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

Report 14 - Winter 2021

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Title
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Executive Summary

The *Catchment and Drinking Water Quality Micro Pollutant Monitoring Program* was launched in mid-2014 with the aim of improving the characterisation and understanding of the micro pollutant risk profile in source water reservoirs through annual summer and winter sampling campaigns. The monitoring program utilising passive samplers was continued in reservoirs in South East Queensland (SEQ) during the third quarter of 2021. These sampling events represent the third 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 two samplers 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 52 different chemicals including 13 OCPs, 7 PAHs, 22 polar pesticides and 10 PPCPs. OCPs were detected at 76% of sites, with Chlorpyrifos (46%) and Dacthal (38%) the most frequently reported. Total ∑OCP water concentrations across sites ranged between 0.010 – 3.84 ng L^{-1} where concentrations were reportable. PAHs were detected at 86% of sites, with Chrysene/Triphenylene (86%) and Fluoranthene (38%) reported at the highest abundance across all sites. Total ∑PAH water concentrations across sites ranged between 0.001 – 0.570 ng L^{-1}. In total, 22 different polar pesticides were reported in 32 sites (86%), with Metsulfuron methyl (59%) and Atrazine (38%) reported at highest abundance across all sites. Total ∑polar pesticides ranged between 0.66 – 211.57 ng L^{-1}. Additionally, 10 PPCPs were detected across sites with highest detection frequencies observed for DEET (14%) and Carbamazepine (8%). Total estimated ∑PPCP water concentrations ranged between 1.880 – 58.0 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 (ADWG 2011) for comparison. No chemicals were present in concentrations that exceeded the ADWG values. In the ecotoxicological setting, chlorpyrifos, metolachlor and tebuthiruon were detected above the thresholds set for 99% species protection but fell 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.

Methodology

Passive water samplers were deployed in periods between July 2021 to August 2021 at 37 sites of SEQ reservoirs/waterways (Table 1) except for sites 28 and 37 which were redeployed between August and September 2021 due to sampler loss and are denoted by "Spare" throughout the report. It should be noted that only redeployed samplers are reported for those sites. Deployments were for periods of 27 to 31 days in duration. 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" (January 2021). 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	Date Deployed	Date Retrieved	Days Deployed	Flow velocity (cm s^{-1})	Comments
SEQ01 : Mary River @ Coles Crossing	MRS-SP012	14/07/2021	11/08/2021	28	3.4	
SEQ02 : Lake MacDonald Intake	LMD-SP001	22/07/2021	19/08/2021	28	3.4	
SEQ04 : Mary River @ Kenilworth	MRS-SP013	13/07/2021	13/08/2021	31	10.5	
SEQ05 : Poona Dam	POD-SP001	7/07/2021	5/08/2021	29	4.6	
SEQ06 : South Maroochy Intake Weir	SOR-SP001	6/07/2021	4/08/2021	29	3.4	
SEQ07 : Yabba Creek @ Jimna Weir	YAC-SP001	13/07/2021	13/08/2021	31	3.4	
SEQ08 : Baroon Pocket Dam	BPD-SP001	29/07/2021	25/08/2021	27	3.9	
SEQ09 : Ewen Maddock Intake	EMD-SP001	8/07/2021	5/08/2021	28	7.7	
SEQ10 : Kilcoy WTP Offtake	SOD-SP010	13/07/2021	10/08/2021	28	3.4	
SEQ11 : Kirkleagh	SOD-SP011	20/07/2021	17/08/2021	28	3.7	
SEQ12 : Somerset Dam Wall	SOD-SP001	20/07/2021	17/08/2021	28	3.6	
SEQ13 : Wivenhoe Dam @ Esk Profiler	WID-SP004	12/07/2021	9/08/2021	28	3.9	
SEQ14 : Wivenhoe Dam Wall @ Profiler	WID-SP001	13/07/2021	10/08/2021	28	6.9	
SEQ17 : Lowood Intake	MBR-SP016	13/07/2021	10/08/2021	28	4	
SEQ18 : Mid Bris River @ Mt Crosby Westbank Offtake Tower	MBR-SP001	13/07/2021	11/08/2021	29	7.8	
SEQ19 : North Pine River @ Dayboro Well	NOD-SP091	20/07/2021	17/08/2021	28	3.4	
SEQ20 : North Pine VPS	NOD-SP001	20/07/2021	17/08/2021	28	5.2	
SEQ21 : Kurwongbah dam wall @ offtake	LAK-SP001	21/07/2021	18/08/2021	28	4.9	
SEQ23 : Herring Lagoon	NSC-SP001	15/07/2021	12/08/2021	28	3.4	
SEQ24 : Leslie Harrison Dam	LHD-SP005	20/07/2021	18/08/2021	29	3.4	

SEQ25 : Wyaralong Dam Wall	WYD-SP001	7/07/2021	4/08/2021	28	4.1	
SEQ26 : Reynolds Creek @ Boonah	MOD-SP027	21/07/2021	17/08/2021	27	3.4	
SEQ27 : Moogerah Dam @ Offtake	MOD-SP002	22/07/2021	17/08/2021	26	7.4	
SEQ28 : Logan River @ Kooralbyn Offtake	LRS-SP017	3/08/2021	6/07/2021	28	27.8	**PDMS cage lost on retrieval due to breakage of deployment wire**
Spare3_SEQ28 : Logan River @ Kooralbyn Offtake	LRS-SP017	4/08/2021	6/09/2021	33	15.9	**Used to re-sample site due to lost PDMS cage**
SEQ29 : Maroon Dam Wall @ Offtake W2 Buoy	MAD-SP004	5/07/2021	2/08/2021	28	7.7	
SEQ30 : Logan River @ Helen St	LRS-SP013	6/07/2021	3/08/2021	28	15.5	
SEQ31 : Rathdowney Weir	LRS-SP016	6/07/2021	3/08/2021	28	4.6	
SEQ32 : Canungra Creek @ Offtake	CAC-SP001	19/07/2021	16/08/2021	28	3.4	
SEQ33 : Little Nerang Dam	LND-NR001	26/07/2021	25/08/2021	30	3.4	
SEQ34 : Hinze Dam Upper Intake	HID-SP001	27/07/2021	24/08/2021	28	3.4	
SEQ35 : Hinze Dam Lower Intake	HID-SP002	27/07/2021	24/08/2021	28	4.9	
SEQ36 : Downstream of Fernvale STP @ Savages CRC	MBR-SP013	14/07/2021	11/08/2021	28	3.4	
Spare1_SEQ37 : Logan River @ Cedar Grove	LRS-SP012	4/08/2021	6/09/2021	33	3.4	**Original kit deployed on 6/7 had been removed or was lost by 3/8.**
SEQ38 : Wappa Dam	WAD-SP001	7/07/2021	5/08/2021	29	3.9	
SEQ39 : Cooloolabin Dam	COD-SP001	6/07/2021	4/08/2021	29	6.7	
SEQ40 : Wivenhoe Dam @ Logans Inlet PRW	WID-SP061	12/07/2021	9/08/2021	28	6.8	
SEQ43 : Enoggera dam wall at offtake	END-SP001	12/07/2021	9/08/2021	28	5.4	

Note:- Flow velocity of 3.4 cm s^{-1} was used where the calculated flow velocity was less than 3.4 cm s^{-1}
Sites with replicate samplers deployed for QA/QC purposes are highlighted in green.

