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

Report 16 – Summer 2022

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Title
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Table of Contents

List of Tables

List of Figures

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 bi-annual summer and winter sampling campaigns. The monitoring program utilising passive samplers was continued in reservoirs in South East Queensland (SEQ) during the first quarter of 2022. 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 due to weather events.

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 67 different chemicals including 17 OCPs, 11 PAHs, 30 polar pesticides and 9 PPCPs. OCPs were detected at 89% of sites, with chlorpyrifos (76%) and dieldrin (78%) the most frequently reported. Total ∑OCP water concentrations across sites ranged between 0.001 – 5.93 ng L^{-1} where concentrations were reportable. PAHs were detected at 83% of sites, with benzo[e]pyrene (62%) and chrysene/triphenylene (54%) reported at the highest abundance across all sites. Total ∑PAH water concentrations across sites ranged between 0.002 – 1.09 ng L^{-1}. In total, 30 different polar pesticides were reported in 34 sites (94%), with carbendazim (78%) and atrazine (70%) reported at highest abundance across all sites. Total ∑polar pesticides ranged between 1.73 – 171 ng L^{-1}. Additionally, 9 PPCPs were detected across sites with highest detection frequencies observed for DEET (78%) and carbamazepine (16%). Total estimated ∑PPCP water concentrations ranged between 0.260 – 71.1 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 analytes exceeded the ADWG values at any site. In the ecotoxicological setting, diazinon, metolachlor, tebuthiuron and chlorpyrifos were often above the thresholds set for 99% species protection, however only diazinon was detected above the 95% protection level at the O'Reilly's Weir site.

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. The first campaigns ran between 2014 and 2020 and an extension of the program has been introduced to extend the use of passive sampling technologies in the monitoring of source water reservoirs over the three-year period (2020 – 2023; summer and winter sampling campaigns). The recent campaign aims to continue to accurately assess the risk from micro pollutants posed to drinking water quality as well as add to a longitudinal dataset to aid catchment management. 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 January 2022 to February 2022 at 38 sites of SEQ reservoirs/waterways (Table 1). Site 30 was lost as a result of flooding. Site 28 was redeployed due to it drying out, and the redeployed sampler (Spare 1, Table 1) was also found dried out and therefore is not reported here. Site 31 (SEQ31 – Rathdowney Weir) was discovered on the shoreline still wet. Dried out samplers are considered compromised and often excluded, however as this sampler was still wet and had resulting flow data in line with previous campaigns, both mass/sampler data and water concentration estimates are included here.

Deployments were for periods of 27 to 42 days in duration. A duplicate sampler was 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)

SEQ22 (North Pine River at Petrie Offtake)

Table 1. *Deployment locations, dates, lengths of deployment period and water velocity measured at each site. Sites highlighted in green indicate where duplicate passive samplers were deployed.*

Site	Site Code	Date Deployed	Date Retrieved	Days Deployed	Flow Velocity (cm/s)	Comments
SEQ01 : Mary River @ Coles Crossing	MRS-SP012	18/01/2022	15/02/2022	28	12.7	
SEQ02 : Lake MacDonald Intake	LMD-SP001	31/01/2022	8/03/2022	36	6.6	
SEQ04 : Mary River @ Kenilworth	MRS-SP013	18/01/2022	15/02/2022	28	12.7	
SEQ05 : Poona Dam	POD-SP001	19/01/2022	16/02/2022	28	4.9	
SEQ06 : South Maroochy Intake Weir	SOR-SP001	19/01/2022	16/02/2022	28	3.4	
SEQ07 : Yabba Creek @ Jimna Weir	YAC-SP001	20/01/2022	17/02/2022	28	3.4	
SEQ08 : Baroon Pocket Dam	BPD-SP001	27/01/2022	24/02/2022	28	6.8	
SEQ09 : Ewen Maddock Intake	EMD-SP001	18/01/2022	15/02/2022	28	9.6	
SEQ10 : Kilcoy WTP Offtake	SOD-SP010	31/01/2022	8/03/2022	36	6.7	
SEQ11 : Kirkleagh	SOD-SP011	31/01/2022	8/03/2022	36	7.5	
SEQ12 : Somerset Dam Wall	SOD-SP001	31/01/2022	8/03/2022	36	7.1	
SEQ13 : Wivenhoe Dam @ Esk Profiler	WID-SP004	18/01/2022	15/02/2022	28	6.7	
SEQ14 : Wivenhoe Dam Wall @ Profiler	WID-SP001	18/01/2022	15/02/2022	28	9.5	

SEQ16 : O'Reillys Weir	**LOC-SP031**	**20/01/2022**	**16/02/2022**	**27**	**3.9**	
SEQ17 : Lowood Intake	**MBR-SP016**	**20/01/2022**	**16/02/2022**	**27**	**6.6**	
SEQ18 : Mid Bris River @ Mt Crosby Westbank Offtake Tower	**MBR-SP001**	**20/01/2022**	**16/02/2022**	**27**	**6.9**	
SEQ19 : North Pine River @ Dayboro Well	**NOD-SP091**	**19/01/2022**	**17/02/2022**	**29**	**15**	
SEQ20 : North Pine VPS	**NOD-SP001**	**20/01/2022**	**17/02/2022**	**28**	**6.1**	
SEQ21 : Kurwongbah dam wall @ offtake	**LAK-SP001**	**19/01/2022**	**16/02/2022**	**28**	**6.7**	
SEQ23 : Herring Lagoon	**NSC-SP001**	**12/01/2022**	**17/02/2022**	**36**	**4.3**	
SEQ24 : Leslie Harrison Dam	**LHD-SP005**	**19/01/2022**	**16/02/2022**	**28**	**6.9**	
SEQ25 : Wyaralong Dam Wall	**WYD-SP001**	**18/01/2022**	**15/02/2022**	**28**	**10.3**	
SEQ26 : Reynolds Creek @ Boonah	**MOD-SP027**	**18/01/2022**	**14/02/2022**	**27**	**5.1**	
SEQ27 : Moogerah Dam @ Offtake	**MOD-SP002**	**18/01/2022**	**15/02/2022**	**28**	**17**	
SEQ28 : Logan River @ Kooralbyn Offtake	**LRS-SP017**	**2/02/2022**	**9/02/2022**	**7**	**26.6**	**Samplers dried out, replaced with Spare 1 - Not reported**
SEQ29 : Maroon Dam Wall @ Offtake W2 Buoy	**MAD-SP004**	**1/02/2022**	**8/03/2022**	**35**	**14.8**	
SEQ30 : Logan River @ Helen St	**LRS-SP013**	**1/02/2022**	**N/A**	**N/A**	**N/A**	**Samplers lost - Not reported**
SEQ31 : Rathdowney Weir	**LRS-SP016**	**2/02/2022**	**10/03/2022**	**36**	**11.1**	**Samplers recovered on shoreline but still wet - Data reported**
SEQ32 : Canungra Creek @ Offtake	**CAC-SP001**	**17/01/2022**	**14/02/2022**	**28**	**9.7**	**1 PFM returned with cut cable tie - its final weight was estimated**
SEQ33 : Little Nerang Dam	**LND-NR001**	**24/01/2022**	**24/02/2022**	**31**	**4.5**	
SEQ34 : Hinze Dam Upper Intake	**HID-SP001**	**25/01/2022**	**22/02/2022**	**28**	**5.7**	
SEQ35 : Hinze Dam Lower Intake	**HID-SP002**	**25/01/2022**	**22/02/2022**	**28**	**9.1**	
SEQ36 : Downstream of Fernvale STP @ Savages CRC	**MBR-SP013**	**19/01/2022**	**16/02/2022**	**28**	**5.7**	
SEQ37 : Logan River @ Cedar Grove	**LRS-SP012**	**2/02/2022**	**16/03/2022**	**42**	**9.6**	**1 PFM lost, 1 PFM returned with cut cable tie - its final weight was estimated**
SEQ38 : Wappa Dam	**WAD-SP001**	**19/01/2022**	**16/02/2022**	**28**	**4.2**	
SEQ39 : Cooloolabin Dam	**COD-SP001**	**18/01/2022**	**16/02/2022**	**29**	**5.5**	
SEQ40 : Wivenhoe Dam @ Logans Inlet PRW	**WID-SP061**	**18/01/2022**	**15/02/2022**	**28**	**9.9**	
SEQ43 : Enoggera dam wall at offtake	**END-SP001**	**20/01/2022**	**25/02/2022**	**36**	**4.7**	
Spare 1 : Logan River @ Kooralbyn Offtake	**LRS-017**	**9/02/2022**	**10/03/2022**	**29**	**22.6**	**Samplers dried out - Not reported**

