38	10	23
β-HCH	3	8	0.09	1.5
chlorpyrifos	34	92	6.80	1700
cis-chlordane (a)	12	32	0.57	1.0
dacthal	36	97	0.47	140
dieldrin	29	78	5.40	70
endosulfan sulfate	37	100	0.12	8.8
endrin	22	59	0.057	0.57
endrin aldehyde	2	5	0.54	0.56
endrin ketone	3	8	0.08	2.2
HCB	2	5	2.50	2.7
heptachlor	7	19	0.80	1.0
heptachlor epoxide B	36	97	0.14	14
op-DDD	23	62	0.09	3.1
op-DDE	4	11	0.04	0.39
op-DDT	23	62	0.01	0.76
pp-DDD	33	89	0.07	13
pp-DDE	36	97	0.09	16
pp-DDT	29	78	0.14	5.2
r-HCH (lindane)	1	3	0.91	0.91
trans-chlordane (r)	19	51	1.2	4.7
<b>Polycyclic aromatic hydrocarbons (PAHs)</b>				
Acenaphthylene	1	3	13	13
Anthracene	2	5	16	21
Fluoranthene	17	46	21	160
Pyrene	10	27	27	100
Benzo (a) anthracene	15	41	1.2	13
Chrysene	32	86	3.0	16
Benzo (b,j,k) fluoranthene	32	86	0.4	5.3
Benzo (e) pyrene	34	92	0.5	7.3
Benzo (a) pyrene	15	41	0.3	2.4
Indeno (1,2,3-cd) pyrene	7	19	0.6	3.0
Benzo (g,h,i) perylene	24	65	0.3	5.2

Table 4. Summary of the number of chemicals accumulated in EDs, percentage of detection at the sites and the range of mass accumulated over 28-33 days (ng ED<sup>-1</sup>).

	Numbers of site detected (n = 37)	% detection	Min detect (ng ED <sup>-1</sup> )	Max detect (ng ED <sup>-1</sup> )
<b>Herbicides and Insecticides</b>				
2,4-D	31	84	0.49	12
2,4-DB	3	8	0.61	18
245-T	1	3	0.15	0.15
Ametryn	2	5	0.14	0.14
Ametryn hydroxy	26	70	0.11	3.4
Atrazine	37	100	0.16	49
Bromacil	3	8	0.35	0.79
Desethyl Atrazine	36	97	0.13	8
Desisopropyl Atrazine	36	97	0.10	8.7
Diazinon	9	24	0.12	0.99
Diuron	33	89	0.13	10
Fluazifop	2	5	0.15	1.3
Haloxyfop	9	24	0.28	3.3
Hexazinone	26	70	0.24	17
Imazethapyr	2	5	0.22	0.30
Imidacloprid	20	54	0.31	3.6
MCPA	22	59	0.38	14
Metalaxyl	12	32	0.10	4.1
Methomyl	3	8	0.09	0.21
Metolachlor	32	86	0.15	124
Metribuzin	4	11	0.11	3.4
Metsulfuron-Methyl	31	84	0.65	9.5
Pendimethalin	1	3	0.34	0.34
Picloram	4	11	0.33	0.59
Prometryn	7	19	0.05	1.7
Propazine	7	19	0.06	0.24
Propiconazole	6	16	0.22	0.83
Propoxur	1	3	0.24	0.24
Simazine	31	84	0.14	56
Simazine hydroxy	19	51	0.15	1.9
Tebuconazole	14	38	0.10	1.4
Tebuthiuron	25	68	0.12	15
Terbuthylazine	11	30	0.13	2.6
Terbuthylazine des ethyl	21	57	0.21	0.91
Triclopyr	19	51	0.16	15
<b>Pharmaceuticals and personal care products (PPCPs)</b>				
Acesulfame	1	3	0.25	0.25
Atenolol	2	5	0.97	5.3
Caffeine	1	3	53	53

Carbamazepine	13	35	0.31	19
Codeine	1	3	3.3	3.3
Fluoxetine	1	3	16	16
Gabapentin	10	27	0.17	4.4
Hydrochlorothiazide	4	11	0.15	3.2
Ibuprofen	1	3	22	22
Iopromide	4	11	0.28	16
Paracetamol	1	3	80	80
Temazepam	5	14	0.37	6.0
Tramadol	1	3	0.62	0.62
Venlafaxine	2	5	4.1	17

Table 5. Summary of glyphosate/ AMPA accumulated in PEs, percentage of detection at the sites and the range of mass accumulated over 28-33 days ( $ng PE^{-1}$ ).

	Numbers of site detected (n = 37)	% detection	Min detect ( $ng PE^{-1}$ )	Max detect ( $ng PE^{-1}$ )
<b>Glyphosate/ Aminomethylphosphonic acid (AMPA)</b>				
Glyphosate	11	30	1.33	76.01
AMPA	4	11	9.90	60.53

Table 6. Summary of PFAS accumulated in PEs, percentage of detection at the sites and the range of mass accumulated over 28-33 -days ( $ng PE^{-1}$ ).

	Numbers of site detected (n = 37)	% detection	Min detect ( $ng PE^{-1}$ )	Max detect ( $ng PE^{-1}$ )
<b>Per- and poly-fluoroalkyl substances (PFAS)</b>				
Perfluoro-n-butanoic acid (PFBA)	20	54	0.41	0.86
Perfluoro-n-pentanoic acid (PFPeA)	22	60	0.14	0.58
Perfluoro-n-hexanoic acid (PFHxA)	8	22	0.11	0.58
Perfluoro-n-heptanoic acid (PFHpA)	5	14	0.30	0.46
Perfluoro-n-octanoic acid (PFOA)	28	76	0.05	0.77
Perfluoro-n-nonanoic acid (PFNA)	2	5	0.09	0.15
Perfluoro-n-decanoic acid (PFDA)	1	3	0.17	0.17
Potassium perfluoro-1-butananesulfonate (PFBS)	11	30	0.08	0.26
Perfluorohexane sulfonate (PFHxS)	15	41	0.06	0.74
Perfluorooctane sulfonate (PFOS)	27	73	0.06	1.10
Sodium perfluoro-1-decanesulfonate (PFDS)	1	3	1.44	1.44
Sodium 1H, 1H, 2H, 2H-perfluorooctane sulfonate (6:2 FTS)	6	16	0.07	0.15

## Organochlorine pesticides (OCPs)

In total, 23 OCPs and pesticides were accumulated in PDMS samplers over the 28 – 33 day deployment period (Table 3, Figure 3, Appendix 1), with the amount of  $\Sigma$ OCPs accumulated ranging between 2.96 – 1895 ng PDMS<sup>-1</sup> for sites SEQ33 (Little Nerang Dam) and SEQ36 (Downstream of Fernvale STP @ Savages CRC), respectively.

The highest frequency of detection was observed for endosulfan sulfate (100%) followed by dacthal, heptachlor epoxide B, and pp-DDE, at 97% detection each. Highest accumulation was observed for chlorpyrifos at 1700 ng PDMS<sup>-1</sup> followed by dacthal at 140 ng PDMS<sup>-1</sup> both from site SEQ36, downstream of Fernvale STP @ Savages CRC. The OCPs accumulated in the greatest abundance between sites were chlorpyrifos (6160 ng PDMS<sup>-1</sup>) > dacthal (560 ng PDMS<sup>-1</sup>) > dieldrin (450 ng PDMS<sup>-1</sup>).

