

Queensland Alliance for Environmental Health Sciences



# Catchment and Drinking Water Quality Micro Pollutant Monitoring

# **Program – Passive Sampling**

Report 20 – Summer 2024

Ryan Shiels, Kristie Thompson and Sarit Kaserzon

# Title

Catchment and Drinking Water Quality Micro Pollutant Monitoring program – Passive Sampling. Report 20 – Summer 2024.

#### 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 authors expressly disclaim 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 authors.

#### **Project Team**

Kristie Thompson, Ryan Shiels, Yan Li, Chris Paxman, Gabriele Elisei, Pritesh Prasad, Joe Clokey, Xuan Qu, 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) <u>k.sarit@uq.edu.au</u>

#### **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	3
List of Figures	3
Executive Summary	4
Introduction	5
Methodology	6
Passive sampler preparation and extraction	7
Analytical methods	8
Data modelling and reporting of results	9
Quality control and assurance (QC/QA) procedures	9
Results	9
Passive flow monitors (PFM) results	9
Chemical analysis results	11
Organochlorine pesticides (OCPs)	16
Polycyclic aromatic hydrocarbons (PAHs)	20
Pesticides	22
Pharmaceuticals and personal care products (PPCPs)	24
Per- and Polyfluoroalkyl Substances (PFAS)	26
Analysis of non-target polar chemicals	28
Analysis of ant bait chemicals	28
Comparison to water quality guideline values	29
Discussion	31
Future recommendations	33
References	34
Appendix 1	36

# List of Tables

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

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<sup>-1</sup>).

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<sup>-1</sup>).

Table 4. Summary of the number of chemicals accumulated in MPT passive samplers, percentage of detection at the sites and the range of mass accumulated over the deployment periods (ng MPT<sup>-1</sup>).

Table 5. List of tentatively identified non-target chemicals in EDs, and the sites in which they were detected.

Table 6. List of tentatively identified ant-bait chemicals in PDMS, and the sites in which they were detected.

Table 7. Threshold chemical guidelines for Australian Drinking Water and Freshwater Aquatic Ecosystems. Values highlighted in yellow exceed the 99% or 95% species protection guideline.

# List of Figures

Figure 1. Preparation of a PDMS passive sampler in a stainless steel cage.

Figure 2. Passive flow monitor (PFM) based water flow velocity estimations (cm s<sup>-1</sup>) at the deployment sites (n=36).

Figure 3. Total mass of 23  $\Sigma$ OCPs (ng PDMS<sup>-1</sup>) (excluding Dacthal) accumulated in PDMS passive samplers at each site.

Figure 4. Total mass of Dacthal (ng PDMS<sup>-1</sup>) accumulated in PDMS passive samplers at each site.

Figure 5. Total estimated water concentrations (ng  $L^{-1}$ ) of 23  $\Sigma$ OCPs (excluding Dacthal) at each site derived from PDMS passive samplers.

Figure 6. Total estimated water concentrations (ng L<sup>-1</sup>) of Dacthal at each site derived from PDMS passive samplers.

Figure 7. Total mass of 9 ΣPAHs (ng PDMS<sup>-1</sup>) accumulated in PDMS passive samplers at each site.

Figure 8. Total estimated water concentrations (ng  $L^{-1}$ ) of 9  $\Sigma$ PAHs at each site derived from PDMS passive samplers.

Figure 9. Total mass of 33  $\Sigma$ polar pesticides (ng ED<sup>-1</sup>) accumulated in ED passive samplers at each site. Figure 10. Total estimated water concentrations (ng L<sup>-1</sup>) of 17  $\Sigma$ polar pesticides at each site derived from ED passive samplers.

Figure 11. Total mass of 6 ΣPPCPs (ng ED<sup>-1</sup>) accumulated in ED passive samplers at each site.

Figure 12. Total estimated water concentrations (ng L<sup>-1</sup>) of 4  $\Sigma$ PPCPs derived from ED passive samplers.

Figure 13. Total mass of ΣPFAS (ng MPT<sup>-1</sup>) accumulated in MPT passive samplers at each site.

Figure 14. Total estimated water concentrations (ng L<sup>-1</sup>) of ΣPFAS derived from MPT passive samplers.

# **Executive Summary**

The Catchment and Drinking Water Quality Micro Pollutant Monitoring Program was launched in mid-2014 with the aim of improving the characterisation and understanding of the micro pollutant risk profile in source water reservoirs through bi-annual summer and winter sampling campaigns. The monitoring program utilising passive samplers was continued in reservoirs in South East Queensland (SEQ) during the first quarter of 2024. 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). This campaign also included analysis of passive sampler extracts for per- and polyfluoroalkyl substances (PFAS). 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 72 different chemicals including 24 OCPs, 9 PAHs, 33 polar pesticides, 1 PFAS and 6 PPCPs. OCPs were detected at 97% of sites, with Dieldrin (92%) and Chlorpyrifos (86%) the most frequently reported. Total  $\sum$ OCP water concentrations across sites ranged between 0.008 – 230 ng L<sup>-1</sup> where concentrations were reportable. PAHs were detected at 97% of sites, with Chrysene/Triphenylene (92%) and Benzo[b,j,k]fluoranthene (86%) reported at the highest abundance across all sites. Total  $\sum$ PAH water concentrations across sites ranged between 0.002 – 0.60 ng L<sup>-1</sup>. In total, 33 different polar pesticides were reported across 34 sites (94%), with Metsulfuron methyl (83%), Diuron (78%) and Terbuthylazine desethyl (78%) reported at highest frequency across all sites. Total  $\sum$  pesticides ranged between 0.380 – 1573 ng L<sup>-1</sup>. Additionally, 6 PPCPs were detected across sites with highest detection frequencies observed for DEET (100%) and Carbamazepine (22%). Total estimated  $\sum$ PPCP water concentrations ranged between 7.52 – 159 ng L<sup>-1</sup> across sites. PFAS analysis resulted in only one reportable concentration).

