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Catchment and Drinking Water Quality Micro Pollutant Monitoring program – Passive Sampling. Report 21 – Winter 2024.

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 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 2024. Results presented provide a continued insight into the water quality of the target catchments and drinking water reservoirs. Samplers were deployed for approximately one month, however some sites needed to be redeployed due to sampler losses.

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), UV filters, organochlorine pesticides (OCPs), fire ant bait chemicals 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 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 68 different chemicals including 14 OCPs, 12 PAHs, 28 polar pesticides and 14 PPCPs. OCPs were detected at 87% of sites, with Chlorpyrifos (68%) and Dieldrin (58%) the most frequently reported. Total ∑OCP water concentrations across sites ranged between 0.010 – 111 ng L^{-1} where concentrations were reportable. PAHs were detected at 95% of sites, with Chrysene/Triphenylene (82%) and Fluoranthene (95%) reported at the highest abundance across all sites. Total ∑PAH water concentrations across sites ranged between 0.028 – 3.67 ng L^{-1}. In total, 28 different polar pesticides were reported in 34 sites (89%), with Metsulfuron methyl (84%) and Terbuthylazine desethyl (55%) the most frequently detected. Total ∑polar pesticides ranged between 0.270 – 241 ng L^{-1}. Additionally, 14 PPCPs were detected across sites with highest detection frequencies observed for DEET (92%) and Paraxanthine (34%). Total estimated ∑PPCP water concentrations ranged between 1.59 – 137 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 for comparison (ANZECC & ARMCANZ 2018). No chemicals were present at 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 Southeast 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 two decades. 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 August 2024 at 38 sites of SEQ reservoirs/waterways (Table 1). Sites 26 and 29 were redeployed due to samplers being lost. Due to one PFM being lost for Site 18, water flow was estimated from a single PFM.

Deployments were for periods of 28 to 38 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	6/08/2024	5/09/2024	30	11.6	
SEQ02 : Lake Macdonald Intake	CSX-LMD-01-OFF-PS	18/07/2024	21/08/2024	34	8	
SEQ04 : Mary River @ Kenilworth	CMV-MRS-40-RIV-PS	2/07/2024	30/07/2024	28	11.3	
SEQ05 : Poona Dam	CMR-POD-01-OFF-PS	16/07/2024	13/08/2024	28	5.3	
SEQ06 : South Maroochy Intake Weir	CMR-SOR-25-OFF-PS	16/07/2024	13/08/2024	28	3.4	
SEQ07 : Yabba Creek @ Jimna	CMV-YAC-01-OFF-PS	2/07/2024	30/07/2024	28	3.4	
SEQ08 : Baroon Pocket Dam	CBT-BPD-15-OFF-PS	25/07/2024	30/08/2024	36	4.3	
SEQ09 : Ewen Maddock	CML-EMD-01-OFF-PS	25/07/2024	30/08/2024	36	7	
SEQ10 : Kilcoy WTP offtake	CST-SOD-90-OFF-PS	9/07/2024	15/08/2024	37	5.4	
SEQ11 : Kirkleagh	CST-SOD-71-OFF-PS	9/07/2024	16/08/2024	38	4.3	
SEQ12 : Somerset Dam Wall	CST-SOD-01-OFF-PS	9/07/2024	16/08/2024	38	4.3	
SEQ13 : Wivenhoe Dam @ Esk	CUB-WID-90-OFF-PS	27/06/2024	27/07/2024	30	4.6	
SEQ14 : Wivenhoe Dam Wall	CUB-WID-01-OFF-PS	27/06/2024	25/07/2024	28	6.7	
SEQ15 : Lockyer Creek @ Lake Clarendon Way	CCK-LOC-50-RIV-PS	2/07/2024	1/08/2024	30	3.4	
SEQ16 : Lockyer Creek @ Patrick's Estate	CCK-LOC-15-RIV-PS	9/07/2024	6/08/2024	28	3.4	
SEQ17 : Lowood Intake	CMB-MBR-80-OFF-PS	9/07/2024	6/08/2024	28	6.9	
SEQ18 : Mt Crosby Westbank Offtake Tower	CMB-MBR-02-OFF-PS	8/07/2024	5/08/2024	28	16.1	**1** PFM lost

SEQ19 : North Pine River @ Dayboro Well	**CPV-NPR-70-OFF-PS**	**16/07/2024**	**20/08/2024**	**35**	**4.5**	
SEQ20 : North Pine VPS	**CPV-NOD-10-OFF-PS**	**26/07/2024**	**23/08/2024**	**28**	**4.5**	
SEQ21 : Lake Kurwongbah	**CPV-LAK-01-OFF-PS**	**17/07/2024**	**20/08/2024**	**34**	**5.4**	
SEQ23 : Herring Lagoon	**CNS-HLA-01-OFF-PS**	**16/07/2024**	**20/08/2024**	**35**	**3.4**	
SEQ24 : Leslie Harrison Dam	**CRL-LHD-05-VPS-PS**	**19/07/2024**	**22/08/2024**	**34**	**4.7**	
SEQ25 : Wyaralong Dam Wall	**CLR-WYD-01-REC-PS**	**5/07/2024**	**2/08/2024**	**28**	**5.2**	
SEQ26 : Reynolds Creek @ Boonah	**CWV-REY-20-OFF-PS**	**28/08/2024**	**29/09/2024**	**32**	**3.4**	**Samplers** lost: replaced by Spare 5
SEQ27 : Moogerah Dam	**CWV-MOD-02-OFF-PS**	**19/07/2024**	**21/08/2024**	**33**	**8**	
SEQ28 : Logan River @ Kooralbyn Offtake	**CLR-LOG-60-OFF-PS**	**4/07/2024**	**1/08/2024**	**28**	**3.4**	
SEQ29 : Maroon Dam Wall	**CLR-MAD-04-OFF-PS**	**2/08/2024**	**3/09/2024**	**32**	**8.9**	**Samplers** lost: replaced by Spare 4
SEQ31 : Rathdowney Weir	**CLR-LOG-80-OFF-PS**	**4/07/2024**	**1/08/2024**	**28**	**3.9**	**ED** muddy
SEQ32 : Canungra Creek @ Offtake	**CLR-CAC-01-OFF-PS**	**22/07/2024**	**19/08/2024**	**28**	**4.4**	
SEQ33 : Little Nerang Dam	**CNR-LND-01-OFF-PS**	**23/07/2024**	**27/08/2024**	**35**	**4.5**	
SEQ34 : Hinze Upper Intake	**CNR-HID-20-OFF-PS**	**25/07/2024**	**28/08/2024**	**34**	**3.7**	
SEQ35 : Hinze Lower Intake	**CNR-HID-01-OFF-PS**	**25/07/2024**	**28/08/2024**	**34**	**5.3**	
SEQ36 : Fernvale STP @ Savages Crossing	**CMB-MBR-60-RIV-PS**	**9/07/2024**	**6/08/2024**	**28**	**17.7**	
SEQ37 : Logan River @ Cedar Grove	**CLR-LOG-12-RIV-PS**	**4/07/2024**	**1/08/2024**	**28**	**3.4**	
SEQ38 : Wappa Dam	**CMR-WAD-01-OFF-PS**	**16/07/2024**	**13/08/2024**	**28**	**4.5**	
SEQ39 : Cooloolabin Dam	**CMR-COD-01-OFF-PS**	**4/07/2024**	**1/08/2024**	**28**	**4.4**	
SEQ40 : Wivenhoe Dam @ Logans Inlet PRW	**CUB-WID-59-PRW-PS**	**27/06/2024**	**25/07/2024**	**28**	**8.6**	
SEQ43 : Enoggera Reservoir	**CLB-END-01-OFF-PS**	**10/07/2024**	**9/08/2024**	**30**	**6.8**	

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) (Figure 1). Polydimethylsiloxane (PDMS) strips in stainless steel cages (Figure 2) 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 an Empore Disk passive sampler.

