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

Report 13 – Winter 2020

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Title
Catchment and Drinking Water Quality Micro Pollutant Monitoring program – Passive Sampling.
Report 1 – Winter 2020.

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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 the third quarter of 2020. These sampling events represent the first of a 3-year monitoring study (encompassing seasonal winter/summer sampling from 2020 – 2023) which follows a previous 6-year study (beginning in 2014) which concluded in the second quarter of 2020. Results presented provide a continued insight into the water quality of the target catchments and drinking water reservoirs. Deployment dates in this report are consistent, with only one sampler requiring redeployment.

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

Chemical analyses of the passive sampler extracts reported 51 different chemicals including 12 OCPs, 9 PAHs, 22 polar pesticides and 9 PPCPs. OCPs were detected at 83% of sites, with dieldrin, dacthal and chlorpyriphos the most frequently reported, and chlorpyrifos showing the highest individual concentration. Total ∑OCP water concentrations across sites ranged between 0.003 – 1.53 ng L^{-1} where concentrations were reportable. PAHs were detected at 89% of sites, with fluoranthene (86%), pyrene (47%) and Benzo[a]anthracene (31%) reported at the highest abundance across all sites. Total ∑PAH water concentrations across sites ranged between 0.03 – 1.47 ng L^{-1}. Twenty-two different polar pesticides were reported in 29 sites (81%), with atrazine (58%), atrazine desisopropyl (42%) and metolachlor (42%) reported at highest abundance across all sites. The highest single concentration was observed for metolachlor at 41.0 ng L^{-1}. Total ∑polar pesticides ranged between 0.91 – 55.0 ng L^{-1}. EightPPCPs were detected across sites with highest detection frequencies observed for DEET (22%), carbamazepine (22%) and naproxen (11%). Total estimated ∑PPCP water concentrations ranged between 1.08 – 20.0 ng L^{-1} across sites.

Australian and New Zealand Guidelines for Drinking Water (ADWG) as well as Fresh and Marine Water Quality values are available for some of these chemicals (ANZECC & ANCANZ 2018) for comparison. No chemicals were present in concentrations that exceeded the ADWG values. In the ecotoxicological setting, chlorpyrifos was often above the thresholds set for 99% species protection but fell well below the 95% protection levels.

Introduction

As the bulk supplier of drinking water to South East Queensland, Seqwater maintains a Catchment and Drinking Water Quality Micro Pollutant Monitoring Program to ensure safe and reliable supply of the region's drinking water source reservoirs. The aim of this program is to identify and understand the presence of micro pollutants in the source water reservoirs as well as to recognise any spatial and temporal trends of micro pollutants. An extension of this program has been introduced to include the use of passive sampling technologies in the monitoring of source water reservoirs over a three year period (2020 – 2023; 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 raises analytical challenges as well as further challenges in obtaining appropriate and representative samples. Grab samples may not offer enough volume to allow sufficient concentration factors for the quantification of micro pollutants and may miss episodic contamination events, given they represent a single point in time. The use of passive sampling technologies has been introduced to complement and overcome some of these challenges, substantially improving chemical pollutant monitoring in liquid phases over the last 15 - 20 years. Benefits of passive sampling tools include *in-situ* concentration of chemical pollutants, increased sensitivity, the provision of time-weighted average concentration estimates for chemicals over periods of ≥ 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 this program.

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

Methodology

Passive water samplers were deployed in periods between August 2020 to October 2020 at 36 sites of SEQ reservoirs/waterways (Table 1). Deployments were for periods of 28 to 29 days in duration. The sampler for site SEQ30 (Logan River @ Helen St) was compromised by its removal from water, therefore a subsequent sampler was redeployed with only the redeployed sampler reported here (Table 1, highlighted in orange). Duplicate samplers were deployed at five randomly selected sites (Table 1, highlighted in green).

The deployment of samplers was conducted in alignment with the "Drinking and Catchment Water Quality Micro Pollutant Passive Sampling Procedure" (December 2020). Table 1 below lists the deployment site locations, site numbers, site codes, deployment and retrieval dates and lengths of deployment periods, as well as the water velocity (cm s^{-1}) estimated at each site.

In this campaign, the following sites were not sampled:

SEQ03 (Borumba Dam)

SEQ15 (Lockyer Creek at Lake Clarendon Way)

SEQ16 (Lockyer Creek at O'Reilly's Weir)

SEQ22 (North Pine River at Petrie Offtake)

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
SEQ01	MRS-SP012	SEQ-MARY RIVER @ COLES CROSSING	31/08/2020	28/09/2020	28	3.4	
SEQ02	LMD-SP001	SEQ-LAKE MACDONALD INTAKE	3/09/2020	1/10/2020	28	5.2	
SEQ04	MRS-SP013	SEQ-MARY RIVER @ KENILWORTH	31/08/2020	28/09/2020	28	3.4	
SEQ05	POD-SP001	SEQ-POONA DAM	2/09/2020	30/09/2020	28	4.2	
SEQ06	SOR-SP001	SEQ-SOUTH MAROOCHY INTAKE WEIR	1/09/2020	30/09/2020	29	3.4	
SEQ07	YAC-SP001	SEQ-YABBA CREEK @ JIMNA WEIR	31/08/2020	28/09/2020	28	3.4	
SEQ08	BPD-SP001	SEQ-BAROON POCKET DAM	3/09/2020	1/10/2020	28	4.5	
SEQ09	EMD-SP001	SEQ-EWEN MADDOCK INTAKE	1/09/2020	29/09/2020	28	5.2	
SEQ10	SOD-SP010	SEQ-KILCOY WTP OFFTAKE	8/09/2020	6/10/2020	28	4.4	
SEQ11	SOD-SP011	SEQ-KIRKLEAGH	8/09/2020	6/10/2020	28	7	
SEQ12	SOD-SP001	SEQ-SOMERSET DAM WALL	8/09/2020	6/10/2020	28	5.1	
SEQ13	WID-SP004	SEQ-WIVENHOE DAM @ ESK PROFILER	10/09/2020	8/10/2020	28	5.7	
SEQ14	WID-SP001	SEQ-WIVENHOE DAM WALL @ PROFILER	10/09/2020	8/10/2020	28	10.1	
SEQ17	MBR-SP016	SEQ-LOWOOD INTAKE	3/09/2020	1/10/2020	28	4.1	
SEQ18	MBR-SP001	SEQ-MID BRIS RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER	4/09/2020	2/10/2020	28	5.3	
SEQ19	NOD-SP091	SEQ-NORTH PINE RIVER @ DAYBORO WELL	1/09/2020	29/09/2020	28	3.4	
SEQ20	NOD-SP001	SEQ-NORTH PINE VPS	1/09/2020	29/09/2020	28	4.5	
SEQ21	LAK-SP001	SEQ-LAKE KURWONGBAH	1/09/2020	29/09/2020	28	4.7	
SEQ23	NSC-SP001	SEQ-HERRING LAGOON	25/08/2020	22/09/2020	28	3.4	
SEQ24	LHD-SP005	SEQ-LESLIE HARRISON DAM	10/09/2020	8/10/2020	28	5.2	
SEQ25	WYD-SP001	SEQ-WYARALONG DAM WALL	3/09/2020	1/10/2020	28	5.1	
SEQ26	MOD-SP027	SEQ-REYNOLDS CREEK @ BOONAH	1/09/2020	29/09/2020	28	3.4	

SEQ27	MOD-SP002	SEQ-MOOGERAH DAM @ OFFTAKE	1/09/2020	29/09/2020	28	8.9	
SEQ28	LRS-SP017	SEQ-LOGAN RIVER @ KOORALBYN OFFTAKE	2/09/2020	30/09/2020	28	9.1	
SEQ29	MAD-SP004	SEQ-MAROON DAM WALL @ OFFTAKE W2 BUOY	1/09/2020	29/09/2020	28	7	
SEQ30	LRS-SP013	SEQ-LOGAN RIVER @ HELEN ST	7/10/2020	4/11/2020	28	14.6	Original sampler was not viable therefore this data represents the redeployed sampler
SEQ31	LRS-SP016	SEQ-RATHDOWNEY WEIR	2/09/2020	30/09/2020	28	3.4	
SEQ32	CAC-SP001	SEQ-CANUNGRA CREEK @ OFFTAKE	27/08/2020	24/09/2020	28	3.4	
SEQ33	LND-SP014	SEQ-LITTLE NERANG DAM	27/08/2020	24/09/2020	28	3.4	
SEQ34	HID-SP001	SEQ-HINZE DAM UPPER INTAKE	26/08/2020	23/09/2020	28	4	
SEQ35	HID-SP002	SEQ-HINZE DAM LOWER INTAKE	26/08/2020	23/09/2020	28	4.8	
SEQ36	MBR-SP013	SEQ-DOWNSTREAM OF FERNVALE STP @ SAVAGES CRC	3/09/2020	1/10/2020	28	4.7	
SEQ37	LRS-SP012	SEQ-LOGAN RIVER @CEDAR GROVE	2/09/2020	30/09/2020	28	3.4	
SEQ38	WAD-SP001	SEQ-WAPPA DAM	2/09/2020	30/09/2020	28	3.8	
SEQ39	COD-SP001	SEQ-COOLOOLABIN DAM	1/09/2020	30/09/2020	29	4.8	
SEQ40	WID-SP061	SEQ-WIVENHOE DAM @ LOGANS INLET PRW	10/09/2020	8/10/2020	28	11.6	

Note:- Flow velocity of 3.4 cm s^{-1} was used where the calculated flow velocity was smaller than 3.4 cm s^{-1}
Sites with replicate samplers deployed for QA/QC purposes are highlighted in green.
Sites where the original sampling kit was replaced and redeployed are highighted in orange.

