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

Report 19 – Winter 2023

Kristie Thompson, Ryan Shiels and Sarit Kaserzon

Title
Catchment and Drinking Water Quality Micro Pollutant Monitoring program – Passive Sampling.
Report 19 – Winter 2023.

Disclaimer
This report and the data present are prepared solely for the use of the person or corporation to whom it is addressed. It may not be used or relied upon by any other person or entity. No warranty is given to any other person as to the accuracy of any of the information, data or opinions expressed herein. The author expressly disclaims all liability and responsibility whatsoever to the maximum extent possible by law in relation to any unauthorized use of this report. The work and opinions expressed in this report are those of the author.

Project Team
Kristie Thompson, Ryan Shiels, Yan Li, Chris Paxman, Gabriele Elisei, Pritesh Prasad, Christina Carswell, Michael Gallen, Tim Reeks, Summer Xia, Jochen Mueller and Sarit Kaserzon.

Direct Enquiries to:

Kristie Thompson
(e) k.leechue@uq.edu.au

Dr. Sarit Kaserzon
(e) k.sarit@uq.edu.au

Dr. Ryan Shiels
(e) r.shiels@uq.edu.au

Queensland Alliance for Environmental Health Sciences (QAEHS)
Formerly National Research Centre for Environmental Toxicology (Entox)
The University of Queensland
20 Cornwall Street, Woolloongabba, Qld 4102
(p) +61 (0)428 532 053
(w) www.uq.edu.au

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 third quarter of 2023. Results presented provide a continued insight into the water quality of the target catchments and drinking water reservoirs. While deployment dates in this report are consistent, at some sites, multiple samplers required redeployment due to unforeseen events resulting in samplers being compromised.

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). Samples were analysed at the Queensland Alliance for Environmental Health Sciences (QAEHS), UQ by LC-QQQ MS/MS (polar compounds), LC-QToF MS/MS (polar chemicals; 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 63 different chemicals including 13 OCPs, 13 PAHs, 27 polar pesticides and 10 PPCPs. OCPs were detected at 92% of sites, with trans-chlordane (79%) and chlorpyrifos (63%) the most frequently reported. Total ∑OCP water concentrations across sites ranged between 0.003 – 24.92 ng L^{-1} where concentrations were reportable. PAHs were detected at 95% of sites, with chrysene/triphenylene (95%) and fluoranthene (66%) reported at the highest abundance across all sites. Total ∑PAH water concentrations across sites ranged between 0.003 – 23.31 ng L^{-1}. In total, 27 different polar pesticides were reported across 30 sites (79%), with metsulfuron methyl (68%) and atrazine (53%) reported at highest frequency across all sites. Total ∑ pesticides ranged between 0.620 – 75 ng L^{-1}. Additionally, 10 PPCPs were detected across sites with highest detection frequencies observed for DEET (50%) and carbamazepine (13%). Total estimated ∑PPCP water concentrations ranged between 0.60 – 48 ng L^{-1} across sites.

Australian Drinking Water Guidelines (ADWG) as well as Australia and New Zealand guidelines for Fresh and Marine Water Quality values are available for some of these chemicals (ANZECC & ARMCANZ 2018) for comparison. No chemicals were present in concentrations that exceeded the ADWG values. In the ecotoxicological setting, diazinon, metolachlor, tebuthiuron and chlorpyrifos were often above the thresholds set for 99% species protection, however there were no chemicals detected above the 95% protection level.

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 a five-year period (2020 – 2025; summer and winter sampling campaigns). The recent campaign aims to continue to 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 raise 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 and September 2023 at 39 sites of SEQ reservoirs/waterways (Table 1). Samplers from Site 30 were removed from the water, and no redeployment was made (not shown). Site 34 was redeployed after samplers were similarly compromised. Due to one PFM being lost for Site 04, water flow was estimated from a single PFM. One of the replicate passive flow monitors (PFMs) was damaged at Site 33, therefore the water flow velocity at the site was also calculated using only the remaining PFM data.

Deployments were for periods of 27 to 36 days in duration. A second sampler was deployed at ten randomly selected sites (Table 1, highlighted in green), with six of these extra samplers as site duplicates. The remaining four were spiked with native target analytes as part of QAEHS routine quality control procedures.

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.

Table 1. *Passive sampler 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)	Comments
SEQ01 : Mary River @ Coles X ing	CMV-MRS-01-OFF-PS	12/07/2023	10/08/2023	29	3.4	
SEQ02 : Lake Macdonald Intake	CSX-LMD-01-OFF-PS	20/07/2023	22/08/2023	33	7.1	
SEQ04 : Mary River @ Kenilworth	CMV-MRS-40-RIV-PS	13/07/2023	11/08/2023	29	3.8	**lost** 1 PFM: used existing PFM x 2
SEQ05 : Poona Dam	CMR-POD-01-OFF-PS	18/07/2023	17/08/2023	30	6.5	
SEQ06 : South Maroochy Intake Weir	CMR-SOR-25-OFF-PS	18/07/2023	17/08/2023	30	3.4	
SEQ07 : Yabba Creek @ Jimna	CMV-YAC-01-OFF-PS	13/07/2023	11/08/2023	29	3.4	
SEQ08 : Baroon Pocket Dam	CBT-BPD-15-OFF-PS	26/07/2023	31/08/2023	36	4.2	
SEQ09 : Ewen Maddock	CML-EMD-01-OFF-PS	5/07/2023	2/08/2023	28	4.9	
SEQ10 : Kilcoy WTP offtake	CST-SOD-90-OFF-PS	11/07/2023	8/08/2023	28	4.2	
SEQ11 : Kirkleagh	CST-SOD-71-OFF-PS	11/07/2023	8/08/2023	28	4.1	
SEQ12 : Somerset Dam Wall	CST-SOD-01-OFF-PS	11/07/2023	8/08/2023	28	3.4	
SEQ13 : Wivenhoe Dam @ Esk	CUB-WID-90-OFF-PS	26/07/2023	22/08/2023	27	5.2	
SEQ14 : Wivenhoe Dam Wall	CUB-WID-01-OFF-PS	26/07/2023	22/08/2023	27	6.2	
SEQ15 : Lockyer Creek @ Lake Clarendon Way	CCK-LOC-50-RIV-PS	6/07/2023	4/08/2023	29	5	
SEQ16 : Lockyer Creek @ Patrick's Estate	CCK-LOC-15-RIV-PS	20/07/2023	17/08/2023	28	3.4	
SEQ17 : Lowood Intake	CMB-MBR-80-OFF-PS	20/07/2023	17/08/2023	28	7.8	
SEQ18 : Mt Crosby Westbank Offtake Tower	CMB-MBR-02-OFF-PS	5/07/2023	2/08/2023	28	5.4	

SEQ19 : North Pine River @ Dayboro Well	CPV-NPR-70-OFF-PS	18/07/2023	17/08/2023	30	3.4	
SEQ20 : North Pine VPS	CPV-NOD-10-OFF-PS	18/07/2023	22/08/2023	35	4.8	
SEQ21 : Lake Kurwongbah	CPV-LAK-01-OFF-PS	19/07/2023	17/08/2023	29	4.2	
SEQ23 : Herring Lagoon	CNS-HLA-01-OFF-PS	18/07/2023	22/08/2023	35	3.4	
SEQ24 : Leslie Harrison Dam	CRL-LHD-05-VPS-PS	20/07/2023	23/08/2023	34	4.7	
SEQ25 : Wyaralong Dam Wall	CLR-WYD-01-REC-PS	7/07/2023	8/08/2023	32	4.1	
SEQ26 : Reynolds Creek @ Boonah	CWV-REY-20-OFF-PS	19/07/2023	18/08/2023	30	3.4	
SEQ27 : Moogerah Dam	CWV-MOD-02-OFF-PS	19/07/2023	18/08/2023	30	8	
SEQ28 : Logan River @ Kooralbyn Offtake	CLR-LOG-60-OFF-PS	6/07/2023	3/08/2023	28	22.1	
SEQ29 : Maroon Dam Wall	CLR-MAD-04-OFF-PS	4/07/2023	2/08/2023	29	8.1	
SEQ31 : Rathdowney Weir	CLR-LOG-80-OFF-PS	6/07/2023	3/08/2023	28	3.4	
SEQ32 : Canungra Creek @ Offtake	CLR-CAC-01-OFF-PS	13/07/2023	18/08/2023	36	3.4	
SEQ33 : Little Nerang Dam	CNR-LND-01-OFF-PS	25/07/2023	29/08/2023	35	4.4	1 PFM had plaster fall out. Used other PFM x 2
SEQ34 : Hinze Upper Intake	CNR-HID-20-OFF-PS	31/08/2023	29/09/2023	29	4.6	Original samplers compromised: replaced with spare kit.
SEQ35 : Hinze Lower Intake	CNR-HID-01-OFF-PS	26/07/2023	31/08/2023	36	5.9	
SEQ36 : Fernvale STP @ Savages Crossing	CMB-MBR-60-RIV-PS	6/07/2023	4/08/2023	29	7.7	
SEQ37 : Logan River @ Cedar Grove	CLR-LOG-12-RIV-PS	6/07/2023	3/08/2023	28	3.4	
SEQ38 : Wappa Dam	CMR-WAD-01-OFF-PS	18/07/2023	17/08/2023	30	3.5	
SEQ39 : Cooloolabin Dam	CMR-COD-01-OFF-PS	6/07/2023	3/08/2023	28	3.4	
SEQ40 : Wivenhoe Dam @ Logans Inlet PRW	CUB-WID-59-PRW-PS	26/07/2023	22/08/2023	27	7	
SEQ43 : Enoggera Reservoir	CLB-END-01-OFF-PS	13/07/2023	10/08/2023	28	3.6	