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 (Figure 1) 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

Passive flow monitors (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 3.4 cm s^{-1} (SEQ34 : Hinze Dam Upper Intake) to 15.9 cm s^{-1} (Spare3_SEQ28 : Logan River @ Kooralbyn Offtake) (Figure 2).

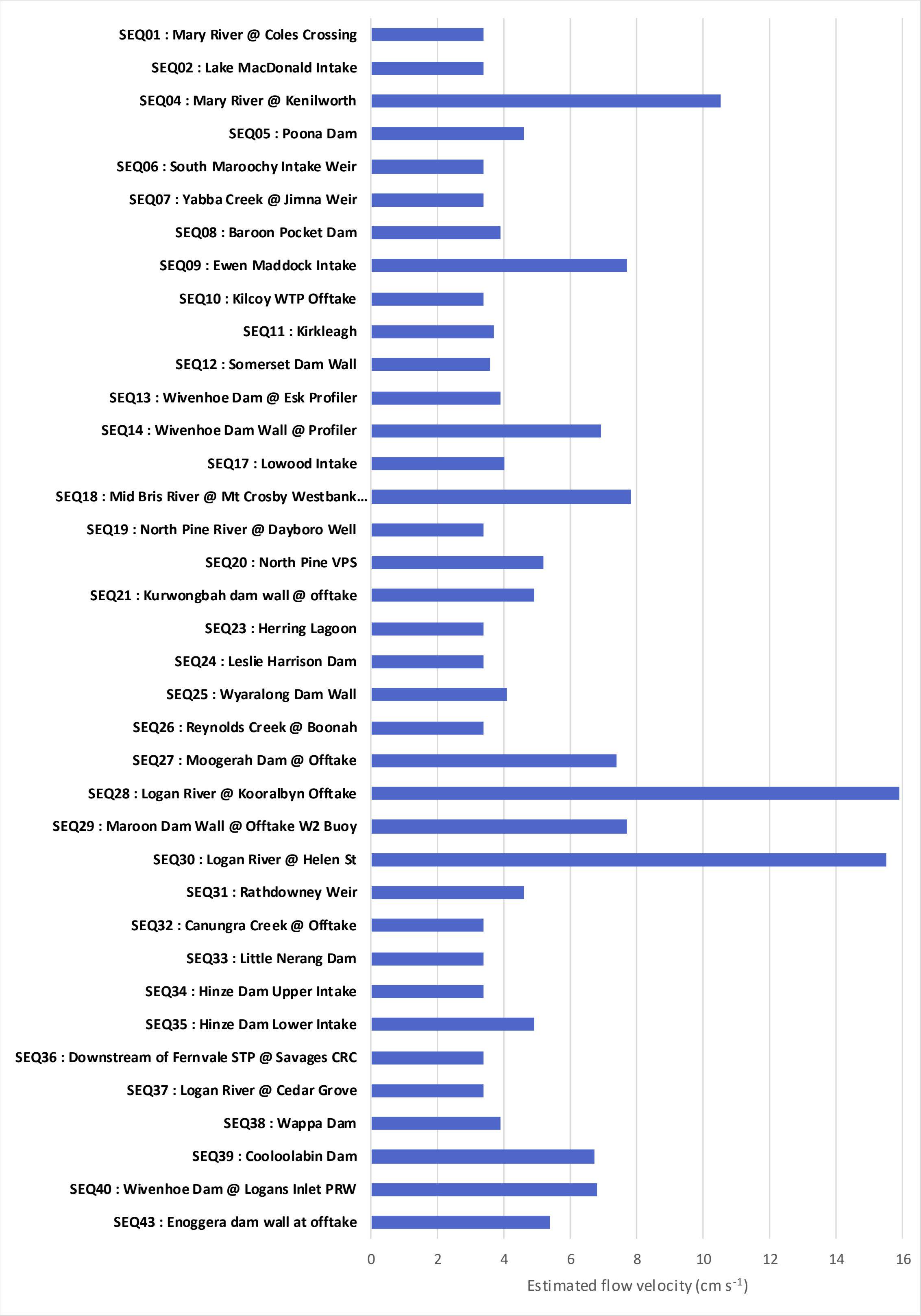

Figure 2. Passive flow monitor (PFM) based water flow velocity estimations (cm s^{-1}) at the deployment sites (n=37).

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 13 OCPs and 7 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% – 46% for OCPs and 3% – 86% for PAHs. Table 3 summarises the polar chemicals quantified via ED (pesticides and PPCPs). A total of 22 pesticides (predominantly herbicides) and 10 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3% - 59% for pesticides and 3% - 14% 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	% Detection	Min reported (ng/PDMS)	Max reported (ng/PDMS)
OCP				
Bifenthrin	**5**	**14%**	**0.802**	**3.5**
Chlorpyrifos	**17**	**46%**	**2.86**	**36**
cis-Chlordane	**2**	**5%**	**0.56**	**0.972**
Dacthal	**14**	**38%**	**2.63**	**31.5**
Dieldrin	**11**	**30%**	**2.64**	**25.7**
Endosulfan sulfate	**4**	**11%**	**1.04**	**2.73**
Heptachlor epoxide b	**3**	**8%**	**1.76**	**9.10**
o,p-DDD	**1**	**3%**	**2.10**	**2.10**
p,p-DDD	**7**	**19%**	**1.34**	**12.1**
p,p-DDE	**7**	**19%**	**1.24**	**5.2**
Permethrin	**6**	**16%**	**2.540**	**5.20**
trans-Chlordane	**1**	**3%**	**1.68**	**1.68**
γ-HCH (Lindane)	**3**	**8%**	**1.81**	**13.9**
PAH				
Acenaphthene	**1**	**3%**	**23**	**23.0**
Benzo[a]anthracene	**1**	**3%**	**1.01**	**1.01**
Benzo[b,j,k]fluoranthene	**2**	**5%**	**0.537**	**0.71**
Chrysene/Triphenylene	**32**	**86%**	**0.51**	**3.09**
Fluoranthene	**14**	**38%**	**5.06**	**19.7**
Phenanthrene	**2**	**5%**	**52**	**63.1**
Pyrene	**7**	**19%**	**7.63**	**15.7**