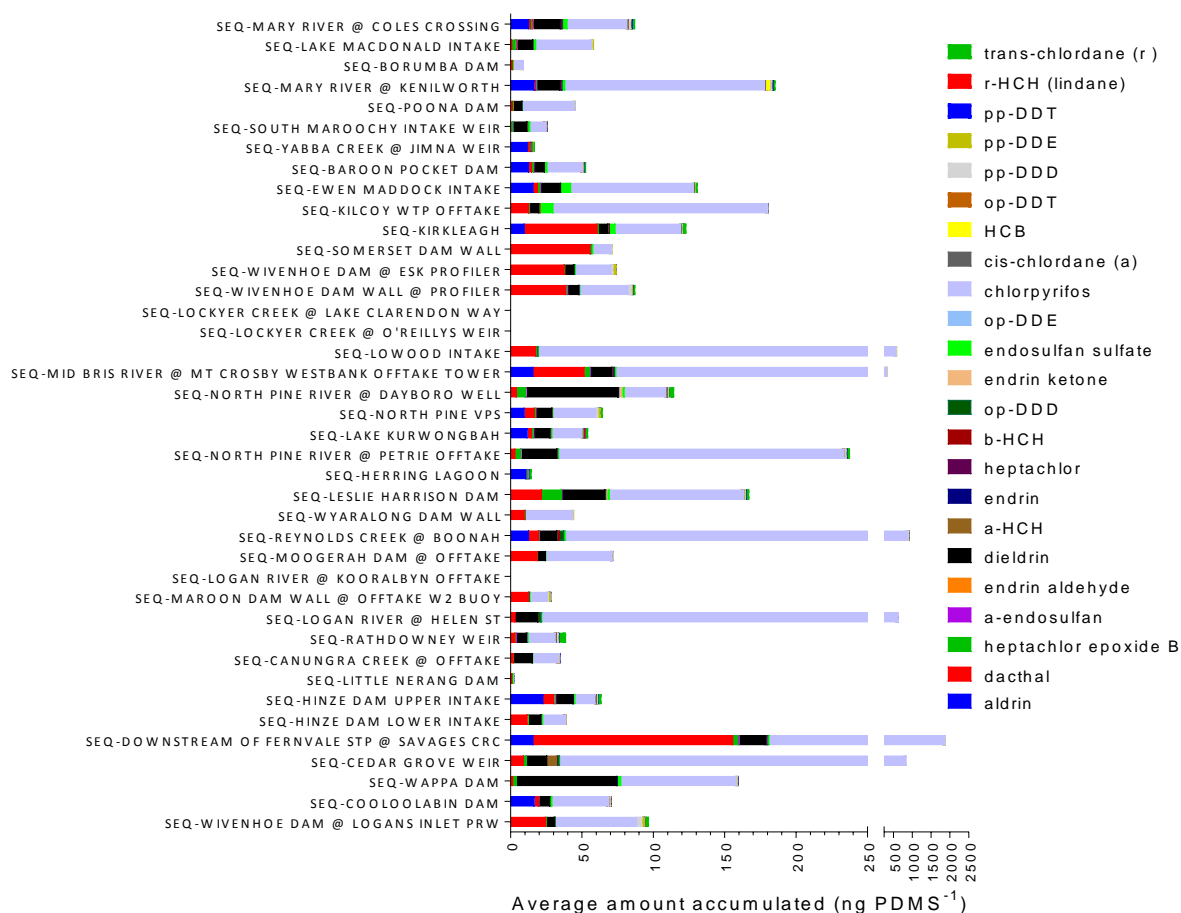


Figure 3. Total amounts of 23  $\Sigma$ OCPs accumulated in PDMS passive samplers.

The conversion of OCP masses accumulated in passive samplers to average water concentrations over the deployment period revealed an estimated water concentration range of  $\Sigma$ OCPs between 0.085 – 27 ng L<sup>-1</sup> for sites SEQ33 (Little Nerang Dam) and SEQ36 (Downstream of Fernvale STP @ Savages CRC), respectively (Figure 4). SEQ37 (Cedar Grove Weir) had the next highest concentration of  $\Sigma$ OCPs of 14 ng L<sup>-1</sup>.

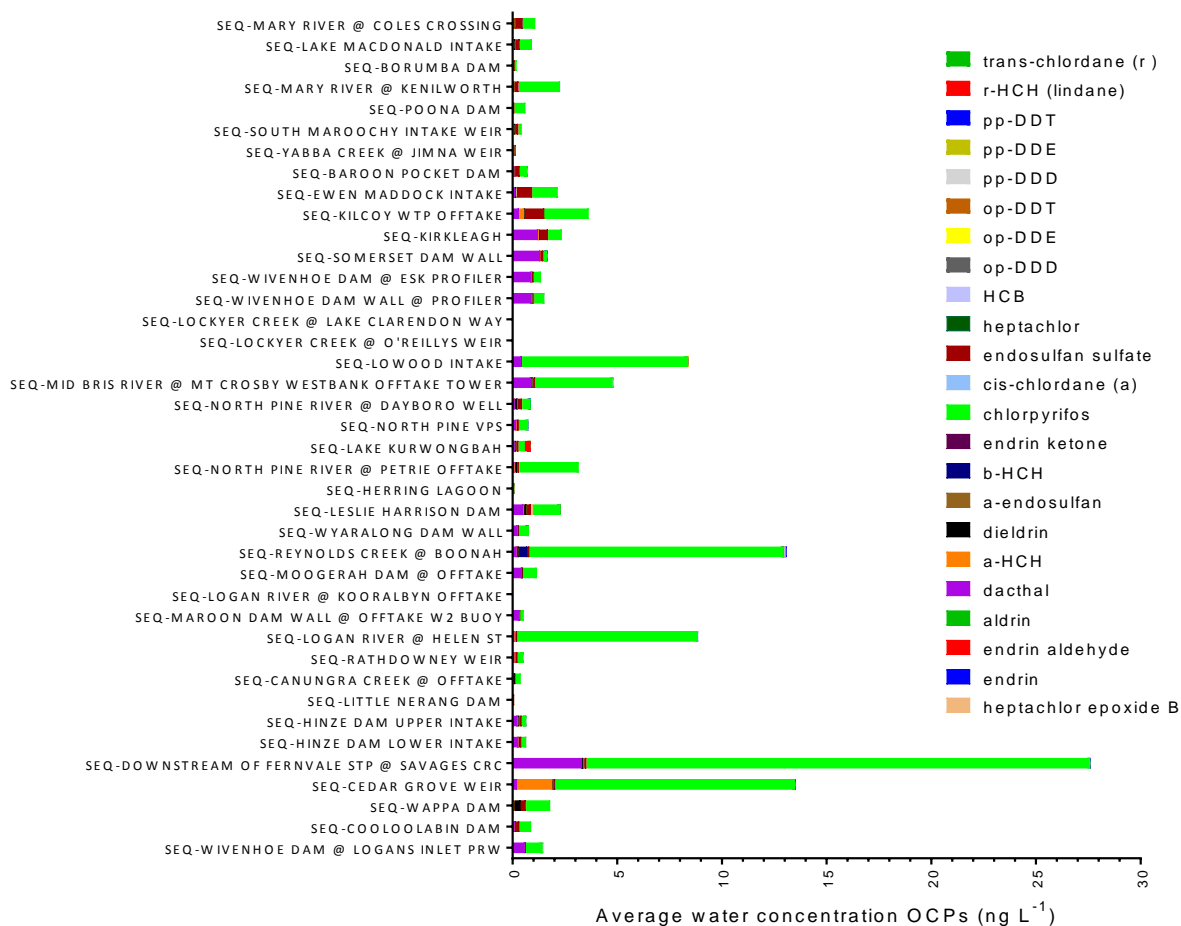


Figure 4. Total estimated water concentrations of 23  $\Sigma$ OCPs derived from accumulation in PDMS.