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.

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 3.4 cm s^{-1} or PFM loss rate equal to 0.58 g d^{-1}; O'Brien *et al.* 2009; 2011b). Therefore, to remain within the accurate mathematical modelling range for PFM-based flow velocity prediction, we applied a minimum flow rate of 3.4 cm s^{-1} for the sites showing flow below this threshold and the minimum atrazine equivalence R_s. This may result in a slight over-estimation of R_s and under-estimation of water concentration estimates (C_w), though we do not expect this to be significant (Kaserzon *et al.* 2014; O'Brien *et al.* 2011b). Average flow velocities estimated from PFMs over the deployment period ranged from between 3.4 cm s^{-1} to 22.1 cm s^{-1} (SEQ28 : Logan River @ Kooralbyn Offtake) (Figure 2).
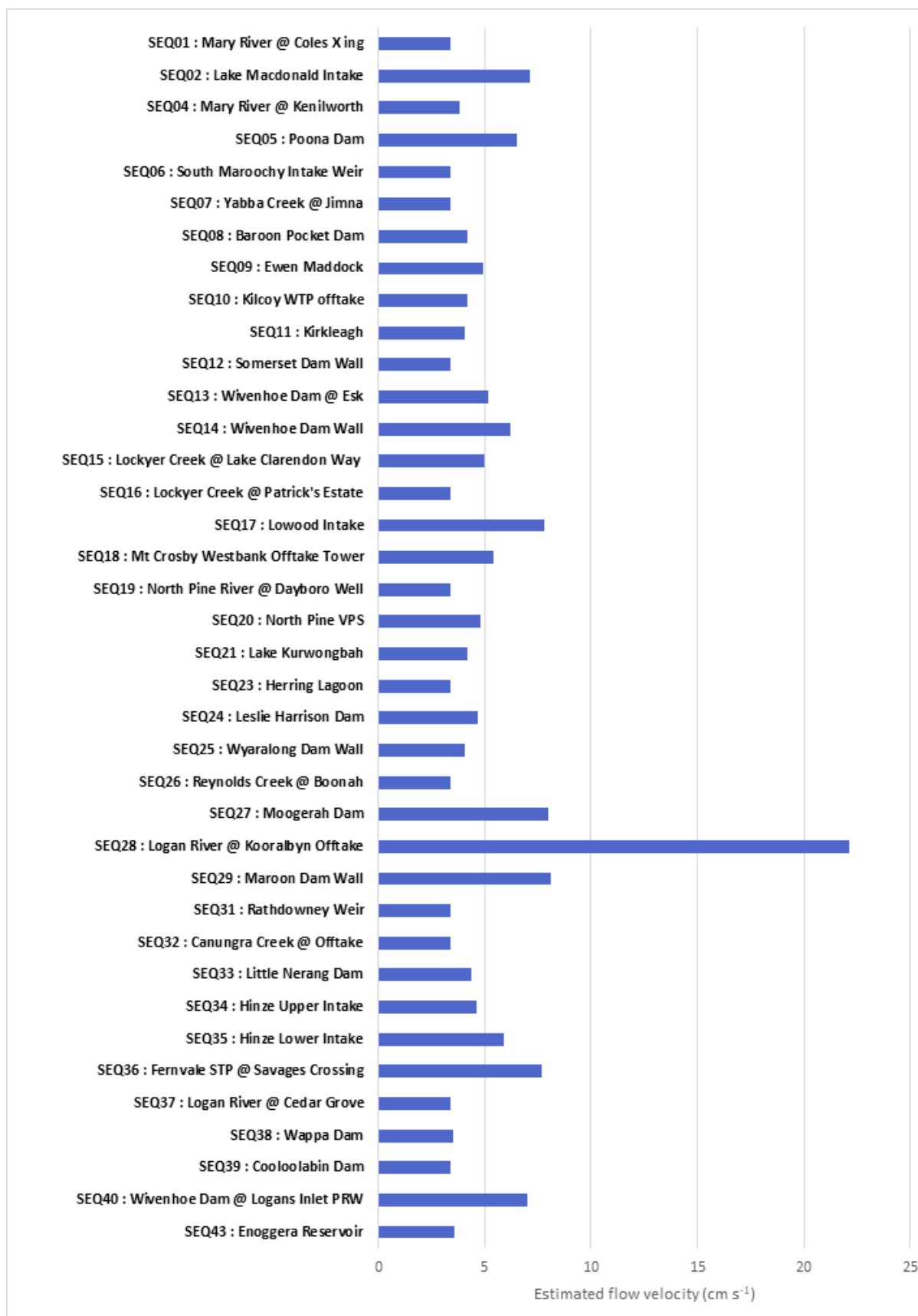
Figure 2. Passive flow monitor (PFM) based water flow velocity estimations (cm s⁻¹) at the deployment sites (n=38).

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 13 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% – 79% for OCPs and 3% – 95% for PAHs. Table 3 summarises the polar chemicals quantified via ED (pesticides and PPCPs). A total of 27 pesticides (predominantly herbicides) and 10 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3% - 68% for pesticides and 3% - 50% 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				
Aldrin	0	0%	0.00	0.00
Azinphos methyl	0	0%	0.00	0.00
Bifenthrin	4	11%	1.39	4.09
Chlorpyrifos	24	63%	2.51	36
cis-Chlordane	16	42%	1.07	8.56
Cypermethrin	0	0%	0.00	0.00
Dacthal	19	50%	4.63	1126
Deltamethrin	0	0%	0.00	0.00
Dieldrin	19	50%	2.66	12.3
Endosulfan sulfate	6	16%	1.03	6.21
Endrin	0	0%	0	0.00
Endrin ketone	0	0%	0	0.00
HCB	8	21%	1.51	2.19
Heptachlor	0	0%	0.00	0.00
Heptachlor epoxide a	0	0%	0.00	0.00
Heptachlor epoxide b	2	5%	2.22	2.9
Methoxychlor	0	0%	0.00	0.00
Mirex	0	0%	0.00	0.00
o,p-DDD	0	0%	0.00	0.00
o,p-DDE	0	0%	0.00	0.00
o,p-DDT	0	0%	0.00	0.00
p,p-DDD	8	21%	1.07	2.40
p,p-DDE	12	32%	1.00	10.0
p,p-DDT	0	0%	0.00	0.00
Pendimethalin	5	13%	10.4	83
Permethrin	2	5%	1.80	2.24
trans-Chlordane	30	79%	1.52	7.2
α-Endosulfan	0	0%	0.00	0.00
α-HCH	0	0%	0.00	0.00
β-endosulfan	0	0%	0.00	0.00
β-HCH	0	0%	0.00	0.00
γ-HCH (Lindane)	0	0%	0.00	0.00