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	Number of sites detected	% Detection	Min reported (ng/ED)	Max reported (ng/ED)
Herbicides and Pesticides				
2,4-D	2	5%	5.73	21.16
Ametryn hydroxy	1	3%	1.75	1.75
Atrazine	14	38%	1.12	10.1
Atrazine desethyl	12	32%	1.18	5.16
Atrazine desisopropyl	10	27%	1.66	3.18
Carbendazim	12	32%	1.11	128.3
Diuron	7	19%	1.00	11.5
Fipronil	3	8%	0.960	2.70
Fluazifop	1	3%	0.340	0.340
Fluroxypyr	1	3%	1.05	1.05
Haloxyfop	1	3%	5.22	5.22
Hexazinone	10	27%	1.05	4.3
Imidacloprid	6	16%	1.07	3.7
MCPA	1	3%	5.03	5.0
Metalaxyl	2	5%	3.910	4.50
Metolachlor (S+R)	7	19%	1.04	28.1
Metsulfuron methyl	22	59%	1.05	33.54
Pendimethalin	1	3%	5.15	5.15
Simazine	12	32%	1.03	20.8
Tebuthiuron	10	27%	1.05	332.3
Terbuthylazine	1	3%	1.57	1.57
Triclopyr	7	19%	5.28	39.9
Pharmaceuticals and personal care products (PPCPs)				
Caffeine	2	5%	42.0	61.8
Carbamazepine	3	8%	3.62	22.47
DEET	5	14%	28.5	128
Diclofenac	3	8%	2.50	3.41
Gabapentin	1	3%	1.32	1.32
Hydrochlorthiazide	1	3%	6.62	6.62
Naproxen	1	3%	5.02	5.02
Oxazepam	3	8%	0.72	3.68
Sulfamethoxazole	3	8%	0.300	8.150
Temazepam	2	5%	1.04	7.34

Organochlorine pesticides (OCPs)

In total, 13 OCPs were accumulated in PDMS samplers over the deployment period (Table 2, Figure 3, Appendix 1), with the amount of ∑OCPs accumulated ranging from below reporting limits (SEQ25 - Wyaralong Dam Wall; SEQ31 - Rathdowney Weir; SEQ39 - Cooloolabin Dam; SEQ08 - Baroon Pocket Dam; SEQ33 - Little Nerang Dam; SEQ35 - Hinze Dam Lower Intake; SEQ04 - Mary River @ Kenilworth; SEQ32 - Canungra Creek @ Offtake) to 82 ng PDMS^{-1} (SEQ24 - Leslie Harrison Dam).

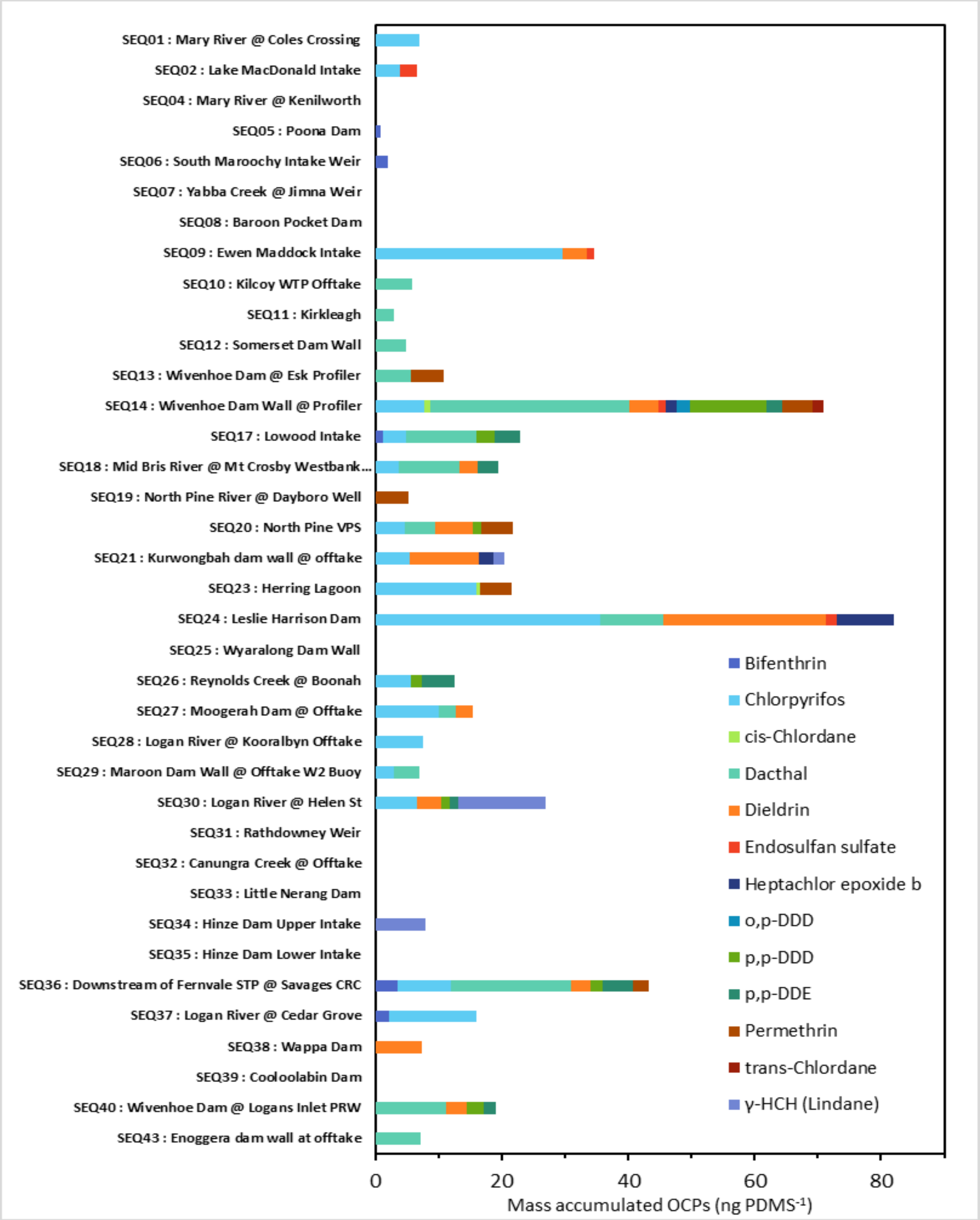

Figure 3. Total mass of 13 ΣOCPs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

Discounting the sites below reporting limits, the conversion of ∑OCP masses accumulated in passive samplers to time-weighted average water concentrations revealed an estimated water concentration range of 0.010 to 3.84 ng L^{-1} (SEQ05 - Poona Dam and SEQ30 - Logan River @ Helen St, respectively; Figure 4).