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, atrazine, diazinon, metolachlor, tebuthiuron and chlorpyrifos were often above the thresholds set for 99% species protection. In two instances, diazinon and metolachlor were 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 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  $\geq$  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<sup>TM</sup> Disk; ED) chemical pollutants have been chosen for deployment in this program. PFAS were also monitored in this campaign at the majority of sites by deployment of microporous polyethylene tube (MPT) passive samplers specialised for PFAS monitoring.

The list of target chemicals for inclusion in the monitoring campaign was identified via a review of the Australian Drinking Water Guidelines (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 product 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 ongoing risk assessment and detection frequency.

# Methodology

Passive water samplers were deployed in periods between January and April 2024 at 38 sites of SEQ reservoirs/waterways (Table 1). Samplers from Site SEQ17 (Lowood Intake) were discovered out of the water and considered compromised and were subsequently redeployed successfully. Samplers from Site SEQ15 (Lockyer Creek @ Lake Clarendon Way) were lost, and subsequently redeployed successfully. Samplers from Site SEQ01 (Mary River @ Coles X ing) were lost, and the subsequent redeployment was also lost, with no further redeployments performed (not shown). Samplers from Site SEQ28 (Logan River @ Kooralbyn Offtake) were not deployed (not shown). PFAS passive samplers were not deployed at Sites SEQ15 (Lockyer Creek @ Lake Clarendon Way), SEQ16 (Lockyer Creek @ Patrick's Estate), SEQ36 (Fernvale STP @ Savages Crossing) and SEQ43 (Enoggera Reservoir).

Deployments were for periods of 27 to 39 days in duration. A second sampler set was deployed at 11 randomly selected sites (Table 1, highlighted in green), with 6 of these extra samplers as site duplicates. Four extra samplers were spiked in the laboratory 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<sup>-1</sup>) estimated at each site.

Site	Site Code	Date	Date	Days	Flow Velocity	Comments
		Deployed	Retrieved	Deployed	(cm/s)	
SEQ02 : Lake Macdonald Intake	CSX-LMD-01- OFF-PS	18/01/2024	22/02/2024	35	11.3	
SEQ04 : Mary River @ Kenilworth	CMV-MRS-40- RIV-PS	18/01/2024	14/02/2024	27	27.8	
SEQ05 : Poona Dam	CMR-POD-01- OFF-PS	16/01/2024	19/02/2024	34	6.4	
SEQ06 : South Maroochy Intake Weir	CMR-SOR-25- OFF-PS	19/02/2024	20/03/2024	30	3.4	
SEQ07 : Yabba Creek @ Jimna	CMV-YAC-01- OFF-PS	18/01/2024	14/02/2024	27	3.4	
SEQ08 : Baroon Pocket Dam	CBT-BPD-15- OFF-PS	19/01/2024	20/02/2024	32	5.7	
SEQ09 : Ewen Maddock	CML-EMD-01- OFF-PS	1/02/2024	6/03/2024	34	5.5	
SEQ10 : Kilcoy WTP offtake	CST-SOD-90- OFF-PS	9/01/2024	7/02/2024	29	10.1	
SEQ11 : Kirkleagh	CST-SOD-71- OFF-PS	9/01/2024	7/02/2024	29	8.4	
SEQ12 : Somerset Dam Wall	CST-SOD-01- OFF-PS	9/01/2024	7/02/2024	29	6.8	
SEQ13 : Wivenhoe Dam @ Esk	CUB-WID-90- OFF-PS	23/01/2024	20/02/2024	28	7.3	
SEQ14 : Wivenhoe Dam Wall	CUB-WID-01- OFF-PS	23/01/2024	20/02/2024	28	9.7	
SEQ15 : Lockyer Creek @ Lake Clarendon Way	CCK-LOC-50- RIV-PS	6/03/2024	5/04/2024	30	5	Initial sampler lost, redeployed sampler. PFAS sampler not deployed at this site
SEQ16 : Lockyer Creek @ Patrick's Estate	CCK-LOC-15- RIV-PS	5/01/2024	6/02/2024	32	8.5	PFAS sampler not deployed at this site