## Polycyclic aromatic hydrocarbons (PAHs)

In total, eleven different PAHs were accumulated in PDMS samplers with an average amount of  $\Sigma$ PAHs accumulated ranging between 0.48 – 330 ng PDMS<sup>-1</sup> for sites SEQ8 (Baroon Pocket Dam) and SEQ27 (Moogerah Dam at Offtake), respectively (Table 3, Figure 5, Appendix 1). The highest frequency of detection was observed for benzo(e)pyrene with 92% detection, followed by chrysene and benzo(bjk)fluoranthene both at 86% detection frequency. The PAHs accumulated in the greatest abundance between sites were fluoranthene (804 ng PDMS<sup>-1</sup>) > pyrene (495 ng PDMS<sup>-1</sup>) > chrysene (203 ng PDMS<sup>-1</sup>).

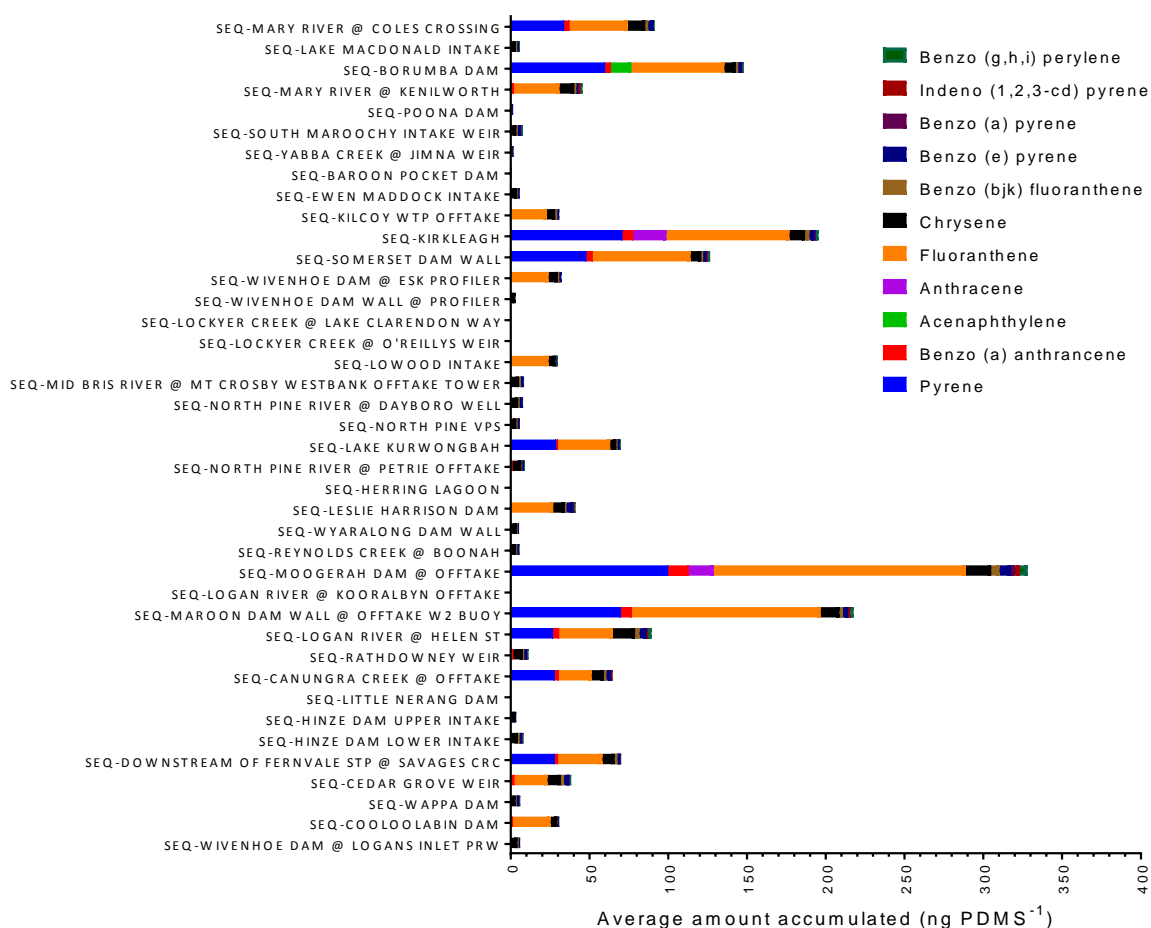


Figure 5. Total amounts of 11  $\Sigma$ PAHs accumulated in PDMS passive samplers.

When converting the masses of accumulated PAHs in passive samplers to average water concentrations over the deployment period, concentrations of  $\Sigma$ PAHs ranged between 0.001 – 2.8 ng L<sup>-1</sup> (Figure 6) for SEQ8 (Baroon Pocket Dam) and SEQ27 (Moogerah Dam @ Offtake), respectively. Thirty-five sites had reportable water concentrations of PAHs. Highest  $\Sigma$ PAH concentrations were observed at site SEQ27 (Moogerah Dam @ Offtake) followed by site SEQ3 (Borumba Dam) and site SEQ29 (Maroon Dam Wall @ Offtake W2 Buoy) with concentrations of 2.8, 1.4, and 1.4 ng L<sup>-1</sup>, respectively.

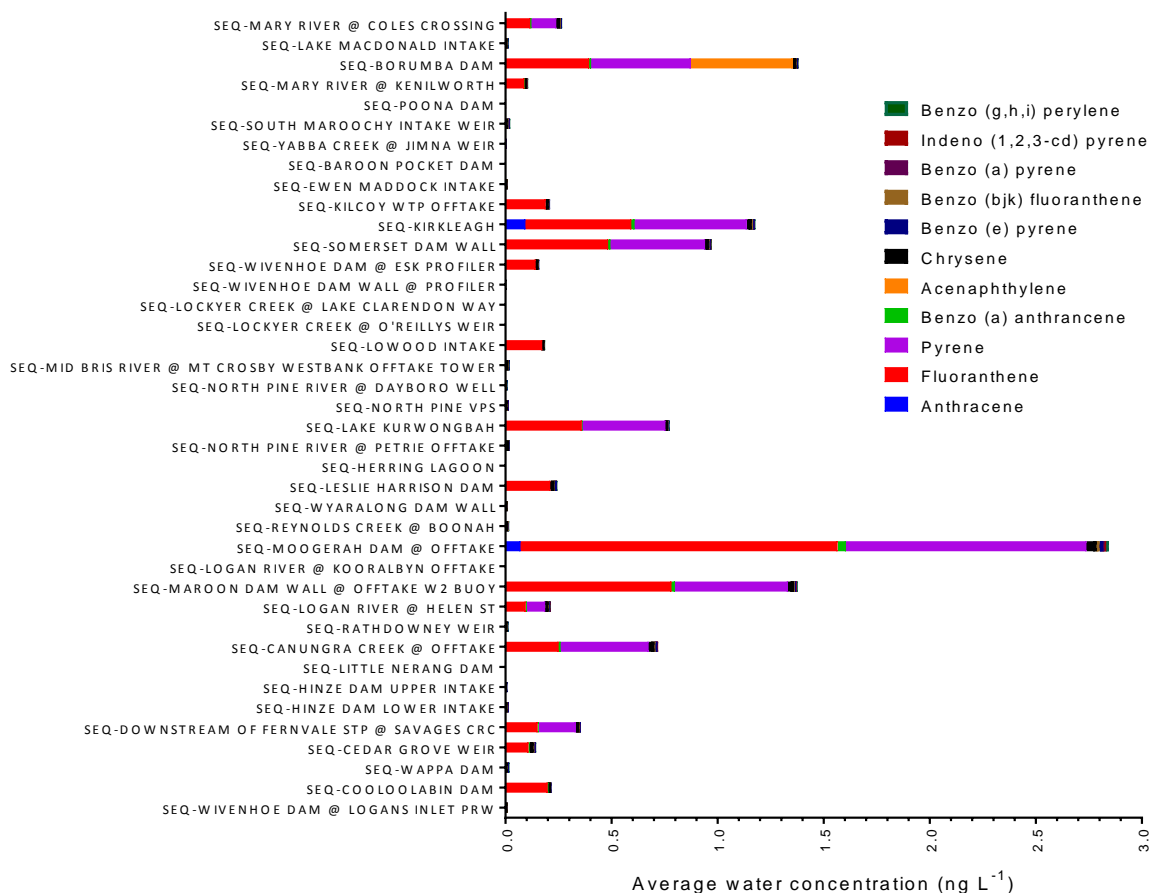


Figure 6. Total estimated water concentrations of 11  $\Sigma$ PAHs.