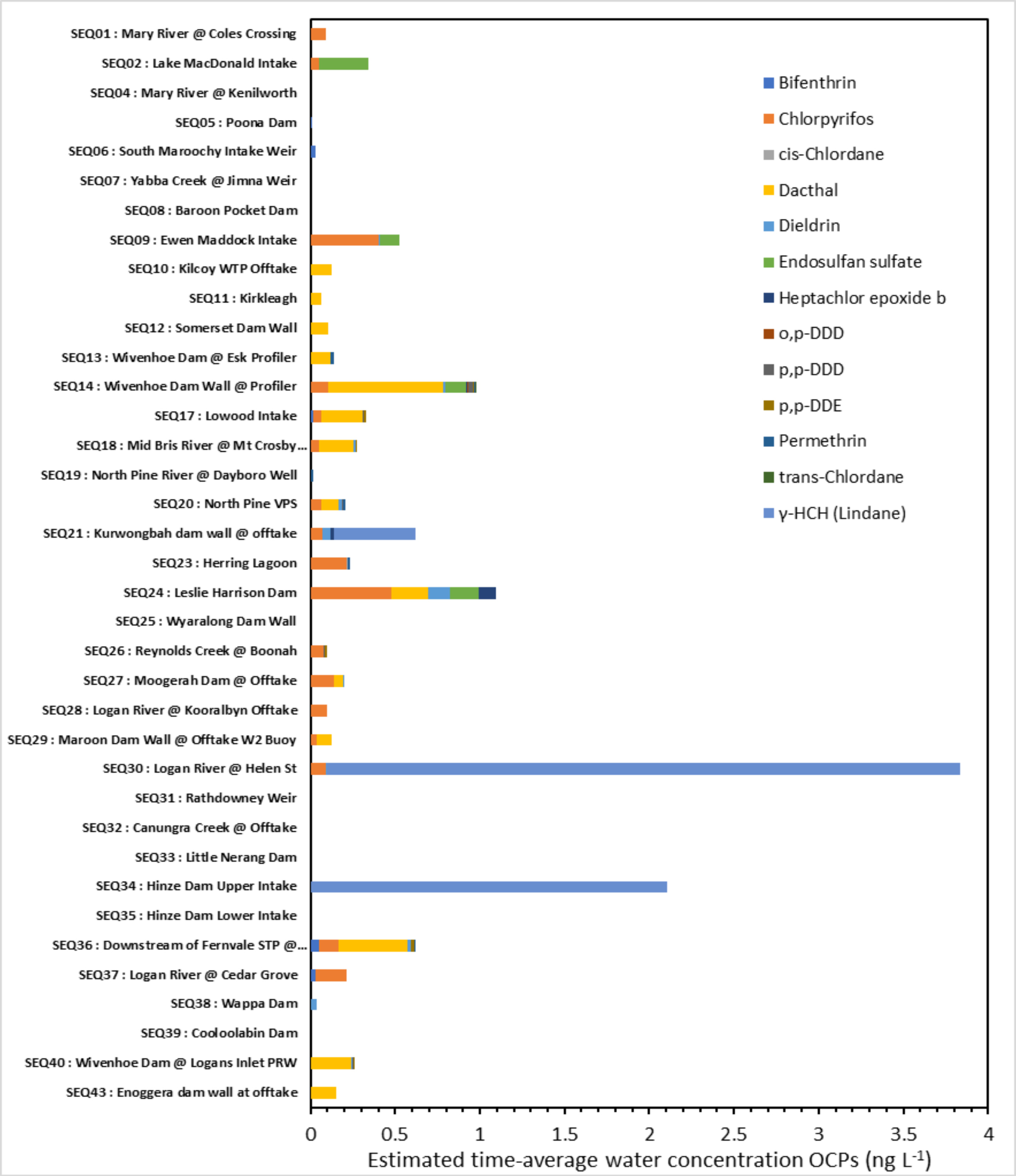

Figure 4. Total estimated water concentrations (ng L^{-1}) of 13 ΣOCPs at each site derived from PDMS passive samplers.

Polycyclic aromatic hydrocarbons (PAHs)

In total, 7 PAHs were accumulated in PDMS samplers over the deployment period (Table 2, Figure 5, Appendix 1), with the amount of ∑PAHs accumulated ranging from below reporting limits (SEQ23 - Herring Lagoon; SEQ07 - Yabba Creek @ Jimna Weir; SEQ34 - Hinze Dam Upper Intake; SEQ19 - North Pine River @ Dayboro Well) to 100 ng PDMS^{-1} (SEQ24 - Leslie Harrison Dam).

Figure 5. Total mass of 7 ΣPAHs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

Discounting the sites below reporting limits, the conversion of ∑PAH masses accumulated in passive samplers to time-weighted average water concentrations revealed an estimated water concentration range of 0.001 to 0.570 ng L^{-1} (SEQ39 - Cooloolabin Dam and SEQ24 - Leslie Harrison Dam, respectively; Figure 6).