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

SEQ17 : Lowood Intake	CMB-MBR-80- OFF-PS	6/02/2024	5/03/2024	28	6.6	Initial sampler compromised, redenloved sampler
SEQ18 : Mt Crosby Westbank Offtake Tower	CMB-MBR-02- OFF-PS	10/01/2024	7/02/2024	28	12.6	
SEQ19 : North Pine River @ Dayboro Well	CPV-NPR-70- OFF-PS	6/02/2024	8/03/2024	31	6.2	
SEQ20 : North Pine VPS	CPV-NOD-10- OFF-PS	15/01/2024	23/02/2024	39	5.8	
SEQ21 : Lake Kurwongbah	CPV-LAK-01- OFF-PS	17/01/2024	21/02/2024	35	6.9	
SEQ23 : Herring Lagoon	CNS-HLA-01- OFF-PS	16/01/2024	20/02/2024	35	3.4	
SEQ24 : Leslie Harrison Dam	CRL-LHD-05- VPS-PS	18/01/2024	22/02/2024	35	5.4	
SEQ25 : Wyaralong Dam Wall	CLR-WYD-01- REC-PS	6/02/2024	6/03/2024	29	5.5	
SEQ26 : Reynolds Creek @ Boonah	CWV-REY-20- OFF-PS	17/01/2024	21/02/2024	35	6.1	
SEQ27 : Moogerah Dam	CWV-MOD- 02-OFF-PS	17/01/2024	21/02/2024	35	10.4	
SEQ29 : Maroon Dam Wall	CLR-MAD-04- OFF-PS	1/02/2024	5/03/2024	33	9.2	
SEQ31 : Rathdowney Weir	CLR-LOG-80- OFF-PS	2/02/2024	6/03/2024	33	10.1	
SEQ32 : Canungra Creek @ Offtake	CLR-CAC-01- OFF-PS	15/01/2024	19/02/2024	35	10	
SEQ33 : Little Nerang Dam	CNR-LND-01- OFF-PS	24/01/2024	27/02/2024	34	3.7	
SEQ34 : Hinze Upper Intake	CNR-HID-20- OFF-PS	25/01/2024	29/02/2024	35	5	
SEQ35 : Hinze Lower Intake	CNR-HID-01- OFF-PS	25/01/2024	29/02/2024	35	6.9	
SEQ36 : Fernvale STP @ Savages Crossing	CMB-MBR-60- RIV-PS	9/01/2024	6/02/2024	28	23.9	PFAS sampler not deployed at this site
SEQ37 : Logan River @ Cedar Grove	CLR-LOG-12- RIV-PS	6/02/2024	6/03/2024	29	4.2	
SEQ38 : Wappa Dam	CMR-WAD-01- OFF-PS	16/01/2024	19/02/2024	34	3.4	
SEQ39 : Cooloolabin Dam	CMR-COD-01- OFF-PS	2/02/2024	7/03/2024	34	4.5	
SEQ40 : Wivenhoe Dam @ Logans Inlet PRW	CUB-WID-59- PRW-PS	23/01/2024	20/02/2024	28	13.8	
SEQ43 : Enoggera Reservoir	CLB-END-01- OFF-PS	11/01/2024	15/02/2024	35	4.4	PFAS sampler not deployed at this site

**Note:-** Flow velocity of 3.4 cm s<sup>-1</sup> was used where the calculated flow velocity was smaller than 3.4 cm s<sup>-1</sup> Sites with replicate samplers deployed for QA/QC purposes are highlighted in green.

#### Passive sampler preparation and extraction

In this campaign, multiple types of passive samplers were deployed at each site. Empore Disk<sup>™</sup> (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. Microporous tubes (MPT) were deployed to detect and quantify the presence of per- and

polyfluoroalkyl substances (PFAS). ED and PDMS passive samplers, as well as PFMs, were prepared and extracted according to previously published procedures and methods described in Kaserzon *et al.* (2017). MPT samplers were prepared and extracted according to Kaserzon *et al.* (2019) and Mackie *et al.* (2024).



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 and MPT extracts were analysed by LC-QQQ MS/MS for polar herbicides, PFAS and PPCPs (112 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 PFAS, herbicides and PPCPs (LC-QQQ MS/MS), OCPs and PAHs (GC-HRMS), and suspect screening of herbicides and PPCPs (LC-QTOF MS/MS) have been detailed previously in Kaserzon *et al.* (2017), Kaserzon *et al.* (2019), Mackie *et al.* (2024), 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<sup>-1</sup> or PFM loss rate equal to 0.58 g d<sup>-1</sup>; 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<sup>-1</sup> for the sites showing flow below this threshold. 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<sup>-1</sup> to 27.8 cm s<sup>-1</sup> (SEQ04 : Mary River @ Kenilworth) (Figure 2).



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

Note: A minimum flow velocity of 3.4 cm s<sup>-1</sup> 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<sup>-1</sup>) is presented in Tables 2, 3 and 4 below. Table 2 summarises the non-polar chemicals quantified via PDMS (OCPs and PAHs). A total of 24 OCPs and 9 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% - 92% for OCPs and 8% - 92% for PAHs. Table 3 summarises the polar chemicals quantified via ED (pesticides and PPCPs). A total of 33 pesticides (predominantly herbicides) and 6 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3% - 83% for pesticides and 3% - 100% for PPCPs. Table 4 summarises the PFAS chemicals quantified via MPT. Only one PFAS accumulated in samplers, with a percent detection at sampling sites of 3% (2.12 ng MPT<sup>-1</sup> at SEQ24 – Somerset Dam Wall).