## Herbicides and insecticides

Over the 28-33 day deployment period, 35 herbicides and insecticides accumulated in ED passive samplers (Table 3, Figure 7, Appendix 1). The average amount of  $\Sigma$ herbicides and insecticides accumulated ranged between 0.17 – 244 ng ED<sup>-1</sup> for sites SEQ23 (Herring Lagoon) and SEQ37 (Cedar Grove Weir), respectively. Out of the 28 priority herbicides and pesticides, 16 were found among sites. The most frequently detected herbicide was atrazine and its breakdown products, desethyl atrazine and desisopropyl atrazine (100%, 97% and 97%, respectively), followed by diuron (89%), metolachlor (86%) and simazine (84%). Herbicides and insecticides were detected at all sites while site SEQ37 (Cedar Grove Weir) showed the highest total accumulation (244 ng ED<sup>-1</sup>), followed by site SEQ36 (Downstream of Fernvale STP at Savages CRC; 161 ng ED<sup>-1</sup>). In both sites high accumulated levels of metolachlor were apparent.

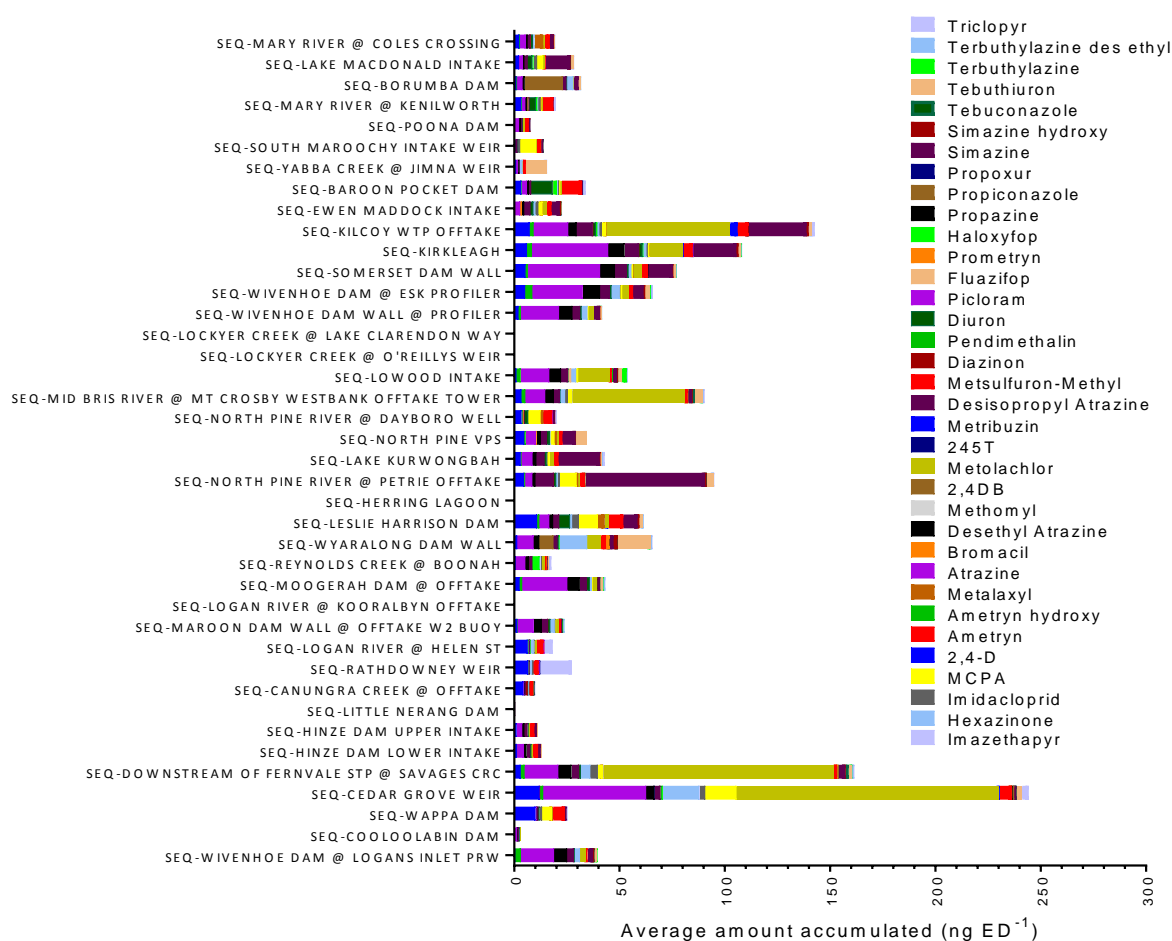


Figure 7. Total amounts of 35  $\Sigma$ herbicides and insecticides accumulated in ED passive samplers.

Water concentrations were estimated for 18 herbicides and insecticides with average total  $\Sigma$  concentrations ranging between 0.16 – 77 ng L<sup>-1</sup> for sites SEQ23 (Herring Lagoon) and SEQ37 (Cedar Grove Weir), respectively (Figure 8). Atrazine was detected in all sites and had the highest total  $\Sigma$  concentration across all sites (161 ng L<sup>-1</sup>).