Passive sampler preparation and extraction

In this campaign, two types of passive samplers were deployed at each site. Empore Disk^{TM} (3M; ED) samplers were deployed to detect and quantify the presence of polar organic pollutants such as herbicides, pharmaceuticals and personal care products (PPCPs). Polydimethylsiloxane (PDMS) strips in stainless steel cages were deployed to quantify the presence of more hydrophobic organic pollutants (non-polar chemicals) such as certain organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs). Passive flow monitors (PFMs) were co-deployed in duplicate with the passive samplers at each site to estimate the water flow conditions during the deployment period. ED and PDMS passive samplers were all prepared and extracted according to previously published procedures and methods described in Kaserzon *et al.* (2017).

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

Analytical methods

Chemical analysis was performed at QAEHS using established standard operating procedures (SOPs). ED extracts were analysed by LC-QQQ MS/MS for polar herbicides and PPCPs (85 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 30 OCPs, 16 PAHs and 1 other Herbicide/Pesticide compounds via GC-HRMS (Appendix 1). The analytical methods for herbicides and PPCPs (LC-QQQ MS/MS), OCPs and PAHs (GC-HRMS), and suspect screening of herbicides and PPCPs (LC-QToF MS/MS) are detailed in previously published reports (Kaserzon *et al.* 2017) and in Quality Protocol: Contract 03944 Micro-Pollutant and Passive Sampler Monitoring program.

Data modelling and reporting of results

Data were modelled and reported according to previously published procedures and methods described in Kaserzon *et al.* (2017).

Quality control and assurance (QC/QA) procedures

Quality control was also carried out in accordance with Quality Protocol: Contract 03944 Micro-Pollutant and Passive Sampler Monitoring program.

Results

PFM results

Two passive flow monitors (PFMs) were deployed at each site to allow for flow rate calculations. Under very low flow conditions the change in mass loss rates from the PFM are too small to provide a reliable measure of flow, and therefore cannot accurately provide flow data for the chemical sampling rate (R_s) calculation (i.e. below a threshold flow of 3.40 cm s^{-1} or PFM loss rate equal to 0.58 g d^{-1}; O'Brien *et al.* 2009; 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 3.40 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 (Kaserzon *et al.* 2014; O'Brien *et al.* 2011b). Average flow velocities estimated from PFMs over the deployment period ranged between 3.40 cm s^{-1} (SEQ07; Yabba Creek @ Jimna Weir) to 14.6 cm s^{-1} (SEQ30; Logan River @ Helen St).

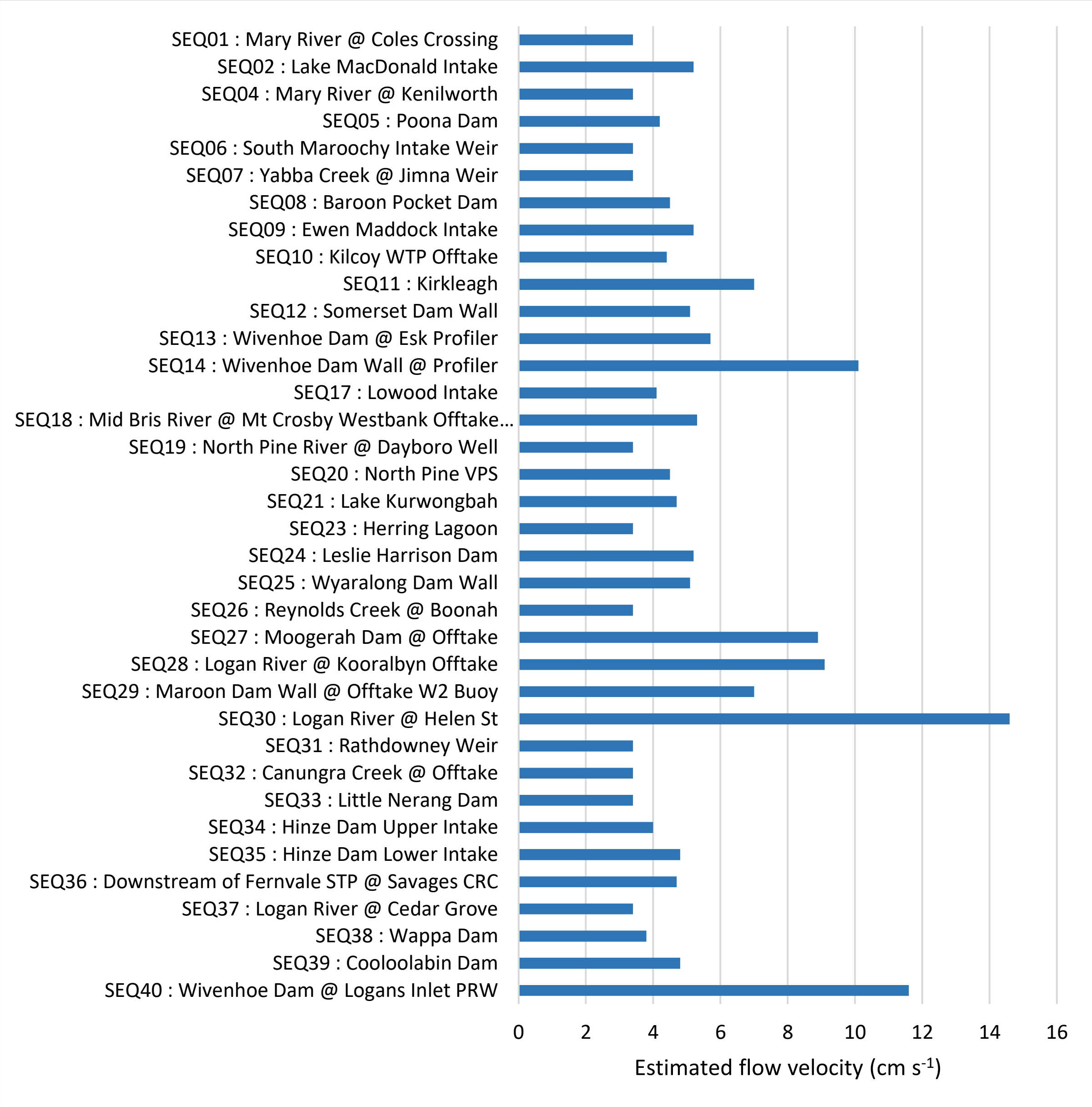

Figure 2. Passive flow monitor (PFM) based water flow velocity estimations (cm s^{-1}) at the deployment sites (n=36).

Note: A minimum flow velocity of 3.4 cm s^{-1} is used to assess flow velocity using Passive Flow Monitors (PFMs).

Chemical analysis results

A summary of the number of chemicals quantified at the sampling sites, the percent detection of each chemical and mass accumulation (ng $sampler^{-1}$) is presented in Tables 2 and 3 below. Table 2 summarises the non-polar chemicals detected via PDMS (OCPs and PAHs). A total of 12 OCPs and 9 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% – 83% for OCPs and 3% – 86% for PAHs. Table 3 summarises the polar chemicals quantified via ED (pesticides and PPCPs). A total of 25 pesticides (predominantly herbicides) and 8 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3% - 58% for pesticides and 3% - 22% for PPCPs.

Table 2. Summary of the number of chemicals accumulated in PDMS passive samplers, percentage of detection at the sites and the range of mass accumulated over the deployment periods (ng PDMS-1).

Analyte	Number of sites detected (n=36)	% Detection	Min reported (ng PDMS -1)	Max reported (ng PDMS -1)
Organochlorine pesticides (OCPs)				
Aldrin	1	3%	0.550	0.550
Chlorpyriphos	18	50%	7.14	77.2
cis-Chlordane	2	6%	0.512	0.895
Dacthal	27	75%	0.540	28.9
Dieldrin	30	83%	1.26	17.0
Endosulfan sulfate	8	22%	1.07	3.55
Etridiazole	4	11%	2.45	7.33
o,p-DDD	2	6%	0.835	1.79
p,p-DDD	11	31%	0.575	10.8
p,p-DDE	9	25%	1.02	4.96
Permethrin	1	3%	11.6	11.6
trans-Chlordane	4	11%	0.949	3.42
Polycyclic aromatic hydrocarbons (PAHs)				
Acenaphthylene	7	19%	4.06	10.9
Anthracene	1	3%	17.9	17.9
Benzo[a]anthracene	11	31%	0.600	9.16
Benzo[e]pyrene	1	3%	16.6	16.6
Benzo[g,h,i]perylene	2	6%	3.20	3.73
Chrysene/Triphenylene	5	14%	7.51	14.1
Fluoranthene	31	86%	8.33	133
Phenanthrene	7	19%	62.3	110
Pyrene	17	47%	11.5	106

Table 3. Summary of the number of chemicals accumulated in ED passive samplers, percentage of detection at the sites and the range of mass accumulated over the deployment periods (ng ED-1).