Figure 2. 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, 2 UV filters and 3 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, to remain within the accurate mathematical modelling range for PFM-based flow velocity prediction, a minimum flow rate of 3.40 cm s^{-1} was applied 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 17.7 cm s^{-1} (SEQ36 : Fernvale STP @ Savages Crossing) (Figure 3).

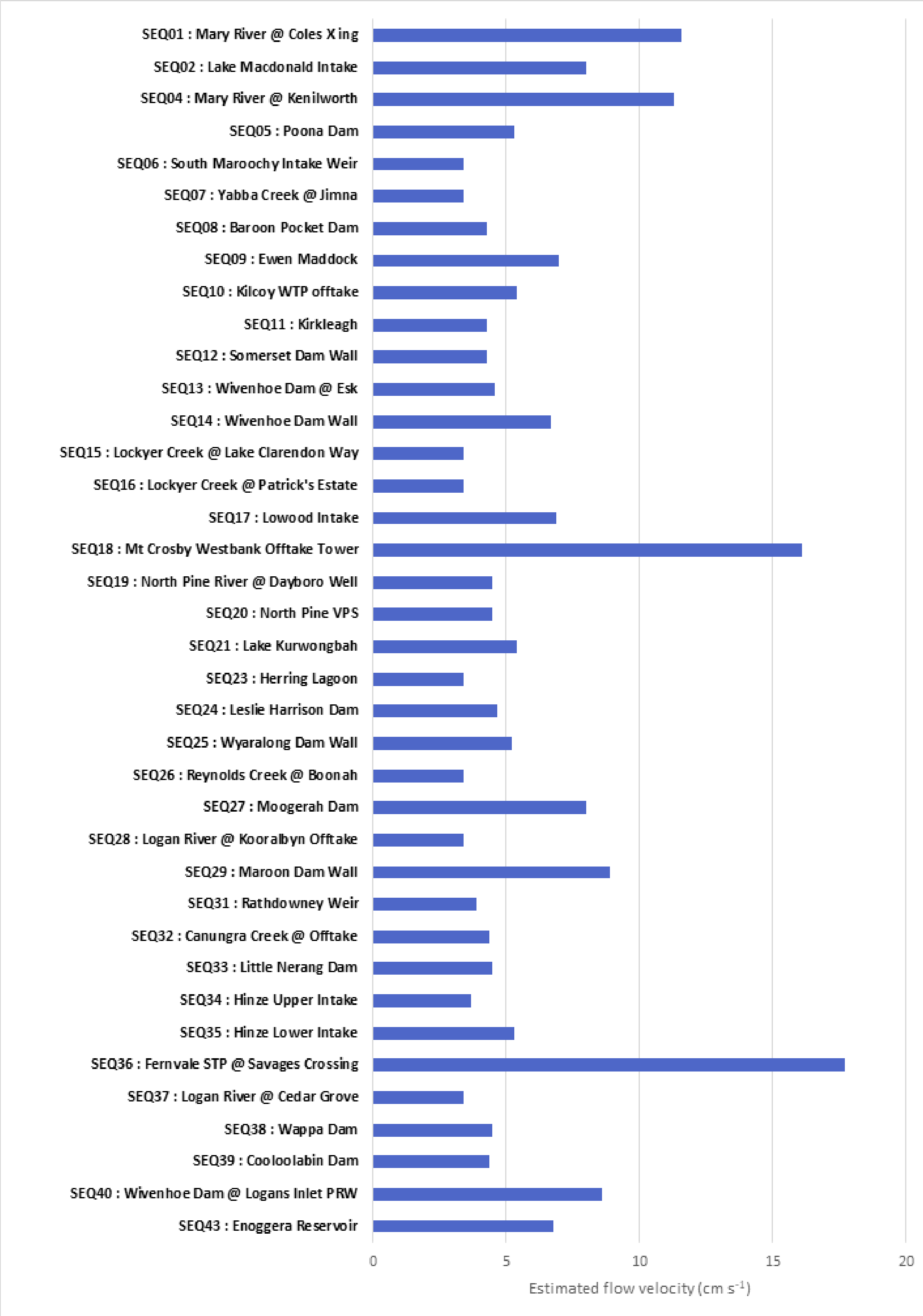

Figure 3. Passive flow monitor (PFM) based water flow velocity estimations (cm s^{-1}) at the deployment sites (n=38).

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, UV filters and PAHs). A total of 14 OCPs and 12 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% – 68% for OCPs and 3% – 95% for PAHs. Table 3 summarises the polar chemicals quantified via ED (pesticides and PPCPs). A total of 28 pesticides (predominantly herbicides) and 14 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3% - 84% for pesticides and 3% - 92% 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%	<LOR	<LOR
Azinphos methyl	0	0%	<LOR	<LOR
Bifenthrin	2	5%	2.32	2.7
Chlorpyrifos	26	68%	2.62	193
cis-Chlordane	9	24%	0.718	6.6
Cypermethrin	0	0%	<LOR	<LOR
Dacthal	21	55%	3.36	5024
Deltamethrin	0	0%	<LOR	<LOR
Dieldrin	22	58%	2.55	20.7
Endosulfan sulfate	4	11%	1.2	8.9
Endrin	0	0%	<LOR	<LOR
Endrin ketone	0	0%	<LOR	<LOR
HCB	0	0%	<LOR	<LOR
Heptachlor	0	0%	<LOR	<LOR
Heptachlor epoxide a	0	0%	<LOR	<LOR
Heptachlor epoxide b	4	11%	1.55	4.7
Methoprene	0	0%	<LOR	<LOR
Methoxychlor	0	0%	<LOR	<LOR
Mirex	0	0%	<LOR	<LOR
o,p-DDD	0	0%	<LOR	<LOR
o,p-DDE	0	0%	<LOR	<LOR
o,p-DDT	0	0%	<LOR	<LOR
p,p-DDD	9	24%	1.26	4.5
p,p-DDE	11	29%	1.08	28.8
p,p-DDT	0	0%	<LOR	<LOR
Pendimethalin	9	24%	6.37	117
Permethrin	0	0%	<LOR	<LOR
Pyriproxyfen	0	0%	<LOR	<LOR
trans-Chlordane	15	39%	2.22	6.0
UV327	0	0%	<LOR	<LOR