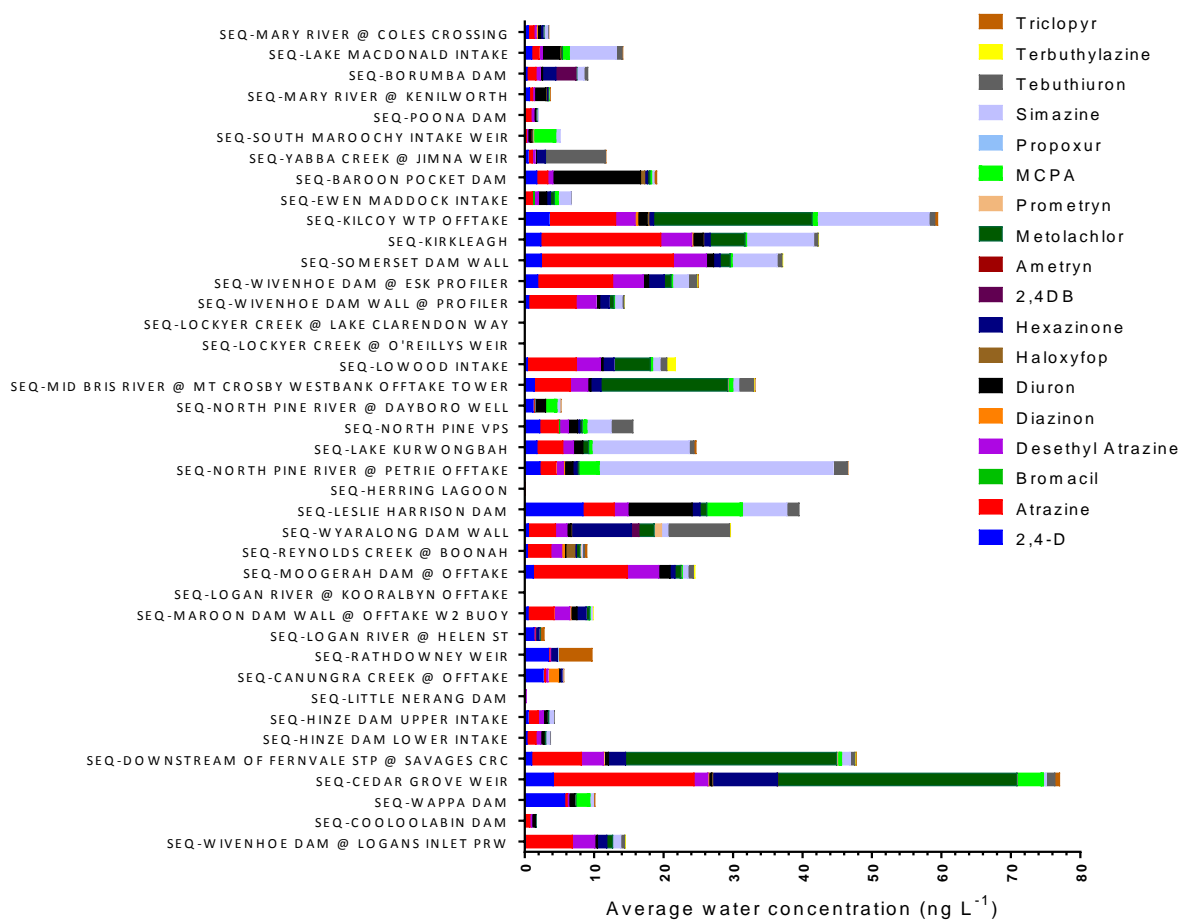


Figure 8. Total estimated water concentrations of 18 herbicides and insecticides.

### Pharmaceuticals and personal care products (PPCPs)

Fourteen PPCPs were detected with the average amount of  $\Sigma$ PPCPs accumulated ranging between 0.23 – 150 ng ED<sup>-1</sup> at sites SEQ17 (Lowood Intake) and SEQ36 (Downstream of Fernvale STP @ Savages CRC), respectively (Table 4, Figure 9, 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 (53 ng ED<sup>-1</sup>), ibuprofen (23 ng ED<sup>-1</sup>) and carbamazepine (20 ng ED<sup>-1</sup>). Most frequently detected were carbamazepine with a detection frequency of 35%, followed by gabapentin at 27%.

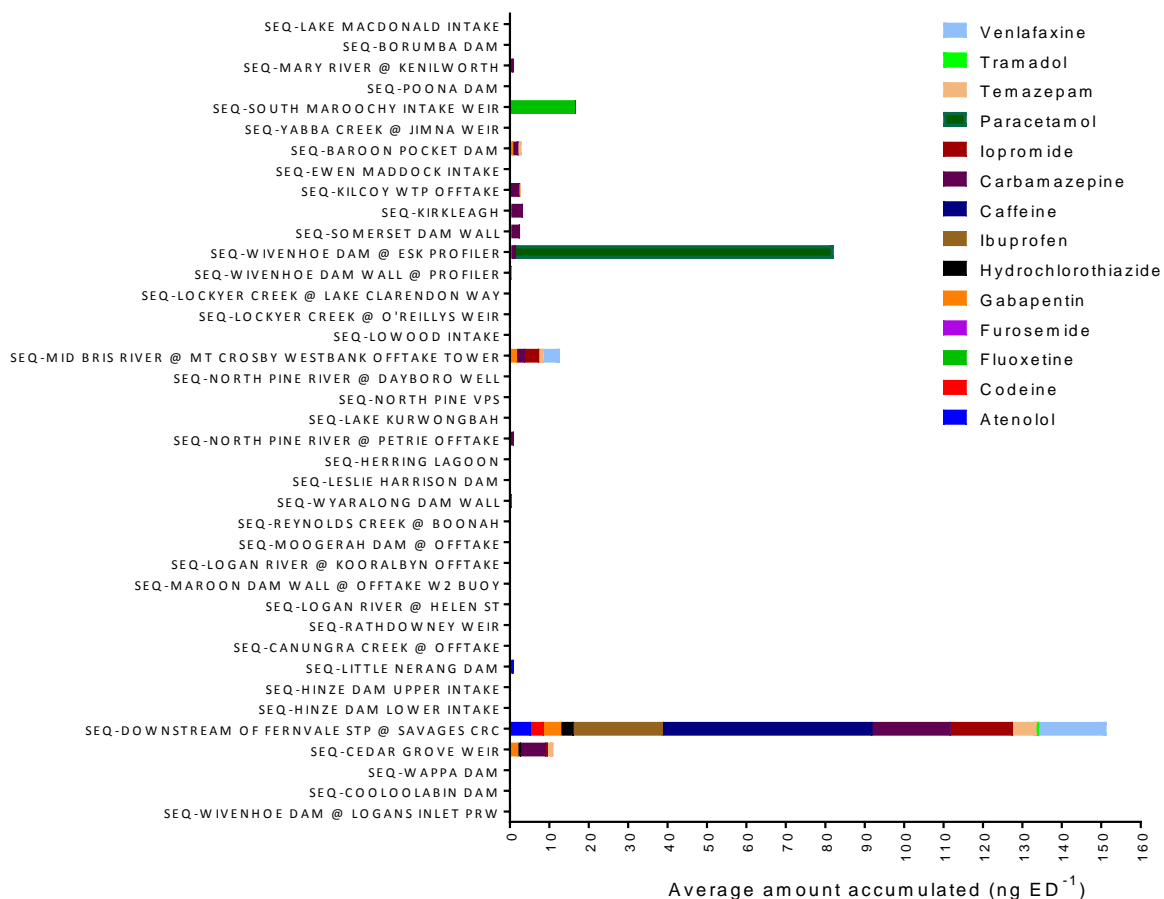


Figure 9. Average amounts of 14 PPCPs accumulated in ED passive samplers.

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 total  $\Sigma$ PPCP water concentrations ranged between 0.08 – 19 ng L<sup>-1</sup> for site SEQ40 (Wivenhoe Dam @ Logans Inlet PRW) and SEQ36 (Downstream of Fernvale STP @ Savages CRC), respectively (Figure 10).



Figure 10. Average estimated water concentrations of 3 PPCPs.

## Glyphosate (N-phosphonomethyl glycine)

This campaign is the first to include results from novel PE passive samplers for detecting glyphosate and aminomethylphosphonic acid (AMPA). The amount of glyphosate and its metabolite AMPA accumulated in PE passive samplers are shown in ng sampler<sup>-1</sup> (Table 5, Figure 11, Appendix 1) and ng L<sup>-1</sup> (Figure 12). Each site had duplicate PE samplers deployed. The results shown were the average value of two duplicate samplers (unless a detection was reported in only one of the two duplicates) with a >80% agreement between duplicates except for SEQ11 Kirkleagh (>70%). Eleven out of thirty-seven sampled sites had glyphosate detected, with AMPA observed at four sites. AMPA was detected at sites that presented highest comparative levels of glyphosate and would typically represent sites where glyphosate treatment was not very recent, allowing time for glyphosate to degrade in the system. The highest detected glyphosate was at site SEQ38 (Wappa Dam) at 76 ng PE<sup>-1</sup> followed by site SEQ10 (Kilcoy WRP Offtake) at 20 ng PE<sup>-1</sup>. The highest detected AMPA was site at SEQ38 (Wappa Dam) at 60 ng PE<sup>-1</sup> followed by site SEQ19 (North Pine River at Dayboro Well) at 25 ng PE<sup>-1</sup>.