PAH				
Acenaphthene	1	3%	12	12
Acenaphthylene	15	39%	5.09	32.7
Anthracene	4	11%	5.7	28.2
Benzo[a]anthracene	5	13%	1.12	4.2
Benzo[a]pyrene	0	0%	0	0.00
Benzo[b,j,k]fluoranthene	21	55%	0.515	1.65
Benzo[e]pyrene	3	8%	1.01	1.49
Benzo[g,h,i]perylene	1	3%	1.27	1.27
Chrysene/Triphenylene	36	95%	0.90	11.3
Dibenz[a,h]anthracene	0	0%	0.00	0.00
Fluoranthene	25	66%	14.8	70.4
Fluorene	2	5%	42.9	45.3
Indeno[1,2,3-c,d]pyrene	0	0%	0	0.00
Naphthalene	1	3%	335	335
Phenanthrene	18	47%	67.3	260
Pyrene	16	42%	13	39.3

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				
2,4,5-T	0	0%	0.00	0.00
2,4-D	3	8%	5.82	21.5
3,4 Dichloroaniline	0	0%	0.00	0.00
Ametryn	0	0%	0.00	0.00
Ametryn hydroxy	1	3%	1.25	1.25
Aminocarb	0	0%	0.00	0.00
Atrazine	20	53%	1.28	12
Atrazine desethyl	12	32%	1.01	3.0
Atrazine desisopropyl	11	29%	1.06	2.26
Bendiocarb	1	3%	1.34	1.34
Bromacil	1	3%	1.26	1.26
Bromoxynil	1	3%	1.69	1.69
Carbaryl	0	0%	0.00	0.00
Carbendazim	2	5%	3.65	14.3
DCPMU	1	3%	0.117	0.117
DCPU	0	0%	0.00	0.00
Diazinon	4	11%	0.106	1.939
Difenoconazole	0	0%	0.00	0.00
Diketonitrile	0	0%	0.000	0.000
Diuron	10	26%	0.501	20.2
Fenuron	0	0%	0.00	0.00
Fipronil	1	3%	0.776	0.78
Fluazifop	0	0%	0.000	0.00
Fluometuron	0	0%	0.00	0.00

Fluroxypyr	0	0%	0.00	0.00
Haloxyfop	1	3%	2.74	2.74
Hexazinone	7	18%	2.40	3.82
Imazapyr	0	0%	0.00	0.00
Imazethapyr	0	0%	0.00	0.00
Imidacloprid	1	3%	14.74	14.7
Malathion	0	0%	0.00	0.00
MCPA	1	3%	16.48	16.48
Metalaxyl	12	32%	0.131	1.95
Methidathion	0	0%	0.00	0.00
Methomyl	1	3%	5.60	5.6
Metolachlor (S+R)	14	37%	1.22	60
Metolcarb	0	0%	0.00	0.00
Metribuzin	0	0%	0.00	0.00
Metsulfuron methyl	26	68%	1.04	8.2
Mexacarbate	0	0%	0.00	0.00
Oryzalin	0	0%	0.00	0.00
Picloram	0	0%	0.00	0.00
Promecarb	0	0%	0.00	0.00
Prometryn	0	0%	0.00	0.00
Propachlor	0	0%	0.00	0.00
Propazine	0	0%	0.00	0.00
Propiconazole	0	0%	0.00	0.00
Propoxur	0	0%	0.00	0.00
Simazine	12	32%	1.09	4.8
Simazine hydroxy	0	0%	0.00	0.00
Tebuconazole	0	0%	0.00	0.00
Tebuthiuron	12	32%	1.08	134
Terbuthylazine	6	16%	1.09	1.88
Terbuthylazine desethyl	17	45%	1.10	5.8
Thiamethoxam	2	5%	6.490	20.12
Triclopyr	3	8%	5.29	11.6
Pharmaceuticals and personal care products (PPCPs)				
Acesulfame	0	0%	0.00	0.00
Atenolol	1	3%	3.47	3.47
Atorvastatin	0	0%	0.00	0.00
Caffeine	0	0%	0	0
Carbamazepine	5	13%	1.16	2.79
Codeine	0	0%	0.00	0.00
DEET	19	50%	16.26	104
Diclofenac	1	3%	0.960	0.960
Gabapentin	1	3%	1.32	1.32
Hydrochlorothiazide	1	3%	1.10	1.10
Iopromide	0	0%	0.00	0.00
Naproxen	3	8%	1.36	19.80
Oxazepam	3	8%	1.38	2.13

Paracetamol	0	0%	0.00	0.00
Paraxanthine	0	0%	0.0	0.0
Salicylic acid	0	0%	0.00	0.00
Sulfadiazine	0	0%	0.000	0.000
Sulfamethoxazole	3	8%	0.371	0.886
Tadalafil	0	0%	0.00	0.00
Temazepam	1	3%	1.34	1.34
Verapamil	0	0%	0.00	0.00

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 (SEQ07 - Yabba Creek @ Jimna; SEQ01 - Mary River @ Coles X ing; SEQ04 - Mary River @ Kenilworth) to 1243 ng PDMS^{-1} (SEQ15 - Lockyer Creek @ Lake Clarendon Way).
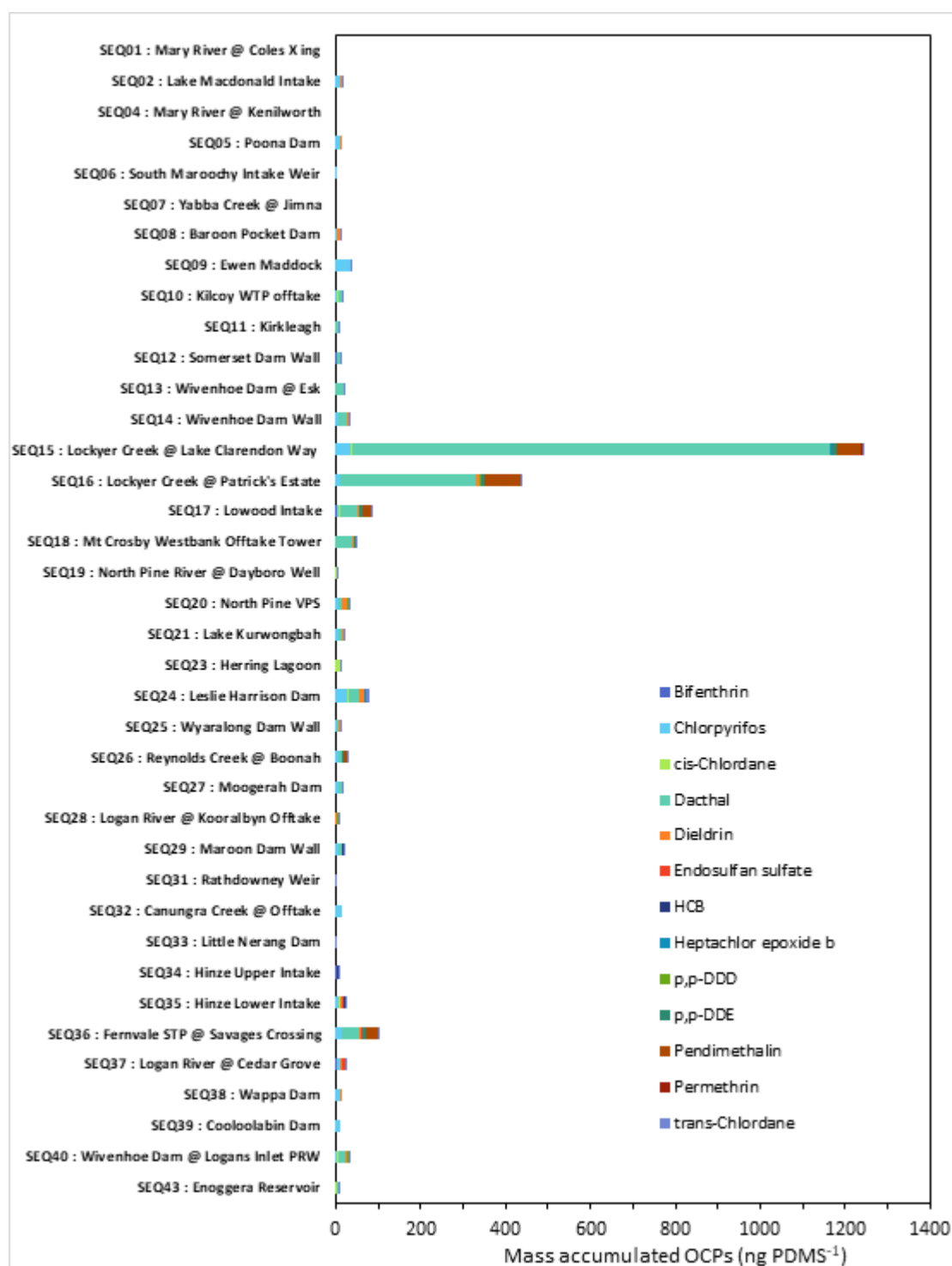
Figure 3. Total mass of 13 ΣOCPs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

