THE UNIVERSITY OF QUEENSLAND AUSTRALIA | Queensland Alliance for Environmental Health Sciences

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

Report 2 – Summer 2021

Ryan Shiels and Sarit Kaserzon

Title
Catchment and Drinking Water Quality Micro Pollutant Monitoring program – Passive Sampling. Report 2 – Summer 2021.

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
Ryan Shiels, Summer Xia, Yan Li, Chris Paxman, Gabriele Elisei, Pritesh Prasad, Christina Carswell, Michael Gallen, Tim Reeks, Geoff Eaglesham, Homa Teimouri Sichani, Olivier Cheneval, Bastian Schulze, Sara Ghorbani Gorji, Jochen Mueller and Sarit Kaserzon.

Direct Enquiries to:

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

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

Chemical analyses of the passive sampler extracts reported 67 different chemicals including 14 OCPs, 9 PAHs, 30 polar pesticides and 14 PPCPs. OCPs were detected at 94% of sites, with Chlorpyrifos (82%) and Dieldrin (65%) the most frequently reported. Total ∑OCP water concentrations across sites ranged between 0.002 – 1.42 ng L^{-1} where concentrations were reportable. PAHs were detected at 65% of sites, with Chrysene/Triphenylene (56%) and Fluoranthene (35%) reported at the highest abundance across all sites. Total ∑PAH water concentrations across sites ranged between 0.002 – 0.673 ng L^{-1}. In total, 30 different polar pesticides were reported in 30 sites (88%), with Atrazine (71%) and Metsulfuron methyl (68%) reported at highest abundance across all sites. Total ∑polar pesticides ranged between 1.07 – 52.7 ng L^{-1}. Additionally, 14 PPCPs were detected across sites with highest detection frequencies observed for DEET (68%) and Carbamazepine (18%). Total estimated ∑PPCP water concentrations ranged between 0.400 – 42.2 ng L^{-1} across sites.

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

Introduction

As the bulk supplier of drinking water to South East Queensland, Seqwater maintains a Catchment and Drinking Water Quality Micro Pollutant Monitoring Program to ensure safe and reliable supply of the region's drinking water source reservoirs. The aim of this program is to identify and understand the presence of micro pollutants in the source water reservoirs as well as to recognise any spatial and temporal trends of micro pollutants. An extension of this program has been introduced to include the use of passive sampling technologies in the monitoring of source water reservoirs over a three year period (2020 – 2023; summer and winter sampling campaigns), in order to accurately assess the risk from micro pollutants posed to drinking water quality. Additional passive samplers may be deployed at sites when required during high rainfall or event periods.

The typically low-level concentrations of micro pollutants present in environmental waters raises analytical challenges as well as further challenges in obtaining appropriate and representative samples. Grab samples may not offer enough volume to allow sufficient concentration factors for the quantification of micro pollutants and may miss episodic contamination events, given they represent a single point in time. The use of passive sampling technologies has been introduced to complement and overcome some of these challenges, substantially improving chemical pollutant monitoring in liquid phases over the last 15 - 20 years. Benefits of passive sampling tools include *in-situ* concentration of chemical pollutants, increased sensitivity, the provision of time-weighted average concentration estimates for chemicals over periods of ≥ 1 month, increased data resolution and risk profiling using a robust scientific methodology. Passive samplers designed to monitor non-polar (polydimethylsiloxane; PDMS) as well as polar (Empore™ Disk; ED) chemical pollutants have been chosen for deployment in this program.

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

Methodology

Passive water samplers were deployed in periods between January 2021 to March 2021 at 36 sites of SEQ reservoirs/waterways (Table 1). Deployments were for periods of 28 to 29 days in duration. The sampler for site SEQ30 (Logan River @ Helen St) was compromised by its removal from water, and is therefore not reported here. Duplicate samplers were deployed at five randomly selected sites (Table 1, highlighted in green).

The deployment of samplers was conducted in alignment with the "Drinking and Catchment Water Quality Micro Pollutant Passive Sampling Procedure" (January 2021). Table 1 below lists the deployment site locations, site numbers, site codes, deployment and retrieval dates and lengths of deployment periods, as well as the water velocity (cm s^{-1}) estimated at each site.

In this campaign, the following sites were not sampled:

SEQ03 (Borumba Dam)

SEQ15 (Lockyer Creek at Lake Clarendon Way)

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

SEQ21 (Lake Kurongbah)

SEQ22 (North Pine River at Petrie Offtake)

SEQ30 (Logan River at Helen St)

Table 1. *Deployment locations, dates, lengths of deployment period and water velocity measured at each site.*