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.

Passive sampler preparation and extraction

In this campaign, two types of passive samplers were deployed at each site. Empore Disk™ (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} (SEQ07 : Yabba Creek @ Jimna Weir) to 17 cm s^{-1} (SEQ27 : Moogerah Dam @ Offtake) (Figure 2).

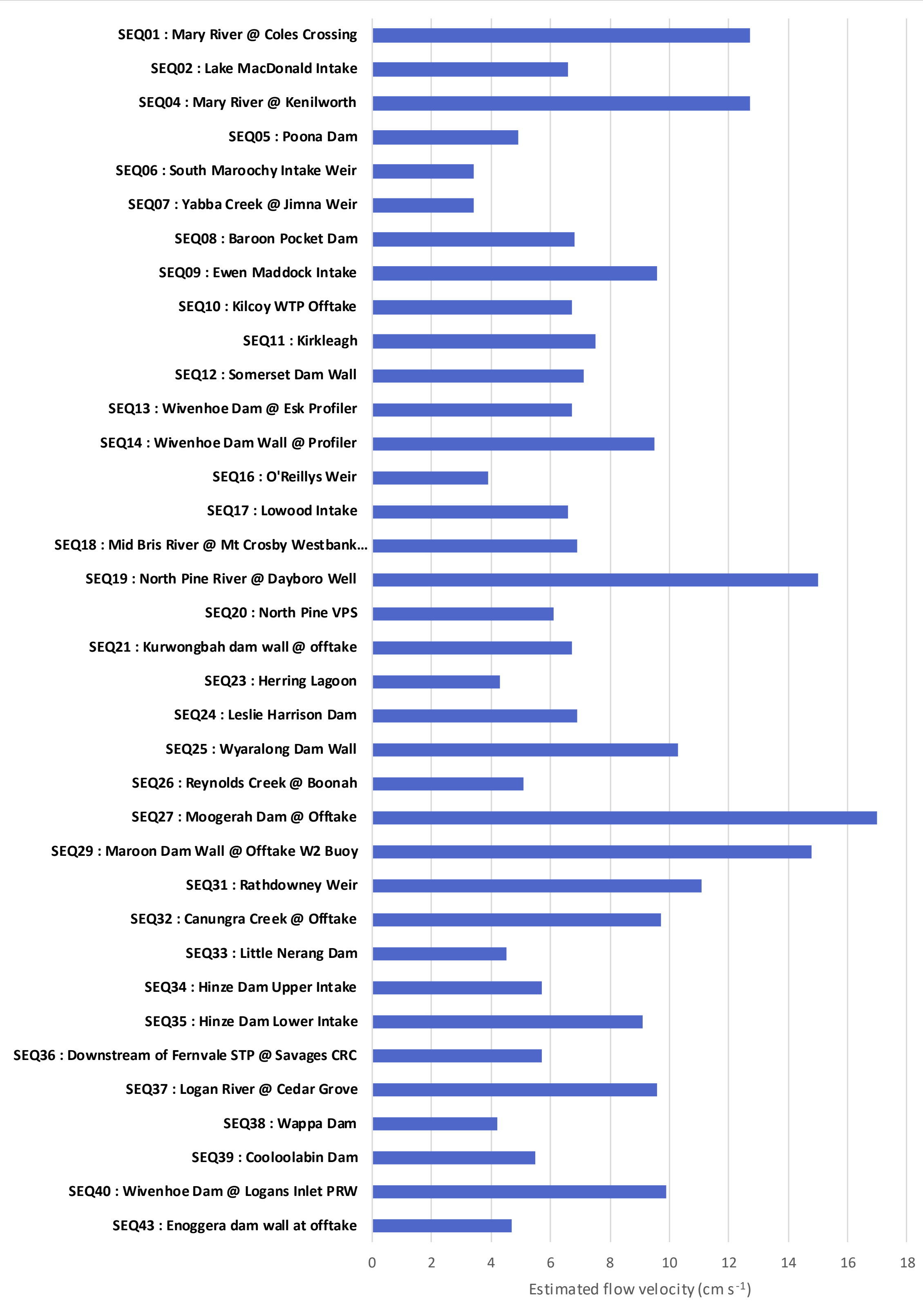

Figure 2. Passive flow monitor (PFM) based water flow velocity estimations (cm s^{-1}) at the deployment sites (n=36).