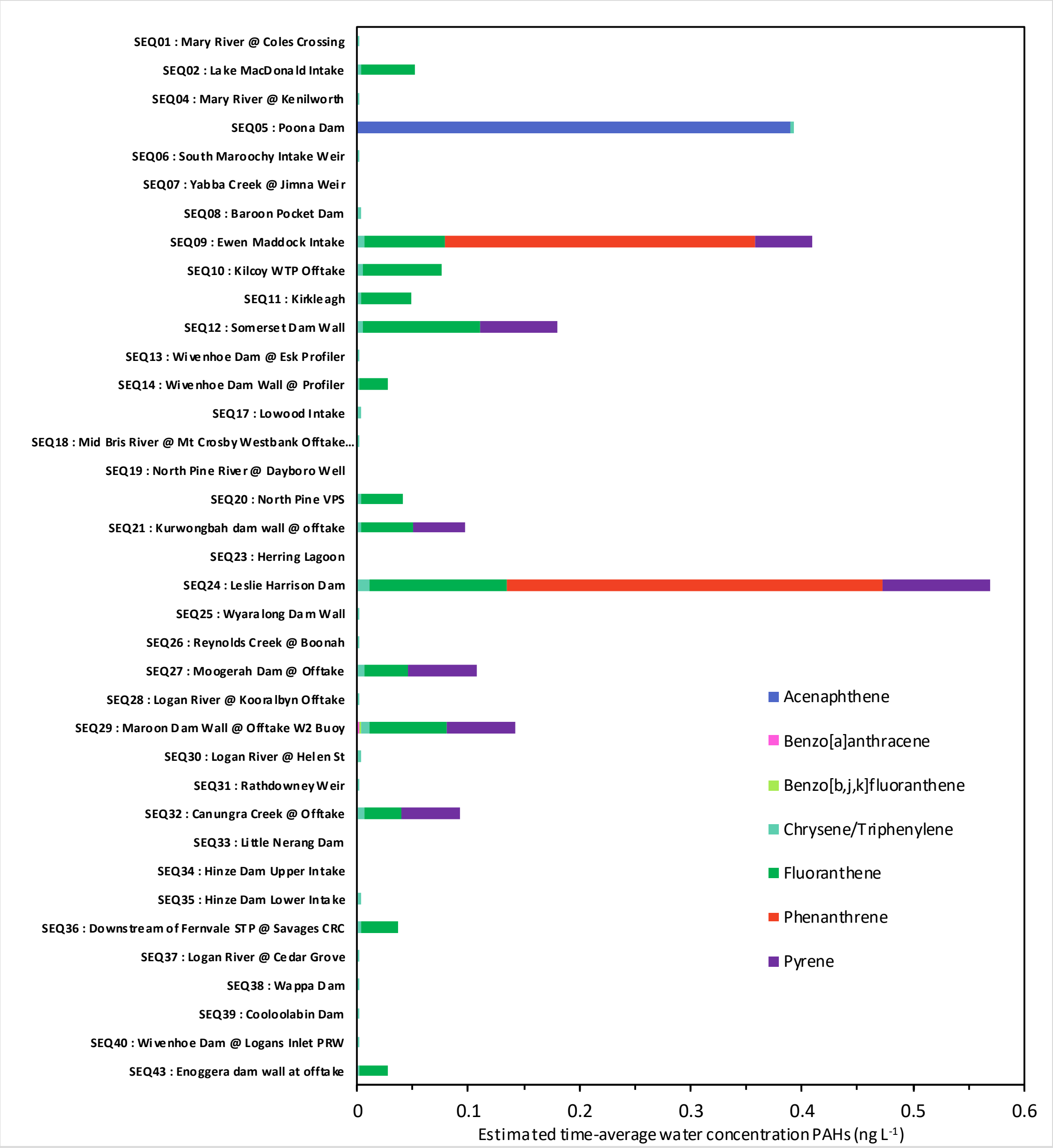

Figure 6. Total estimated water concentrations (ng L^{-1}) of 7 ΣPAHs at each site derived from PDMS passive samplers.

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 ranged from below reporting limits (SEQ43 - Enoggera dam wall at offtake; SEQ23 - Herring Lagoon; SEQ33 - Little Nerang Dam; SEQ39 - Cooloolabin Dam) to 346 ng ED^{-1}(SEQ24 - Leslie Harrison Dam).