Site	Site Code	Date Deployed	Date Retrieved	Days Deployed	Flow velocity (cm/s)	Comments
SEQ01 : Mary River @ Coles Crossing	MRS-SP012	21/01/2021	18/02/2021	28	3.4	
SEQ02 : Lake MacDonald Intake	LMD-SP001	20/01/2021	17/02/2021	28	6.8	
SEQ04 : Mary River @ Kenilworth	MRS-SP013	21/01/2021	18/02/2021	28	13.6	
SEQ05 : Poona Dam	POD-SP001	15/01/2021	12/02/2021	28	4.7	
SEQ06 : South Maroochy Intake Weir	SOR-SP001	15/01/2021	12/02/2021	28	3.4	
SEQ07 : Yabba Creek @ Jimna Weir	YAC-SP001	19/01/2021	16/02/2021	28	3.4	
SEQ08 : Baroon Pocket Dam	BPD-SP001	27/01/2021	24/02/2021	28	5.6	
SEQ09 : Ewen Maddock Intake	EMD-SP001	22/01/2021	19/02/2021	28	6	
SEQ10 : Kilcoy WTP Offtake	SOD-SP010	12/01/2021	10/02/2021	29	4.9	
SEQ11 : Kirkleagh	SOD-SP011	12/01/2021	10/02/2021	29	8.2	
SEQ12 : Somerset Dam Wall	SOD-SP001	12/01/2021	10/02/2021	29	6.2	
SEQ13 : Wivenhoe Dam @ Esk Profiler	WID-SP004	12/01/2021	9/02/2021	28	5.7	
SEQ14 : Wivenhoe Dam Wall @ Profiler	WID-SP001	13/01/2021	10/02/2021	28	11.2	
SEQ17 : Lowood Intake	MBR-SP016	12/01/2021	9/02/2021	28	6.5	
SEQ18 : Mid Bris River @ Mt Crosby Westbank Offtake Tower	MBR-SP001	27/01/2021	24/02/2021	28	13.7	
SEQ19 : North Pine River @ Dayboro Well	NOD-SP091	18/01/2021	15/02/2021	28	3.9	
SEQ20 : North Pine VPS	NOD-SP001	18/01/2021	15/02/2021	28	5.2	

SEQ23 : Herring Lagoon	**NSC-SP001**	18/01/2021	**15/02/2021**	28	3.4	
SEQ24 : Leslie Harrison Dam	**LHD-SP005**	20/01/2021	**17/02/2021**	28	5.9	
SEQ25 : Wyaralong Dam Wall	**WYD-SP001**	21/01/2021	**18/02/2021**	28	7.2	
SEQ26 : Reynolds Creek @ Boonah	**MOD-SP027**	19/01/2021	**16/02/2021**	28	4.4	
SEQ27 : Moogerah Dam @ Offtake	**MOD-SP002**	19/01/2021	**16/02/2021**	28	12.3	
SEQ28 : Logan River @ Kooralbyn Offtake	**LRS-SP017**	21/01/2021	**18/02/2021**	28	21	
SEQ29 : Maroon Dam Wall @ Offtake W2 Buoy	**MAD-SP004**	1/02/2021	**1/03/2021**	28	10	
SEQ31 : Rathdowney Weir	**LRS-SP016**	21/01/2021	**18/02/2021**	28	8.8	
SEQ32 : Canungra Creek @ Offtake	**CAC-SP001**	18/01/2021	**17/02/2021**	30	7	
SEQ33 : Little Nerang Dam	**LND-NR001**	25/01/2021	**22/02/2021**	28	11.2	
SEQ34 : Hinze Dam Upper Intake	**HID-SP001**	27/01/2021	**24/02/2021**	28	5.4	
SEQ35 : Hinze Dam Lower Intake	**HID-SP002**	27/01/2021	**24/02/2021**	28	8.3	
SEQ36 : Downstream of Fernvale STP @ Savages CRC	**MBR-SP013**	12/01/2021	**9/02/2021**	28	4.8	
SEQ37 : Logan River @ Cedar Grove	**LRS-SP012**	21/01/2021	**18/02/2021**	28	4.5	
SEQ38 : Wappa Dam	**WAD-SP001**	15/01/2021	**12/02/2021**	28	3.4	
SEQ39 : Cooloolabin Dam	**COD-SP001**	15/01/2021	**12/02/2021**	28	4.8	
SEQ40 : Wivenhoe Dam @ Logans Inlet PRW	**WID-SP061**	12/01/2021	**9/02/2021**	28	13.4	

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} (SEQ38 : Wappa Dam) to 21 cm s^{-1} (SEQ28 : Logan River @ Kooralbyn Offtake) (Figure 2).