Analyte	Number of	%	Min reported	Max reported		
	sites detected	Detection	(ng/PDMS)	(ng/PDMS)		
OCP						
Aldrin	0	0%	0.00	0.00		
Azinphos methyl	0	0%	0.00	0.00		
Bifenthrin	22	61%	1.03	11.8		
Chlorpyrifos	31	86%	5.17	499		
cis-Chlordane	21	58%	0.79	21.6		
Cypermethrin	3	8%	8.86	16.3		
Dacthal	12	33%	2.69	10315		
Deltamethrin	1	3%	3.63	3.63		
Dieldrin	33	92%	2.86	89.9		
Endosulfan sulfate	12	33%	1.05	16.6		
Endrin	3	8%	1.75	2.64		
Endrin ketone	2	6%	2.35	2.91		
НСВ	0	0%	0.00	0.00		
Heptachlor	0	0%	0.00	0.00		
Heptachlor epoxide a	0	0%	0.00	0.00		
Heptachlor epoxide b	10	28%	1.57	27.8		
Methoxychlor	0	0%	0.00	0.00		
Mirex	0	0%	0.00	0.00		
o,p-DDD	7	19%	1.15	3.71		
o,p-DDE	2	6%	1.43	2.16		
o,p-DDT	1	3%	5.93	5.93		
p,p-DDD	11	31%	1.10	13.1		
p,p-DDE	14	39%	1.39	146		
p,p-DDT	4	11%	4.97	23.3		
Pendimethalin	4	11%	11.4	268		
Permethrin	1	3%	52.7	52.7		
trans-Chlordane	18	50%	4.05	41.3		
α-Endosulfan	3	8%	2.25	5.80		
α-ΗCΗ	3	8%	1.09	3.15		
β-endosulfan	2	6%	1.85	5.36		
β-НСН	5	14%	0.630	102		

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<sup>-1</sup>).

γ-HCH (Lindane)	0	0%	0.00	0.00
		РАН		
Acenaphthene	0	0%	0.00	0.00
Acenaphthylene	0	0%	0.00	0.00
Anthracene	0	0%	0.00	0.00
Benzo[a]anthracene	6	17%	1.35	5.70
Benzo[a]pyrene	3	8%	1.16	1.28
Benzo[b,j,k]fluoranthene	31	86%	0.504	3.16
Benzo[e]pyrene	17	47%	1.19	3.72
Benzo[g,h,i]perylene	5	14%	1.02	2.33
Chrysene/Triphenylene	33	92%	0.610	11.9
Dibenz[a,h]anthracene	0	0%	0.00	0.00
Fluoranthene	4	11%	37.6	95.8
Fluorene	0	0%	0.00	0.00
Indeno[1,2,3-c,d]pyrene	3	8%	1.08	1.81
Naphthalene	0	0%	0.00	0.00
Phenanthrene	0	0%	0.00	0.00
Pyrene	6	17%	13.6	53.1

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	%	Min reported	Max reported			
	detected	Detection	(ng/ED)	(ng/ED)			
Herbicides and Pesticides							
2,4,5-T	1	3%	1.62	1.62			
2,4-D	10	28%	6.07	32.8			
3,4 Dichloroaniline	0	0%	0.00	0.00			
Ametryn	0	0%	0.00	0.00			
Ametryn hydroxy	6	17%	1.12	3.41			
Aminocarb	0	0%	0.00	0.00			
Atrazine	27	75%	1.08	1847			
Atrazine desethyl	24	67%	1.09	79.4			
Atrazine desisopropyl	22	61%	1.24	33.1			
Bendiocarb	0	0%	0.00	0.00			
Bromacil	1	3%	11.2	11.2			
Bromoxynil	0	0%	0.00	0.00			
Carbaryl	0	0%	0.00	0.00			
Carbendazim	13	36%	1.24	26.1			
DCPMU	3	8%	0.160	0.350			
DCPU	0	0%	0.00	0.00			
Diazinon	20	56%	0.170	26.4			
Difenoconazole	0	0%	0.00	0.00			
Diketonitrile	4	11%	0.120	0.180			
Diuron	28	78%	0.540	10.4			
Fenuron	0	0%	0.00	0.00			
Fipronil	9	25%	0.580	14.4			

Eluszifon	F	1 / 0/	0.620	2 47
Fluazilop	5	14%	0.030	2.47
Flumentarion	0	0%	0.00	0.00
Fluroxypyr	0	0%	0.00	0.00
Наюхутор	8	22%	2.31	27.2
Hexazinone		31%	1.68	5.67
Imazapyr	0	0%	0.00	0.00
Imazethapyr	0	0%	0.00	0.00
Imidacioprid	14	39%	1.38	39.4
Malathion	0	0%	0.00	0.00
МСРА	7	19%	6.04	20.8
Metalaxyl	14	39%	0.160	8.20
Methidathion	0	0%	0.00	0.00
Methomyl	3	8%	2.93	9.10
Metolachlor (S+R)	22	61%	1.16	2007
Metolcarb	0	0%	0.00	0.00
Metribuzin	7	19%	1.47	13.5
Metsulfuron methyl	30	83%	1.11	16.8
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	1	3%	1.04	1.04
Propachlor	0	0%	0.00	0.00
Propazine	4	11%	1.34	18.8
Propiconazole	5	14%	1.31	5.74
Propoxur	0	0%	0.00	0.00
Simazine	16	44%	1.35	47.8
Simazine hydroxy	0	0%	0.00	0.00
Tebuconazole	10	28%	1.10	7.01
Tebuthiuron	17	47%	1.44	169
Terbuthylazine	20	56%	1.24	7.34
Terbuthylazine desethyl	28	78%	1.00	10.6
Thiamethoxam	5	14%	2.16	47.5
Triclopyr	11	31%	7.14	95.0
Pharma	ceuticals and perso	nal care product	ts (PPCPs)	
Acesulfame	0	0%	0.00	0.00
Atenolol	0	0%	0.00	0.00
Atorvastatin	0	0%	0.00	0.00
Caffeine	1	3%	108	108
Carbamazepine	8	22%	1.13	4.79
Codeine	0	0%	0.00	0.00
DEET	36	100%	21.8	437
Diclofenac	0	0%	0.00	0.00
Gabapentin	0	0%	0.00	0.00
Hydrochlorothiazide	0	0%	0.00	0.00
	~	0,0	5.00	0.00