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 17 OCPs and 11 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% – 76% for OCPs and 3% – 62% for PAHs. Table 3 summarises the polar chemicals quantified via ED (pesticides and PPCPs). A total of 30 pesticides (predominantly herbicides) and 9 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3% - 78% for pesticides and 3% - 78% 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	11	30%	2.96	31.5
Chlorpyrifos	28	76%	3.35	184
cis-Chlordane	24	65%	1.54	6.64
Dacthal	11	30%	2.71	144
Dieldrin	29	78%	2.50	34.4
Endosulfan sulfate	4	11%	1.24	9.24
Endrin ketone	1	3%	1.57	1.60
HCB	2	5%	3.65	9.8
Heptachlor epoxide b	9	24%	1.72	9.91
Mirex	1	3%	1.13	1.10
o,p-DDD	5	14%	1.09	4.88
p,p-DDD	12	32%	1.01	20.7
p,p-DDE	16	43%	1.04	27.4
p,p-DDT	1	3%	3.80	3.80
Permethrin	6	16%	1.56	6.80
trans-Chlordane	15	41%	4.39	19.8
α-HCH	2	5%	1.23	1.80
		PAH		
Acenaphthene	1	3%	45.8	45.8
Anthracene	4	11%	6.69	19.8
Benzo[a]anthracene	7	19%	3.47	29.7
Benzo[a]pyrene	2	5%	4.12	5.61
Benzo[b,j,k]fluoranthene	5	14%	3.33	12.2
Benzo[e]pyrene	23	62%	1.13	9.97
Benzo[g,h,i]perylene	8	22%	1.05	7.60
Chrysene/Triphenylene	20	54%	5.03	34.0
Fluoranthene	15	41%	17.0	188
Indeno[1,2,3-c,d]pyrene	5	14%	1.10	4.19
Pyrene	1	3%	182	182

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	6	16%	5.206	131.331
3,4 Dichloroaniline	1	3%	1.01	1.01
Ametryn hydroxy	3	8%	1.58	1.80
Atrazine	26	70%	1.02	44.8
Atrazine desethyl	17	46%	1.31	8.44
Atrazine desisopropyl	20	54%	1.21	4.90
Bromacil	3	8%	1.82	5.59
Bromoxynil	1	3%	1.042	1.042
Carbendazim	29	78%	1.02	29.2
DCPMU	1	3%	0.523	0.523
Diazinon	15	41%	0.29	9.29
Diuron	12	32%	1.07	15.4
Fipronil	9	24%	0.510	6.93
Fluazifop	4	11%	0.575	1.243
Haloxyfop	7	19%	1.18	15.24
Hexazinone	9	24%	1.01	10.3
Imidacloprid	17	46%	1.15	27.3
Metalaxyl	15	41%	0.100	4.15
Methomyl	1	3%	1.43	1.43
Metolachlor (S+R)	22	59%	1.32	135.5
Metribuzin	1	3%	2.19	2.19
Metsulfuron methyl	24	65%	1.59	19.64
Propiconazole	5	14%	1.51	11.9
Simazine	15	41%	1.10	25.1
Tebuconazole	6	16%	1.14	6.10
Tebuthiuron	17	46%	1.07	287.9
Terbuthylazine	9	24%	1.17	6.17
Terbuthylazine desethyl	15	41%	1.09	4.34
Thiamethoxam	1	3%	4	4
Triclopyr	10	27%	6.91	84.8
Pharmaceuticals and personal care products (PPCPs)				
Acesulfame	2	5%	1.50	169
Caffeine	1	3%	59.5	59.5
Carbamazepine	6	16%	1.21	4.44
DEET	29	78%	22.1	176
Oryzalin	1	3%	0.72	0.72
Oxazepam	1	3%	2.07	2.07
Sulfadiazine	1	3%	0.665	0.665
Sulfamethoxazole	3	8%	0.138	1.030
Temazepam	1	3%	1.51	1.51

Organochlorine pesticides (OCPs)

In total, 17 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 (SEQ33 - Little Nerang Dam; SEQ34 - Hinze Dam Upper Intake; SEQ23 - Herring Lagoon) to 341 ng PDMS^{-1} (SEQ16 - O'Reillys Weir).

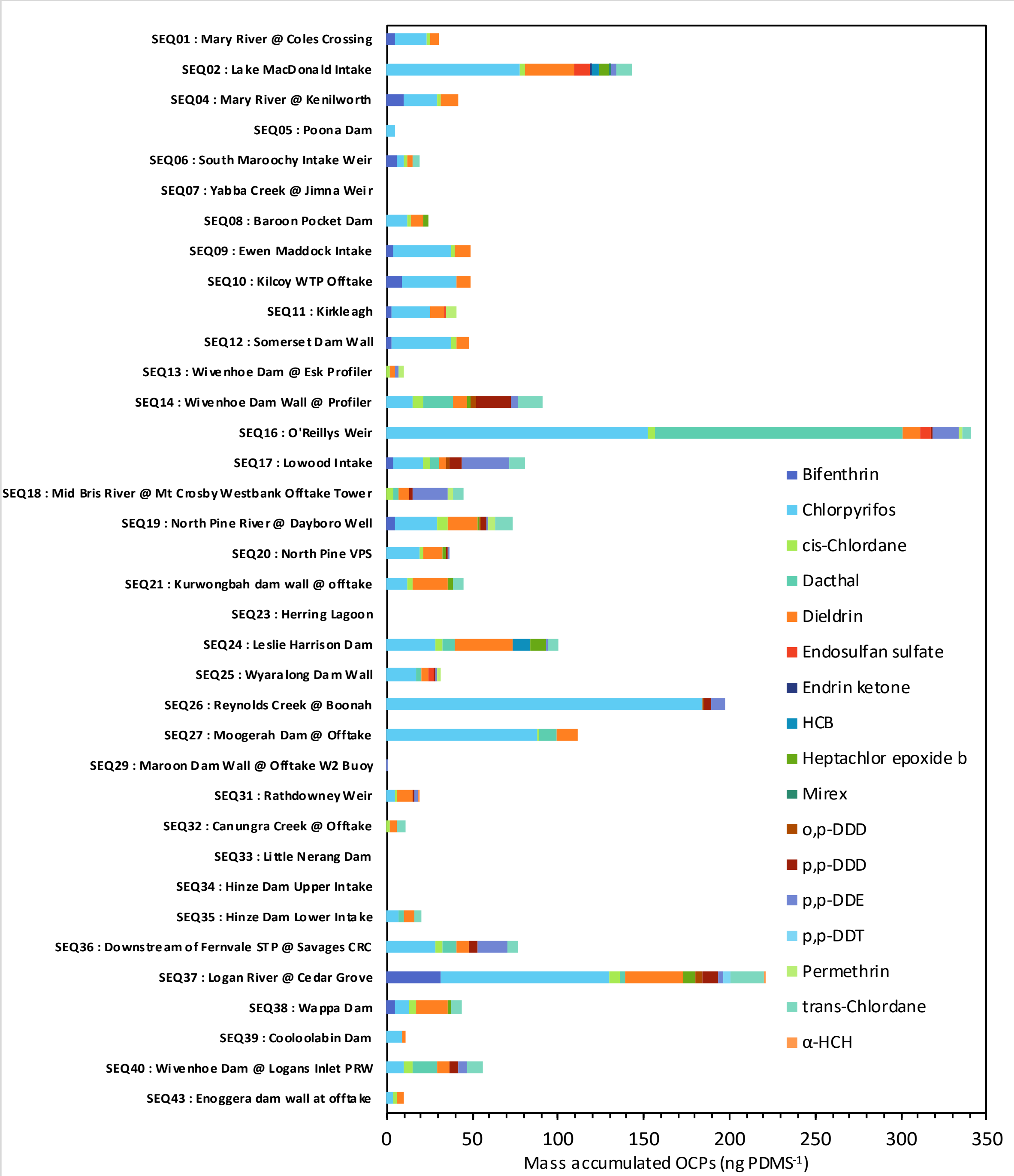

Figure 3. Total mass of 17 ΣOCPs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

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 0.001 to 5.93 ng L^{-1} (SEQ29 - Maroon Dam Wall @ Offtake W2 Buoy and SEQ16 - O'Reillys Weir, respectively; Figure 4).