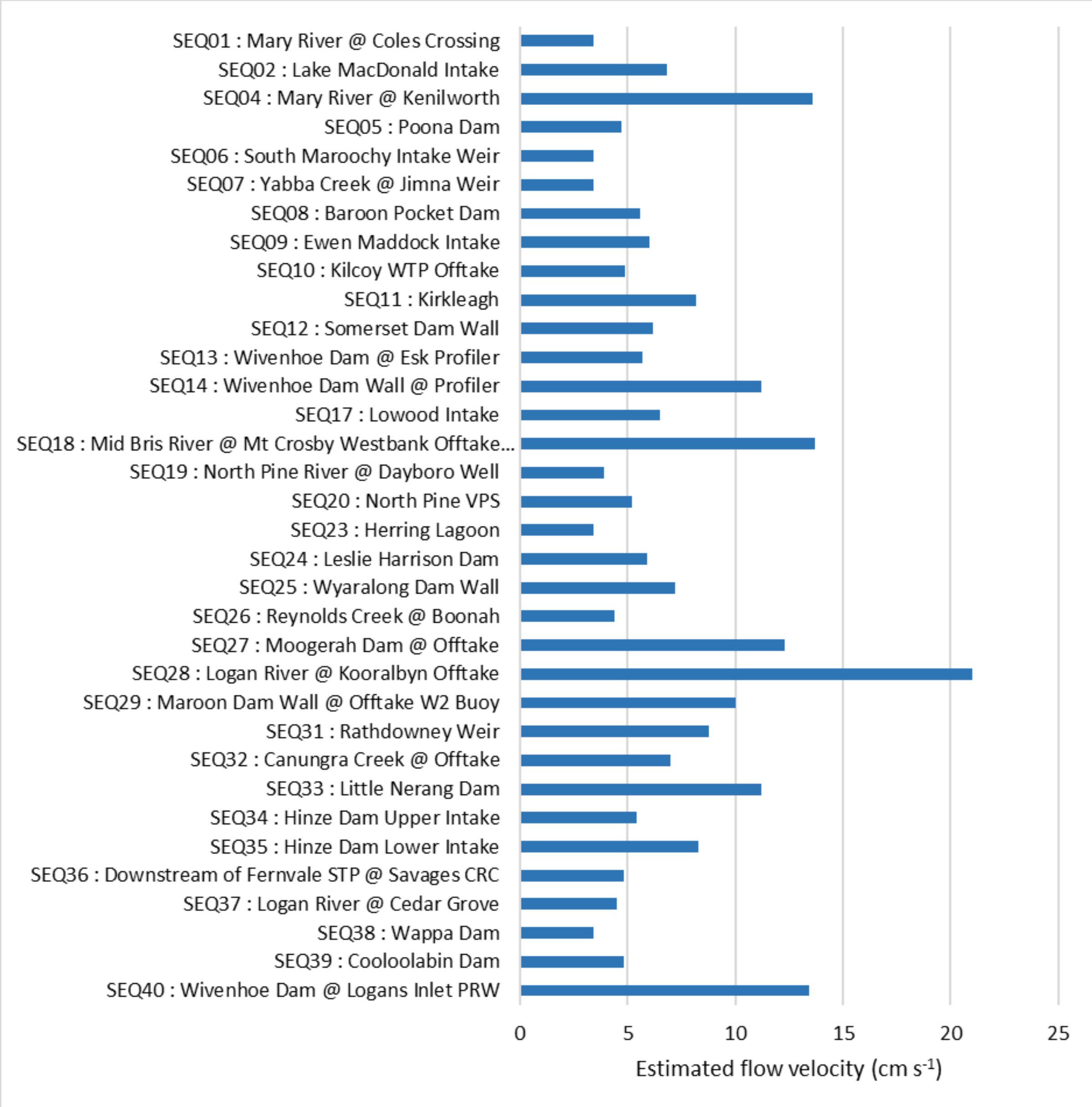

Figure 2. Passive flow monitor (PFM) based water flow velocity estimations (cm s^{-1}) at the deployment sites (n=34).

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 14 OCPs and 9 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% – 82% for OCPs and 6% – 56% for PAHs. Table 3 summarises the polar chemicals quantified via ED (pesticides and PPCPs). A total of 30 pesticides (predominantly herbicides) and 15 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3% - 69% for pesticides and 3% - 66% 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 $PDMS^{-1}$)	Max reported (ng $PDMS^{-1}$)
Organochlorine pesticides (OCP)				
Chlorpyrifos	28	82%	2.56	101
Cypermethrin	3	9%	1.22	13.4
Dacthal	4	12%	2.97	12.4
Dieldrin	22	65%	2.56	19.3
Endosulfan sulfate	1	3%	1.03	1.03
Heptachlor epoxide a	1	3%	9.67	9.67
Heptachlor epoxide b	3	9%	1.54	8.92
o,p-DDD	3	9%	1.19	4.56
p,p-DDD	8	24%	1.14	26.2
p,p-DDE	11	32%	1.03	13.1
p,p-DDT	3	9%	3.51	6.41
Permethrin	5	15%	0.730	8.68
trans-Chlordane	2	6%	1.62	2.71
β-endosulfan	1	3%	12.6	12.6
polycyclic aromatic hydrocarbons (PAHs)				
Benzo[a]anthracene	6	18%	1.32	7.89
Benzo[a]pyrene	2	6%	1.06	2.74
Benzo[b,j,k]fluoranthene	6	18%	0.73	3.91
Benzo[e]pyrene	5	15%	1.03	3.78
Benzo[g,h,i]perylene	3	9%	1.15	3.63
Chrysene/Triphenylene	19	56%	1.00	9.69
Fluoranthene	12	35%	6.02	86.4
Indeno[1,2,3-c,d]pyrene	2	6%	1.91	2.39
Pyrene	9	26%	8.98	55.9

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^{-1})	Max reported (ng ED^{-1})
Herbicides and Pesticides				
3,4 Dichloroaniline	3	9%	5.44	8.31
Ametryn hydroxy	9	26%	1.25	2.99
Atrazine	24	71%	1.26	27.1
Atrazine desethyl	15	44%	1.36	7.48
Atrazine desisopropyl	17	50%	1.05	4.88
Bromacil	2	6%	1.14	1.47
Carbendazim	18	53%	2.02	20.8