UV328	2	5%	4.36	7.1
α-Endosulfan	0	0%	<LOR	<LOR
α-HCH	0	0%	<LOR	<LOR
β-endosulfan	0	0%	<LOR	<LOR
β-HCH	4	11%	0.509	4.4
γ-HCH (Lindane)	1	3%	1.31	1.3
PAH				
Acenaphthene	0	0%	<LOR	<LOR
Acenaphthylene	10	26%	5.2	38.0
Anthracene	2	5%	5.47	28.1
Benzo[a]anthracene	8	21%	1	8.9
Benzo[a]pyrene	1	3%	1.17	1.2
Benzo[b,j,k]fluoranthene	13	34%	0.717	370
Benzo[e]pyrene	14	37%	1.1	2.4
Benzo[g,h,i]perylene	1	3%	1.5	1.5
Chrysene/Triphenylene	31	82%	1.12	21.0
Dibenz[a,h]anthracene	0	0%	<LOR	<LOR
Fluoranthene	36	95%	5.05	151
Fluorene	1	3%	70.2	70.2
Indeno[1,2,3-c,d]pyrene	0	0%	<LOR	<LOR
Naphthalene	0	0%	<LOR	<LOR
Phenanthrene	17	45%	41.2	184
Pyrene	22	58%	7.52	82.2

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%	<LOR	<LOR
2,4-D	11	29%	5.09	15.9
3,4 Dichloroaniline	0	0%	<LOR	<LOR
Ametryn	0	0%	<LOR	<LOR
Ametryn hydroxy	4	11%	1.20	1.93
Aminocarb	0	0%	<LOR	<LOR
Atrazine	17	45%	1.14	13
Atrazine desethyl	14	37%	1.00	3.8
Atrazine desisopropyl	15	39%	1.08	2.33
Bendiocarb	0	0%	<LOR	<LOR
Bromacil	0	0%	<LOR	<LOR
Bromoxynil	0	0%	<LOR	<LOR
Carbaryl	0	0%	<LOR	<LOR
Carbendazim	7	18%	2.35	10.6
DCPMU	2	5%	0.180	0.250

DCPU	1	3%	0.81	0.81
Diazinon	15	39%	0.130	4.09
Difenoconazole	0	0%	<LOR	<LOR
Diketonitrile	0	0%	<LOR	<LOR
Diuron	18	47%	0.520	12.4
Fenuron	0	0%	<LOR	<LOR
Fipronil	2	5%	1.00	2.41
Fluazifop	0	0%	<LOR	<LOR
Fluometuron	0	0%	<LOR	<LOR
Fluroxypyr	0	0%	<LOR	<LOR
Haloxyfop	2	5%	2.13	4.44
Hexazinone	10	26%	1.09	3.36
Imazapyr	0	0%	<LOR	<LOR
Imazethapyr	0	0%	<LOR	<LOR
Imidacloprid	6	16%	1.49	5.1
Malathion	0	0%	<LOR	<LOR
MCPA	1	3%	9.36	9.36
Metalaxyl	16	42%	0.110	1.16
Methidathion	0	0%	<LOR	<LOR
Methomyl	1	3%	1.63	1.6
Metolachlor (S+R)	15	39%	1.11	270
Metolcarb	0	0%	<LOR	<LOR
Metribuzin	0	0%	<LOR	<LOR
Metsulfuron methyl	32	84%	1.06	25.0
Mexacarbate	0	0%	<LOR	<LOR
Oryzalin	0	0%	<LOR	<LOR
Picloram	0	0%	<LOR	<LOR
Promecarb	0	0%	<LOR	<LOR
Prometryn	1	3%	4.88	4.88
Propachlor	0	0%	<LOR	<LOR
Propazine	0	0%	<LOR	<LOR
Propiconazole	1	3%	1.27	1.27
Propoxur	0	0%	<LOR	<LOR
Simazine	13	34%	1.05	6.9
Simazine hydroxy	0	0%	<LOR	<LOR
Tebuconazole	2	5%	1.39	2.60
Tebuthiuron	10	26%	1.55	82
Terbuthylazine	16	42%	1.02	4.93
Terbuthylazine desethyl	21	55%	1.00	4.3
Thiamethoxam	2	5%	7.20	9.96
Triclopyr	1	3%	8.39	8.4
Pharmaceuticals and personal care products (PPCPs)				
Acesulfame	0	0%	<LOR	<LOR

Atenolol	**1**	**3%**	**1.53**	**1.53**
Atorvastatin	**0**	**0%**	**<LOR**	**<LOR**
Caffeine	**9**	**24%**	**25**	**45**
Carbamazepine	**4**	**11%**	**3.60**	**5.85**
Codeine	**1**	**3%**	**1.86**	**1.86**
DEET	**35**	**92%**	**5.76**	**185**
Diclofenac	**2**	**5%**	**0.350**	**1.030**
Gabapentin	**3**	**8%**	**1.23**	**6.99**
Hydrochlorothiazide	**2**	**5%**	**1.34**	**1.42**
Iopromide	**0**	**0%**	**<LOR**	**<LOR**
Naproxen	**1**	**3%**	**3.52**	**3.52**
Oxazepam	**3**	**8%**	**2.17**	**2.50**
Paracetamol	**0**	**0%**	**<LOR**	**<LOR**
Paraxanthine	**13**	**34%**	**2.7**	**14.5**
Salicylic acid	**0**	**0%**	**<LOR**	**<LOR**
Sulfadiazine	**1**	**3%**	**1.60**	**1.60**
Sulfamethoxazole	**4**	**11%**	**0.140**	**1.52**
Tadalafil	**0**	**0%**	**<LOR**	**<LOR**
Temazepam	**2**	**5%**	**1.41**	**1.68**
Verapamil	**0**	**0%**	**<LOR**	**<LOR**

Organochlorine pesticides (OCPs)

In total, 14 OCPs were accumulated in PDMS samplers over the deployment period across 33 of the 38 sites (Table 2, Figure 4, Appendix 1), with the amount of ∑OCPs accumulated ranging from below reporting limits (SEQ06 - South Maroochy Intake Weir; SEQ32 - Canungra Creek @ Offtake; SEQ28 - Logan River @ Kooralbyn Offtake; SEQ31 - Rathdowney Weir; SEQ07 - Yabba Creek @ Jimna) to 5373 ng PDMS^{-1} (SEQ16 - Lockyer Creek @ Patrick's Estate).