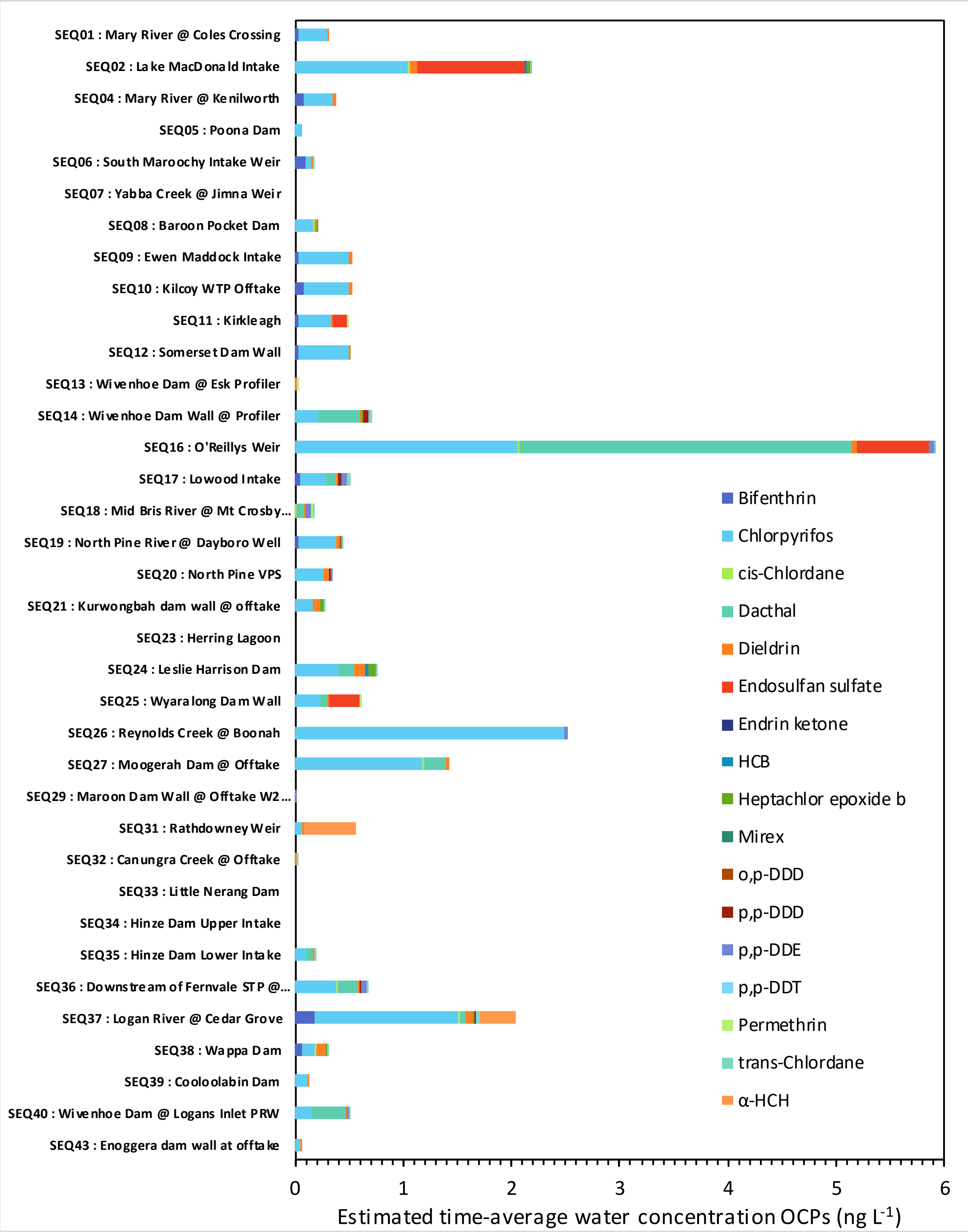

Figure 4. Total estimated water concentrations (ng L^{-1}) of 17 ΣOCPs at each site derived from PDMS passive samplers.

Polycyclic aromatic hydrocarbons (PAHs)

In total, 11 PAHs were accumulated in PDMS samplers over the deployment period (Table 2, Figure 5, Appendix 1), with the amount of ∑PAHs accumulated ranging from below reporting limits (SEQ23 - Herring Lagoon; SEQ05 - Poona Dam; SEQ08 - Baroon Pocket Dam; SEQ13 - Wivenhoe Dam @ Esk Profiler; SEQ26 - Reynolds Creek @ Boonah) to 493 ng $PDMS^{-1}$ (SEQ27 - Moogerah Dam @ Offtake).