DCPMU	**2**	**6%**	**0.260**	**0.270**
Diketonitrile	**7**	**21%**	**0.100**	**0.150**
Diuron	**7**	**21%**	**1.08**	**43.7**
Fipronil	**2**	**6%**	**0.660**	**2.53**
Fluazifop	**3**	**9%**	**0.199**	**0.400**
Haloxyfop	**2**	**6%**	**1.84**	**2.04**
Hexazinone	**13**	**38%**	**1.06**	**18.0**
Imidacloprid	**7**	**21%**	**1.23**	**11.0**
MCPA	**4**	**12%**	**7.52**	**14.8**
Metalaxyl	**8**	**24%**	**0.150**	**1.29**
Methomyl	**4**	**12%**	**1.48**	**7.76**
Metolachlor (S+R)	**17**	**50%**	**1.23**	**29.5**
Metribuzin	**3**	**9%**	**1.39**	**1.66**
Metsulfuron methyl	**23**	**68%**	**1.01**	**9.88**
Prometryn	**3**	**9%**	**1.13**	**2.88**
Propiconazole	**5**	**15%**	**1.28**	**13.4**
Simazine	**16**	**47%**	**1.06**	**10.1**
Simazine hydroxy	**1**	**3%**	**1.30**	**1.30**
Tebuconazole	**5**	**15%**	**1.12**	**2.02**
Tebuthiuron	**14**	**41%**	**1.12**	**52.8**
Terbuthylazine	**4**	**12%**	**1.12**	**1.91**
Terbuthylazine desethyl	**6**	**18%**	**1.00**	**2.25**
Triclopyr	**3**	**9%**	**6.38**	**11.4**
Pharmaceuticals and personal care products (PPCPs)				
Acesulfame	**1**	**3%**	**8.17**	**8.17**
Atorvastatin	**1**	**3%**	**2.66**	**2.66**
Caffeine	**3**	**9%**	**30.8**	**80.1**
Carbamazepine	**6**	**18%**	**1.07**	**6.25**
Codeine	**1**	**3%**	**3.31**	**3.31**
DEET	**23**	**68%**	**11.9**	**118**
Diclofenac	**1**	**3%**	**1.32**	**1.32**
Gabapentin	**3**	**9%**	**1.26**	**2.42**
Oxazepam	**2**	**6%**	**1.69**	**3.45**
Paraxanthine	**1**	**3%**	**14.0**	**14.0**
Sulfadiazine	**2**	**6%**	**0.560**	**0.907**
Sulfamethoxazole	**4**	**12%**	**0.170**	**0.700**
Temazepam	**2**	**6%**	**1.52**	**2.04**
Trimethoprim	**1**	**3%**	**0.100**	**0.100**

Organochlorine pesticides (OCPs)

In total, 14 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 (SEQ19 - North Pine River @ Dayboro Well) to 142 ng $PDMS^{-1}$ (SEQ28 - Logan River @ Kooralbyn Offtake).

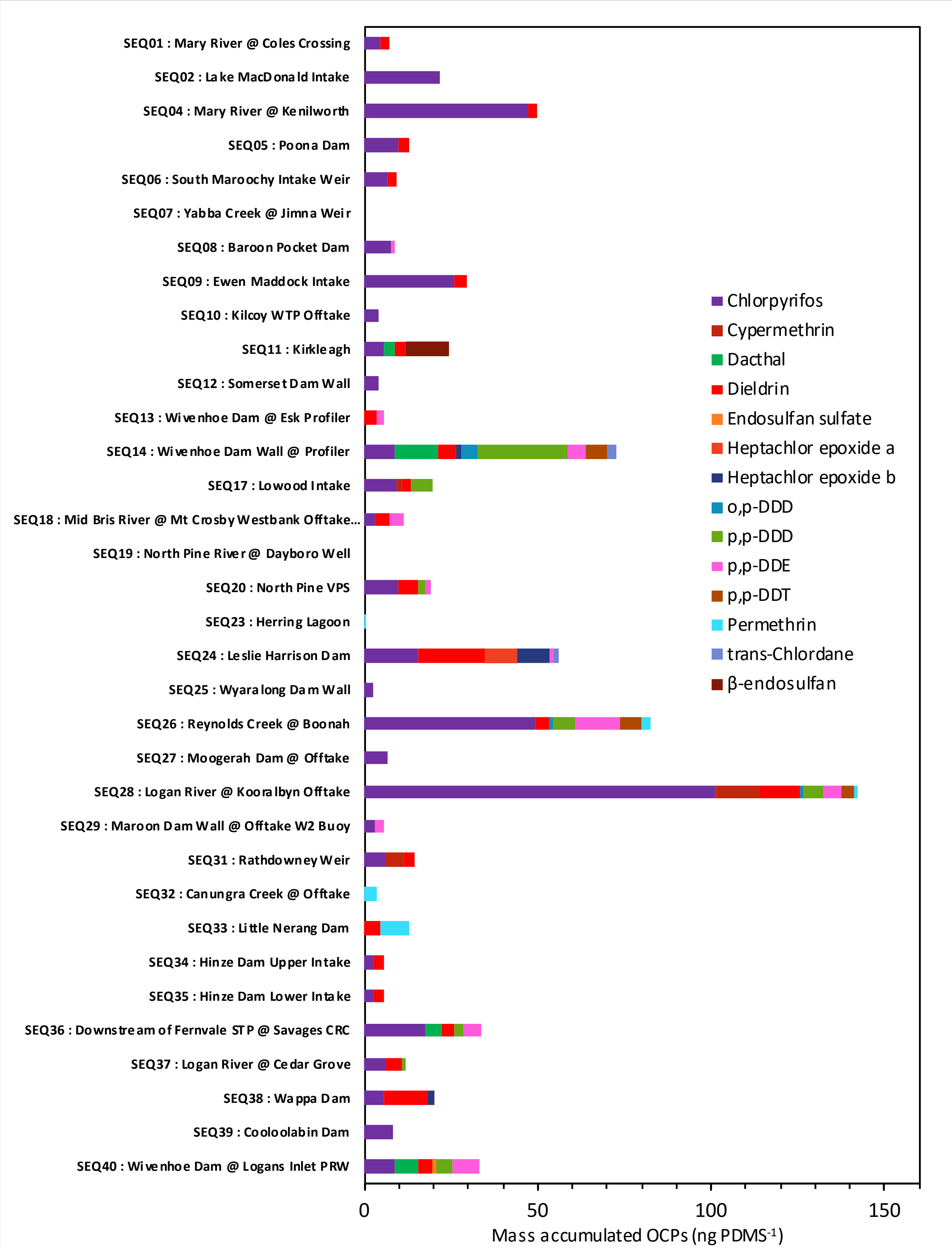

Figure 3. Total mass of 14 ΣOCPs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

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 0.002 to 1.42 ng L^{-1} (SEQ23 - Herring Lagoon and SEQ28 - Logan River @ Kooralbyn Offtake, respectively; Figure 4).