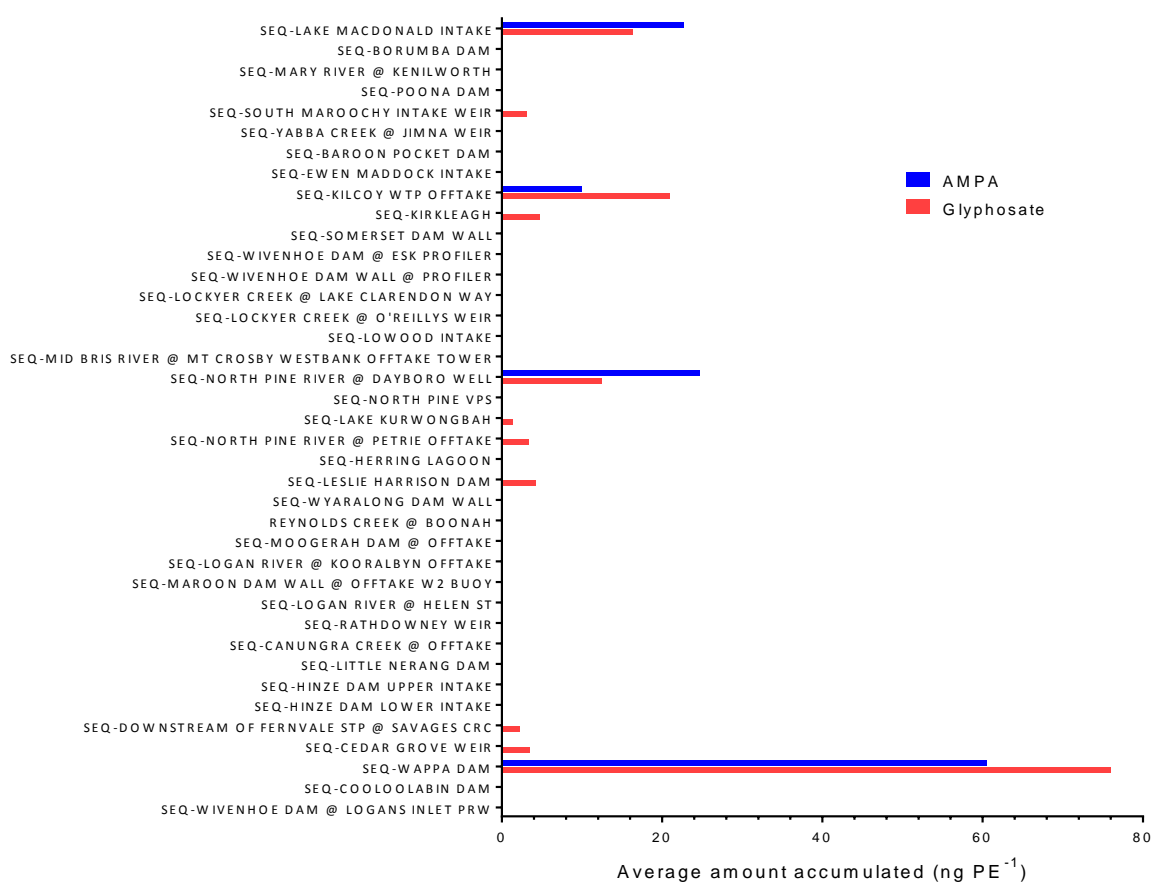


Figure 11. Averaged amount (ng per sampler) of glyphosate and AMPA accumulated in PE passive samplers at each site.

Water concentrations were estimated for glyphosate and AMPA (Figure 12, Appendix 1) with glyphosate concentrations ranging between 1.8 - 104 ng L<sup>-1</sup> for sites SEQ21 (Lake Kurwongbah) and SEQ38 (Wappa Dam), respectively. AMPA concentrations ranged between 20 – 125 ng L<sup>-1</sup> for sites SEQ10 (Kilcoy WTP Offtake) and SEQ38 (Wappa Dam), respectively.

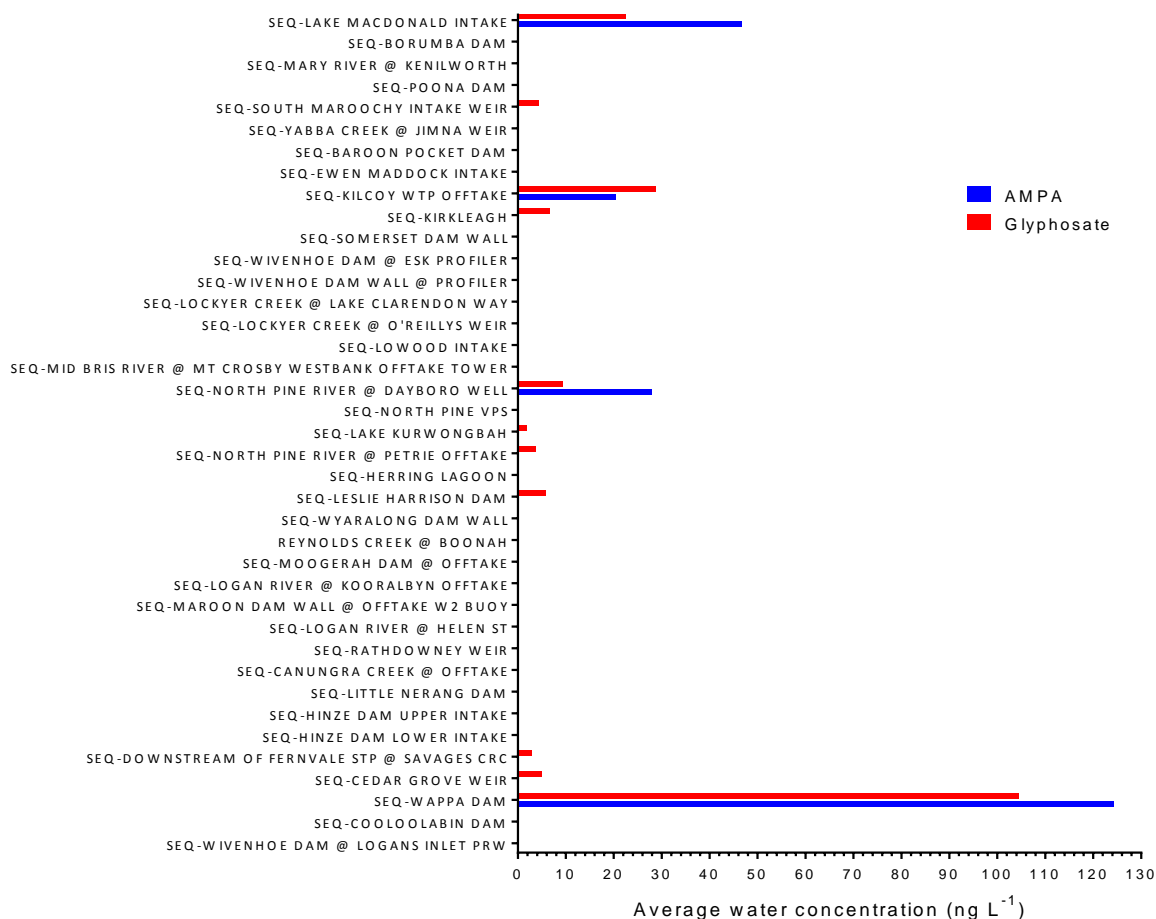


Figure 12. Average estimated water concentrations of glyphosate and AMPA.

### Per- and poly-fluoroalkyl substances (PFAS)

This campaign is the first to include results from using PE passive samplers for detecting a range of PFAS. Twelve PFAS were detected in PE samplers across 34 sites. Each site had duplicate samplers and the results are plotted to show the average amount of PFAS accumulated in  $\text{ng sampler}^{-1}$  (Table 6, Figure 13, Appendix 1) and  $\text{ng L}^{-1}$  (Figure 14). The total accumulated PFOS/ PFHxS and PFOA are plotted in Figure 15 as a comparison to current health based guidance values (Table 8).

The highest total accumulated PFAS detected was SEQ24 (Leslie Harrison Dam) at  $6.7 \text{ ng PE}^{-1}$  followed by site SEQ21 (Lake Kurwongbah) at  $3.2 \text{ ng PE}^{-1}$ . The most frequently detected PFAS was PFOA at 76% of sites, followed by PFOS at 73%, PFPeA at 60% and PFBA at 54% (Table 6).