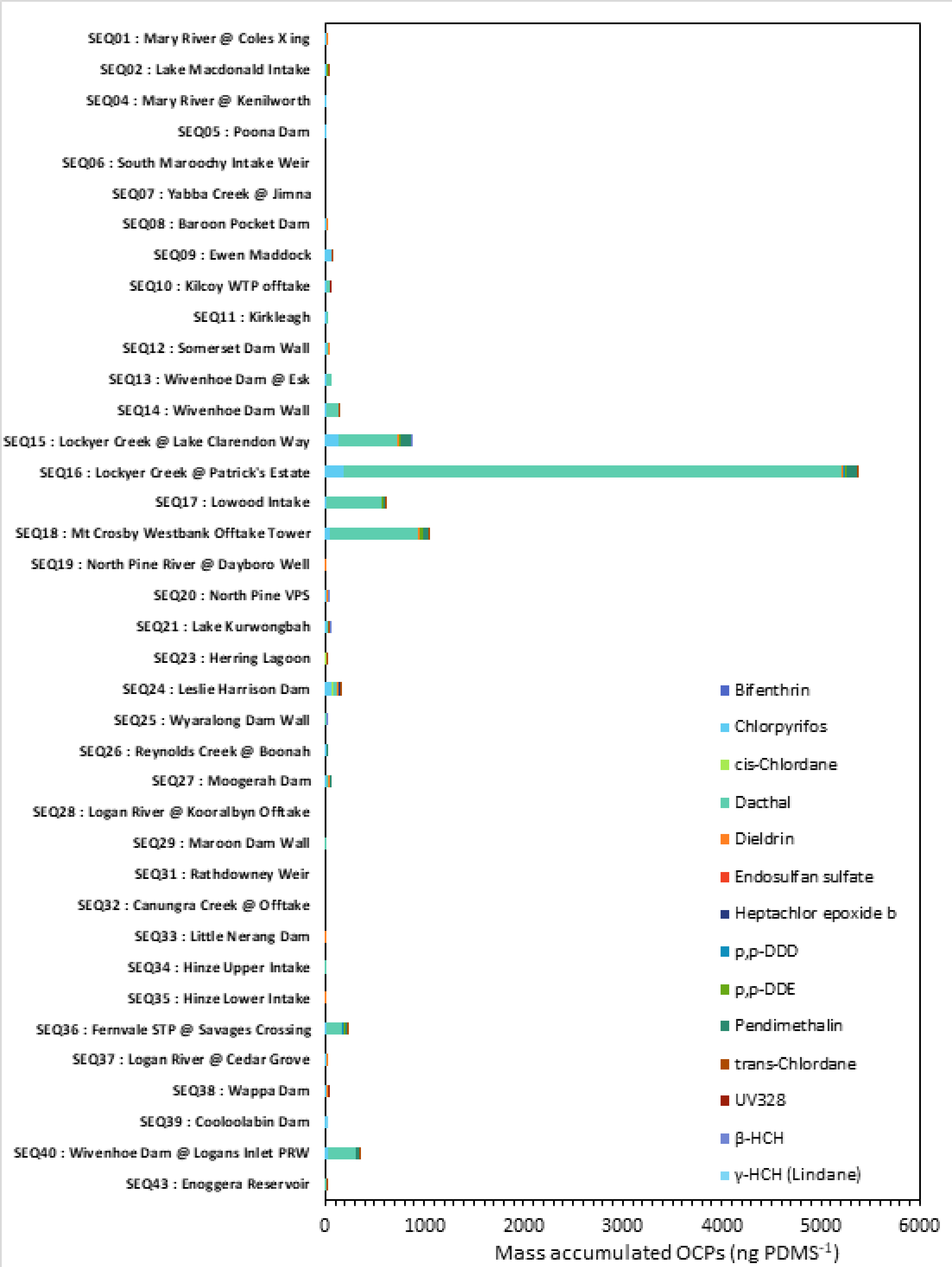

Figure 4. Total mass of 14 ΣOCPs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

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 111 ng L^{-1} (SEQ33 - Little Nerang Dam and SEQ16 - Lockyer Creek @ Patrick's Estate, respectively; Figure 5).

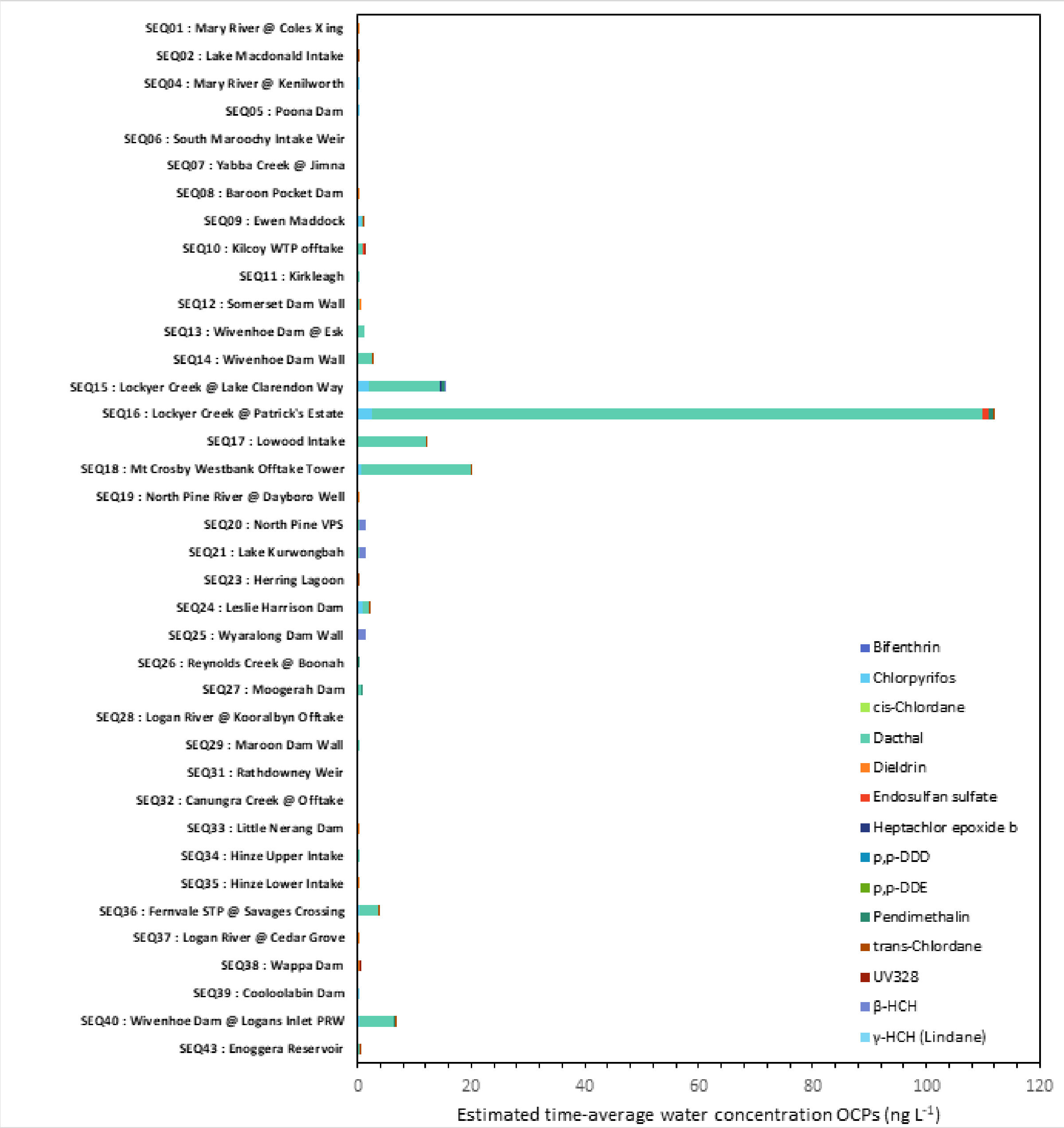

Figure 5. Total estimated water concentrations (ng L^{-1}) of 14 ΣOCPs at each site derived from PDMS passive samplers.