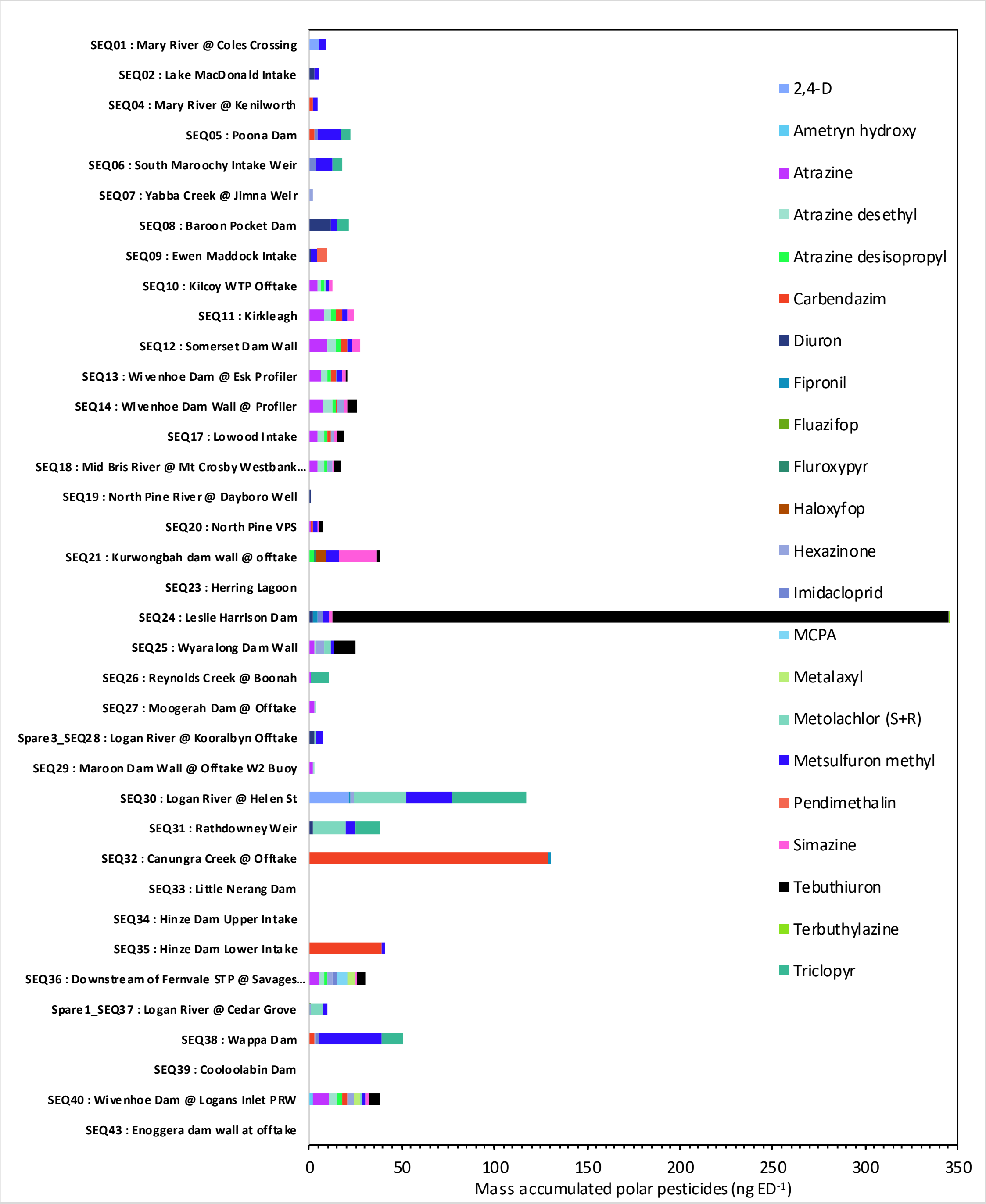

Figure 7. Total mass of 22 Σpolar pesticides (ng ED^{-1}) accumulated in ED passive samplers at each site.

Water concentrations were estimated for the polar pesticides accumulated where sampling rates have been previously calibrated. From the 22 chemicals reported, 14 were converted to time-weighted average water ∑concentrations. Discounting the sites below reporting limits, these water concentrations ranged between 0.66 and 211.57 ng L^{-1} (SEQ09 - Ewen Maddock Intake and SEQ24 - Leslie Harrison Dam, respectively; Figure 8).

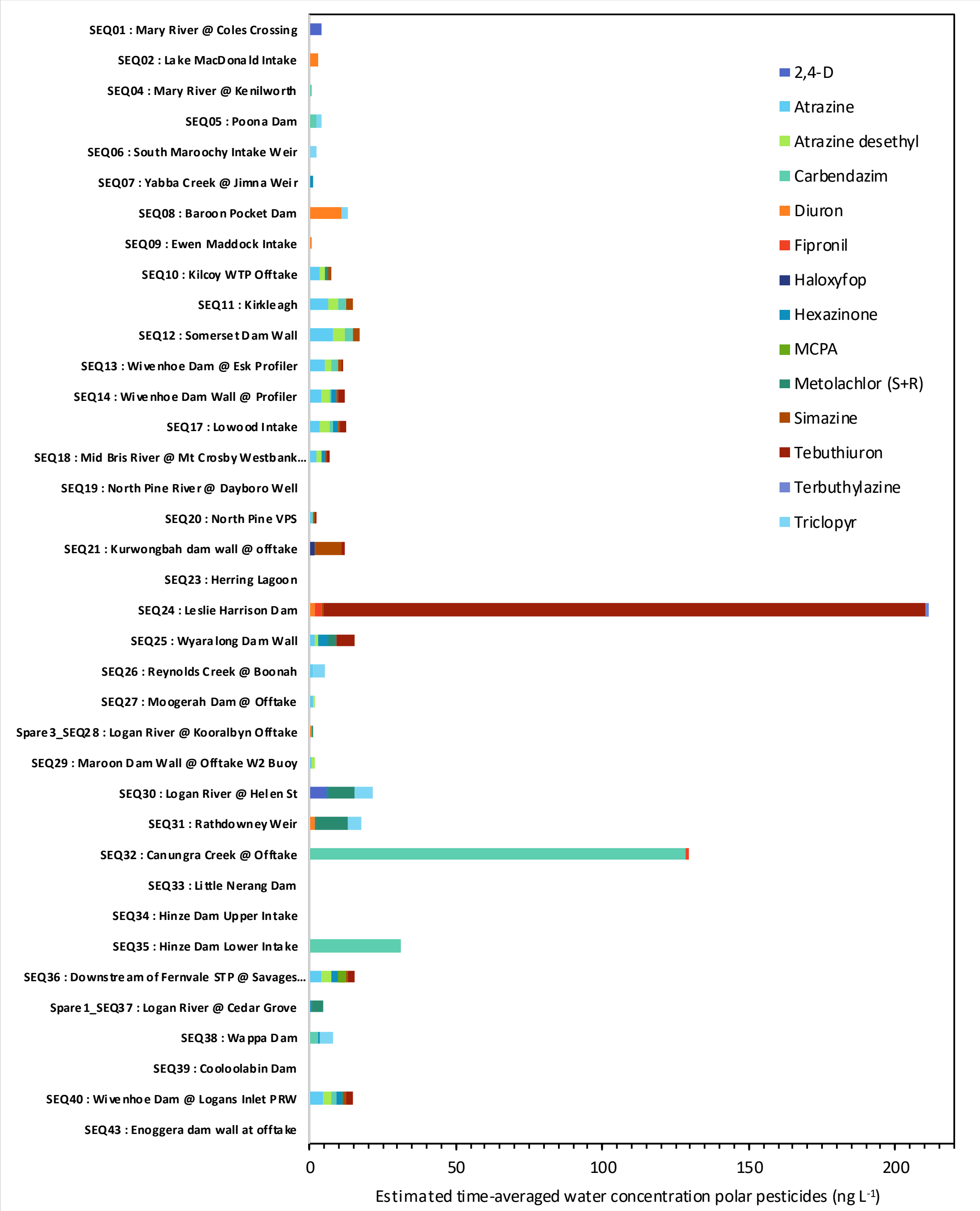

Figure 8. Total estimated water concentrations (ng L^{-1}) of 14 Σpolar pesticides at each site derived from ED passive samplers.

Pharmaceuticals and personal care products (PPCPs)

In total, 10 PPCPs were reported (Table 3, Figure 9, Appendix 1) with the average amount of ΣPPCPs accumulated ranging from below reporting limits for most sites to 177.69 ng ED^{-1} (SEQ18 - Mid Bris River @ Mt Crosby Westbank Offtake Tower).