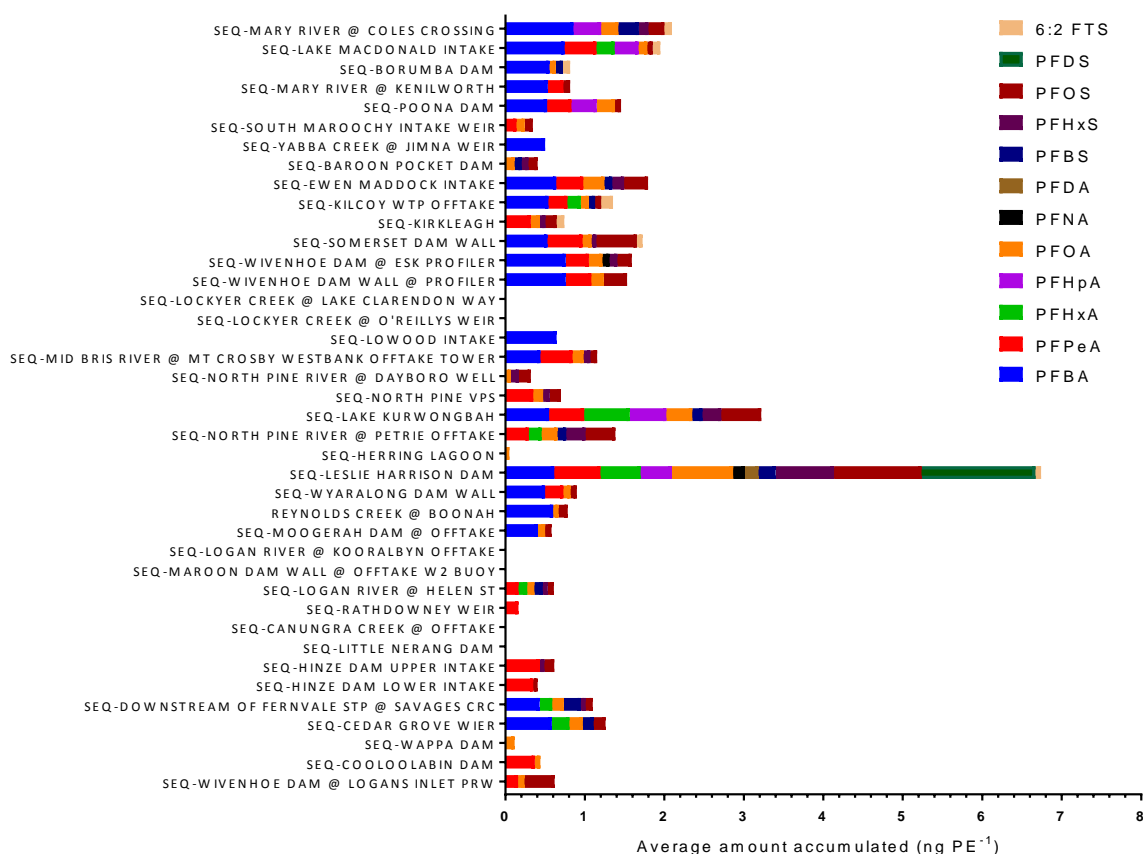


Figure 13. Average amount of twelve PFAS accumulated in PE passive samplers.



Water concentrations were estimated for nine PFAS (Figure 14, Appendix 1) with total ΣPFAS concentrations ranging between 0.3 – 30 ng L<sup>-1</sup> for sites SEQ23 (Herring Lagoon) and SEQ24 (Leslie Harrison Dam), respectively.

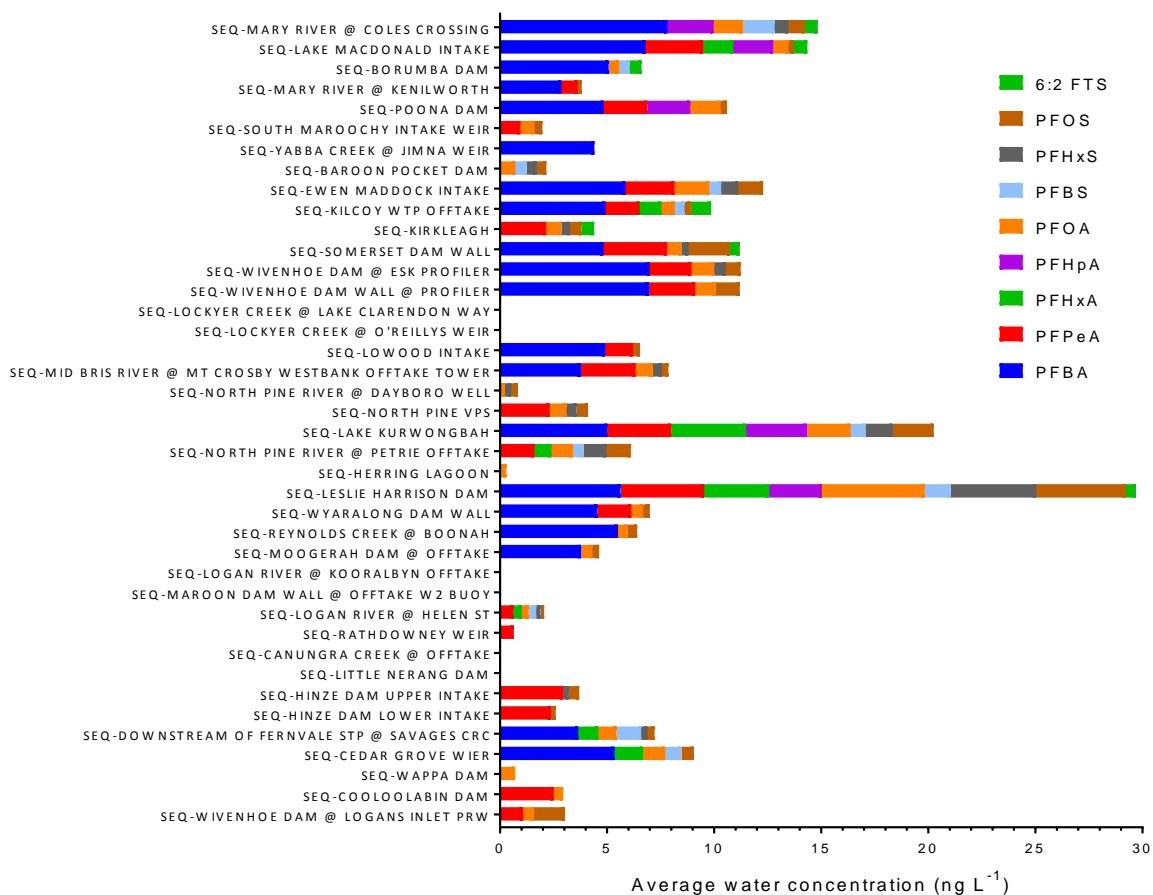


Figure 14. Total average estimated water concentrations of nine PFAS.



Figure 15. Total average estimated water concentrations of PFOS, PFHxS and PFAS.

### 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, two non-target chemicals were detected from this library: carbaryl and carbendazim (Table 7). In addition to the suspect library search, a broader scale non-target search was performed on all ED sample extracts from this season (although this investigation does not form part of the deliverables for this project).