Discounting the sites below reporting limits, the conversion of ΣOCP masses accumulated in passive samplers to time-weighted average water concentrations revealed an estimated water concentration range of 0.003 to 24.9 ng L^{-1} (SEQ33 - Little Nerang Dam and SEQ15 - Lockyer Creek @ Lake Clarendon Way , respectively; Figure 4).
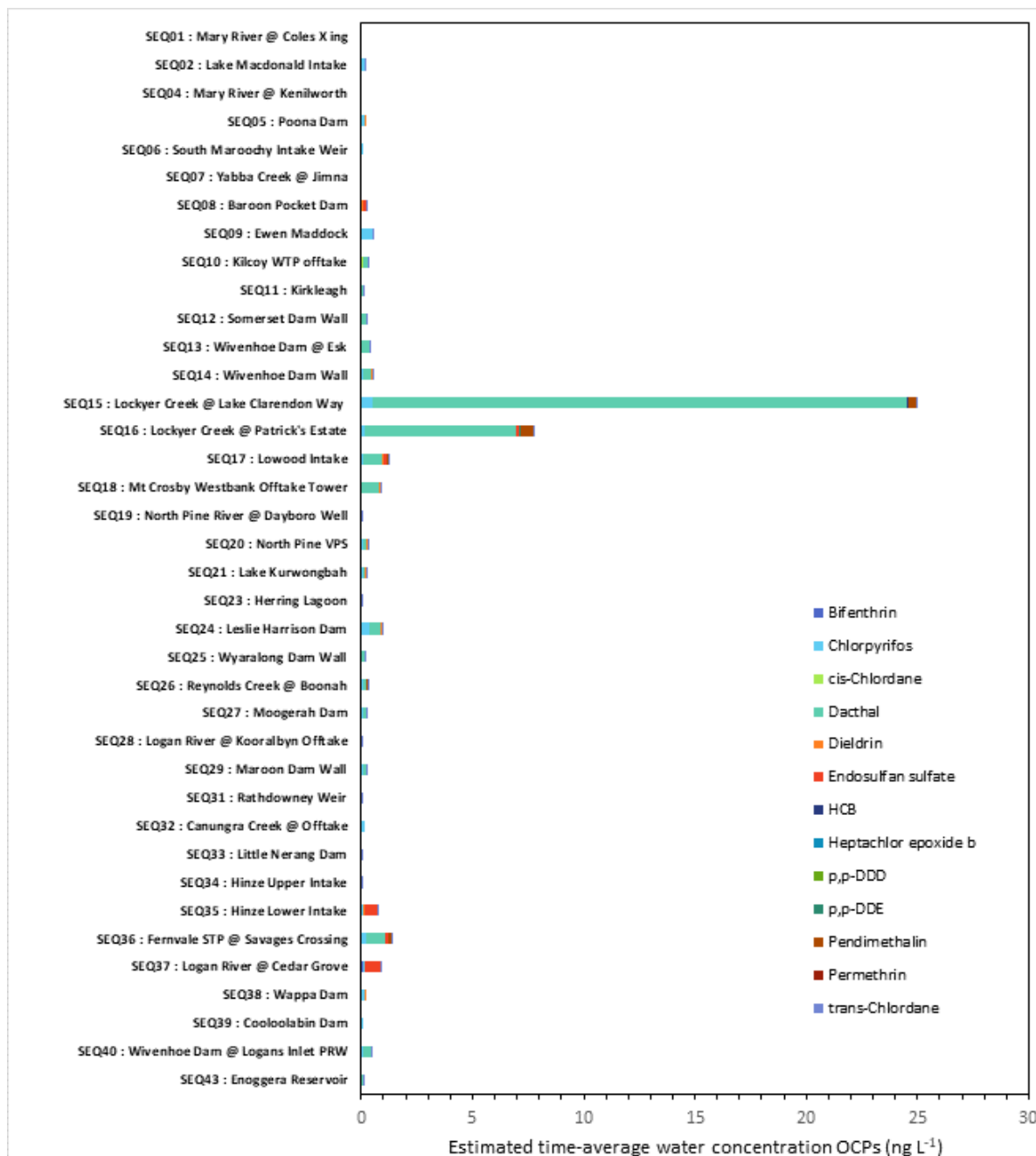
Figure 4. Total estimated water concentrations (ng L⁻¹) of 13 ΣOCPs at each site derived from PDMS passive samplers.

Polycyclic aromatic hydrocarbons (PAHs)

In total, 13 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 (SEQ19 - North Pine River @ Dayboro Well; SEQ07 - Yabba Creek @ Jimna) to 471 ng PDMS⁻¹ (SEQ20 - North Pine VPS).
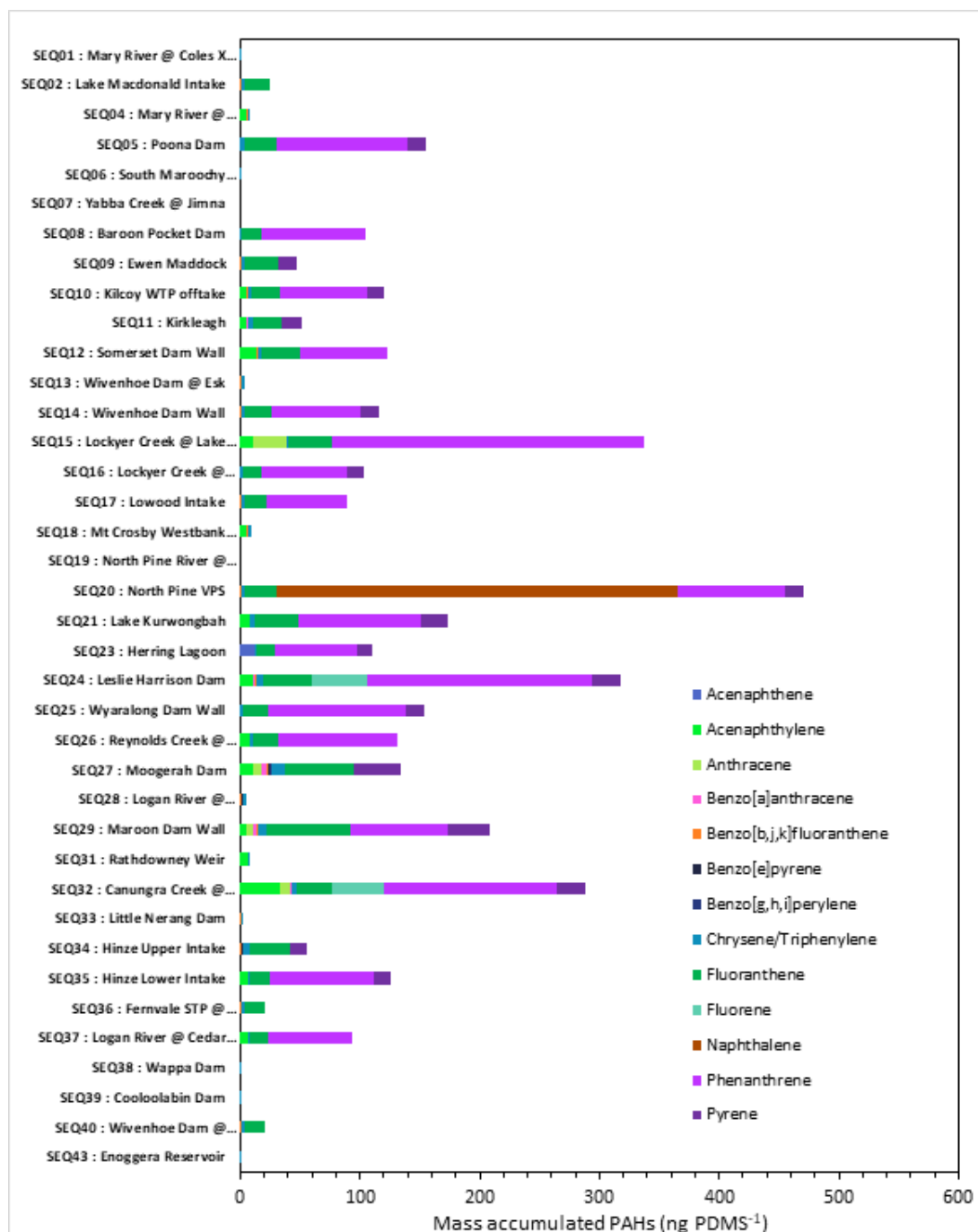
Figure 5. Total mass of 13 ΣPAHs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