Polycyclic aromatic hydrocarbons (PAHs)

In total, 12 PAHs were accumulated in PDMS samplers over the deployment period (Table 2, Figure 6, Appendix 1), with the amount of ∑PAHs accumulated ranging from below reporting limits (SEQ07 - Yabba Creek @ Jimna; SEQ37 - Logan River @ Cedar Grove) to 544 ng $PDMS^{-1}$ (SEQ29 - Maroon Dam Wall).

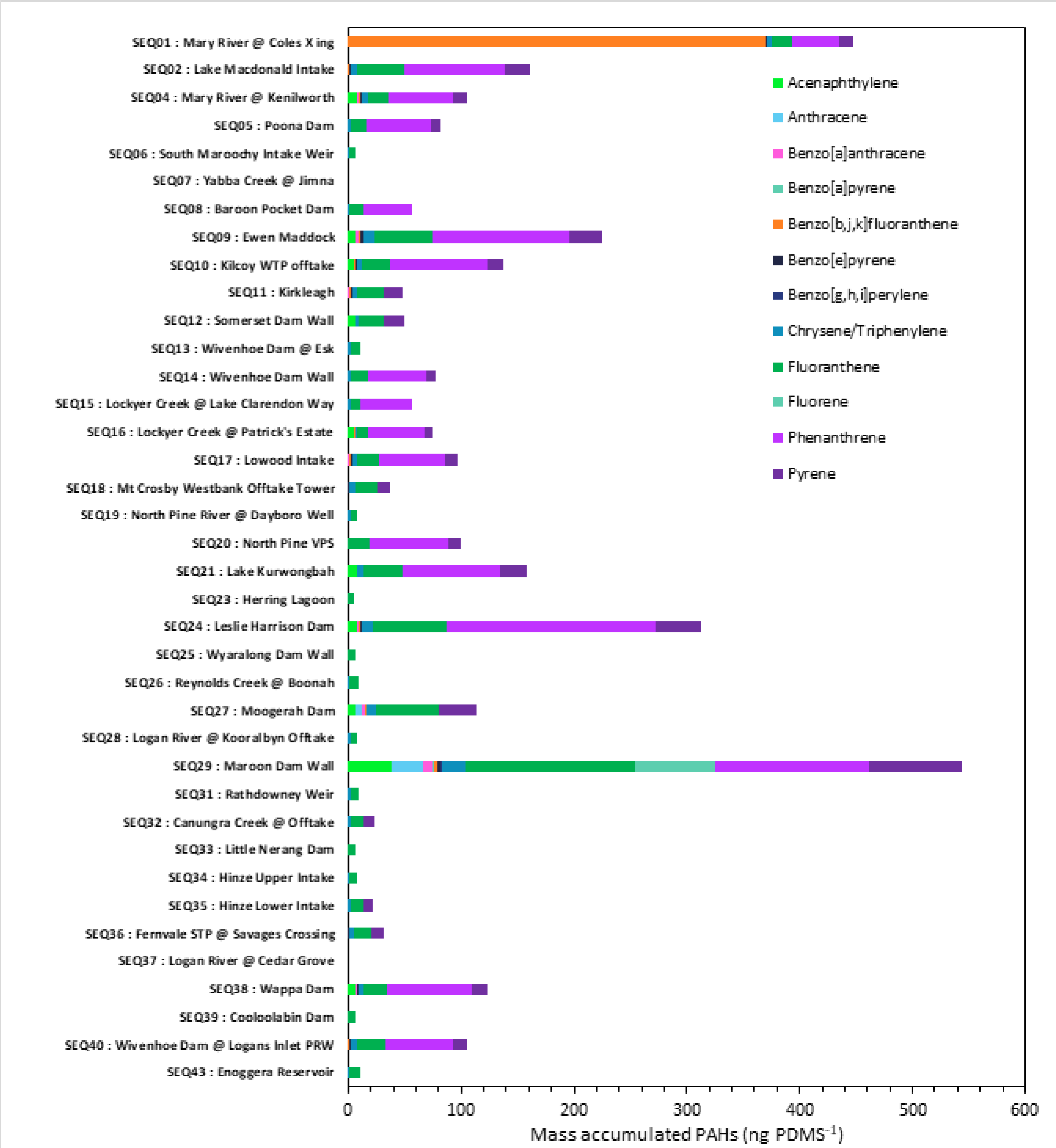

Figure 6. Total mass of 12 ΣPAHs (ng $PDMS^{-1}$) accumulated in PDMS passive samplers at each site.

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 0.028 to 3.67 ng L^{-1} (SEQ23 - Herring Lagoon and SEQ29 - Maroon Dam Wall, respectively; Figure 7).

Figure 7. Total estimated water concentrations (ng L^{-1}) of 12 ΣPAHs at each site derived from PDMS passive samplers.

Pesticides

Over the deployment period, 28 polar pesticides (including herbicides, fungicides and insecticides) accumulated in ED passive samplers (Table 3, Figure 8, Appendix 1). The ∑polar pesticides accumulated ranged from below reporting limits (SEQ23 - Herring Lagoon; SEQ33 - Little Nerang Dam; SEQ07 - Yabba Creek @ Jimna; SEQ43 - Enoggera Reservoir; SEQ39 – Cooloolabin Dam) to 342 ng ED^{-1} (SEQ15 - Lockyer Creek @ Lake Clarendon Way).