Iopromide	0	0%	0.00	0.00
Naproxen	0	0%	0.00	0.00
Oxazepam	0	0%	0.00	0.00
Paracetamol	0	0%	0.00	0.00
Paraxanthine	1	3%	63.6	63.6
Salicylic acid	0	0%	0.00	0.00
Sulfadiazine	3	8%	0.660	1.01
Sulfamethoxazole	3	8%	0.230	0.580
Tadalafil	0	0%	0.00	0.00
Temazepam	0	0%	0.00	0.00
Verapamil	0	0%	0.00	0.00

Table 4. Summary of the number of chemicals accumulated in MPT passive samplers, percentage of detection at the sites and the range of mass accumulated over the deployment periods (ng MPT<sup>-1</sup>).

Analyte	Acronym	Number of sites detected	% Detection	Min reported (ng/MPT)	Max reported (ng/MPT)
Per and	d Polyfluoroalk	yl Substance	(PFAS)		
Perfluorobutanoic acid	PFBA	1	3%	2.12	2.12
Perfluoropentanoic acid	PFPeA	0	0%	0.00	0.00
Perfluorohexanoic acid	PFHxA	0	0%	0.00	0.00
Perfluoroheptanoic acid	PFHpA	0	0%	0.00	0.00
Perfluorooctanoic acid	PFOA	0	0%	0.00	0.00
Total (linear + branched) Perfluorooctanoic acid	PFOA total	0	0%	0.00	0.00
Perfluorononanoic acid	PFNA	0	0%	0.00	0.00
Perfluorodecanoic acid	PFDA	0	0%	0.00	0.00
Perfluoroundecanoic acid	PFUnDA	0	0%	0.00	0.00
Perfluorododecanoic acid	PFDoDA	0	0%	0.00	0.00
6:2 Fluorotelomer carboxylic acid	6:2 FTCA	0	0%	0.00	0.00
8:2 Fluorotelomer carboxylic acid	8:2 FTCA	0	0%	0.00	0.00
5:3 Fluorotelomer carboxylic acid	5:3 FTCA	0	0%	0.00	0.00
6:2 Fluorotelomer sulfonamido propyl betaine	6:2 FTAB	0	0%	0.00	0.00
Trifluoromethoxy propoxy propanoate	ADONA	0	0%	0.00	0.00
Hexafluoropropylene oxide dimer acid	GenX	0	0%	0.00	0.00
Perfluoropropane sulfonate	PFPrS	0	0%	0.00	0.00
Perfluorobutane sulfonate	PFBS	0	0%	0.00	0.00
Perfluoropentane sulfonate	PFPeS	0	0%	0.00	0.00
Perfluorohexane sulfonate	PFHxS	0	0%	0.00	0.00
Total (linear + branched) Perfluorohexane sulfonate	PFHxS total	0	0%	0.00	0.00
Perfluoroheptane sulfonate	PFHpS	0	0%	0.00	0.00
Perfluorooctane sulfonate	PFOS	0	0%	0.00	0.00

Total (linear + branched) Perfluorooctane sulfonate	PFOS total	0	0%	0.00	0.00
8-Chloroperfluoro-1- octanesulfonate	8CI-PFOS	0	0%	0.00	0.00
9-Chlorohexadecafluoro-3- oxanonane-1-sulfonate	9CI-F53B	0	0%	0.00	0.00
Perfluoroethylcyclohexane sulfonate	PFECHS	0	0%	0.00	0.00
Perfluorobutane sulfonamide	FBSA	0	0%	0.00	0.00
Perfluorohexane sulfonamide	FHxSA	0	0%	0.00	0.00
Perfluorooctane sulfonamide	FOSA	0	0%	0.00	0.00
N-ethyl-fluorooctane sulfonamidoacetic acid	N-EtFOSAA	0	0%	0.00	0.00
N-methyl-fluorooctane sulfonamidoacetic acid	N-MeFOSAA	0	0%	0.00	0.00
4:2-Fluorotelomer sulfonate	4:2 FTS	0	0%	0.00	0.00
6:2-Fluorotelomer sulfonate	6:2 FTS	0	0%	0.00	0.00
8:2-Fluorotelomer sulfonate	8:2 FTS	0	0%	0.00	0.00

#### Organochlorine pesticides (OCPs)

In total, 24 OCPs were accumulated in PDMS samplers over the deployment period (Table 2, Figures 3 and 4, Appendix 1), with the amount of  $\Sigma$ OCPs accumulated ranging from below reporting limits to 11215 ng PDMS<sup>-1</sup> (SEQ16 - Lockyer Creek @ Patrick's Estate).