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 0.003 to 23.3 ng L^{-1} (SEQ06 - South Maroochy Intake Weir and SEQ20 - North Pine VPS, respectively; Figure 6).
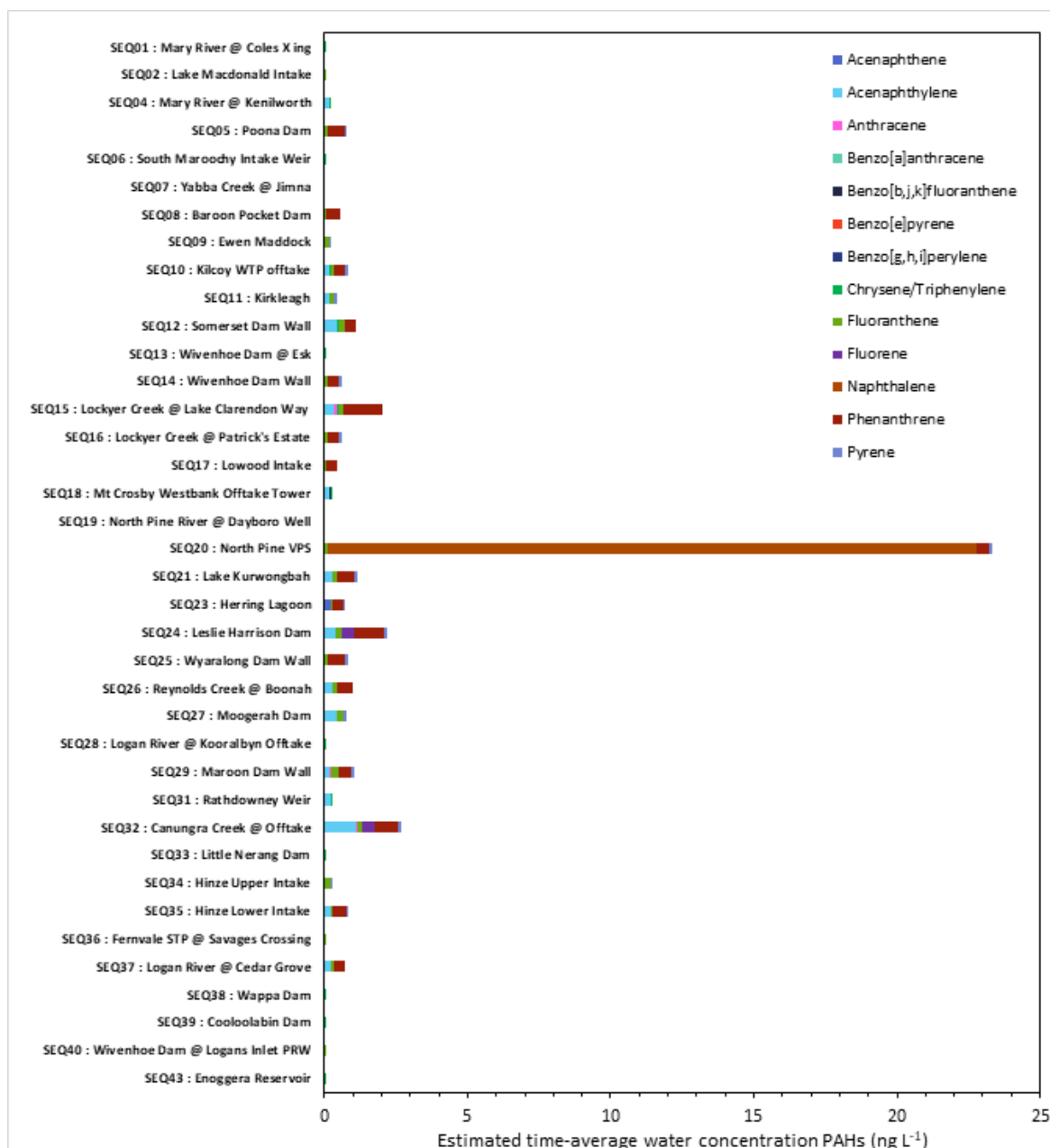
Figure 6. Total estimated water concentrations (ng L^{-1}) of 13 ΣPAHs at each site derived from PDMS passive samplers.

Pesticides

Over the deployment period, 27 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 (SEQ32 - Canungra Creek @ Offtake; SEQ07 - Yabba Creek @ Jimna; SEQ23 - Herring Lagoon; SEQ19 - North Pine River @ Dayboro Well; SEQ43 - Enoggera Reservoir; SEQ33 - Little Nerang Dam; SEQ04 - Mary River @ Kenilworth ; SEQ01 - Mary River @ Coles X ing) to 181 ng ED^{-1} (SEQ24 - Leslie Harrison Dam).
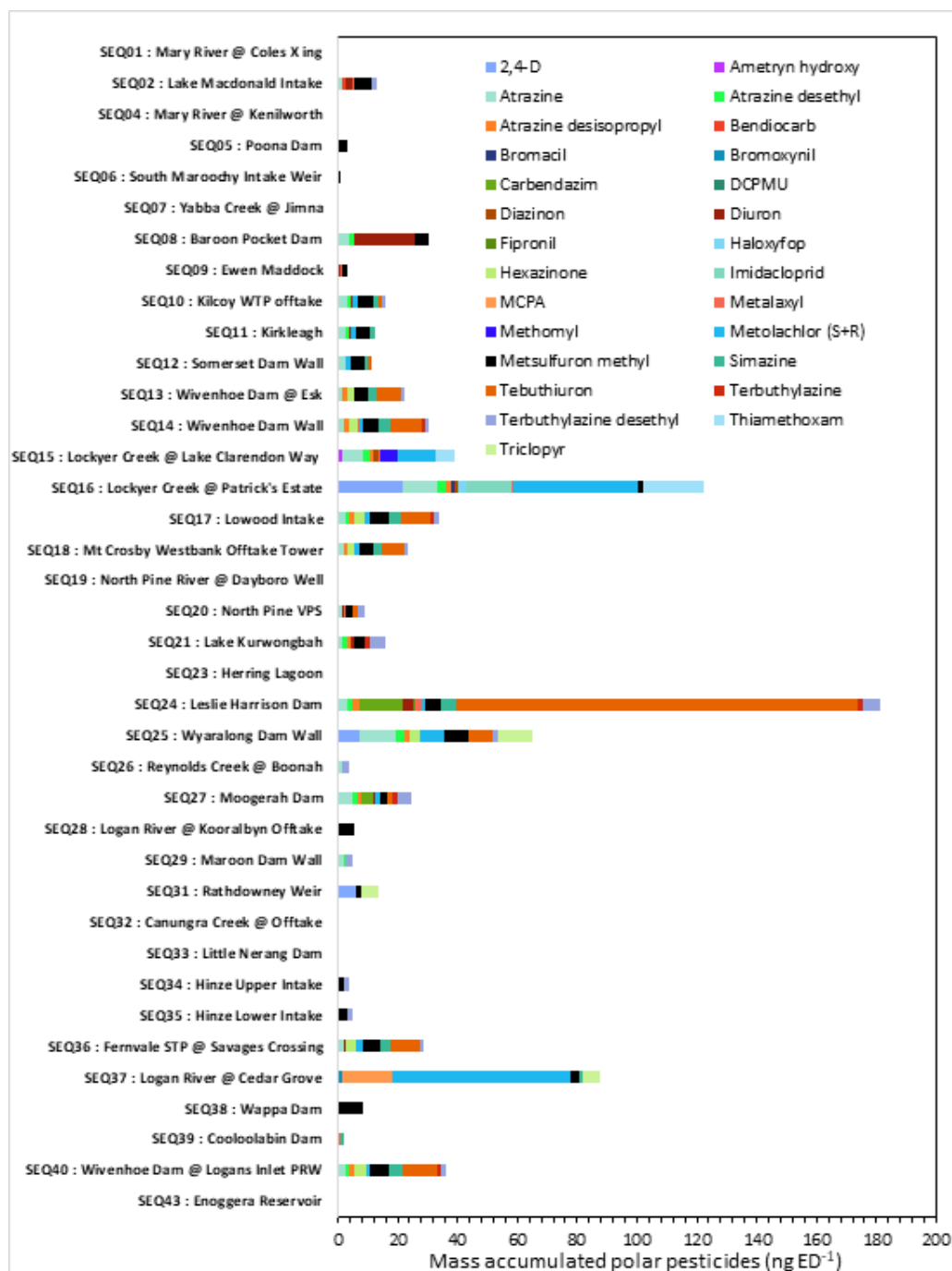
Figure 7. Total mass of 27 Σpolar pesticides (ng ED^{-1}) accumulated in ED passive samplers at each site.