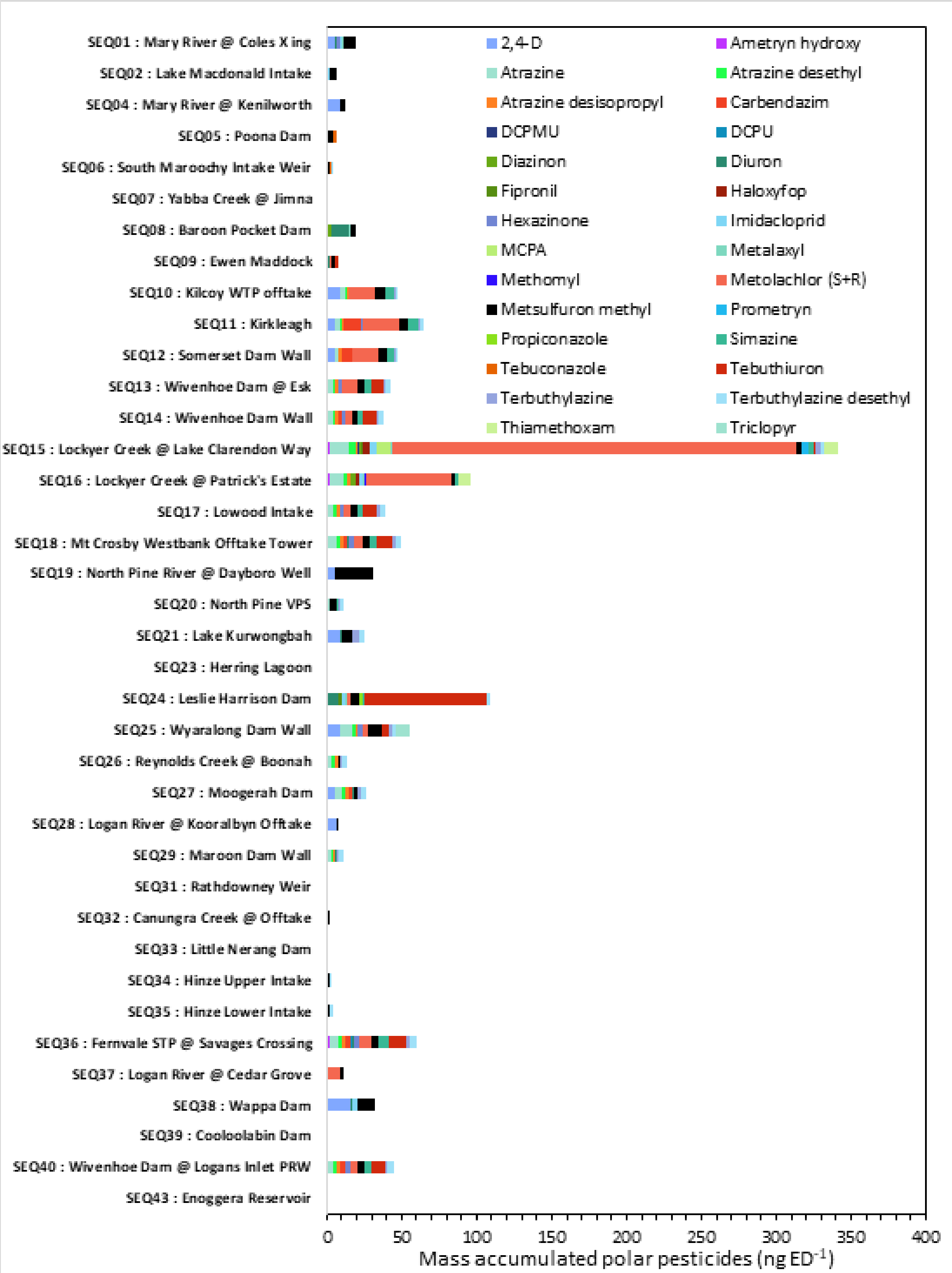

Figure 8. Total mass of 28 Σpolar pesticides (ng ED^{-1}) accumulated in ED passive samplers at each site.

Water concentrations were estimated for the polar pesticides accumulated where sampling rates have been previously calibrated. From the 28 chemicals reported, 16 were converted to time-weighted average water ∑concentrations. Discounting the sites below reporting limits, these water concentrations ranged between 0.270 and 241 ng L^{-1} (SEQ32 - Canungra Creek @ Offtake and SEQ15 - Lockyer Creek @ Lake Clarendon Way, respectively; Figure 9).

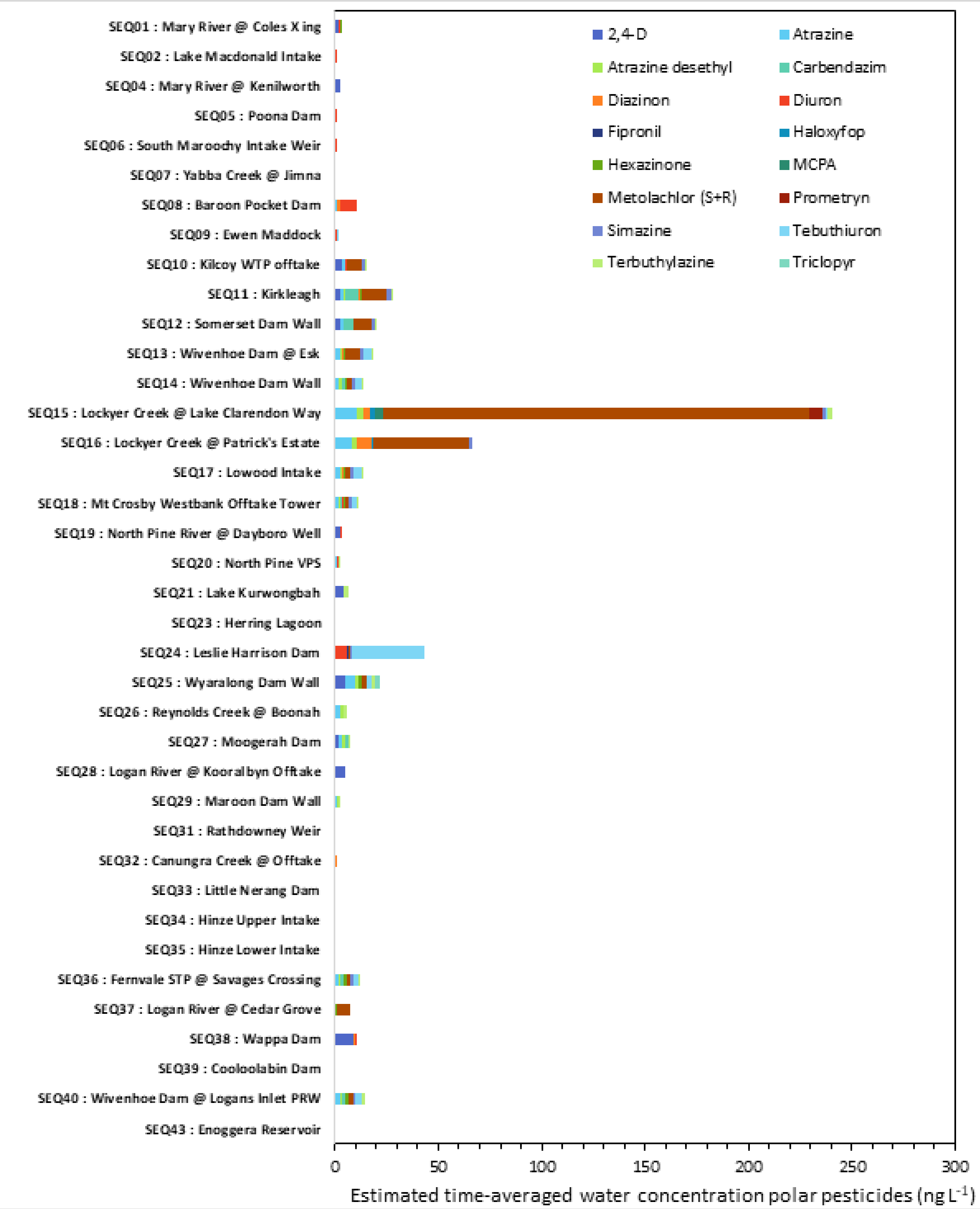

Figure 9. Total estimated water concentrations (ng L^{-1}) of 16 Σpolar pesticides at each site derived from ED passive samplers.