Figure 3. Total mass of 23 ΣOCPs (ng PDMS<sup>-1</sup>) (excluding Dacthal) accumulated in PDMS passive samplers at each site.



Figure 4. Total mass of Dacthal (ng PDMS<sup>-1</sup>) accumulated in PDMS passive samplers at each site.

Discounting the sites below reporting limits, the conversion of  $\sum OCP$  masses accumulated in passive samplers to time-weighted average water concentrations revealed an estimated water concentration range of 0.008 to 230 ng L<sup>-1</sup> (SEQ23 - Herring Lagoon and SEQ16 - Lockyer Creek @ Patrick's Estate, respectively; Figures 5 and 6).



Figure 5. Total estimated water concentrations (ng  $L^{-1}$ ) of 23  $\Sigma$ OCPs (excluding Dacthal) at each site derived from PDMS passive samplers.



Figure 6. Total estimated water concentrations (ng  $L^{-1}$ ) of Dacthal 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 7, Appendix 1), with the amount of  $\Sigma$ PAHs accumulated ranging from below reporting limits to 175 ng PDMS<sup>-1</sup> (SEQ29 - Maroon Dam Wall).



Figure 7. Total mass of 9 ΣPAHs (ng PDMS<sup>-1</sup>) accumulated in PDMS passive samplers at each site.

Discounting the sites below reporting limits, the conversion of  $\Sigma$ PAH masses accumulated in passive samplers to time-weighted average water concentrations revealed an estimated water concentration range of 0.002 to 0.60 ng L<sup>-1</sup> (SEQ06 - South Maroochy Intake Weir and SEQ12 - Somerset Dam Wall, respectively; Figure 8).



Figure 8. Total estimated water concentrations (ng  $L^{-1}$ ) of 9  $\Sigma$ PAHs at each site derived from PDMS passive samplers.

# Pesticides

Over the deployment period, 33 polar pesticides (including herbicides, fungicides and insecticides) accumulated in ED passive samplers (Table 3, Figure 9, Appendix 1). The ∑polar pesticides accumulated ranged from below reporting limits (SEQ23 - Herring Lagoon; SEQ07 - Yabba Creek @ Jimna) to 4192 ng ED<sup>-1</sup> (SEQ16 - Lockyer Creek @ Patrick's Estate).



Figure 9. Total mass of 33 Σpolar pesticides (ng ED<sup>-1</sup>) 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 33 chemicals reported, 17 were converted to time-weighted average water  $\sum$  concentrations. Discounting the sites below reporting limits, these water concentrations ranged between 0.380 and 1573 ng L<sup>-1</sup> (SEQ43 - Enoggera Reservoir and SEQ16 - Lockyer Creek @ Patrick's Estate, respectively; Figure 10).



Figure 10. Total estimated water concentrations (ng  $L^{-1}$ ) of 17  $\Sigma$ polar pesticides at each site derived from ED passive samplers.

# Pharmaceuticals and personal care products (PPCPs)

In total, 6 PPCPs were reported (Table 3, Figure 11, Appendix 1) with the average amount of  $\Sigma$ PPCPs accumulated ranging from 7.52 ng ED<sup>-1</sup> (SEQ14 - Wivenhoe Dam Wall) to 608 ng ED<sup>-1</sup> (SEQ36 - Fernvale STP @ Savages Crossing).



Figure 11. Total mass of 6  $\Sigma$ PPCPs (ng ED<sup>-1</sup>) accumulated in ED passive samplers at each site.

Of the 6 reported PPCPs, 4 were able to be converted into estimated time-weighted average water concentrations. Discounting the sites below reporting limits, these  $\Sigma$ PPCP water concentrations ranged between 7.52 and 159 ng L<sup>-1</sup> (sites SEQ14 - Wivenhoe Dam Wall and SEQ09 - Ewen Maddock, respectively; Figure 12).



Figure 12. Total estimated water concentrations (ng  $L^{-1}$ ) of 4  $\Sigma$ PPCPs derived from ED passive samplers.

# Per- and Polyfluoroalkyl Substances (PFAS)

Across the deployment period, PFAS amounts were below reporting limits at all sites where MPT samplers were included except for perfluorobutanoic acid (PFBA) which had a reportable amount of 2.12 ng MPT<sup>-1</sup> (SEQ12 - Somerset Dam Wall) (Figure 13). This was converted into an estimated time-weighted average water concentration of 13.4 ng L<sup>-1</sup> (Figure 14).



Figure 13. Total mass of  $\Sigma$ PFAS (ng MPT<sup>-1</sup>) accumulated in MPT passive samplers at each site.



Figure 14. Total estimated water concentrations (ng  $L^{-1}$ ) of  $\Sigma$ PFAS derived from MPT 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 mass spectral libraries revealed tentative detection of 3 compounds (Table 5). 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.