Analyte	Numbers of sites detected (n = 36)	% Detection	Min reported (ng ED-1)	Max reported (ng ED-1)
Herbicides and Insecticides				
2,4-D	2	6%	5.81	8.92
Ametryn hydroxy	9	25%	1.00	1.92
Atrazine	21	58%	1.02	25.8
Atrazine desethyl	14	39%	2.05	6.55
Atrazine desisopropyl	15	42%	1.01	4.05
Bromacil	1	3%	1.30	1.30
Carbendazim	3	8%	1.29	4.16
Diuron	4	11%	1.25	27.8
Fipronil	1	3%	2.31	2.31
Haloxyfop	1	3%	1.19	1.19
Hexazinone	13	36%	1.11	9.19
Imidacloprid	1	3%	1.89	1.89

MCPA	1	3%	11.0	11.0
Metalaxyl	6	17%	0.100	0.570
Metolachlor (S+R)	15	42%	1.00	50.5
Metsulfuron methyl	14	39%	1.26	4.14
Propoxur	1	3%	1.34	1.34
Simazine	14	39%	1.30	13.2
Simazine hydroxy	6	17%	1.01	2.71
Tebuthiuron	10	28%	1.09	10.6
Terbuthylazine	1	3%	1.51	1.51
Terbuthylazine desethyl	1	3%	15.8	15.8
Pharmaceuticals and personal care products (PPCPs)				
Carbamazepine	8	22%	1.08	6.36
DEET	8	22%	16.0	39.3
Diclofenac	1	3%	1.16	1.16
Hydrochlorthiazide	2	6%	1.03	4.02
Naproxen	4	11%	24.1	73.3
Oxazepam	2	6%	0.330	0.620
Sulfamethoxazole	3	8%	0.340	2.11
Temazepam	1	3%	3.99	3.99

Organochlorine pesticides (OCPs)

In total, 12 OCPs were accumulated in PDMS samplers over the deployment period (Table 2, Figure 4, Appendix 1), with the amount of ∑OCPs accumulated ranging from below reporting limits to 106 ng $PDMS^{-1}$ for site SEQ24 (Leslie Harrison Dam). The site with the smallest reportable amount was SEQ23 (Herring Lagoon) with 0.900 ng $PDMS^{-1}$ arising solely from cis-chlordane.

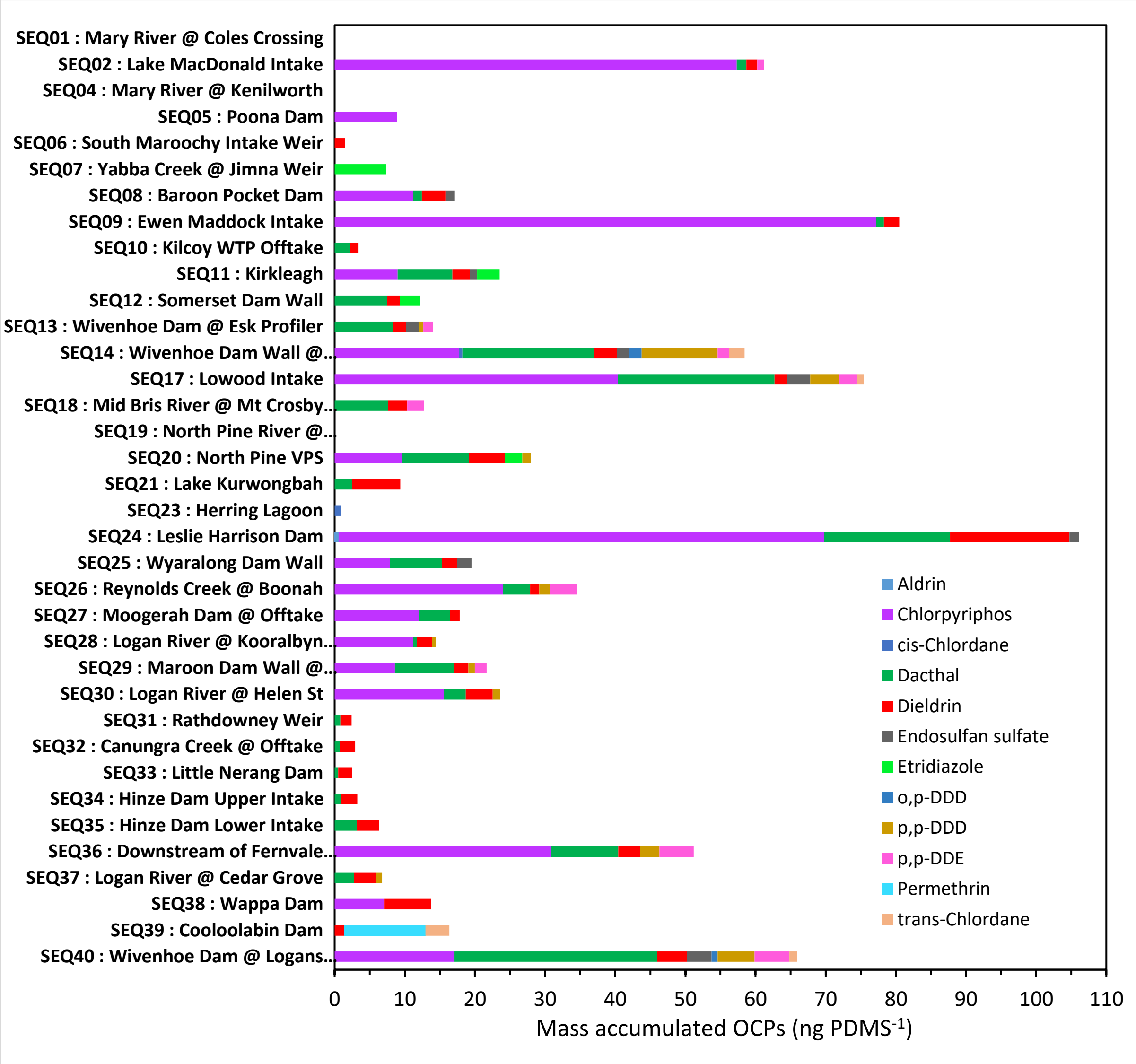

Figure 3. Total mass of 12 ΣOCPs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

The conversion of OCP masses accumulated in passive samplers to time-weighted average water concentrations revealed an estimated water concentration range of ∑OCPs from below reporting limit to 1.53 ng L^{-1}. Sites with ∑OCPs below reporting limits include SEQ01 (Mary River @ Coles Crossing), SEQ04 (Mary River @ Kenilworth) and SEQ19 (North Pine River @ Herring Lagoon) while the greatest time-average water ∑concentration was SEQ24 (Leslie Harrison Dam) at 1.53 ng L^{-1} and the second greatest was SEQ17 (Lowood Intake) at 1.41 ng L^{-1} (Figure 4).

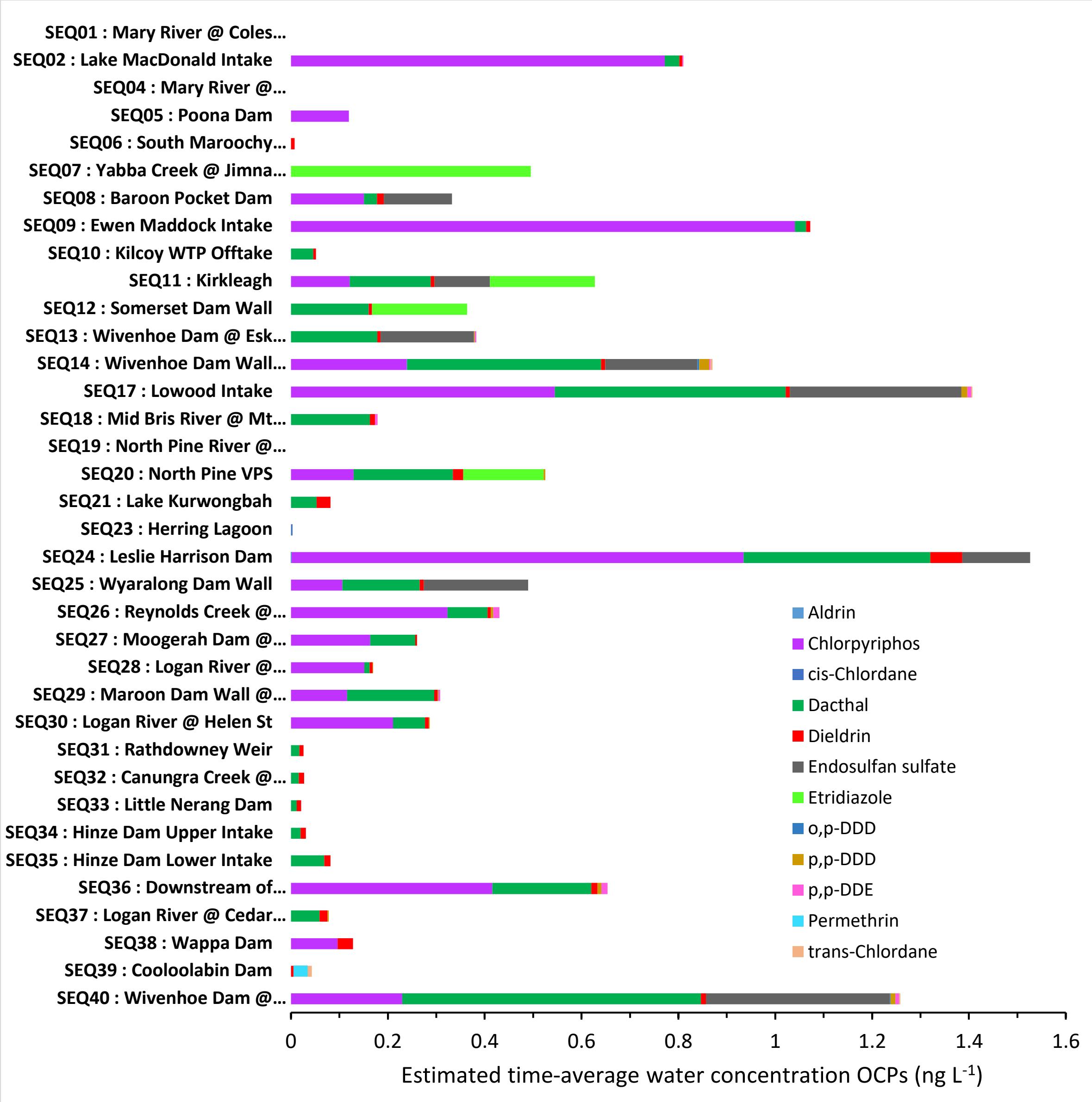

Figure 4. Total estimated water concentrations (ng L^{-1}) of 12 ΣOCPs at each site derived from PDMS passive samplers.