Pharmaceuticals and personal care products (PPCPs)

In total, 14 PPCPs were reported (Table 3, Figure 10, Appendix 1) with the average amount of ΣPPCPs accumulated ranging from 1.59 ng ED^{-1} (SEQ01 - Mary River @ Coles X ing) to 250 ng ED^{-1} (SEQ37 - Logan River @ Cedar Grove).

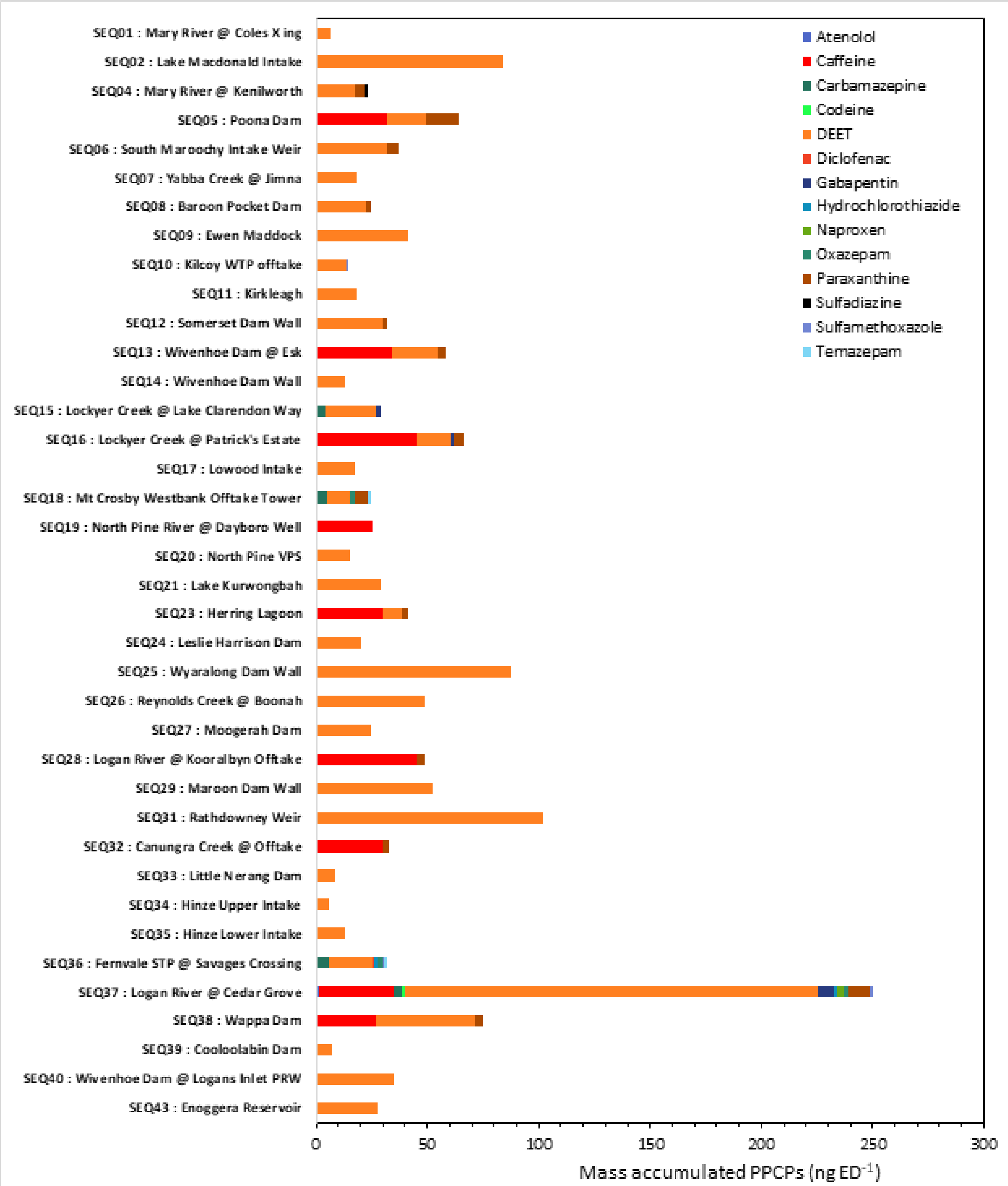

Figure 10. Total mass of 14 ΣPPCPs (ng ED^{-1}) accumulated in ED passive samplers at each site.

Of the 14 reported PPCPs, 7 were converted into estimated time-weighted average water concentrations. Discounting the sites below reporting limits, these ∑PPCP water concentrations ranged between 1.59 and 137 ng L^{-1} (sites SEQ01 - Mary River @ Coles X ing and SEQ37 - Logan River @ Cedar Grove, respectively; Figure 11).