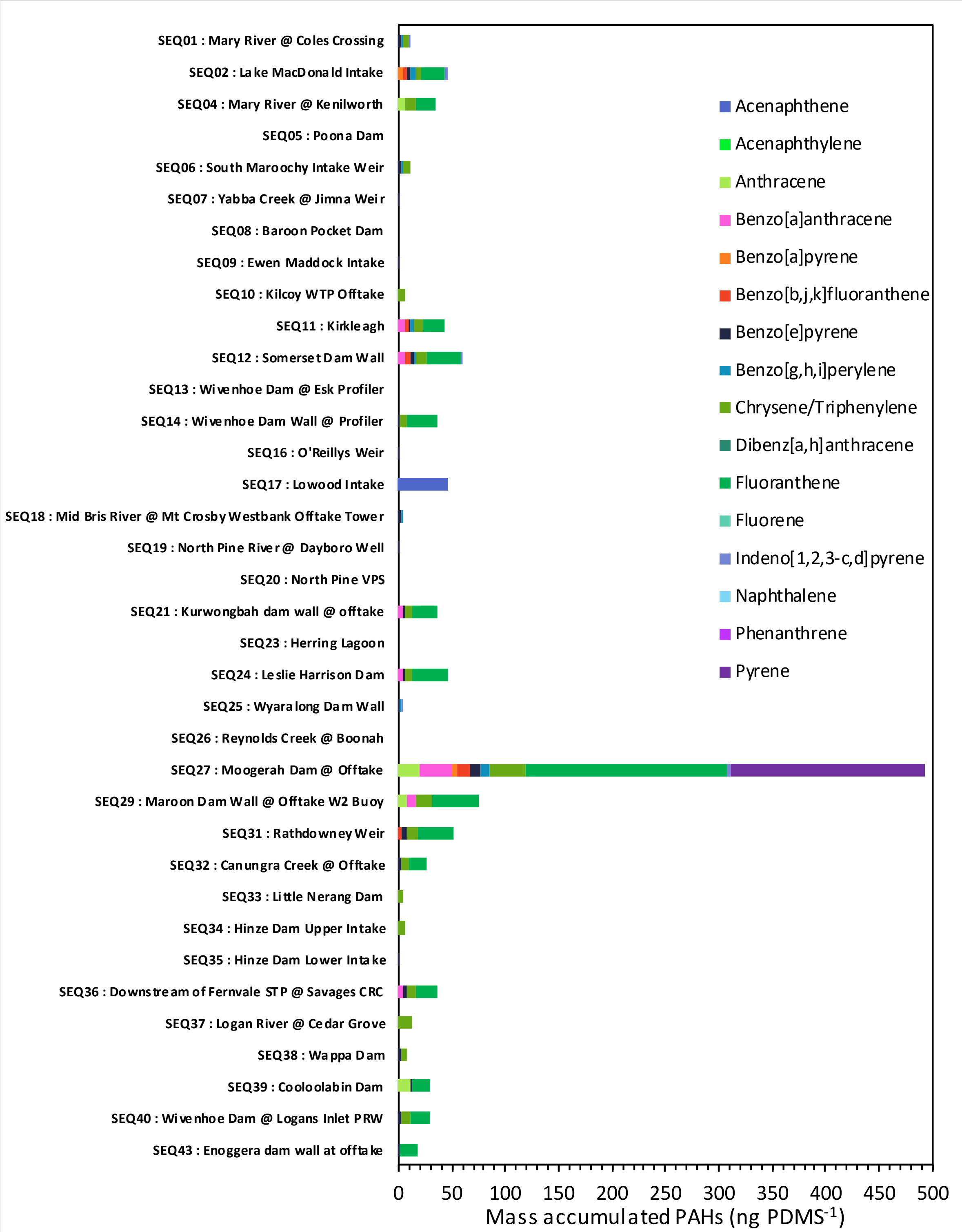

Figure 5. Total mass of 11 ΣPAHs (ng $PDMS^{-1}$) accumulated in PDMS passive samplers at each site.

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 0.002 to 1.09 ng L^{-1} (SEQ19 - North Pine River @ Dayboro Well and SEQ27 - Moogerah Dam @ Offtake, respectively; Figure 6).

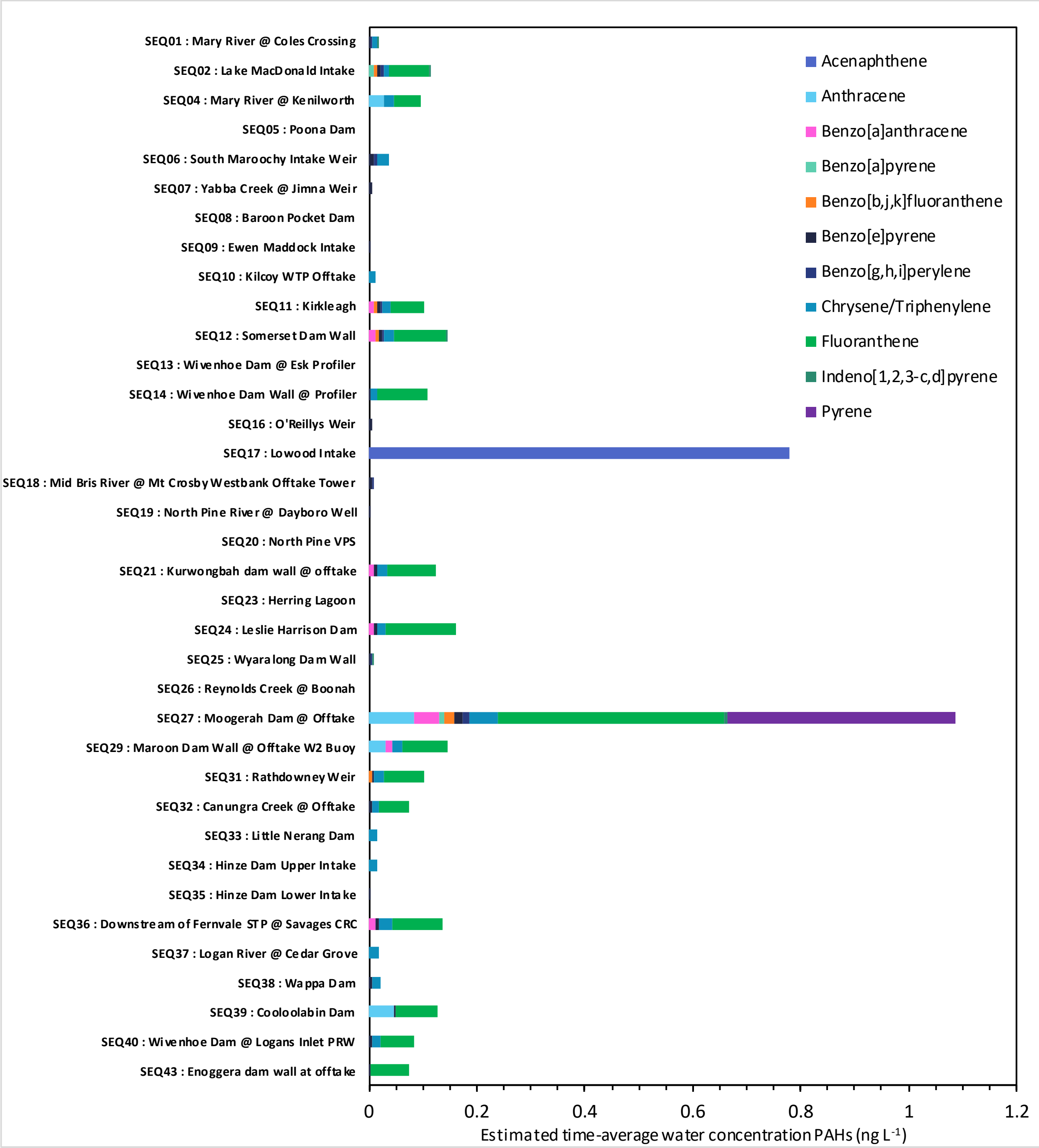

Figure 6. Total estimated water concentrations (ng L^{-1}) of 11 ΣPAHs at each site derived from PDMS passive samplers.

Pesticides

Over the deployment period, 30 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) to 365 ng ED^{-1}(SEQ24 - Leslie Harrison Dam).