Polycyclic aromatic hydrocarbons (PAHs)

In total, 9 PAHs were accumulated in PDMS samplers with amounts of ∑PAHs ranging from below reportable amounts at SEQ05, 06, 19 and 33 (Poona Dam, South Maroochy Intake Weir, North Pine River @ Dayboro Well and Little Nerang Dam, respectively) up to 272 ng $PDMS^{-1}$ at SEQ12 (Somerset Dam wall) (Table 2, Figure 5 and Appendix 1). The site with the smallest reportable ∑PAHs was SEQ07 (Yabba Creek @ Jimna Weir) with 5.74 ng $PDMS^{-1}$ arising predominantly from Acenaphthylene (4.94 ng $PDMS^{-1}$; Figure 5).

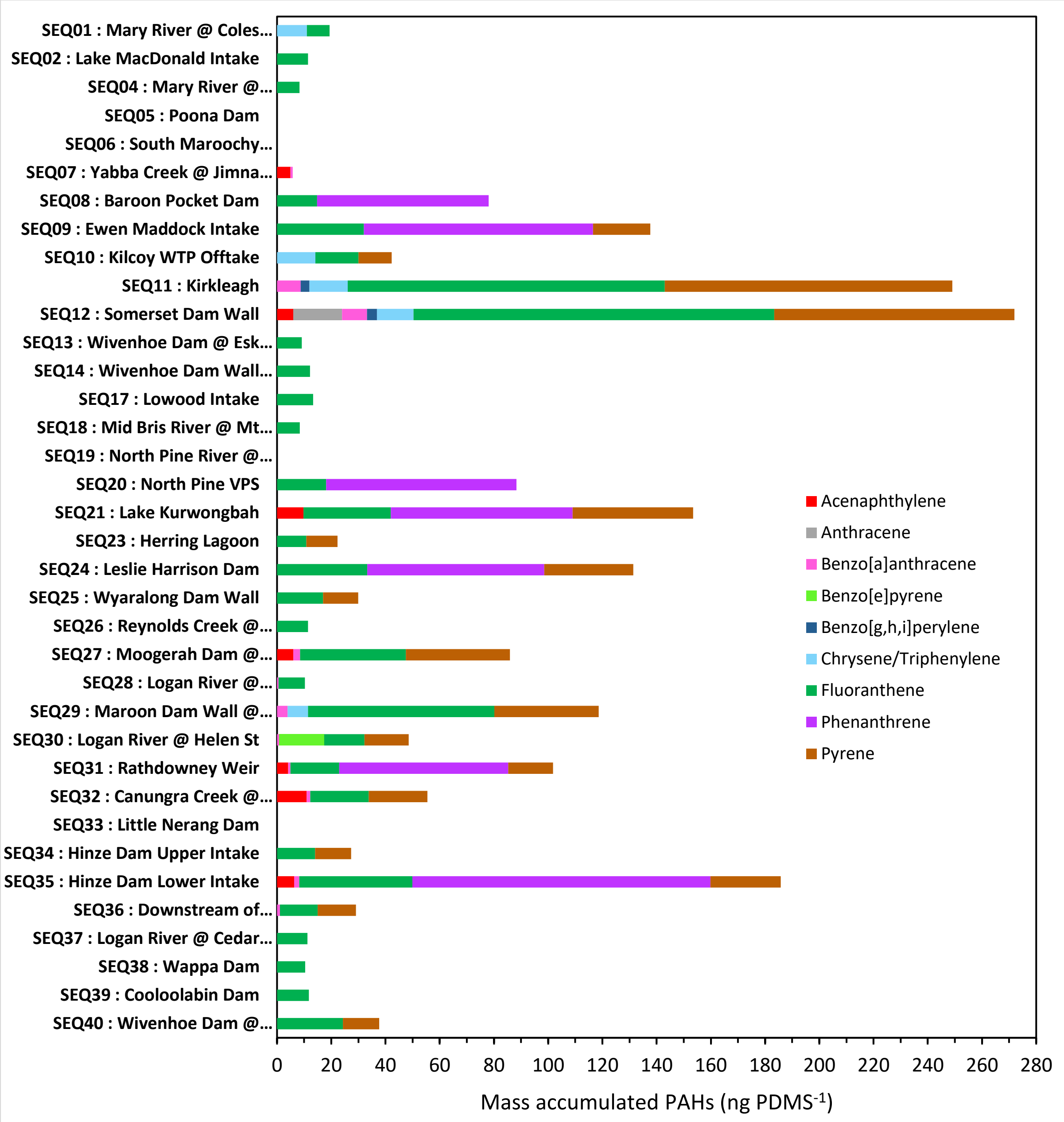

Figure 5. Total mass of 9 ΣPAHs (ng $PDMS^{-1}$) accumulated in PDMS passive samplers at each site.

The conversion of PAH masses accumulated in passive samplers to time-weighted average water concentrations revealed an estimated water ∑concentration range from below reportable concentrations to 1.47 ng L^{-1} (

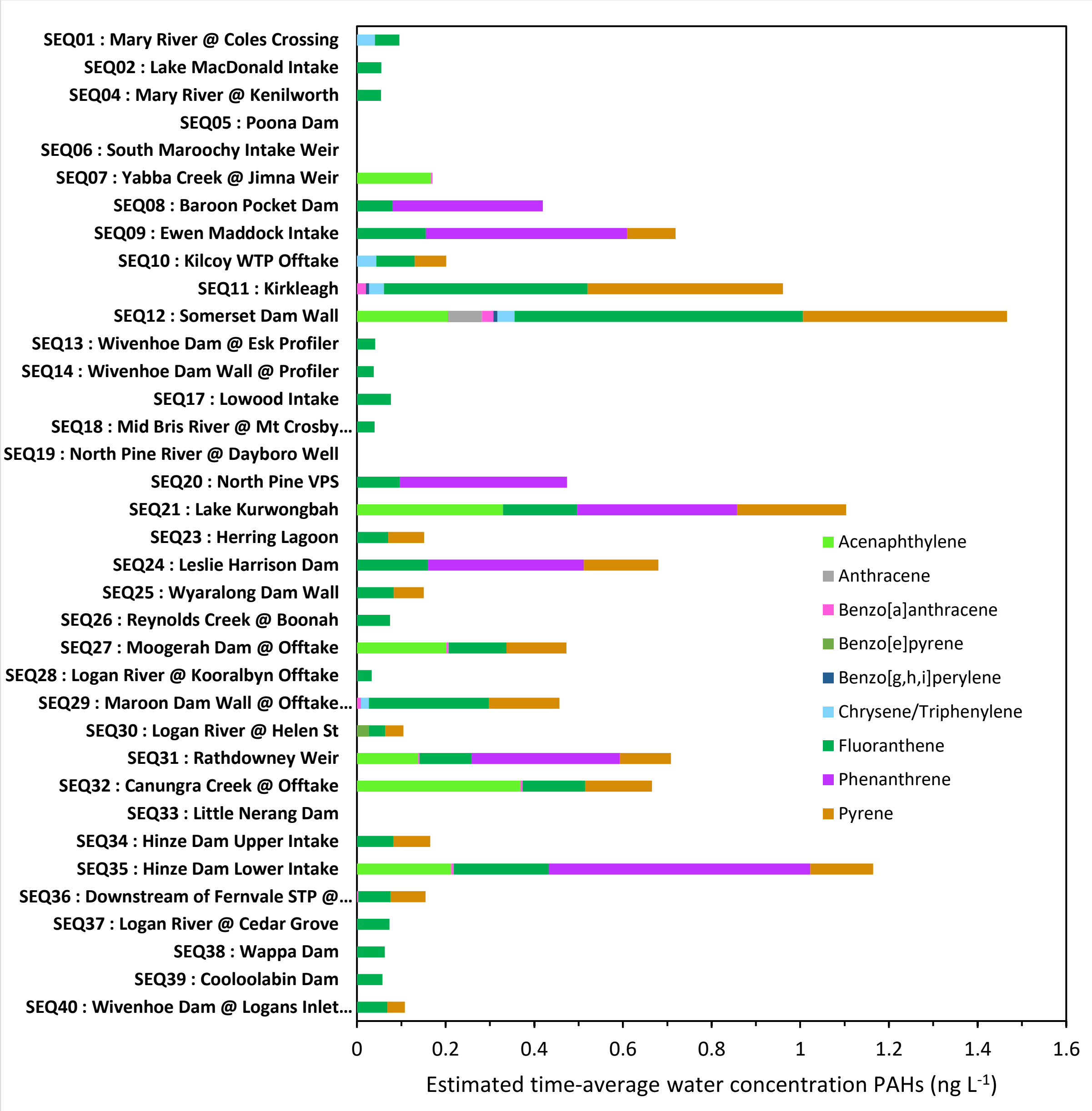

Figure 6). The smallest reportable concentration estimate for ∑PAHs among all sites was SEQ28 (Logan River @ Kooralbyn Offtake) at 0.032 ng L^{-1} and the greatest average concentration was observed for SEQ12 (Somerset Dam Wall) at 1.47 ng L^{-1}. The second and third greatest concentrations were SEQ35 (Hinze Dam Lower Intake) at 1.16 ng L^{-1} and SEQ21 (Lowood Intake) at 1.10 ng L^{-1} (Figure 6), respectively.