Figure 4. Total estimated water concentrations (ng L^{-1}) of 14 ΣOCPs at each site derived from PDMS passive samplers.

Polycyclic aromatic hydrocarbons (PAHs)

In total, 9 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 (SEQ35 - Hinze Dam Lower Intake; SEQ37 - Logan River @ Cedar Grove; SEQ34 - Hinze Dam Upper Intake; SEQ19 - North Pine River @ Dayboro Well; SEQ33 - Little Nerang Dam; SEQ05 - Poona Dam; SEQ06 - South Maroochy Intake Weir; SEQ38 - Wappa Dam; SEQ07 - Yabba Creek @ Jimna Weir; SEQ08 - Baroon Pocket Dam; SEQ23 - Herring Lagoon) to 172 ng $PDMS^{-1}$ (SEQ12 - Somerset Dam Wall).

Figure 5. Total mass of 9 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 0.673 ng L^{-1} (SEQ04 - Mary River @ Kenilworth and SEQ12 - Somerset Dam Wall, respectively; Figure 6).

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

Pesticides

Over the deployment period, 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 (SEQ33 - Little Nerang Dam; SEQ23 - Herring Lagoon; SEQ32 - Canungra Creek @ Offtake) to 114 ng ED^{-1}(SEQ36 - Downstream of Fernvale STP @ Savages CRC).

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 1.07 and 52.7 ng L^{-1} (SEQ31 - Rathdowney Weir and SEQ36 - Downstream of Fernvale STP @ Savages CRC, 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, 14 PPCPs were reported (Table 3, Figure 9, Appendix 1) with the average amount of ΣPPCPs accumulated ranging from below reporting limits (SEQ17 - Lowood Intake; SEQ19 - North Pine River @ Dayboro Well; SEQ23 - Herring Lagoon; SEQ09 - Ewen Maddock Intake; SEQ07 - Yabba Creek @ Jimna Weir; SEQ34 - Hinze Dam Upper Intake) to 118 ng ED^{-1} (SEQ27 - Moogerah Dam @ Offtake).