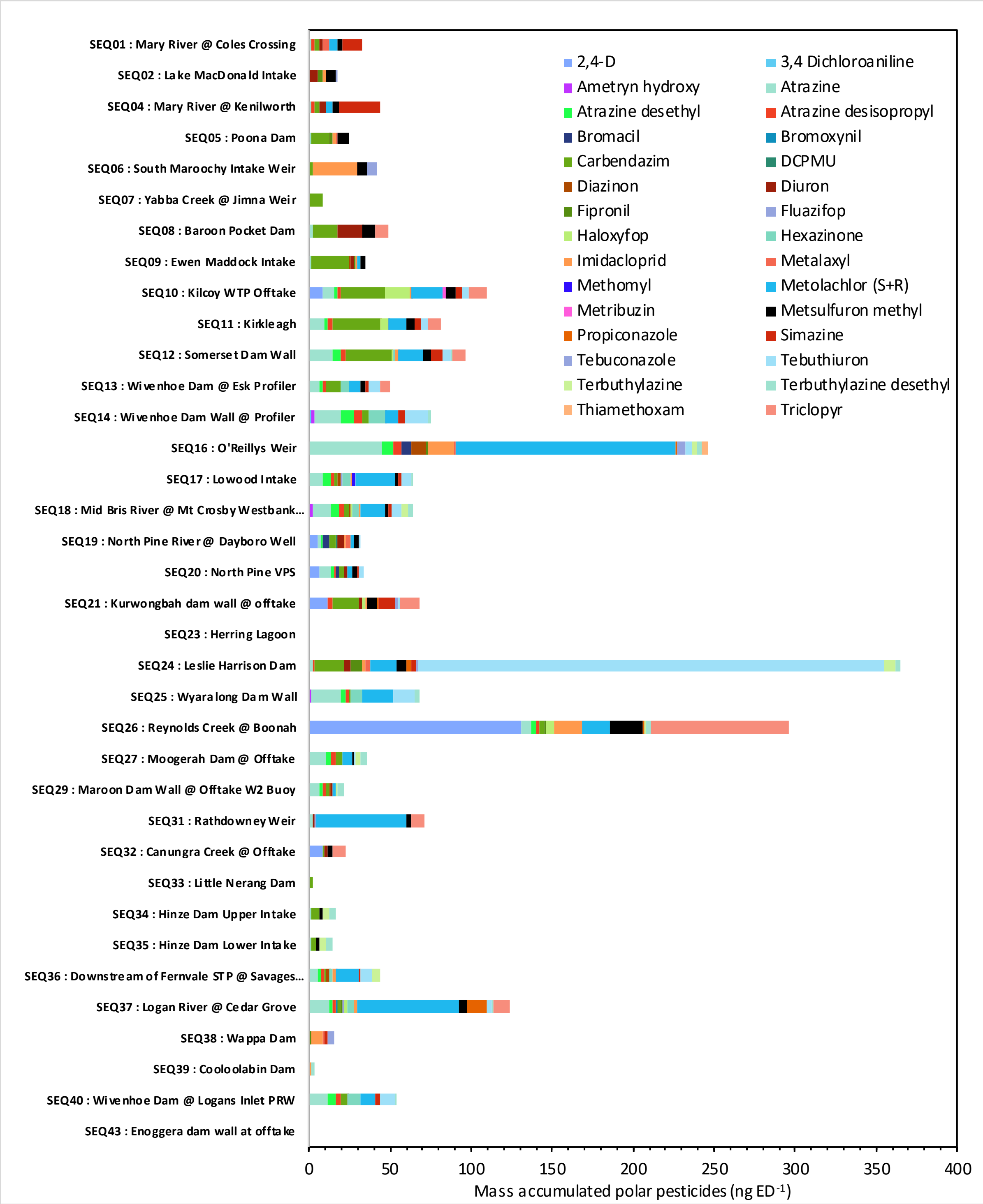

Figure 7. Total mass of 30 Σpolar pesticides (ng ED^{-1}) accumulated in ED passive samplers at each site.

Water concentrations were estimated for the polar pesticides accumulated where sampling rates have been previously calibrated. From the 30 chemicals reported, 15 were converted to time-weighted average water ∑concentrations. Discounting the sites below reporting limits, these water concentrations ranged between 1.73 and 171 ng L^{-1} (SEQ33 - Little Nerang Dam and SEQ16 - O'Reillys Weir, respectively; Figure 8).

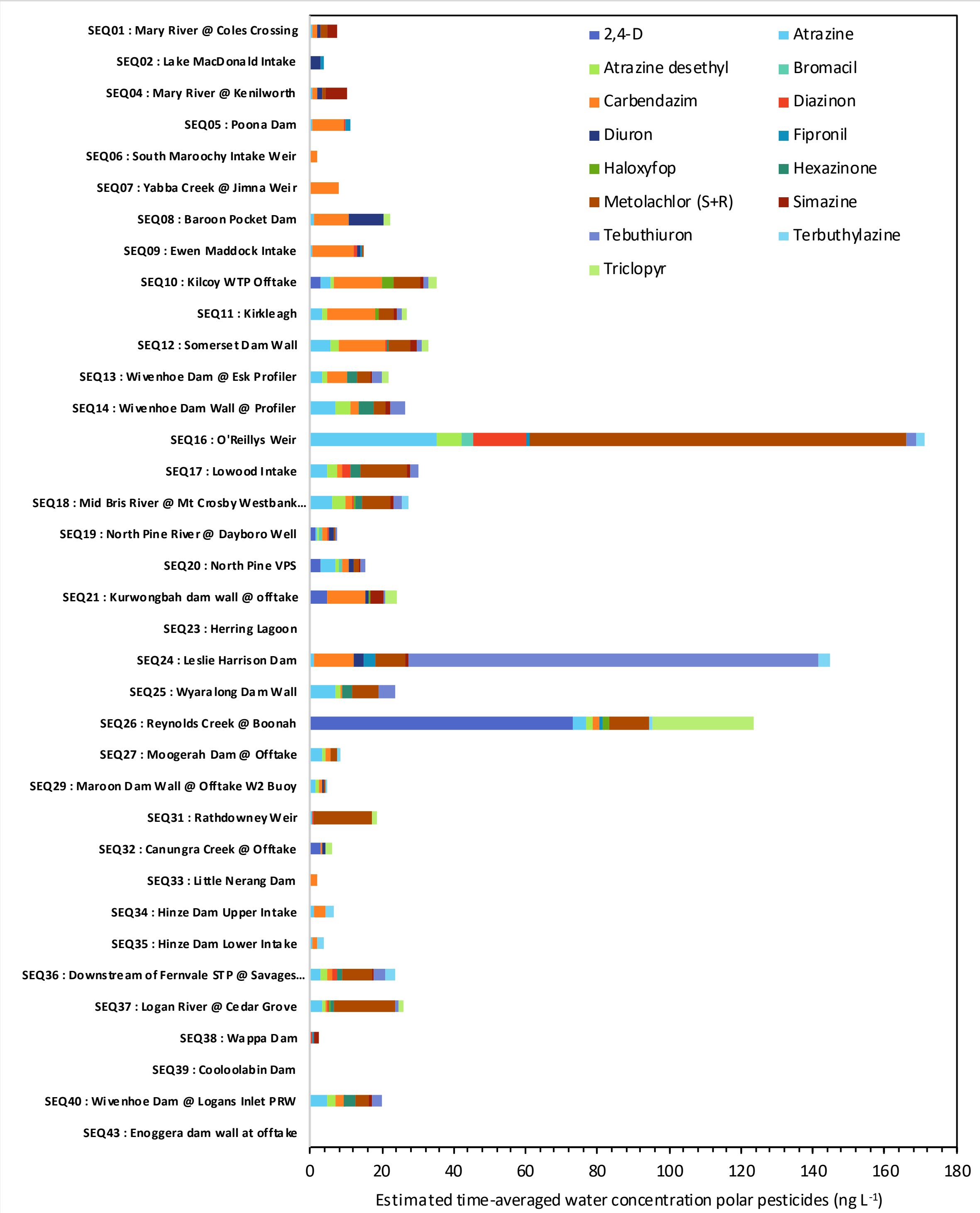

Figure 8. Total estimated water concentrations (ng L^{-1}) of 15 Σpolar pesticides at each site derived from ED passive samplers.