Chemical Name	Description	Sites with tentative detects
Fenobucarb	Carbamate insecticide	SEQ15 : Lockyer Creek @ Lake Clarendon Way
	- moderately toxic	SEQ18 : Mt Crosby Westbank Offtake Tower
		SEQ24 : Leslie Harrison Dam
Mexacarbate	Veterinary antibiotic	SEQ02: Lake Macdonald Intake
	<ul> <li>toxic to algae</li> </ul>	SEQ05: Poona Dam
		SEQ08: Baroon Pocket Dam
		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
		SEQ20: North Pine VPS
		SEQ21: Lake Kurwongbah
		SEQ24: Leslie Harrison Dam
		SEQ25: Wyaralong Dam Wall
		SEQ26: Reynolds Creek @ Boonah
		SEQ27: Moogerah Dam
		SEQ29: Maroon Dam Wall
		SEQ31: Rathdowney Weir
		SEQ35: Hinze Lower Intake
		SEQ36: Fernvale STP @ Savages Crossing
		SEQ37: Logan River @ Cedar Grove
		SEQ39: Cooloolabin Dam
		SEQ40: Wivenhoe Dam @ Logans Inlet PRW
Phenethylamine	Central nervous system stimulant	SEQ12 : Somerset Dam Wall
	(can be naturally occurring)	SEQ21 : Lake Kurwongbah
		SEQ20 : North Pine VP

Table 5. List of tentatively identified non-target chemicals in EDs, and the sites in which they were detected.

# Analysis of ant bait chemicals

Along with the target list of polar and non-polar chemicals identified for investigation (ED and PDMS samplers, respectively), the screening for two ant-bait chemicals, Methoprene and Pyriproxyfen was performed to investigate their presence in water systems following their reported recent use during this campaign. Analytical standards were available and targeted analysis was performed on both ED

and PDMS samplers however detects were only identified in PDMS. While quantification was not possible, tentative identification was made where suspect spectra met strict criteria as established in QAEHS standard operating procedures for targeted analysis (Table 6).

<b>Chemical Name</b>	Description	Sites with tentative detects
Methoprene	Terpenoid insecticide - insect growth regulator	SEQ15 : Lockyer Creek @ Lake Clarendon Way SEQ36: Fernvale STP @ Savages Crossing
Pyriproxyfen	Pyridine-based insecticide	SEQ06 : South Maroochy Intake Weir SEQ16: Lockyer Creek @ Patrick's Estate SEQ29: Maroon Dam Wall SEQ36: Fernvale STP @ Savages Crossing

Table 6. List of tentatively identified ant-bait chemicals in PDMS, and the sites in which they were detected.

# Comparison to water quality guideline values

A selection of water guideline values and species protection values are provided in Table 7. 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.

ANZECC & ARMCANZ have set freshwater guideline chemical concentration values for 99% and 95% species protection levels. Exceedances of the 99% species protection level were observed in the estimated time-averaged water concentrations for atrazine, diazinon, metolachlor, tebuthiuron and chlorpyrifos with diazinon and metolachlor also observed to exceed the 95% species protection guideline.

Table 7. Threshold chemical guidelines for Australian Drinking Water and Freshwater Aquatic Ecosystems. Valueshighlighted in yellow exceed the 99% or 95% species protection guideline.

Australian Drinking Water Guidelines 6 (2011) Version 3.6 Updated December 2021		ANZECC & ARMCANZ (updated 2023) Default guideline values for freshwater		This campaign
Herbicides & Insecticides	Guideline value (ng L <sup>-1</sup> )	99% species protection value (ng L <sup>.</sup> 1)	95% species protection value (ng L <sup>-1</sup> )	Highest Reported Value (ng L <sup>-1</sup> )
Atrazine	20000	700	13000	728
Ametryn	70000	N/A	N/A	N/A
Bromacil	400000	N/A	N/A	3.0
Bromoxynil	10000	N/A	N/A	N/A
Carbaryl	30000	N/A	N/A	N/A
Carbendazim	90000	N/A	N/A	12.1
Cypermethrin	200000	N/A	N/A	N/A
Diazinon	4000	0.03	10	31.6
Diuron	20000	N/A	N/A	6.4
Fipronil	700	13	18	6.18
Fluometuron	70000	N/A	N/A	N/A
Haloxyfop	1000	N/A	N/A	5.58
Hexazinone	400000	N/A	N/A	3.23
Imazapyr	9000000	N/A	N/A	N/A
МСРА	40000	N/A	N/A	4.99
Malathion	70000	2	50	N/A
Methomyl	20000	500	3500	N/A
Metolachlor (S+R)	300000	8.4	460	776