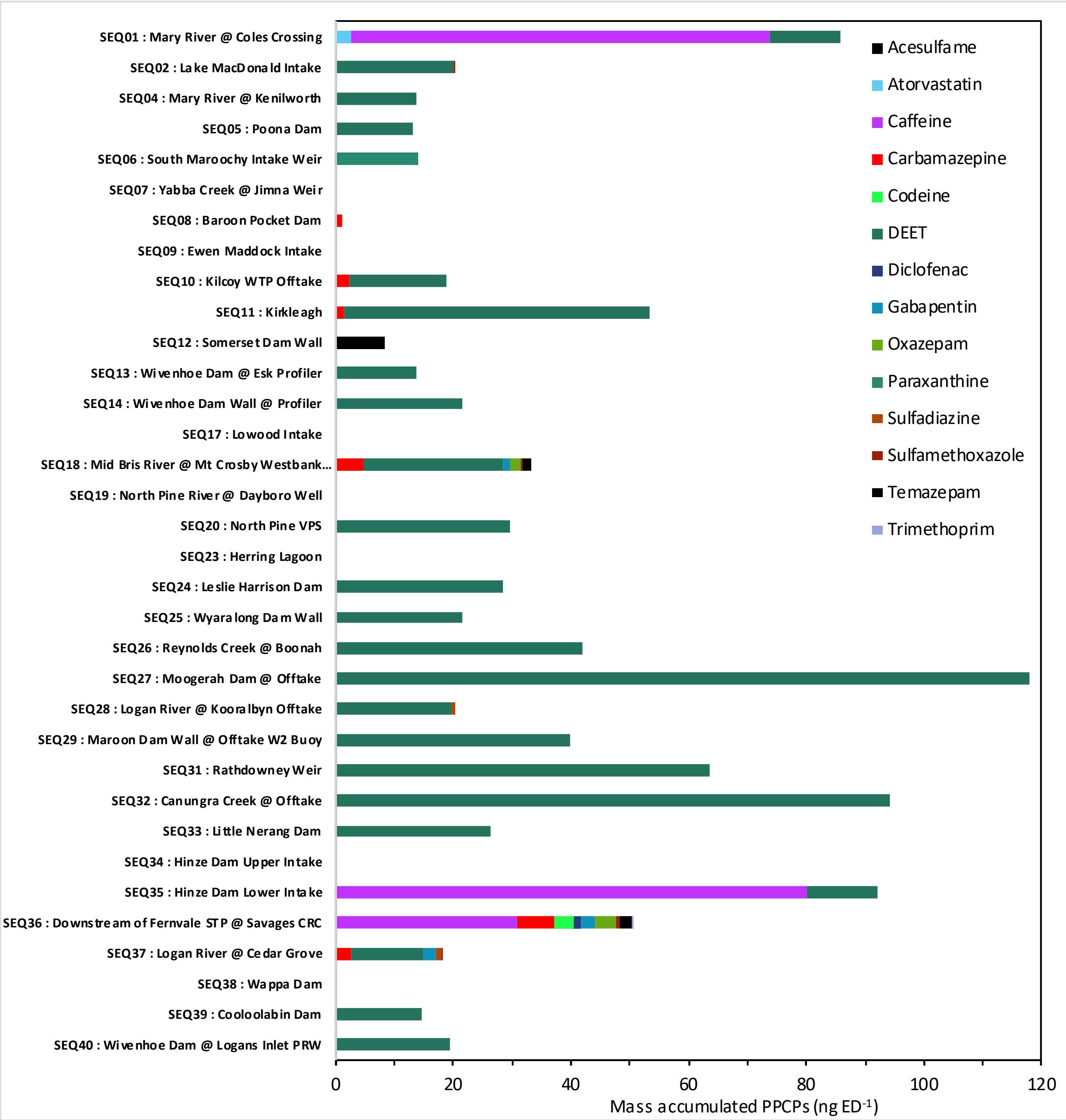

Figure 9. Total mass of 14 ΣPPCPs (ng ED^{-1}) accumulated in ED passive samplers at each site.

Of the 14 reported PPCPs, 6 were able to be converted into estimated time-weighted average water concentrations. Discounting the sites below reporting limits, these ∑PPCP water concentrations ranged between 0.400 and 42.2 ng L^{-1} (sites SEQ08 - Baroon Pocket Dam and SEQ01 - Mary River @ Coles Crossing, respectively; Figure 10).

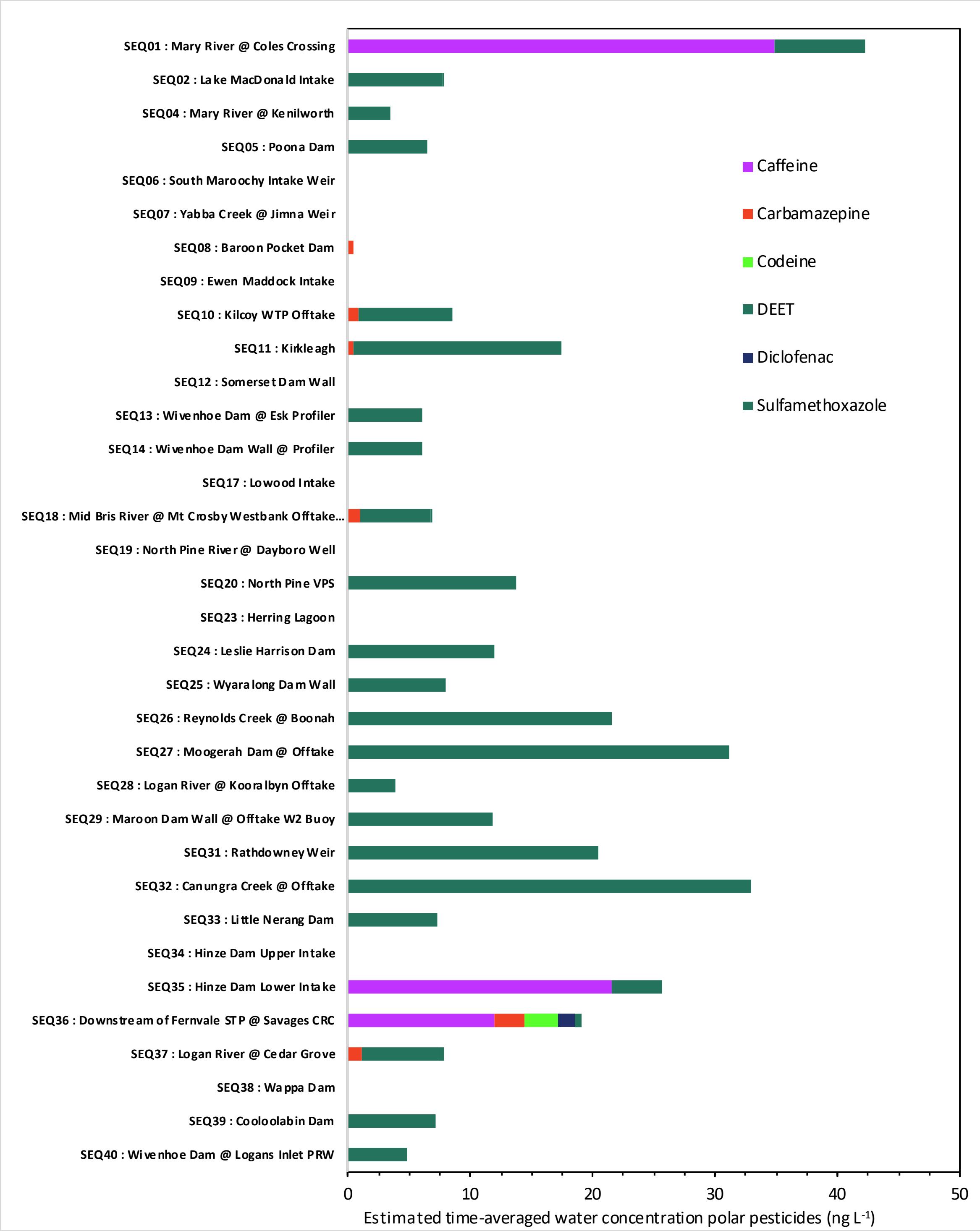

Figure 10. Total estimated water concentrations (ng L^{-1}) of 6 ΣPPCPs.