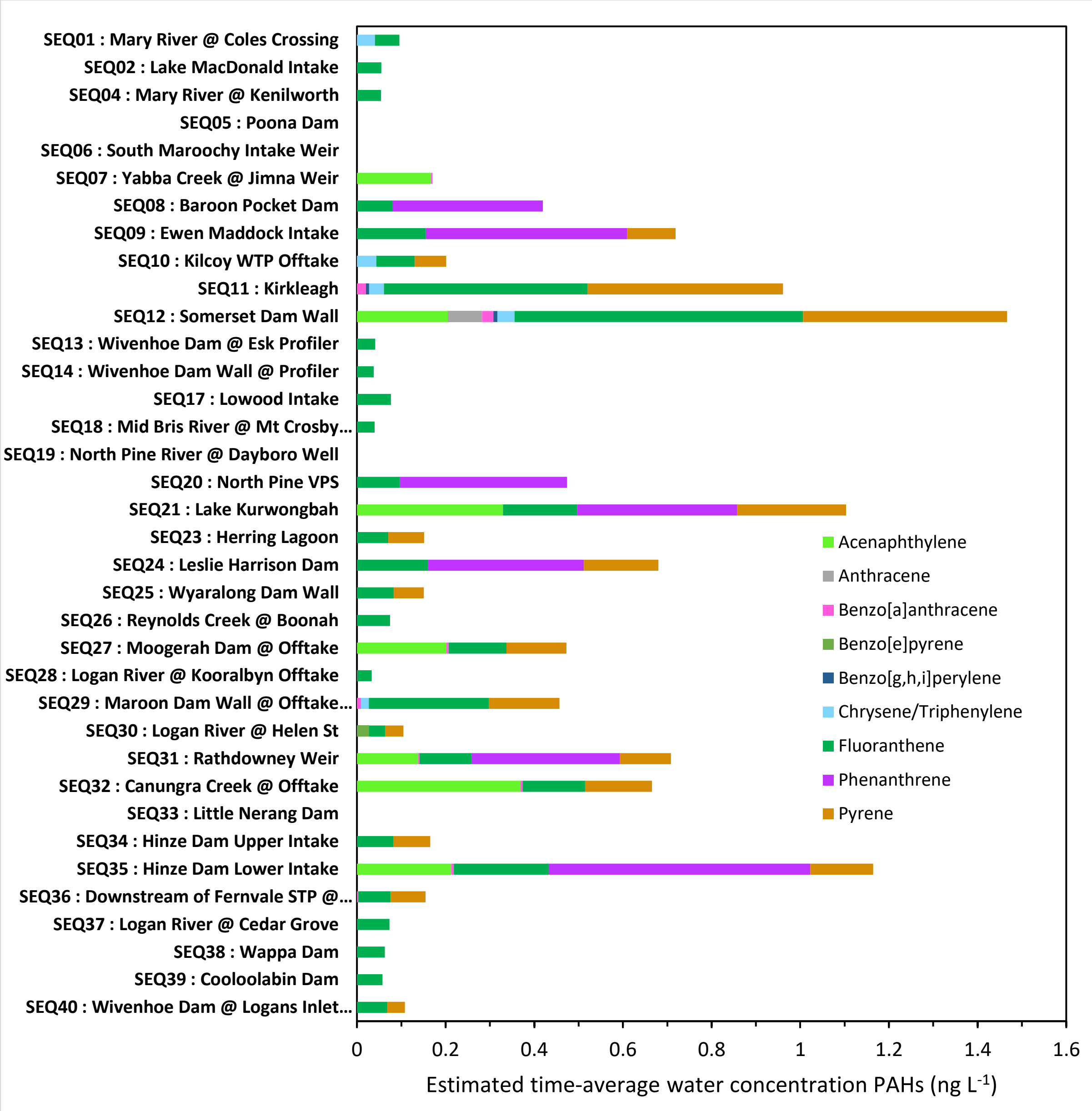

Figure 6. Total estimated water concentrations (ng L^{-1}) of 9 ΣPAHs at each site derived from PDMS passive samplers.

Pesticides

Over the deployment period, 22 polar pesticides (including herbicides, fungicides and insecticides) accumulated in ED passive samplers (

Table 3, Figure 7, Appendix 1). The ∑polar pesticides accumulated were below reporting limits for sites SEQ05 (Poona Dam), 06 (South Maroochy Intake Weir), 7 (Yabba Creek @ Jimna Weir), 23 (Herring Lagoon), 31 (Rathdowney Weir), 33 (Little Nerang Dam) and 34 (Hinze Dam Upper Intake) and the greatest amount reported was for SEQ37 (Logan River @ Cedar Grove) at 76.0 ng ED^{-1}.

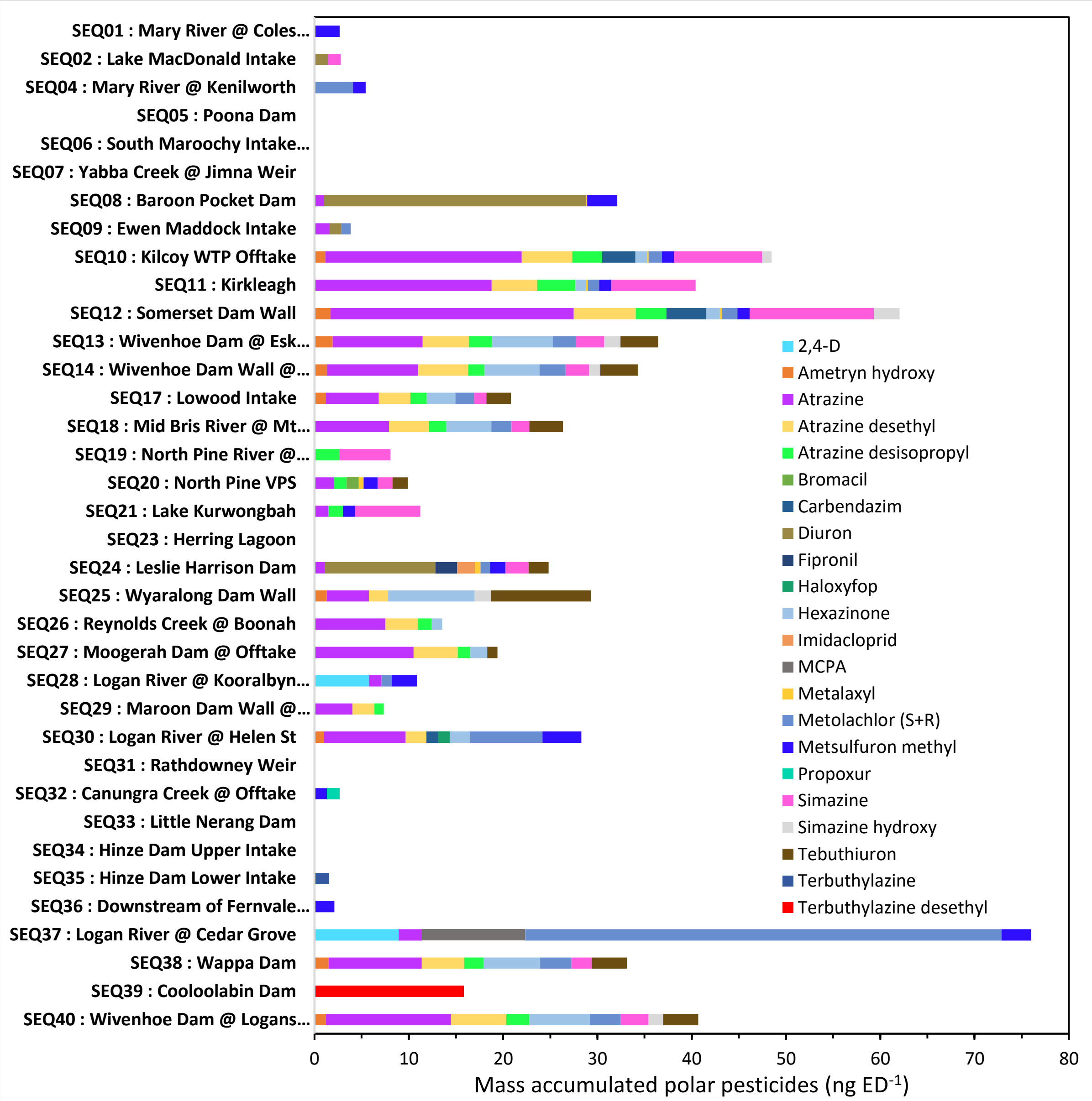

Figure 7. Total mass of 22 Σpolar pesticides (ng ED^{-1}) accumulated in ED passive samplers at each site.