Water concentrations were estimated for the polar pesticides accumulated where sampling rates have been previously calibrated. From the 27 chemicals reported, 16 were converted to time-weighted average water Σconcentrations. Discounting the sites below reporting limits, these water concentrations ranged between 0.62 and 75 ng L^{-1} (SEQ39 - Cooloolabin Dam and SEQ24 - Leslie Harrison Dam, respectively; Figure 8).

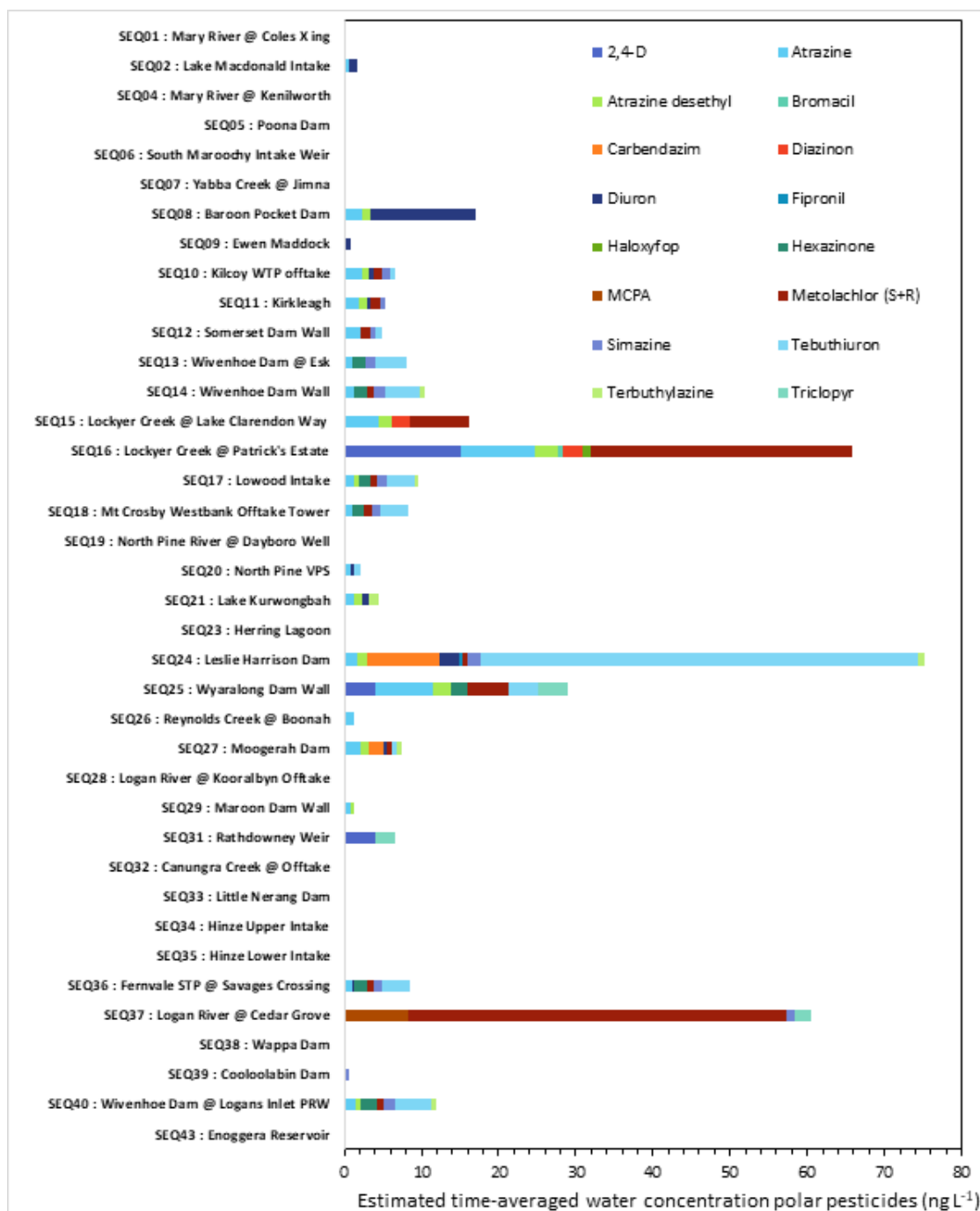*Figure 8. Total estimated water concentrations (ng L^{-1}) of 16 Σpolar pesticides at each site derived from ED passive samplers.*

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 0.60 ng ED^{-1} (SEQ12 - Somerset Dam Wall) to 104 ng ED^{-1} (SEQ05 - Poona Dam).

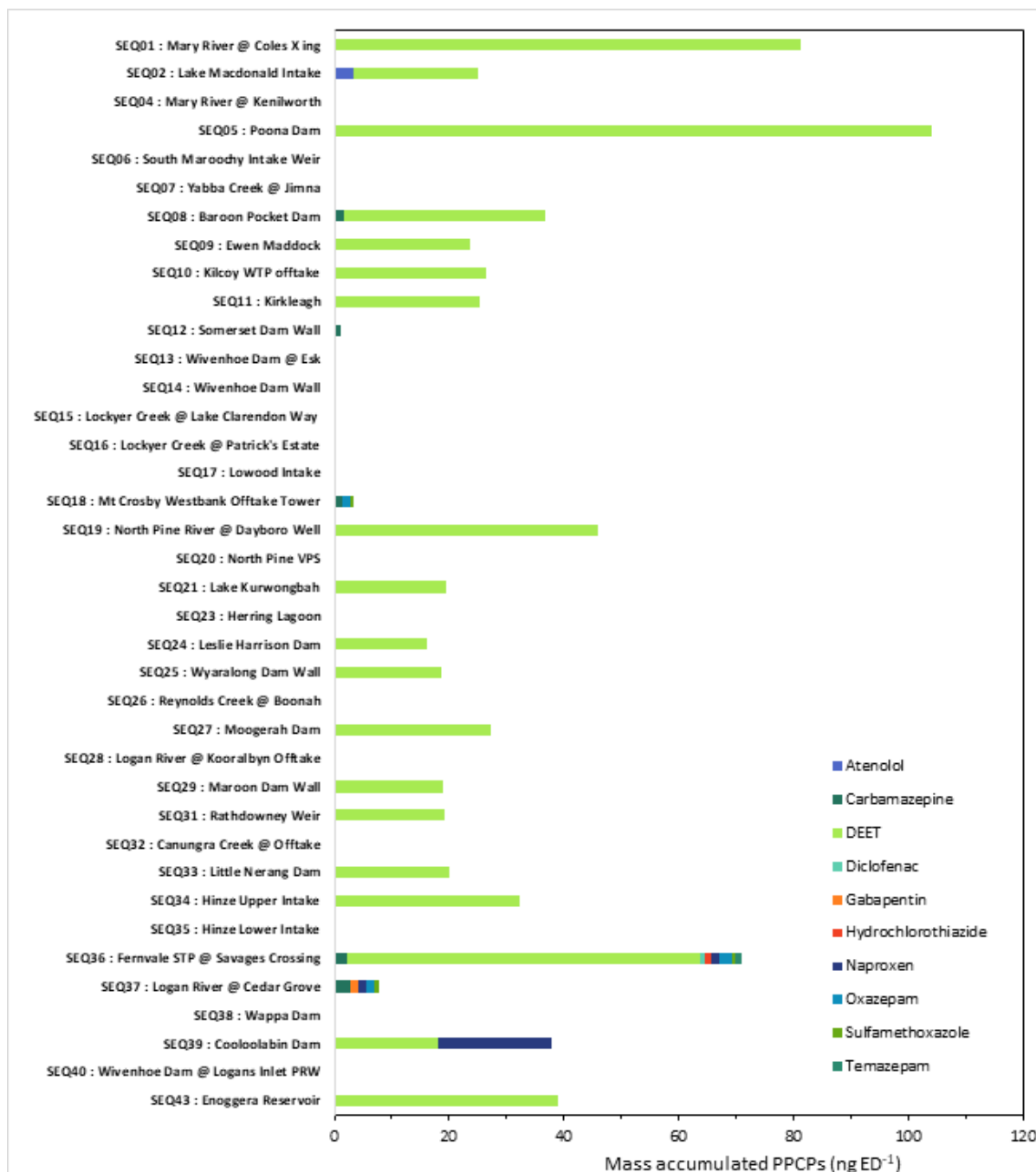*Figure 9. Total mass of 10 ∑PPCPs (ng ED⁻¹) accumulated in ED passive samplers at each site.*