Pharmaceuticals and personal care products (PPCPs)

In total, 9 PPCPs were reported (Table 3, Figure 9, Appendix 1) with the average amount of ΣPPCPs accumulated ranging from below reporting limits (SEQ32 - Canungra Creek @ Offtake; SEQ06 - South Maroochy Intake Weir; SEQ11 - Kirkleagh; SEQ35 - Hinze Dam Lower Intake; SEQ07 - Yabba Creek @ Jimna Weir) to 176 ng ED^{-1} (SEQ17 - Lowood Intake).

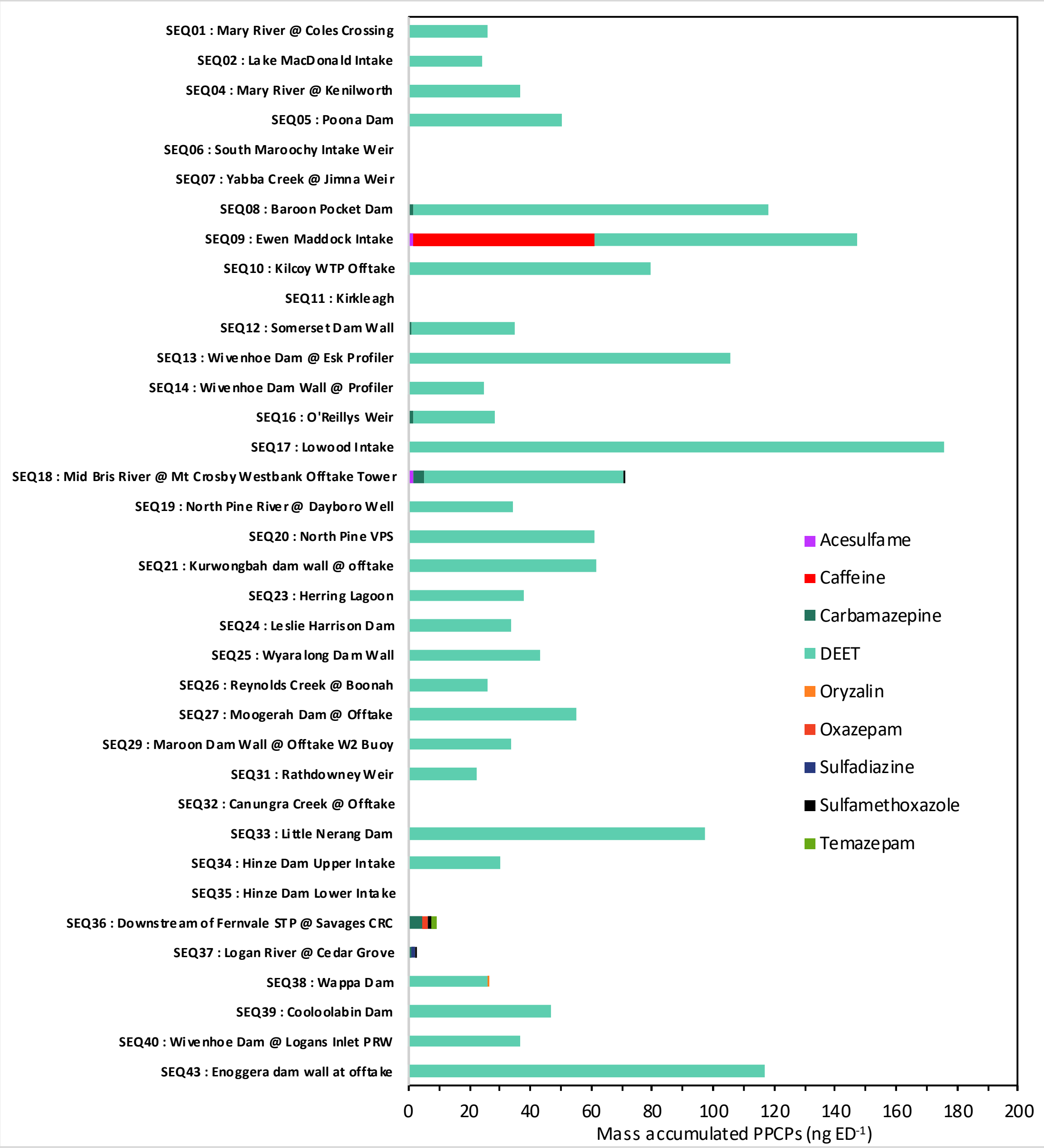

Figure 9. Total mass of 9 ΣPPCPs (ng ED^{-1}) accumulated in ED passive samplers at each site.

Of the 9 reported PPCPs, 4 were able to be converted into estimated time-weighted average water concentrations. Discounting the sites below reporting limits, these ∑PPCP water concentrations ranged between 0.26 and 71.1 ng L^{-1} (sites SEQ37 - Logan River @ Cedar Grove and SEQ17 - Lowood Intake, respectively; Figure 10).