Water concentrations were estimated for the polar pesticides accumulated where sampling rates have been previously calibrated. From the 22 chemicals reported, 15 were converted to time-weighted average water ∑concentrations which ranged from below reporting limits to 55.2 ng L^{-1}. The greatest average water ∑concentrations was reported for SEQ37 (Logan River @ Cedar Grove) and the smallest reportable average ∑concentration was SEQ32 (Canungra Creek @ Offtake) at 0.910 ng L^{-1}.

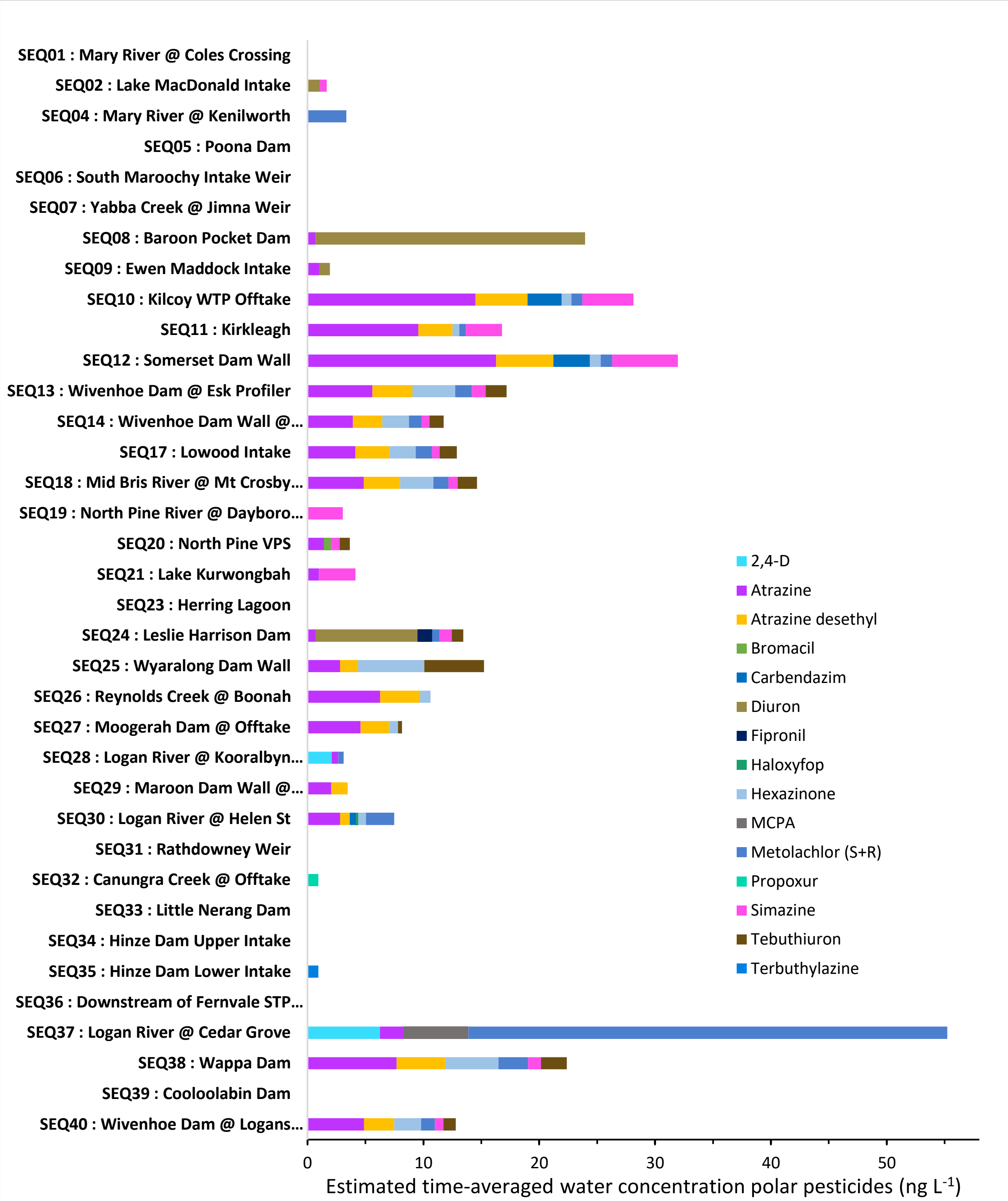

Figure 8. Total estimated water concentrations (ng L^{-1}) of 15 Σpolar pesticides at each site derived from ED passive samplers.

Pharmaceuticals and personal care products (PPCPs)

Eight PPCPs were reported with the average amount of ΣPPCPs accumulated ranging from below reporting limits for half of all sites (18 sites total; Figure 9) and up to 95.6 ng ED^{-1} at SEQ12 (Somerset Dam Wall). Interestingly, the greatest variety of PPCPs were detected at SEQ38 (Wappa Dam).

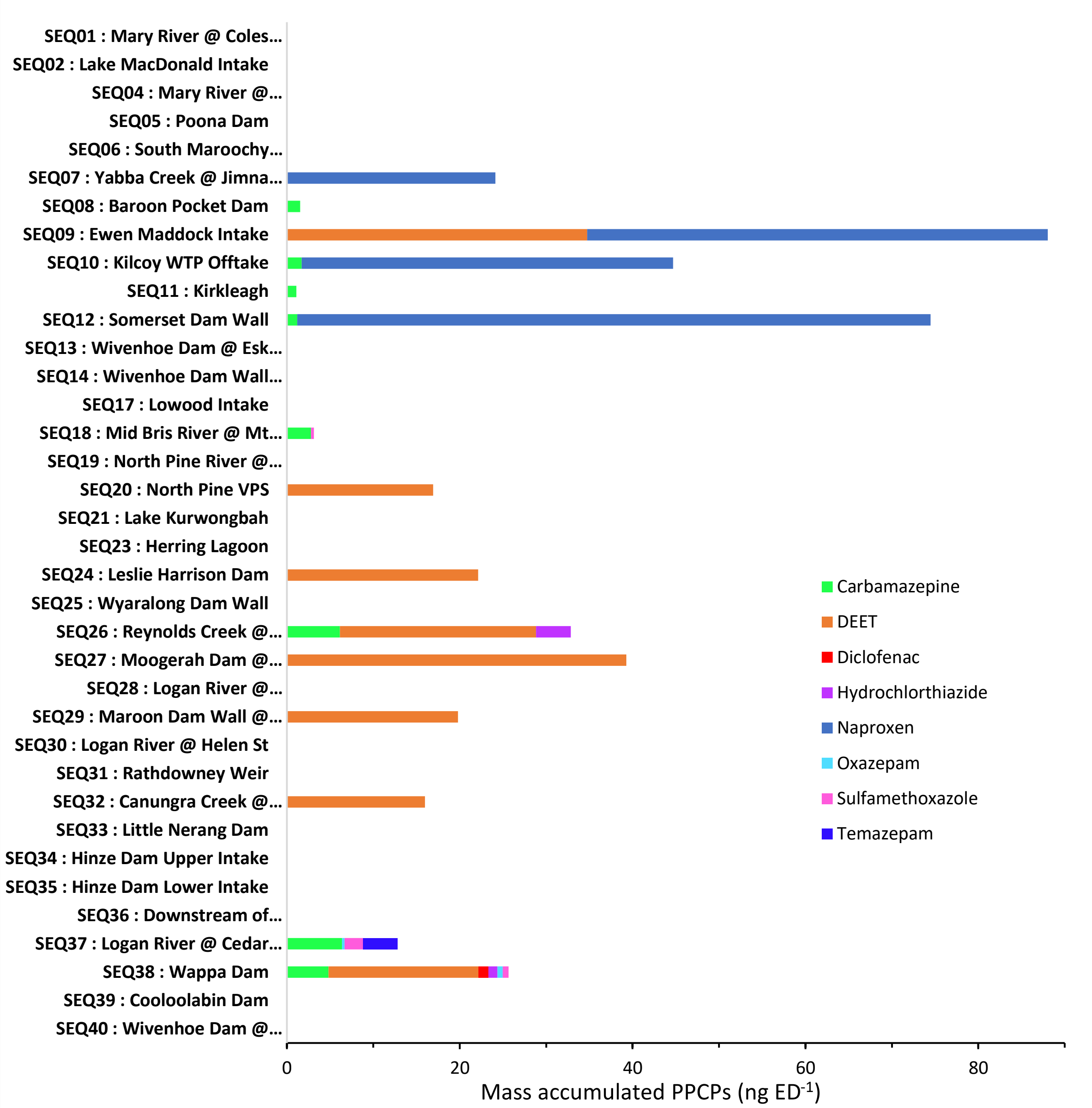

Figure 9. Total mass of 8 ΣPPCPs (ng ED^{-1}) accumulated in ED passive samplers at each site.

Of the 8 reported PPCPs, 5 were able to be converted into estimated time-weighted average water concentrations. Discounting the sites below reporting limits, these ∑PPCP water concentrations ranged between 1.08 and 20.0 ng L^{-1} for site SEQ11 (Kirkleagh) and site SEQ26 (Reynolds Creek @ Boonah), respectively (Figure 10).