Analysis of non-target polar chemicals

Along with the target list of polar chemicals identified for investigation, the screening for an additional 45 herbicides and PPCP chemicals that have the potential to transport to waterways has been performed to investigate their presence in the water systems. During this sampling season no compounds of interest were detected, however a larger screening through additional pesticide, pharmaceutical and personal care product libraries revealed tentative detection of 23 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
3-Hydroxycarbofuran	pesticide	SEQ12 : Somerset Dam Wall
Aminocarb	pesticide	SEQ29 : Maroon Dam Wall @ Offtake W2 Buoy
Benalaxyl	fungicide	SEQ08 : Baroon Pocket Dam SEQ10 : Kilcoy WTP Offtake SEQ19 : North Pine River @ Dayboro Well SEQ24 : Leslie Harrison Dam SEQ28 : Logan River @ Kooralbyn Offtake SEQ31 : Rathdowney Weir
Bifenazate	pesticide	SEQ28 : Logan River @ Kooralbyn Offtake SEQ31 : Rathdowney Weir
Bupirimate	herbicide	SEQ04 : Mary River @ Kenilworth
Cycloheximide	naturally occurring fungicide	SEQ04 : Mary River @ Kenilworth
Cycluron	pesticide	SEQ31 : Rathdowney Weir
Cymoxanil	fungicide	SEQ02 : Lake MacDonald Intake
Disulfoton	insecticide	SEQ07 : Yabba Creek @ Jimna Weir SEQ08 : Baroon Pocket Dam
Fenobucarb	pesticide	SEQ10 : Kilcoy WTP Offtake SEQ11 : Kirkleagh
Fenuron	pesticide	SEQ08 : Baroon Pocket Dam SEQ17 : Lowood Intake SEQ36 : Downstream of Fernvale STP @ Savages CRC
Imazaquin	herbicide	SEQ39 : Cooloolabin Dam
Methabenzthiazuron	herbicide	SEQ08 : Baroon Pocket Dam
Metolcarb	insecticide	SEQ10 : Kilcoy WTP Offtake SEQ13 : Wivenhoe Dam @ Esk Profiler SEQ20 : North Pine VPS SEQ24 : Leslie Harrison Dam SEQ27 : Moogerah Dam @ Offtake SEQ29 : Maroon Dam Wall @ Offtake W2 Buoy
Mexacarbate	pesticide	SEQ05 : Poona Dam SEQ09 : Ewen Maddock Intake SEQ10 : Kilcoy WTP Offtake SEQ11 : Kirkleagh SEQ12 : Somerset Dam Wall SEQ13 : Wivenhoe Dam @ Esk Profiler
Monolinuron	systemic herbicide and an algaecid	SEQ04 : Mary River @ Kenilworth
Oxadixyl	pesticide	SEQ10 : Kilcoy WTP Offtake
Propisochlor	herbicide	SEQ31 : Rathdowney Weir
Pyracarbolid	pesticide	SEQ14 : Wivenhoe Dam Wall @ Profiler
Sethoxydim	herbicide	SEQ20 : North Pine VPS
Simetryn	pesticide	SEQ25 : Wyaralong Dam Wall
Stachybotrylactam	mycotoxin	SEQ02 : Lake MacDonald Intake
Zolmitriptan	migraine treatment	SEQ02 : Lake MacDonald Intake

Comparison to water quality guideline values

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

Exceedances for eco-toxicological guidelines were observed in the estimated time-averaged water concentrations chlorpyrifos. ANZECC & ANCANZ have set chlorpyrifos freshwater guideline values of 0.04 and 10 ng L^{-1} for 99% and 95% level species protection, respectively. Tebuthiuron also has guidelines values of 20 and 2200 ng L^{-1} for 99% and 95%, respectively. In total, 24 and 1 site(s) exceeded the 99% species protection guideline for chlorpyrifos and tebuthiuron, respectively. No sites exceeded the 95% species protection guideline values.

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

Australian Drinking Water Guidelines 6 (2011)		Trigger values for freshwater		This campaign
Version 3.5 Updated August 2018 (ng L^{-1})		99% species protection value (ng L^{-1})	95% species protection value (ng L^{-1})	Highest Reported Value (ng L^{-1})
Herbicides & Insecticides				
Atrazine	20000	700	13000	14.1
Ametryn	70000	N/A	N/A	#N/A
Bromacil	400000	N/A	N/A	#N/A
Carbaryl	30000	N/A	N/A	#N/A
Carbendazim	90000	N/A	N/A	16.4
Diuron	20000	N/A	N/A	27.4
Fluometuron	70000	N/A	N/A	#N/A
Haloxyfop	1000	N/A	N/A	0.800
Hexazinone	400000	N/A	N/A	11.6
MCPA	40000	N/A	N/A	6.83
Malathion	700000	2	50	#N/A
Methomyl	20000	N/A	N/A	#N/A
Metolachlor	300000	N/A	N/A	#N/A
Metsulfuron methyl	40000	N/A	N/A	#N/A
Pendimethalin	400000	N/A	N/A	#N/A
Picloram	300000	N/A	N/A	#N/A
Propazine	50000	N/A	N/A	#N/A
Propiconazole	100000	N/A	N/A	#N/A
Simazine	20000	200	3200	3.69
Tebuthiuron	N/A	20	2200	23.2
Terbuthylazine	10000	N/A	N/A	0.900
Triclopyr	20000	N/A	N/A	4.79
2,4-D	30000	140000	280000	#N/A
2,4,5-T	100000	3000	36000	#N/A