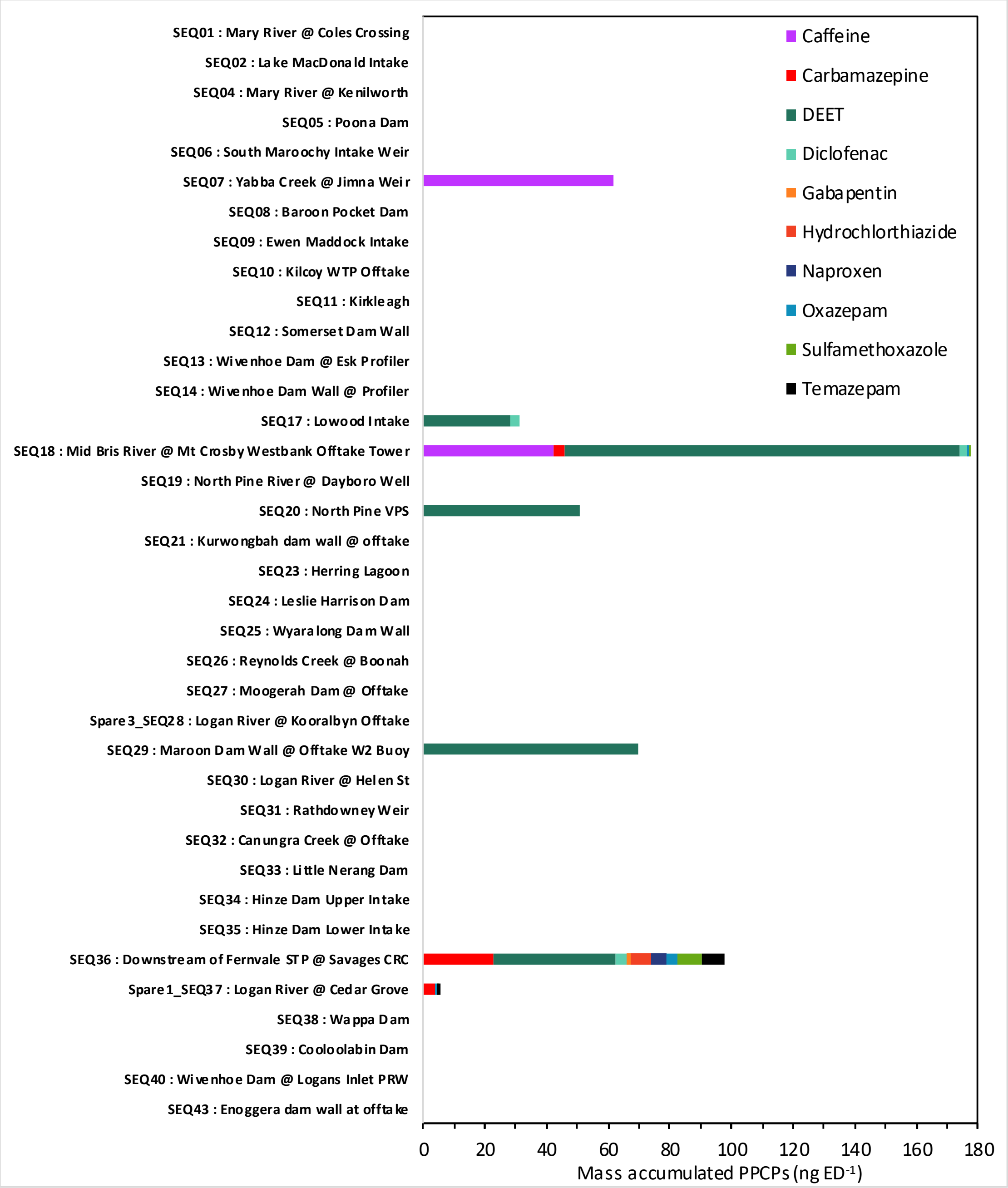

Figure 9. Total mass of 10 ΣPPCPs (ng ED^{-1}) accumulated in ED passive samplers at each site.

Of the 10 reported PPCPs, 6 were able to be converted into estimated time-weighted average water concentrations. Discounting the sites below reporting limits, these ∑PPCP water concentrations ranged between 1.880 and 58.0 ng L^{-1} (sites Spare1_SEQ37 - Logan River @ Cedar Grove and SEQ18 - Mid Bris River @ Mt Crosby Westbank Offtake Tower, respectively; Figure 10).

Figure 10. Total estimated water concentrations (ng L^{-1}) of 6 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 20 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 MS^2 spectral library match scores exceed >99% 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 Tentative Detects
Amicarbazone	Herbicide	SEQ37 : Logan River @ Cedar Grove SEQ40 : Wivenhoe Dam @ Logans Inlet PRW
Aminocarb	Insecticide	SEQ09 : Ewen Maddock Intake SEQ11 : Kirkleagh SEQ12 : Somerset Dam Wall SEQ14 : Wivenhoe Dam Wall @ Profiler SEQ24 : Leslie Harrison Dam SEQ25 : Wyaralong Dam Wall SEQ27 : Moogerah Dam @ Offtake SEQ29 : Maroon Dam Wall @ Offtake W2 Buoy SEQ35 : Hinze Dam Lower Intake SEQ37 : Logan River @ Cedar Grove SEQ40 : Wivenhoe Dam @ Logans Inlet PRW
Carbetamide	Carbamate insecticide	SEQ30 : Logan River @ Helen St
Dextrorphan	Cough supressant	SEQ36 : Downstream of Fernvale STP @ Savages CRC
Fenobucarb	Carbamate insecticide	SEQ30 : Logan River @ Helen St SEQ07 : Yabba Creek @ Jimna Weir
Fenpropidin	Fungicide	SEQ08 : Baroon Pocket Dam
Fenuron	Herbicide	SEQ01 : Mary River @ Coles Crossing SEQ04 : Mary River @ Kenilworth SEQ08 : Baroon Pocket Dam SEQ12 : Somerset Dam Wall SEQ13 : Wivenhoe Dam @ Esk Profiler SEQ21 : Kurwongbah dam wall @ offtake SEQ28 : Logan River @ Kooralbyn Offtake SEQ40 : Wivenhoe Dam @ Logans Inlet PRW
Fluotrimazole	Fungicide	SEQ39 : Cooloolabin Dam
Formetanate	Insecticide	SEQ05 : Poona Dam SEQ25 : Wyaralong Dam Wall SEQ37 : Logan River @ Cedar Grove
Lenacil	Diazine herbicide	SEQ05 : Poona Dam SEQ07 : Yabba Creek @ Jimna Weir SEQ18 : Mid Bris River @ Mt Crosby Westbank Offtake Tower
Metamitron	Herbicide	SEQ27 : Moogerah Dam @ Offtake SEQ28 : Logan River @ Kooralbyn Offtake SEQ31 : Rathdowney Weir
Metazachlor	Herbicide	SEQ09 : Ewen Maddock Intake
Methabenzthiazuron	Herbicide	SEQ24 : Leslie Harrison Dam SEQ12 : Somerset Dam Wall SEQ38 : Wappa Dam
Methiocarb	Carbamate pesticide	SEQ08 : Baroon Pocket Dam SEQ34 : Hinze Dam Upper Intake
Mexacarbate	Carbamate pesticide	SEQ02 : Lake MacDonald Intake SEQ27 : Moogerah Dam @ Offtake
Norcotinine	Nicotine metabolite	SEQ36 : Downstream of Fernvale STP @ Savages CRC
Nordoxepin	Antidepressant metabolite	SEQ01 : Mary River @ Coles Crossing
Pirimicarb	Carbamate insecticide	SEQ04 : Mary River @ Kenilworth SEQ26 : Reynolds Creek @ Boonah
Propham	Herbicide	SEQ33 : Little Nerang Dam SEQ36 : Downstream of Fernvale STP @ Savages CRC
Tricyclazole	Fungicide	SEQ27 : Moogerah Dam @ Offtake