The suspect search revealed an additional 12 compounds not previously targeted. These comprise mainly of insecticides, fungicides and an antibiotic (Table 4). Any new chemicals tentatively identified here will be added to the non-target library list for investigation in future sampling campaigns. Performing full non-target suspect 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 7. List of tentatively identified non-target chemicals in EDs, and the sites in which they were detected. Chemicals were tentatively identified using suspect screening and library matching. Note: All chemicals listed here are only tentatively identified.*

Chemical Name	Description	Sites with Tentative detects
Carbaryl	Insecticide	SEQ38 (WAPPA DAM), SEQ17 (LOWOOD INTAKE)
Carbendazim	Fungicide	SEQ2 (LAKE MACDONALD INTAKE), SEQ14 (WIVENHOE DAM WALL @ PROFILER), SEQ40 (WIVENHOE DAM @ LOGANS INLET PRW)
Cyproconazole	Fungicide	SEQ5 (POONA DAM)
Dimethoate	Organophosphate insecticide	SEQ10 (KILCOY WTP OFFTAKE)
Fenthion	Organothiophosphate insecticide	SEQ1 (MARY RIVER @ COLES CROSSING)
Hexythiazox	Pesticide	SEQ3 (BORUMBA DAM), SEQ17 (LOWOOD INTAKE)
Linuron	Herbicide	SEQ34 (HINZE DAM UPPER INTAKE)
Pencycuron	Fungicide	SEQ4 (MARY RIVER @ KENILWORTH), SEQ9 (EWEN MADDOCK INTAKE), SEQ10 (KILCOY WTP OFFTAKE), SEQ12 (SOMERSET DAM WALL), SEQ1 (MID BRIS RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER), SEQ24 (LESLIE HARRISON DAM), SEQ37 (LOGAN RIVER @ CEDAR GROVE), SEQ39 (COOLOOLABIN DAM), SEQ17 (LOWOOD INTAKE)
Phorate-sulfoxide	Pesticide	SEQ39 (COOLOOLABIN DAM)
Propachlor	Herbicide	SEQ8 (BAROON POCKET DAM), SEQ22 (NORTH PINE RIVER @ PETRIE OFFTAKE)
Propazine	Herbicide	SEQ1 (MARY RIVER @ COLES CROSSING)
Propyzamide	Herbicide	SEQ32 (CANUNGRA CREEK @ OFFTAKE)
Pyrimethanil	Fungicide	SEQ31 (RATHDOWNEY WEIR)
Sulphadiazine	Antibiotic	SEQ36 (DOWNSTREAM FERVALE STP @ SAVAGES CRC)

## Summary

A wide range of organic micro-pollutants were detected at all thirty-seven sampling locations during the summer 2018 deployment period. In summary, 23 OCPs were detected at all monitoring sites; the majority of chemicals were present at very low levels ( $< 27 \text{ ng L}^{-1} \Sigma\text{OCPs}$ ) which may indicate residue background levels because of years of persistent use and subsequent deregulation. Most site profiles are dominated by endosulfan sulfate, dacthal, pp-DDE, heptachlor epoxide B and chlorpyrifos. Australia has set chlorpyrifos environmental water guideline values of 0.04 and 10  $\text{ng L}^{-1}$  for 99% and 95% species protection, respectively.

PAHs were detected at 34 sites with profiles dominated by benzo(e)pyrene, benzo(b)k)pyrene and chrysene (Table 3). Eleven PAHs were detected across sites, though overall maximum  $\Sigma\text{PAHs}$  were below  $2.8 \text{ ng L}^{-1}$ , 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 all sites with 16 out of 28 detected falling within the priority category. The highest total  $\Sigma\text{herbicides}$  and insecticides detected was  $77 \text{ ng L}^{-1}$ . A triazine class herbicide (atrazine and its degradation products) was the most commonly detected with frequencies of detection of 100% and 97% respectively, followed by diuron and metolachlor with a frequency of detection at 89% and 86% of sites, respectively. 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 13 out of 37 sites with site SEQ36 (Downstream of Fernvale STP @ Savages CRC) containing the highest PPCPs with total concentrations of  $19 \text{ ng L}^{-1}$ . The predominant PPCP was carbamazepine at 35% 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.

This is the first sampling campaign to include glyphosate. Glyphosate was detected at 11 out of 37 sites with the highest concentration observed at site SEQ38 (Wappa Dam) at  $104 \text{ ng L}^{-1}$  followed by site SEQ10 (Kilcoy WRP Offtake) at  $28 \text{ ng L}^{-1}$ . AMPA was detected at four sites with the highest detected level at site SEQ38 (Wappa Dam) at  $124 \text{ ng L}^{-1}$  followed by site SEQ2 (Lake Macdonald Intake) at  $46 \text{ ng L}^{-1}$ . Detection of glyphosate where no AMPA was observed may indicate recent application where degradation was not yet significant. Monitoring sites where AMPA was detected indicate application events that were not necessarily recent. The ratio between glyphosate and AMPA varied, as expected, and is likely influenced by application time and the time in which samplers were removed from the water system.

Glyphosate is the most widely used herbicide worldwide (826,000 tons per year) (Benbrook 2016). It is the active ingredient in the Roundup weed killers and a number of other commercial products. Due to its quick and effective action on weed control, glyphosate is consistently applied for agricultural, roadside and urban weed control, including direct spraying of aquatic weeds on water bodies (Beeton *et al.* 2006). In the environment, glyphosate degrades to aminomethylphosphonic acid (AMPA). This process is primarily dependent on microbial activity (Ghassemi *et al.* 1981). Due to its widespread use, it is predicted that glyphosate is ubiquitous in many environmental matrices. The physico-chemical properties of glyphosate (i.e. highly polar and ionic in environmental matrices) mean that the sampling and consequent analysis of this herbicide have been both challenging and costly (Fauvelle *et al.* 2017). This campaign represents the first passive sampler for glyphosate and AMPA to be applied to a

monitoring program, globally, and the first snap shot of the occurrence of glyphosate and AMPA in the SEQ aquatic environment. Levels reported here were below the Australian Drinking Water Guideline (2000) value of  $1 \text{ mg L}^{-1}$  (Table 8).

Passive (PE) samplers were deployed for the first time at all 37 monitoring sites to detect levels of per- and poly-fluoroalkyl substances (PFAS). PFAS were detected at 34 sites with PFOA at 76% of sites, followed by PFOS at 73%, PFPeA at 60% and PFBA at 54% (Table 6). The highest total  $\Sigma$ PFAS concentrations were observed at site SEQ24 (Leslie Harrison Dam) ( $30 \text{ ng L}^{-1}$ ). 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).

### 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. Diazinon exceeded the 99% species protection value at each of the sites it was detected at, although did not exceed the 95% species protection guideline. Chlorpyrifos exceeded the 95% species protection value of 10 ng L<sup>-1</sup> at SEQ36 (Downstream of Fernvale STP @ Savages CRC), SEQ26 (Reynolds Creek @ Boonah) and SEQ37 (Cedar Grove Weir) with 24 ng L<sup>-1</sup>, 12 ng L<sup>-1</sup> and 11 ng L<sup>-1</sup>, respectively.

Although globally and in Australia, bans and restrictions have been applied on some PFAS (i.e. PFOS and PFOA) due to indication of 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, PFOS and PFHxS (for which regulatory guidelines are available, Table 8) across all monitoring sites are 15, 130, and 18 times below the current regulatory guidelines in Australia, respectively.

Table 8. Guidelines for Australian Drinking Water and Freshwater Aquatic Ecosystems.

ANZECC & ANCANZ (2000) Trigger values for freshwater			
	Australian Drinking Water Guidelines 6 (2011) (ng L <sup>-1</sup> )	99% species protection (ng L <sup>-1</sup> )	95% species protection (ng L <sup>-1</sup> )
<b>Herbicides &amp; Insecticides</b>			
Atrazine	20000	700	13000
Bromacil	400000	N/A	N/A
Diazinon	4000	0.03	10
Diuron	20000	N/A	N/A
Haloxfop	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
<b>OCPs</b>			
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
<b>Glyphosate/ AMPA</b>			
Glyphosate	1000000	N/A	N/A
AMPA	N/A	N/A	N/A
<b>PFAS</b>			
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

### Future recommendations

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

- Continued temporal and seasonal comparisons will be further assessed as data from additional sampling campaigns is provided to assess if any trends emerge between sites / seasons.
- The addition of PFAS and glyphosate 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<sup>-1</sup>) and estimated average water concentrations over the deployment periods (ng L<sup>-1</sup>) (28-33 days).