Of the 10 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 0.60 and 48 ng L⁻¹ (sites SEQ12 - Somerset Dam Wall and SEQ01 - Mary River @ Coles X ing, respectively; Figure 10).
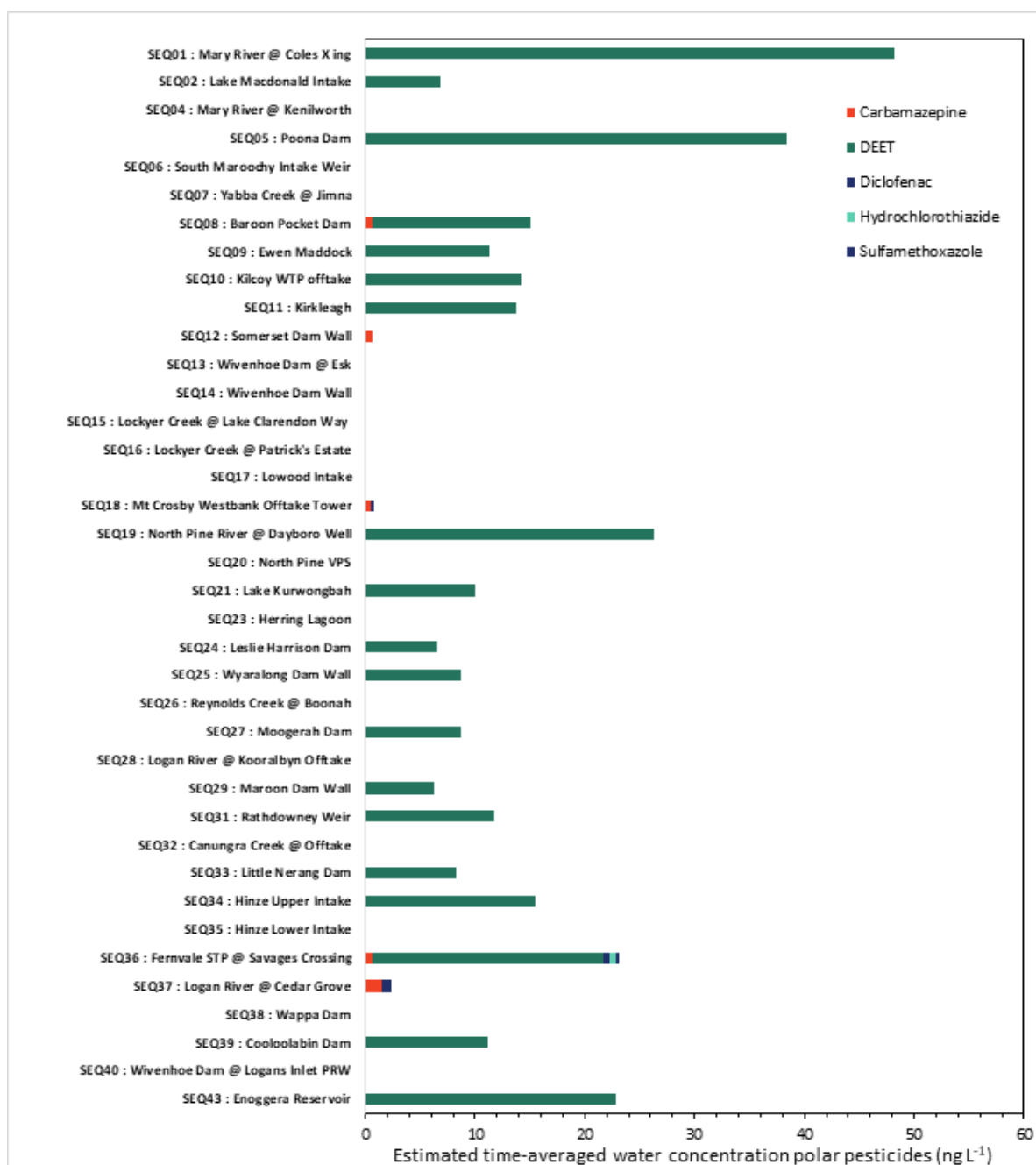
Figure 10. Total estimated water concentrations (ng L^{-1}) of 5 ΣPPCPs derived from ED passive samplers.

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. It is noted that to fully confirm the identification and quantification of these analytes, the use of appropriate chemical standards would be necessary. Tentative identifications are considered when the suspect spectra met strict criteria (strong signal/noise of >3, reverse dot product score >90%) and mass errors were <5 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
Azoxystrobin acid	Azoxystrobin breakdown product	SEQ02 : Lake Macdonald Intake SEQ05 : Poona Dam SEQ06 : South Maroochy Intake Weir SEQ15 : Lockyer Creek @ Lake Clarendon Way SEQ16 : Lockyer Creek @ Patrick's Estate SEQ17 : Lowood Intake SEQ18 : Mt Crosby Westbank Offtake Tower SEQ24 : Leslie Harrison Dam SEQ26 : Reynolds Creek @ Boonah SEQ36 : Fernvale STP @ Savages Crossing SEQ38 : Wappa Dam
Boscalid	Fungicide	SEQ15 : Lockyer Creek @ Lake Clarendon Way SEQ18 : Mt Crosby Westbank Offtake Tower SEQ24 : Leslie Harrison Dam
Tylosin	Veterinary antibiotic - toxic to algae	SEQ02 : Lake Macdonald Intake SEQ13 : Wivenhoe Dam @ Esk SEQ14 : Wivenhoe Dam Wall SEQ16 : Lockyer Creek @ Patrick's Estate SEQ25 : Wyaralong Dam Wall SEQ35 : Hinze Lower Intake SEQ36 : Fernvale STP @ Savages Crossing SEQ37 : Logan River @ Cedar Grove SEQ38 : Wappa Dam SEQ39 : Cooloolabin Dam SEQ40 : Wivenhoe Dam @ Logans Inlet PRW SEQ43 : Enoggera Reservoir
Phenethylamine	Central nervous system stimulant (can be naturally occurring)	SEQ04 : Mary River @ Kenilworth SEQ05 : Poona Dam SEQ10 : Kilcoy WTP offtake SEQ11 : Kirkleagh SEQ15 : Lockyer Creek @ Lake Clarendon Way SEQ17 : Lowood Intake SEQ27 : Moogerah Dam

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. Comparisons were made with those chemicals converted to a water concentration.

Exceedances for eco-toxicological guidelines were observed in the estimated time-averaged water concentrations for diazinon, metolachlor, tebuthiuron and chlorpyrifos. ANZECC & ARMCANZ have set diazinon freshwater guideline values of 0.03 and 10 ng L^{-1} for 99% and 95% species protection levels, respectively. There were no sites with any detections in excess of the 95% species protection guideline

for any chemical. Furthermore, totals of 4, 3, 1 and 24 sites exceeded the 99% species protection guidelines for diazinon, metolachlor, tebuthiuron and chlorpyrifos, respectively (Table 5).

Table 5. Threshold chemical guidelines for Australian Drinking Water and Freshwater Aquatic Ecosystems. Values highlighted in yellow exceed the 99% species protection guideline.