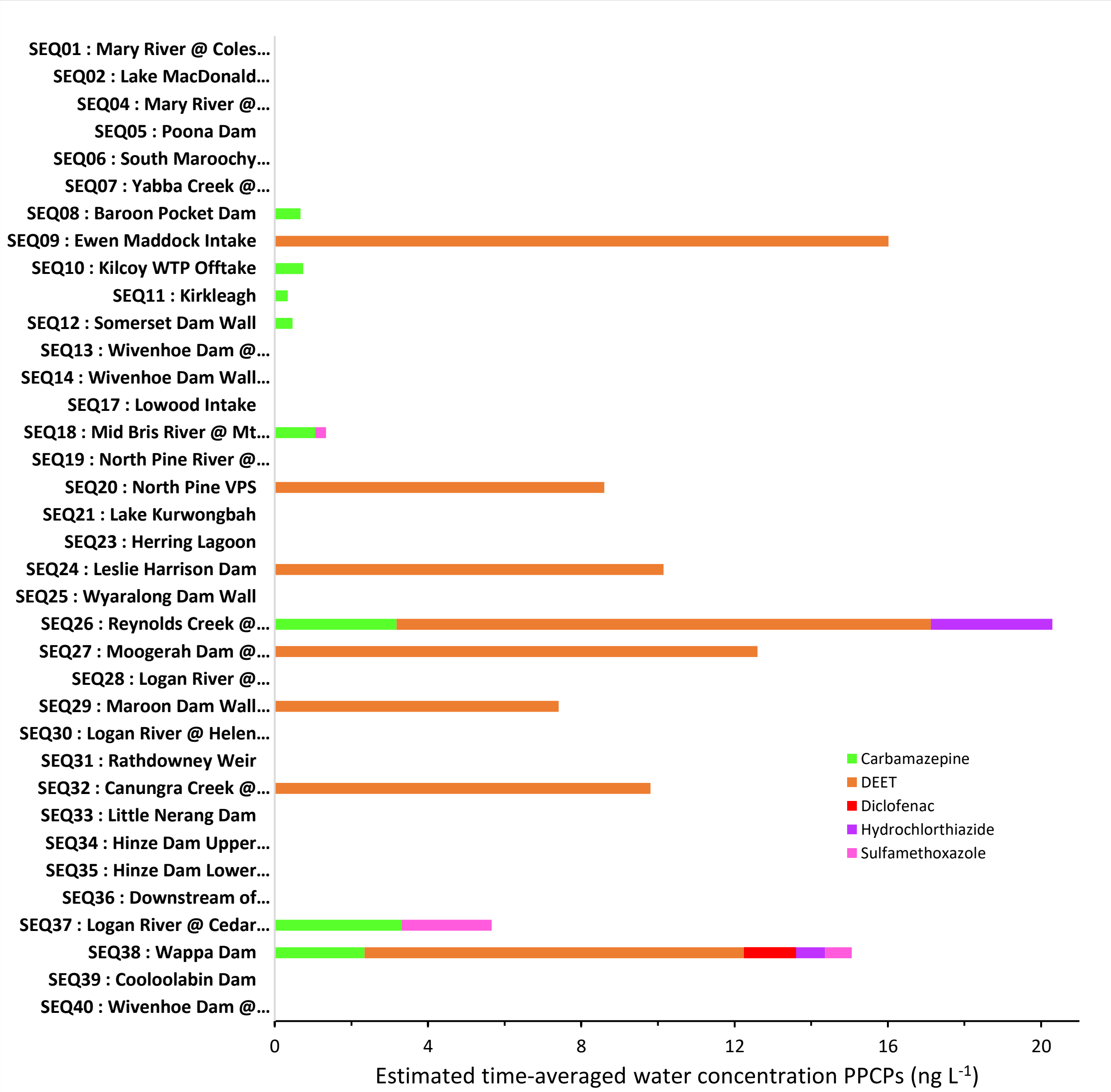

Figure 10. Total estimated water concentrations (ng L^{-1}) of 5 ΣPPCPs.

Analysis of non-target polar chemicals

Along with the target list of polar chemicals identified for investigation, the screening for an additional 45 herbicides and PPCP chemicals that have the potential to transport to waterways has been performed to investigate their presence in the water systems. During this sampling season no compounds of interest were detected, however a larger screening through additional pesticide, pharmaceutical and personal care product libraries revealed tentative detection of four compounds (Table 4). The suspect screening provides tentative identification of the presence / absence of these chemicals. We note that in order to fully confirm the identification and quantification of these analytes, the use of appropriate chemical standards would be necessary. Tentative identifications are considered when spectral library match scores exceed >98% and mass errors were <3 ppm.

Table 4. List of tentatively identified non-target chemicals in EDs, and the sites in which they were detected.

Chemical name	Description	Sites with tentativle detects
Acetochlor	Herbicide	SEQ-WIVENHOE DAM @ LOGANS INLET PRW (SEQ40)
Alachlor	Herbicide	SEQ-WIVENHOE DAM @ ESK PROFILER (SEQ13); SEQ-REYNOLDS CREEK @ BOONAH (SEQ26)
Aminocarb	Insecticide	RIVER @ KENILWORTH (SEQ04); SEQ-LESLIE HARRISON DAM (SEQ24); SEQ-WYARALONG DAM WALL (SEQ25); SEQ-MAROON DAM WALL @ OFFTAKE W2 BUOY (SEQ29); SEQ-LITTLE NERANG DAM (SEQ33); SEQ-HINZE DAM UPPER INTAKE (SEQ34); SEQ-DOWNSTREAM OF FERNVALE STP @ SAVAGES CRC (SEQ36); SEQ-LOGAN RIVER @CEDAR GROVE
Chlordimeform	Insecticide	SEQ-REYNOLDS CREEK @ BOONAH (SEQ26)
Cyanazine	Triazine herbicide	SEQ-MARY RIVER @ COLES CROSSING (SEQ01); SEQ-KILCOY WTP OFFTAKE (SEQ10); SEQ-WIVENHOE DAM @ ESK PROFILER (SEQ13); SEQ-MID BRIS RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER (SEQ18)
Cycloxydim	Herbicide	SEQ-WAPPA DAM (SEQ38)
Cyprodinil	Fungicide	SEQ-LAKE MACDONALD INTAKE (SEQ02); SEQ-KILCOY WTP OFFTAKE (SEQ10); SEQ-SOMERSET DAM WALL (SEQ12); SEQ-LOWOOD INTAKE (SEQ17)
Cyromazine	Insecticide	SEQ-KILCOY WTP OFFTAKE (SEQ10); SEQ-WIVENHOE DAM @ ESK PROFILER (SEQ13); SEQ-MOOGERAH DAM @ OFFTAKE (SEQ27)
Dicyclanil	Insecticide	SEQ-LAKE MACDONALD INTAKE (SEQ02); SEQ-YABBA CREEK @ JIMNA WEIR (SEQ07); SEQ-BAROON POCKET DAM (SEQ08); SEQ-EWEN MADDOCK INTAKE (SEQ09)
Diethofencarb	Antifungal	SEQ-YABBA CREEK @ JIMNA WEIR (SEQ07); SEQ-KILCOY WTP OFFTAKE (SEQ10)
Difenoxuron	Herbicide	SEQ-WIVENHOE DAM @ ESK PROFILER (SEQ13)
Difenzoquat	Herbicide	SEQ-WIVENHOE DAM WALL @ PROFILER (SEQ14); SEQ-MOOGERAH DAM @ OFFTAKE (SEQ27); SEQ-MAROON DAM WALL @ OFFTAKE W2 BUOY (SEQ29)
Diphenamid	Herbicide	SEQ-WIVENHOE DAM @ ESK PROFILER (SEQ13); SEQ-WIVENHOE DAM WALL @ PROFILER (SEQ14); SEQ-LOWOOD INTAKE (SEQ17); SEQ-NORTH PINE VPS (SEQ20); SEQ-MOOGERAH DAM @ OFFTAKE (SEQ27); SEQ-
Ethofumesate	Herbicide	SEQ-MID BRIS RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER (SEQ18); SEQ-HINZE DAM LOWER INTAKE (SEQ35)
Fuberidazole	Fungicide	SEQ-YABBA CREEK @ JIMNA WEIR (SEQ07); SEQ-SOMERSET DAM WALL (SEQ12); SEQ-MID BRIS RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER (SEQ18); SEQ-REYNOLDS CREEK @ BOONAH (SEQ26)
Imazaquin	Herbicide	SEQ-LOGAN RIVER @ KOORALBYN OFFTAKE (SEQ28)
isoprocarb	Insecticide	SEQ-MARY RIVER @ COLES CROSSING (SEQ01); SEQ-KILCOY WTP OFFTAKE (SEQ10); SEQ-SOMERSET DAM WALL (SEQ12); SEQ-NORTH PINE VPS (SEQ20); SEQ-LOGAN RIVER
Mepanipyrim	Fungicide	SEQ-KIRKLEAGH (SEQ11); SEQ-SOMERSET DAM WALL (SEQ12); SEQ-WIVENHOE DAM WALL @ PROFILER (SEQ14); SEQ-LAKE KURWONGBAH (SEQ21); SEQ-REYNOLDS CREEK @ BOONAH (SEQ26); SEQ-MOOGERAH DAM @ OFFTAKE (SEQ27); SEQ-WIVENHOE DAM @ LOGANS INLET PRW (SEQ40)
Metolcarb	Insecticide	SEQ-MAROON DAM WALL @ OFFTAKE W2 BUOY (SEQ29); SEQ-HINZE DAM UPPER INTAKE (SEQ34); SEQ-HINZE DAM LOWER INTAKE (SEQ35)
Promecarb	Insecticide	SEQ-MARY RIVER @ COLES CROSSING (SEQ01); SEQ-KIRKLEAGH (SEQ11); SEQ-SOMERSET DAM WALL (SEQ12); SEQ-MOOGERAH DAM @ OFFTAKE (SEQ27); SEQ-RATHDOWNEY WEIR (SEQ31); SEQ-WAPPA DAM (SEQ38)
Propisochlor	Herbicide	SEQ-SOUTH MAROOCHY INTAKE WEIR (SEQ06); SEQ-KIRKLEAGH (SEQ11); SEQ-MID BRIS RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER (SEQ18)
Rotenone	Insecticide	SEQ-WYARALONG DAM WALL (SEQ25); SEQ-DOWNSTREAM OF FERNVALE STP @ SAVAGES CRC (SEQ36)
Sethoxydim	Herbicide	SEQ-EWEN MADDOCK INTAKE (SEQ09); SEQ-SOMERSET DAM WALL (SEQ12); SEQ-REYNOLDS CREEK @ BOONAH (SEQ26)
Tetramethrin	Insecticide	SEQ-LOGAN RIVER @ HELEN ST (SEQ30)