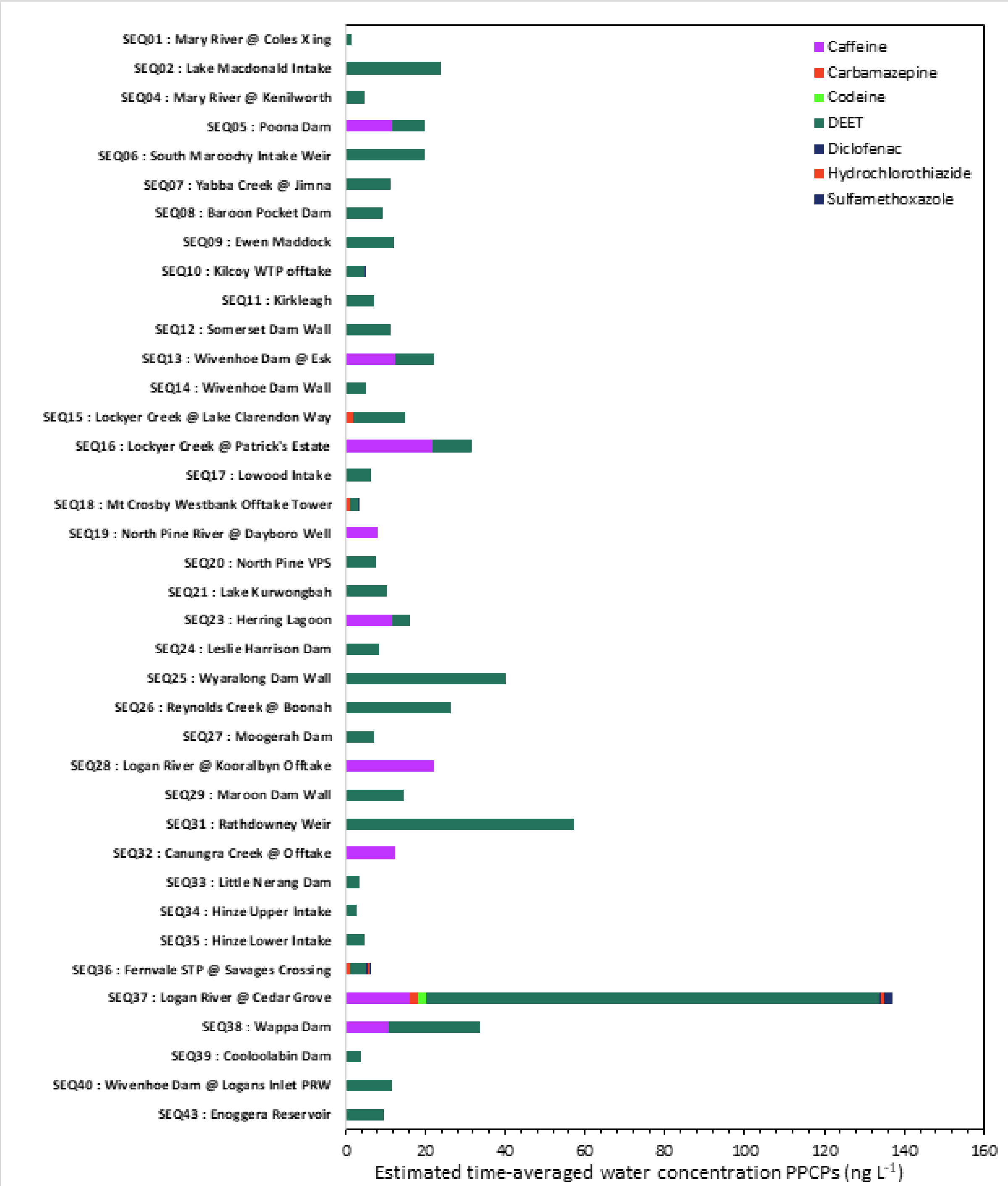

Figure 11. Total estimated water concentrations (ng L^{-1}) of 7 ΣPPCPs derived from ED passive samplers.

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 2 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
Metolachlor-ESA	Metolachlor breakdown product	SEQ01 : Mary River @ Coles X ing SEQ04 : Mary River @ Kenilworth SEQ05 : Poona Dam SEQ06 : South Maroochy Intake Weir SEQ09 : Ewen Maddock SEQ10 : Kilcoy WTP offtake SEQ11 : Kirkleagh SEQ12 : Somerset Dam Wall SEQ13 : Wivenhoe Dam @ Esk SEQ14 : Wivenhoe Dam Wall SEQ15 : Lockyer Creek @ Lake Clarendon Way SEQ16 : Lockyer Creek @ Patrick's Estate SEQ17 : Lowood Intake SEQ18 : Mt Crosby Westbank Offtake Tower SEQ19 : North Pine River @ Dayboro Well SEQ21 : Lake Kurwongbah SEQ24 : Leslie Harrison Dam SEQ25 : Wyaralong Dam Wall SEQ29 : Maroon Dam Wall SEQ31 : Rathdowney Weir SEQ36 : Fernvale STP @ Savages Crossing SEQ37 : Logan River @ Cedar Grove SEQ38 : Wappa Dam SEQ40 : Wivenhoe Dam @ Logans Inlet PRW
3-Formylindole	Tryptophan Metabolite	SEQ04 : Mary River @ Kenilworth SEQ05 : Poona Dam SEQ12 : Somerset Dam Wall SEQ15 : Lockyer Creek @ Lake Clarendon Way

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, and not all compounds have guideline values available. However, given the levels observed, and the comparisons that were able to be made, we believe it is unlikely there would be any further 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 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 detected in excess of the 95% species protection guideline for any chemical. Furthermore, totals of 15, 4, 1 and 25 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 (updated 2023) 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	N/A
Bromoxynil	10000	N/A	N/A	N/A
Carbaryl	30000	N/A	N/A	N/A
Carbendazim	90000	N/A	N/A	6.72
Cypermethrin	200000	N/A	N/A	N/A
Diazinon	4000	0.03	10	6.820
Diuron	20000	N/A	N/A	8.3
Fipronil	700	13	18	1.17
Fluometuron	70000	N/A	N/A	N/A
Haloxyfop	1000	N/A	N/A	1.80
Hexazinone	400000	N/A	N/A	1.67
Imazapyr	9000000	N/A	N/A	N/A
MCPA	40000	3000	7700	4.44
Malathion	70000	2	50	N/A
Methomyl	20000	500	3500	N/A
Metolachlor (S+R)	300000	8.4	460	206
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	6300	87000	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	2.46
Tebuthiuron	N/A	20	2200	34.9
Terbuthylazine	10000	N/A	N/A	2.41

Triclopyr	**20000**	**N/A**	**N/A**	**2.64**
2,4-D	**30000**	**140000**	**280000**	**9.18**
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**	**2.6**
Cypermethrin	**200000**	**1**	**6**	**N/A**
DDT	**9000**	**6**	**10**	**0.066**
Dieldrin	**300**	**N/A**	**N/A**	**0.071**
Aldrin	**300**	**N/A**	**N/A**	**N/A**
Endosulfan	**20000**	**30**	**200**	**0.949**
Endrin	**N/A**	**10**	**20**	**N/A**
Heptachlor	**300**	**10**	**90**	**N/A**
HCB		**50**	**100**	**N/A**
Pendimethalin	**400000**	**N/A**	**N/A**	**0.8**
γ-HCH (Lindane)	**10000**	**70**	**200**	**0.4**
γ-HCH (Lindane)	**10000**	**70**	**200**	**0.4**
Methoxychlor	**300000**	**N/A**	**N/A**	**N/A**
PAHs				
Anthracene	**N/A**	**10**	**400**	**0.134**
Benzo[a]pyrene	**10**	**100**	**200**	**0.002**
Fluoranthene	**N/A**	**1000**	**1400**	**0.475**
Naphthalene	**N/A**	**2500**	**16000**	**N/A**
Phenanthrene	**N/A**	**600**	**2000**	**0.990**

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 33 sites (87%), the concentrations were low (total ∑OCPs <111 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. Chlorpyrifos was the most frequently detected OCP, reported at 26 sites (68% of sites) and dieldrin was the second most frequent at 22 sites (58% of sites). Dacthal (also known as chlorthal-dimethyl) is a herbicide that was used on a wide variety of fruit and vegetable crops until its use was banned by the APVMA in October 2024 (APVMA, 2024). Dacthal was the OCP found at the highest concentration, detected at SEQ16 - Lockyer Creek @ Patrick's Estate at 107 ng L^{-1}. This is lower than levels found at the same site during the Summer 2024 sampling period (220 ng L^{-1}) (Shiels *et al.* 2024), but higher than the previous year (6.8 ng L^{-1}, Winter 2023).

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). Several 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). Fluoranthene was the most frequently detected PAH (95% detection) although this was at low levels, with a maximum concentration of 0.45 ng L^{-1} at site SEQ29 - Maroon Dam Wall.

Polar pesticides (herbicides, insecticides and fungicides) were reported at 34 sites. The two most frequently reported pesticides were Metsulfuron methyl (detected at 32 sites; 84%) and Terbuthylazine desethyl (detected at 21 sites; 55%), a breakdown product of terbuthylazine, 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 methyl 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 decades. 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 (92% 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 Paraxanthine (detected at 34% of sites). Paraxanthine is a caffeine metabolite, often detected in water impacted by wastewater effluent. 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.

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Appendix 1

See enclosed excel file ‘SEQW results_Winter_2024.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}).

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