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 for chlorpyrifos, metolachlor and tebuthiuron. ADWG (2011) have set chlorpyrifos freshwater guideline values of 0.04 and 10 ng L^{-1} for 99% and 95% level species protection, respectively. Metolachlor has guideline values of 8.4 and 460 ng L^{-1} for 99% and 95%, respectively. Tebuthiuron has guideline values of 20 and 2200 ng L^{-1} for 99% and 95%, respectively. In total, 16, 2 and 1 site(s) exceeded the 99% species protection guideline for chlorpyrifos, metolachlor and tebuthiuron, respectively. No sites exceeded the 95% species protection guideline values.

Table 5. Threshold chemical guidelines for Australian Drinking Water and Freshwater Aquatic Ecosystems. Values highlighted in yellow exceed the 95% species protection guideline.

Australian Drinking Water Guidelines 6 (2011) Version 3.6 Updated March 2021		ANZECC & ANCANZ (2021) Trigger values for freshwater		
Herbicides & Insecticides		**99% species protection value (ng L^{-1})**	**95% species protection value (ng L^{-1})**	**This campaign Highest Reported Value (ng L^{-1})**
Atrazine	20000	700	13000	8.2
Ametryn	70000	N/A	N/A	N/A
Bromacil	400000	N/A	N/A	N/A
Bromoxynil	10000	N/A	N/A	N/A
Carbaryl	30000	N/A	N/A	N/A
Carbendazim	90000	N/A	N/A	128.4
Cypermethrin	200000	N/A	N/A	N/A
Diazinon	4000	0.03	10	N/A
Diuron	20000	N/A	N/A	10.9
Fipronil	700	N/A	N/A	1.9
Fluometuron	70000	N/A	N/A	N/A
Haloxyfop	1000	N/A	N/A	1.8
Hexazinone	400000	N/A	N/A	3.2
Imazapyr	9000000	N/A	N/A	N/A
MCPA	40000	N/A	N/A	2.6
Malathion	70000	2	50	N/A
Methomyl	20000	N/A	N/A	N/A
Metolachlor (S+R)	300000	8.4	460	11.6
Metribuzin	70000	N/A	N/A	N/A
Metsulfuron methyl	40000	3.7	18	N/A
Oryzalin	400000	N/A	N/A	N/A
Pendimethalin	400000	N/A	N/A	N/A
Picloram	300000	N/A	N/A	N/A
Propachlor	70000	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	9.2
Tebuthiuron	N/A	20	2200	205.6
Terbuthylazine	10000	N/A	N/A	1.2
Triclopyr	20000	N/A	N/A	6.3
2,4-D	30000	140000	280000	5.6
2,4,5-T	100000	3000	36000	N/A
3,4-Dichloroaniline	N/A	1300	3000	N/A
OCPs				
Azinphos methyl	30000	10	20	N/A
Chlordane	2000	30	80	N/A
Chlorpyrifos	10000	0.04	10	0.5
Cypermethrin	200000	N/A	N/A	N/A
DDT	9000	6	10	0.038
Dieldrin	300	N/A	N/A	0.1
Aldrin	300	N/A	N/A	N/A
Endosulfan	20000	30	200	N/A
Endrin	N/A	10	20	N/A
Heptachlor	300	10	90	N/A
γ-HCH (Lindane)	10000	70	200	3.7
Methoxychlor	300000	N/A	N/A	N/A
PAHs				
Anthracene	N/A	10	400	N/A
Benzo[a]pyrene	10	N/A	N/A	N/A
Fluoranthene	N/A	1000	1400	0.1
Naphthalene	10	2500	16000	N/A
Phenanthrene	N/A	600	2000	0.3

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 28 sites (76%), the concentrations were very low (Total ∑OCPs <3.84 ng L^{-1}). Compounds still in use such as chlorpyrifos were reported at higher concentrations, consistent with ongoing inputs to the environment. 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 chlorpyrifos is warranted to estimate any future risk. Dacthal was the second most detected OCP, reported at 14 sites. Dieldrin has been used is use since the 1950's as an insecticide particularly as a termite treatment. It has been banned in Australia since 1987, though remains persistent in the environment due to its low breakdown rates.

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. Reportable concentrations of PAHs were detected at 32 sites, including Chrysene/Triphenylene and Fluoranthene at low levels (<0.390 ng L^{-1}).

Polar pesticides (herbicides, insecticides and fungicides) were reported at 32 sites. The most frequently reported herbicide metsulfuron methyl (detected at 22 sites; 59%) is used in sugarcane and other farming crop as a broad spectrum pre- and early post-emergent control for various grass and broadleaf weeds. Contemporary herbicides can remain in soils for several months and can migrate from soil to groundwater or transport to waterways via runoff and flooding events. Some 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). Often, such herbicides are used in conjunction with diuron and hexazinone, two herbicides also frequently observed. Herbicides with some soil mobility are generally transported to the aquatic environment through runoff and/or percolation to groundwater. The broad-spectrum herbicide tebuthiuron was detected at 12 (32%) of sites. Of note was its detection at SEQ24: Leslie Harrison Dam, with a reported concentration of 250.7 ng L^{-1}. The remainder of detections were < 6 ng L^{-1}.

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. The second most frequently reported PPCP was Carbamazepine, detected at 8% of sites. 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). 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

Recommendations for future work 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 and establish micro-pollutants concentration profile baseline for each monitored system.

- 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 ‘SEQW21_Client Report.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}).