Australian Drinking Water Guidelines 6 (2011) Version 3.6 Updated December 2021		ANZECC & ARMCANZ (2021) Trigger values for freshwater		This campaign
Herbicides & Insecticides	Guideline value (ng L⁻¹)	99% species protection value (ng L⁻¹)	95% species protection value (ng L⁻¹)	Highest Reported Value (ng L⁻¹)
Atrazine	20000	700	13000	10
Ametryn	70000	N/A	N/A	N/A
Bromacil	400000	N/A	N/A	0.7
Bromoxynil	10000	N/A	N/A	N/A
Carbaryl	30000	N/A	N/A	N/A
Carbendazim	90000	N/A	N/A	9.46
Cypermethrin	200000	N/A	N/A	N/A
Diazinon	4000	0.03	10	2.4
Diuron	20000	N/A	N/A	13.7
Fipronil	700	N/A	N/A	0.37
Fluometuron	70000	N/A	N/A	N/A
Haloxyfop	1000	N/A	N/A	1.19
Hexazinone	400000	N/A	N/A	2.28
Imazapyr	9000000	N/A	N/A	N/A
MCPA	40000	N/A	N/A	8.37
Malathion	70000	2	50	N/A
Methomyl	20000	N/A	N/A	N/A
Metolachlor (S+R)	300000	8.4	460	49
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	1.80
Tebuthiuron	N/A	20	2200	56.7
Terbuthylazine	10000	N/A	N/A	1.15
Triclopyr	20000	N/A	N/A	3.76
2,4-D	30000	140000	280000	15.1
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	0.48
Cypermethrin	200000	N/A	N/A	N/A
DDT	9000	6	10	0.04
Dieldrin	300	N/A	N/A	0.04
Aldrin	300	N/A	N/A	N/A
Endosulfan	20000	30	200	0.66
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	0.12
Benzo[a]pyrene	10	N/A	N/A	N/A
Fluoranthene	N/A	1000	1400	0.311
Naphthalene	N/A	2500	16000	22.6
Phenanthrene	N/A	600	2000	1.39

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 OCPs were reported at 35 sites (92%), the concentrations were low (total ∑OCPs <24.92 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. Trans-chlordane was the most frequently detected OCP, reported at 30 sites (79% of sites) and chlorpyrifos was the second most frequent at 24 sites (63% of sites). Chlordane has been used since the 1950s as an insecticide, particularly as a termite treatment. It has been banned in Australia since 1988, though remains persistent in the environment due to its low breakdown rate. Dacthal (also known as chlorthal-dimethyl) is a herbicide used on a wide variety of fruit and vegetable crops. Dacthal was the OCP found at the highest concentration, detected at two sites along Lockyer Creek (SEQ15 - Lockyer Creek @ Lake Clarendon Way and SEQ16 - Lockyer Creek @ Patrick's Estate, 24.1 ng L^{-1} and 6.8 ng L^{-1}, respectively). These levels are similar to those found at the same sites during the winter 2022 sampling period, 27.2 ng L^{-1} at SEQ15 and 17.1 ng L^{-1} at SEQ16 (Shiels and Kaserzon 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 36 of the 38 sites (95% detection frequency). Chrysene/triphenylene was the most frequently detected PAH (95% detection) although this was at low levels, with a maximum concentration of 0.024 ng/L at site SEQ27 - Moogerah Dam.

Polar pesticides (herbicides, insecticides and fungicides) were reported at 30 sites. The two most frequently reported pesticides were Metsulfuron methyl (detected at 26 sites; 68%) and Atrazine (detected at 20 sites; 53%) which are both 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, terbuthylazine, hexazinone and degradation products such as terbuthylazine desethyl, 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 metsulfuron 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). They 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 (50% of sites) which can often be attributed to background contamination due to requirements of field staff to use insect repellent products in the field which contain deet. The second most frequently reported PPCP was carbamazepine (detected at 13% 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 that 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.

References

Andreozzi R., Marotta R., Pinto G. & Pollio A. (2002). Carbamazepine in water: persistence in the environment, ozonation treatment and preliminary assessment on algal toxicity. Water Research 36(11) 2869 - 2877

ANZECC & ARMCANZ (2018). Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Volume 1 The Guidelines. National Water Quality Management Strategy No. 4., Australian & New Zealand Environment & Conservation Council and the Agriculture & Resource Management Council of Australia & New Zealand.

NHMRC, NRMMC (2011) Australian Drinking Water Guidelines Paper 6. Version 3.5; Updated _AUGUST 2018_. National Water Quality Management Strategy. National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia, Canberra.

APVMA (2010). Endosulfan Chemical Review - 9. Implementation review process workflow, Australian Pesticides and Veterinary Medicines Authority, Australian Government.

APVMA (2011a). Atrazine. Environmental Assessment, Australian Pesticides and Veterinary Medicines Authority, Australian Government.

APVMA (2011b). Chlorpyrifos. Environmental Assessment, Australian Pesticides and Veterinary Medicines Authority, Australian Government.

APVMA (2016). Permit to allow minor use of an agvet chemical product for the control of stinging nettle in lettuce crops. Australian Pesticides and Veterinary Medicines Authority, Australian Government.

Beeton R, Buckley K, Jones G, Morgan D, Reichelt R, Trewin D. (2006). Australian State of the Environment Committee 2006. Independent report to the Australian Government Minister for the Environment and Heritage. Department of the Environment and Heritage.

Benbrook, C.M. (2016). Trends in glyphosate herbicide use in the United States and globally. Environ. Sci. Eur. 28.

Kaserzon, S.L., Hawker, D.W., Kennedy, K., Bartkow, M., Carter, S., Booij, K., Mueller, J.M. (2014). Characterisation and comparison of the uptake of ionizable and polar pesticides, pharmaceuticals and personal care products by POCIS and Chemcatchers. Environ. Sci.: Processes Impacts 16: 2517–2526

Kaserzon, S., Yeh, R., Thompson, K., Paxman, C., Gallen, C., Elisei, G., Prasad, P., Schacht, V., Van Niekerk, S., Verhagen, R., Vijayasarathy, S., Gallen, G., Reeks, T., Jiang, H., Eaglesham, G. and Mueller, J. (2018). Catchment and Drinking Water Quality Micro Pollutant Monitoring Program – Passive Sampling Report 8 – Summer 2018 and summary report, prepared for Seqwater, August 2018.

Kot, A., Zabiegala, B., Namiesnik, J. (2000). Passive sampling for long-term monitoring of organic pollutants in water. Trends in Analytical Chemistry 19 (7):446-459

Liu, N., Jin, X., Yan, Z. et al. (2020). Occurrence and multiple-level ecological risk assessment of pharmaceuticals and personal care products (PPCPs) in two shallow lakes of China. Environmental Sciences Europe 32 (69) 378 - 387

Nguyen, T.C., Loganathan, P., Nguyen, T.V., Vigneswaran, S., Kandasamy, J., Slee, D., Stevenson, G., Naidu, R. (2014). Polycyclic aromatic hydrocarbons in road-deposited sediments, water sediments, and soils in Sydney, Australia: Comparisons of concentration distribution, sources and potential toxicity. Ecotoxicology and Environmental Safety 104:339–348

O'Brien, D., Chiswell, B., Mueller, J. F. (2009). A novel method for the in situ calibration of flow effects on a phosphate passive sampler. Journal of Environmental Monitoring 11: 201-219

O'Brien, D., Booij, K., Hawker, D., Mueller, J.F. (2011a). Method for the in Situ Calibration of a Passive Phosphate Sampler in Estuarine and Marine Waters. Environmental Science & Technology 45 (7): 2871-2877

O'Brien, D., Bartkow, M., Mueller, J.F. (2011b). Determination of deployment specific chemical uptake rates for SDB-RPS EmporeTM disk using a passive flow monitor. Chemosphere 83 (9): 1290-1295

Shiels, R., and Kaserzon, S. (2022). Catchment and Drinking Water Quality Micro Pollutant Monitoring program – Passive Sampling. Report 17 – Winter 2022, prepared for Seqwater, December 2022.

Toms, L.M., Harden, F., Hobson, P., Sjodin, A., Mueller, J. (2012) Temporal trend of organochlorine pesticides in Australia. In Mueller, Jochen & Gaus, Caroline (Eds.) Organohalogen Compounds, International Advisory Board and Dioxin20XX.org, Cairns, QLDVrana, B., Greenwood, R., Mills, G., Dominiak, E., Svensson, K., Knutsson, J., Morrison, G. (2005). Passive sampling techniques for monitoring pollutants in water. Trends in Analytical Chemistry 10: 845-868

Appendix 1

See enclosed excel file 'SEQW results_Winter_2023.xlsx'

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}).