3,4-Dichloroaniline	N/A	1300	3000	#N/A
OCPs				
Chlordane	2000	30	800	#N/A
Chlorpyrifos	10000	0.04	10	1.36
DDT	9000	6	10	0.076
Dieldrin	300	N/A	N/A	0.069
Aldrin	300	N/A	N/A	#N/A
Endosulfan	20000	30	200	0.961
Endrin	N/A	10	20	#N/A
Heptachlor	300	10	90	#N/A
r-HCH (lindane)	10000	70	200	#N/A
PAHs				
Benzo[a]pyrene	10	N/A	N/A	0.006
Naphthalene	10	2500	16000	#N/A

Discussion

OCPs were first introduced into Australia in the mid-1940s and were applied in many commercial products in different forms (such as powders and liquids). At one time up to 150 commercial products containing OCPs may have been registered in Australia. This followed a period of widespread use until the 1970s when recognition of risks related to OCPs resulted in reduced use and their ultimate ban in the 1980s. Since then, human biomonitoring studies in blood and breastmilk have showed the substantial decline of these chemicals from the early 1980s to the 1990s after which levels appear to plateau (Toms *et al.* 2012). Although a few OCPs were reported at 32 sites (94%) all monitoring sites, the concentrations were very low (Total ∑OCPs <1.42 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 22 sites. Dieldrin has been used is use since the 1950's as an insecticide particularly as a termite treatment. It has been banned in Australia since 1987, though remains persistent in the environment due to its low breakdown rates.

PAHs are ubiquitous in the environment and are introduced via anthropogenic sources primarily as a result of incomplete combustion as well as via natural sources (i.e. forest fires and the transformation of biogenic precursors) (Nguyen *et al.* 2014). A number of PAHs have been included as chemicals of concern under the Stockholm Convention on Persistent Organic Pollutants (2011) due to their toxic and carcinogenic properties. They enter aquatic systems via storm water runoff from urban and industrial areas, roads and spills as well as via recreational activities such as boating. PAHs can undergo long-range atmospheric transport and deposition and are distributed in waterways during intense rainfall and flooding (Nguyen *et al.* 2014). The hydrophobic nature of PAHs typically results in low concentrations in water as they generally associate with particulate matter and sediment. Twenty-two sites showed reportable concentrations of PAHs including chrysene, fluoranthene and pyrene at low levels (<0.673 ng L^{-1}). The decrease in reported PAH amounts in this campaign compared to previous reports from the previous campaigns may be due to a combination of decreased rainfall and subsequent runoff in winter, and at sites like Somerset Dam, decreased recreational boating activities which may have further decreased following a decrease in interstate and international tourism due to COVID restrictions.

Polar pesticides (herbicides, insecticides and fungicides) were reported at 30 sites. The most frequently reported herbicide atrazine (detected at 24 sites; 71%) 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. Herbicides with some soil mobility are generally transported to the aquatic environment through runoff and/or percolation to groundwater. Some areas of South-East Queensland experienced lower than average rainfall in January 2021 (BOM 2021), which may explain the decrease in detections compared to previous campaign. This increase may also be due to the seasonal nature of agriculture and pesticide applications.

Pharmaceuticals and personal care products have emerged as a major group of environmental contaminants over the past decade. Some polar organic chemicals persist through wastewater treatment processes resulting in their continuous release into the aquatic environment (Kaserzon *et al.* 2014). The most frequently reported PPCP was DEET which is often attributed to background contamination due to high DEET application by field staff, to combat insect bites. If reported values for DEET are ignored, then the total number of sites with measurable PPCP water concentrations drops to 8. Of these, the primary contributor is carbamazepine, detected at 18% of sites and the antibiotic sulfamethoxazole detected at 4 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). Sulfamethoxazole is reported to have a breakdown rate in soil water environments of ~ 47 days. The contribution of pharmaceuticals and personal care products can be an indicator of systems which are used for human recreational activities or which receive some degree of treated effluent.

Future recommendations

Several recommendations for future work are suggested to build upon the preliminary findings in the current report.

- Continue temporal and seasonal comparisons to assess if any new trends emerge between sites and seasons.

- Review 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.

BOM (Bureau of Meteorology) (2020). Web page: Queensland in September 2020: above average rainfall, and warm days and nights in the west url: http://www.bom.gov.au/climate/current/month/qld/archive/202009.summary.shtml. Accessed 18/12/2020. Australian Government

Kaserzon, S., O'Malley, E., Thompson, K., Paxman, C., Elisei, G., Eaglesham, G., Gallen, M. and Mueller, J. (2017). Catchment and Drinking Water Quality Micro Pollutant Monitoring Program – Passive Sampling Report 6 – Summer 2017 and summary report, prepared for Seqwater, 11 August 2017.

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

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

Vrana, 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

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.

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, QLD

Appendix 1

See enclosed excel file '**SEQW21_Summer_Client_Report.xls**'

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

Appendix 2

See enclosed excel file '**SEQW21_Summer_Flupropanate_Client_Report.xls**'

Reporting sheet listing flupropanate investigated at SEQ05: Poona Dam, listing levels accumulated in Polyethylene (PE) passive samplers and ED passive samplers (ng $sampler^{-1}$) and estimated average water concentrations over the deployment periods (ng L^{-1}).