Comparison to water quality guideline values

A selection of water guideline values and species protection values are provided in Table 5. No compounds with an available Australian drinking water guideline (ADWG) value were reported with estimated average concentrations above the ADWG value. This analysis is somewhat limited in that not all reported compounds were able to be converted to a water concentration. However, given the levels observed, and the comparisons that were able to be made, we believe it is unlikely there would be exceedances attributed to any of the compounds reported as mass per sampler.

Exceedances for eco-toxicological guidelines were observed in the estimated time-averaged water concentrations chlorpyrifos. ANZECC & ANCANZ have set chlorpyrifos freshwater guideline values of 0.04 and 10 ng L^{-1} for 99% and 95% level species protection, respectively. Eighteen sites (ranging between 0.096 (SEQ38) – 1.04 ng L^{-1} (SEQ09)) exceeded the 99% species protection guideline. No sites exceeded the 95% species protection guideline values.

Table 5. Threshold chemical guidelines for Australian Drinking Water and Freshwater Aquatic Ecosystems

Australian Drinking Water Guidelines 6 (2011) Version 3.5 Updated August 2018 (ng L^{-1})		ANZECC & ANCANZ (2018) Trigger values for freshwater		This campaign
		99% species protection value (ng L^{-1})	95% species protection value (ng L^{-1})	Highest Reported Value (ng L^{-1})
Herbicides & Insecticides				
Atrazine	20000	700	13000	16.3
Ametryn	70000	N/A	N/A	N/A
Bromacil	400000	N/A	N/A	0.610
Carbaryl	30000	N/A	N/A	N/A
Carbendazim	90000	N/A	N/A	3.15
Diuron	20000	N/A	N/A	23.3
Fluometuron	70000	N/A	N/A	N/A
Haloxyfop	1000	N/A	N/A	0.200
Hexazinone	400000	N/A	N/A	5.70
MCPA	40000	N/A	N/A	5.57
Malathion	700000	2	50	N/A
Methomyl	20000	N/A	N/A	N/A
Metolachlor	300000	N/A	N/A	41.4
Metsulfuron methyl	40000	N/A	N/A	N/A
Pendimethalin	400000	N/A	N/A	N/A
Picloram	300000	N/A	N/A	N/A
Propazine	50000	N/A	N/A	N/A
Propiconazole	100000	N/A	N/A	N/A
Simazine	20000	200	3200	5.65
Tebuthiuron	N/A	20	2200	5.15
Terbuthylazine	10000	N/A	N/A	0.92
Triclopyr	20000	N/A	N/A	N/A
2,4-D	30000	140000	280000	6.26
2,4,5-T	100000	3000	36000	N/A
3,4-Dichloroaniline	N/A	1300	3000	N/A
OCPs				
Chlordane	2000	30	800	0.008
Chlorpyrifos	10000	0.04	10	1.04
DDT	9000	6	10	N/A
Dieldrin and Aldrin	300	N/A	N/A	0.028
Endosulfan	20000	30	200	N/A
Endrin	N/A	10	20	N/A
Heptachlor	300	10	90	N/A
r-HCH (lindane)	10000	70	200	N/A
PAHs				

Benzo(a)pyrene	10	N/A	N/A	0.026
Naphthalene	10	2500	16000	N/A

Discussion

OCPs were first introduced into Australia in the mid-1940s and were applied in many commercial products in different forms (such as powders and liquids). At one time up to 150 commercial products containing OCPs may have been registered in Australia. This followed a period of widespread use until the 1970s when recognition of risks related to OCPs resulted in reduced use and their ultimate ban in the 1980s. Since then, human biomonitoring studies in blood and breastmilk have showed the substantial decline of these chemicals from the early 1980s to the 1990s after which levels appear to plateau (Toms *et al.* 2012). Although a few OCPs were reported at almost all monitoring sites, the concentrations were very low. The legacy compounds (those now banned) such as endosulfan and DDT, were at levels below the limit of reporting (typically < 0.02 ng L^{-1}). Compounds still in use such as dacthal and chlorpyrifos were reported at higher concentrations, consistent with ongoing inputs to the environment. Dacthal is currently permitted for the use of controlling stinging nettle in lettuce crops (APVMA 2016) and may be in use close to these sites. The insecticide chlorpyrifos was introduced in 1965 and has been included in many products and formulations aimed at agricultural, urban, commercial and residential uses. Although regulation measures have been put in place in Australia (APVMA 2011b) the chemical has not been strictly banned. A search of the APVMA PubCris database reveals 72 currently registered or approved products containing chlorpyrifos. A continued review of both dacthal and chlorpyrifos is warranted to estimate any future risk.

PAHs are ubiquitous in the environment and are introduced via anthropogenic sources primarily as a result of incomplete combustion as well as via natural sources (i.e. forest fires and the transformation of biogenic precursors) (Nguyen *et al.* 2014). A number of PAHs have been included as chemicals of concern under the Stockholm Convention on Persistent Organic Pollutants (2011) due to their toxic and carcinogenic properties. They enter aquatic systems via storm water runoff from urban and industrial areas, roads and spills as well as via recreational activities such as boating. PAHs can undergo long-range atmospheric transport and deposition and are distributed in waterways during intense rainfall and flooding (Nguyen *et al.* 2014). The hydrophobic nature of PAHs typically results in low concentrations in water as they generally associate with particulate matter and sediment. Thirty-two sites showed reportable concentrations of PAHs including acenaphthylene, anthracene, benzo[a]anthracene, benzo[e]pyrene, benzo[g,h,i]perylene, fluoranthene and phenanthrene at low levels (<1 ng L^{-1}). The decrease in reported PAH amounts in this campaign compared to report 12 from the previous campaign may be due to a combination of decreased rainfall and subsequent runoff in winter, and at sites like Somerset Dam, decreased recreational boating activities which may have further decreased following a decrease in interstate and international tourism due to COVID restrictions.

Polar pesticides (herbicides, insecticides and fungicides) were reported at 29 sites. The most frequently reported herbicide atrazine is used in sugarcane and other farming crop as a broad spectrum pre- and early post-emergent control for various grass and broadleaf weeds. Triazine herbicides such as atrazine, simazine, hexazinone and degradation products such as atrazine desisopropyl and atrazine desethyl can remain in soils for several months and can migrate from soil to groundwater or transport to waterways via runoff and flooding events. Atrazine and simazine have been widely used in Australia and are registered for 1600 uses including weed control in orchards and various crops (APVMA 2011a; ANZECC & ARMCANZ 2018). It can be used in conjunction with diuron and hexazinone, two herbicides also frequently observed at relatively high levels. Herbicides with some soil mobility are generally transported to the aquatic environment through runoff and/or percolation to groundwater. Some areas of South-East Queensland experienced lower than average rainfall in September 2020 (BOM 2020), which may explain the decrease in detections from Report 12 in the previous campaign. This increase may also be due to the seasonal nature of agriculture and pesticide applications.

Pharmaceuticals and personal care products have emerged as a major group of environmental contaminants over the past decade. Some polar organic chemicals persist through wastewater treatment processes resulting in their continuous release into the aquatic environment (Kaserzon *et al.* 2014). The most frequently reported PPCP was DEET which is often attributed to background contamination due to high DEET application by field staff, to combat insect bites. If reported values for DEET are ignored, then the total number of sites with measurable PPCP water concentrations drops to 8. Of these, the primary contributor is carbamazepine, detected at 8 sites (22%) and the sole PPCP at 4 of these. The persistence of carbamazepine to biodegradation has been previously noted, and it is frequently observed in wastewater influent and effluent as well as general aquatic environments (Andreozzi *et al.* 2002, Liu *et al.* 2020). Interestingly, Site SEQ36, located downstream of a STP, had no detectable ∑PPCP concentrations in this campaign which may be in part due to a sub-optimal deployment or sampling error. The contribution of pharmaceuticals and personal care products can be an indicator of systems which are used for human recreational activities or which receive some degree of treated effluent.

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.

- Review sampler deployment at SEQ36 (Downstream of Fernvale STP), and include a duplicate sampler for future deployments.

- Review target compound lists to see if those frequently non-detected are better replaced with other targets.

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Appendix 1

See enclosed excel file 'SEQW results_Summer2020.xls'

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