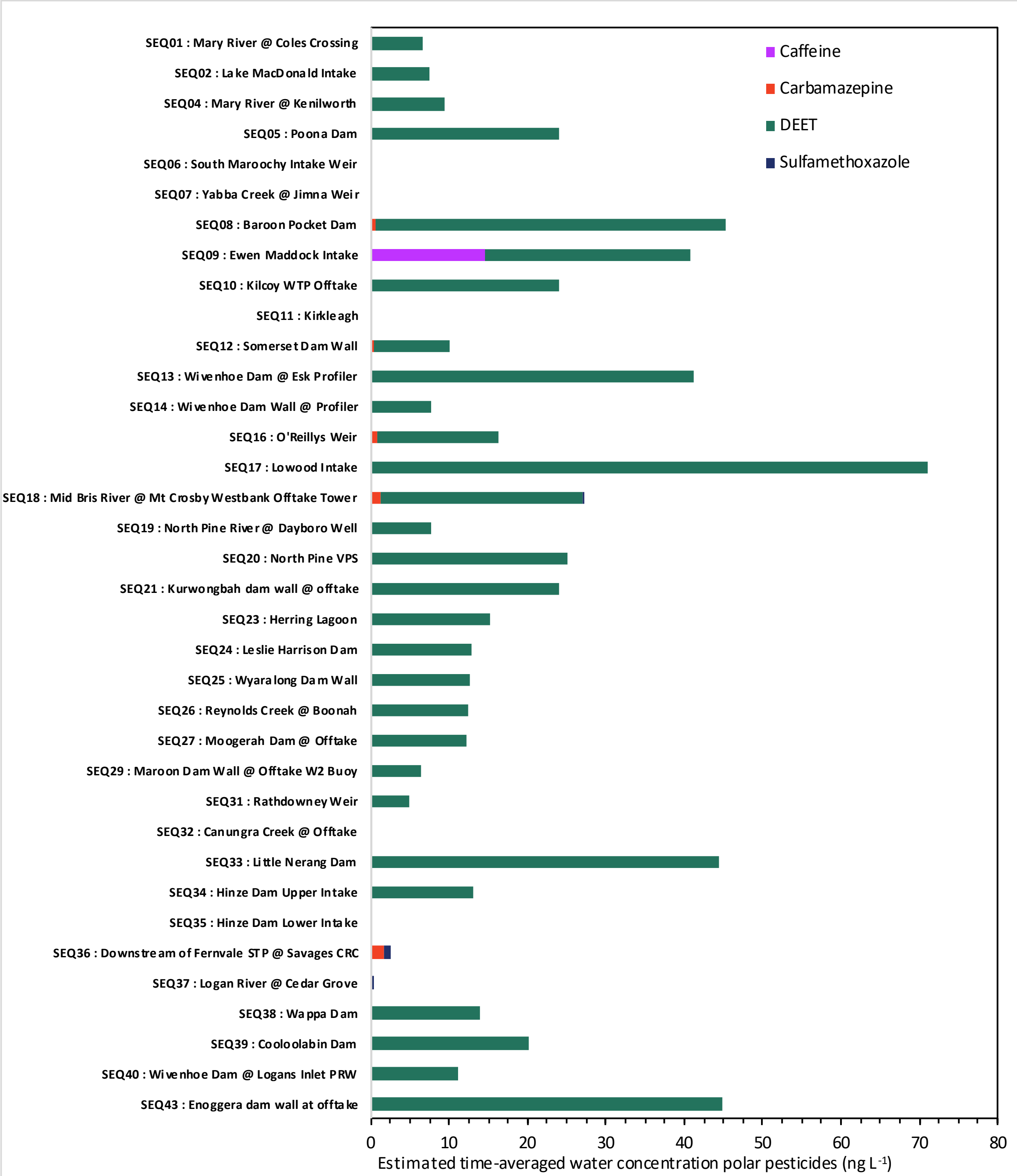

Figure 10. Total estimated water concentrations (ng L^{-1}) of 4 ΣPPCPs.

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 4 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 tentative detects
Bifenazate	Insecticide	SEQ31 : Rathdowney Weir SEQ17 : Lowood Intake SEQ27 : Moogerah Dam @ Offtake SEQ05 : Poona Dam SEQ34 : Hinze Dam Upper Intake SEQ04 : Mary River @ Kenilworth SEQ07 : Yabba Creek @ Jimna Weir
Carbetamide (NIST)	Herbicide	SEQ14 : Wivenhoe Dam Wall @ Profiler
Carbofuran	Carbamate pesticide	SEQ14 : Wivenhoe Dam Wall @ Profiler
Diethofencarb	Carbamate fungicide	SEQ34 : Hinze Dam Upper Intake SEQ43 : Enoggera dam wall at offtake

Comparison to water quality guideline values

A selection of water guideline values and species protection values are provided in Table 5. For analytes where conversion to water concentrations was possible, no exceedances of ADWG values were observed. Exceedances for eco-toxicological guidelines were observed in the estimated time-averaged water concentrations for diazinon, metolachlor, tebuthiuron and chlorpyrifos. ANZECC & ANCANZ have set diazinon freshwater guideline values of 0.03 and 10 ng L^{-1} for 99% and 95% species protection levels, respectively. The site SEQ16 – O'Reillys Weir exceeded the 99% species protection guideline value for diazinon with a concentration of 14.7 ng L^{-1}. Additional sites exceeded the 95% value. Additionally, metolachlor, tebuthiuron and chlorpyrifos have guideline values of 8.4 and 460 ng L^{-1}, 20 and 2200 ng L^{-1}, and 0.4 and 10 ng L^{-1} for 99% and 95%, respectively. In total, 6, 1 and 28 sites exceeded the 95% species protection guidelines for metolachlor, tebuthiuron and chlorpyrifos, respectively.

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

Herbicides & Insecticides	Australian Drinking Water Guidelines 6 (2011) Version 3.6 Updated March 2021 Guideline value (ng L⁻¹)	ANZECC & ANCANZ (2021) Trigger values for freshwater 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	35.4
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	13.4
Cypermethrin	200000	N/A	N/A	N/A
Diazinon	4000	0.03	10	14.7
Diuron	20000	N/A	N/A	9.7
Fipronil	700	N/A	N/A	3.1
Fluometuron	70000	N/A	N/A	N/A
Haloxyfop	1000	N/A	N/A	3.2
Hexazinone	400000	N/A	N/A	4.2
Imazapyr	9000000	N/A	N/A	N/A
MCPA	40000	N/A	N/A	N/A
Malathion	70000	2	50	N/A
Methomyl	20000	N/A	N/A	N/A
Metolachlor (S+R)	300000	8.4	460	105.1
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	6.0
Tebuthiuron	N/A	20	2200	114.2
Terbuthylazine	10000	N/A	N/A	3.1
Triclopyr	20000	N/A	N/A	28.3
2,4-D	30000	140000	280000	73.0
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	2.5
Cypermethrin	200000	N/A	N/A	N/A
DDT	9000	6	10	0.086
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	N/A
Methoxychlor	300000	N/A	N/A	N/A
PAHs				
Anthracene	N/A	10	400	0.1
Benzo[a]pyrene	10	N/A	N/A	0.0
Fluoranthene	N/A	1000	1400	0.4
Naphthalene	10	2500	16000	N/A
Phenanthrene	N/A	600	2000	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 32 sites (89%), the concentrations were low (Total ∑OCPs <5.93 ng L^{-1}). Compounds still in use such as chlorpyrifos was 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. Dieldrin was the second most detected OCP, reported at 29 sites. Dieldrin has been used 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. OCP amounts were greater than the Summer 2021 campaign, which may be partially due to a comparative increase in rainfall across South-East Queensland in 2022.

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 30 sites, including Benzo[e]pyrene and Chrysene/Triphenylene at low levels (<0.78 ng L^{-1}).

Polar pesticides (herbicides, insecticides and fungicides) were reported at 34 sites. The most frequently reported pesticide carbendazim (detected at 29 sites; 78%) is used to control fungal diseases in some crops including fruit trees. The second most frequently reported pesticide was Atrazine (detected at 26 sites; 70%) 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.

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 (78% of sites) 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 16% 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 that build upon the findings in the current report.

- Continue temporal/ seasonal and spatial comparisons to investigate long term trends between sites and seasons.
- 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_Summer2022.xlsx_REISSUE'

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}).