Metribuzin	70000	N/A	N/A	N/A			
Metsulfuron	40000	3.7	18	N/A			
methyl	400000	NI / A	NI/A	N/A			
	400000	N/A	N/A	N/A			
Pendimethalin	40000	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	12.6			
Tebuthiuron	N/A	20	2200	63.7			
Terbuthylazine	10000	N/A	N/A	2.72			
Triclopyr	20000	N/A	N/A	24.0			
2,4-D	30000	140000	280000	10.7			
2,4,5-T	100000	3000	36000	N/A			
3,4-	N/A	1200	2000	N/A			
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	6.73			
Cypermethrin	200000	N/A	N/A	0.028			
DDT	9000	6	10	0.253			
Dieldrin	300	N/A	N/A	0.275			
Aldrin	300	N/A	N/A	N/A			
Endosulfan	20000	30	200	2.14			
Endrin	N/A	10	20	0.008			
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	N/A			
Benzo[a]pyrene	10	100	200	0.003			
Fluoranthene	N/A	1000	1400	0.361			
Naphthalene	10	2500	16000	N/A			
Phenanthrene	N/A	600	2000	N/A			
PFAS							
PFOA	560	N/A	N/A	N/A			
PFOS + PFHxS	70	N/A	N/A	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 shown a 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 (97%), the concentrations were low (total  $\mathcal{F}$ OCPs <230 ng L<sup>-1</sup>). 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. Dieldrin was the most frequently detected OCP, reported at 33 sites (92% of sites) and Chlorpyrifos was the second most frequent at 31 sites (86% of sites). Dieldrin 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 and was the OCP observed at the highest concentration in this campaign (SEQ16 - Lockyer Creek @ Patrick's Estate; 220 ng L<sup>-1</sup>). This is an increase compared with levels found at this site in the two prior campaigns, which reported Dacthal values for this site at 1.06 and 6.79 ng  $L^{-1}$  in the summer 2023 and winter 2023 campaigns, respectively (Shiels and Kaserzon, 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). 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 stormwater 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 35 of the 36 sites (97% detection frequency). Chrysene/Triphenylene was the most frequently detected PAH (92% detection) although this was at low levels, with a maximum concentration of 0.021 ng/L 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 30 sites; 83%) and Diuron and Terbuthylazine desethyl (detected at 28 sites; 78%) which are 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) and can often 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 (100% of sites) which can often be attributed

to background contamination due to requirements of field staff to use insect repellent products in the field that contain DEET. The second most frequently reported PPCP was Carbamazepine (detected at 22% of sites). The resistance 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 that are used for human recreational activities, or that receive some degree of treated effluent.

Per- and polyfluoroalkyl substances (PFAS) have been in use since the 1950s as components of Aqueous Film-forming Foams (AFFF) in firefighting products as well as in a range of consumer products such as non-stick pans, textiles and fabrics, food packaging materials, finishing products and personal use products (Xiao et al. 2017, Dewapriya et al. 2023). Although PFAS are not manufactured in Australia, their use in a wide variety of products, as well as their persistence in the environment has led to concerns about their presence in waterways (Ackerman Grunfeld et al., 2024). During this monitoring period, of the 35 target PFAS analytes, only the presence of PFBA was detected at levels above reporting limits at site SEQ24 (Somerset Dam Wall). The previous PFAS monitoring campaign conducted in summer 2018 showed a total of 12 PFAS detected across 34 out of 37 sites (Kaserzon et al., 2018) with most detections close to the analytical limit of reporting. The lower detection rates of PFAS observed in this current campaign could be attributed to differences in sample matrix and analytical LOQs between the two monitoring periods. In both campaigns detections were in the low parts per trillion concentration range and close to the analytical limits of reporting. Three PFAS (PFOS, PFHxS and PFOA) are currently regulated in Australia. The ADWG's are 560 ng L<sup>-1</sup> for PFOA and 70 ng  $L^{-1}$  for PFOS and PFHxS combined, and the NHMRC guidelines for recreational water are 10  $\mu$ g  $L^{-1}$  for PFOA and 2 µg L<sup>-1</sup> for PFOS and PFHxS combined (NHMRC, 2019). None of the regulated PFAS were detected above the limits of reporting (i.e., 3.4 to 4.8 ng L<sup>-1</sup>) in any of the sites sampled.

# **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

Ackerman Grunfeld, D., Gilbert, D., Hou, J., Jones, A. M., Lee, M. J., Kibbey, T. C. G., & O'Carroll, D. M. (2024). Underestimated burden of per- and polyfluoroalkyl substances in global surface waters and groundwaters. Nature Geoscience, 17(4), 340-346. https://doi.org/10.1038/s41561-024-01402-8

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.

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.

Dewapriya, P., Chadwick, L., Gorji, S. G., Schulze, B., Valsecchi, S., Samanipour, S., Thomas, K. V., & Kaserzon, S. L. (2023). Per- and polyfluoroalkyl substances (PFAS) in consumer products: Current knowledge and research gaps. Journal of Hazardous Materials Letters, 4, 100086. https://doi.org/https://doi.org/10.1016/j.hazl.2023.100086

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., 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., 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.

Kaserzon, S., Vijayasarathy, S., Bräunig, J., Mueller, L., Hawker, D.W., Thomas, K.V., Mueller, J.F. (2019). Calibration and validation of a novel passive sampling device for the time integrative

monitoring of per- and polyfluoroalkyl substances (PFASs) and precursors in contaminated groundwater. Journal of Hazardous Materials 366: 423-431.

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.

Mackie, R., Hawker, D.W., Ghorbani Gorji, S., Booij, K., Qu, X., Bowles, K., Shea, S., Higgins, C.P., Kaserzon, S., (2024). Application of a microporous polyethylene tube passive sampler for monitoring per- and polyfluoroalkyl substances in wastewater influent and effluent. ACS - ES & T Water, 4 (5), 2281-2291.

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.

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

NHMRC (2019). Guidance on Per and Polyfluoroalkyl (PFAS) in Recreational Water, National Health and Medical Research Council, Canberra.

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. (2023). Catchment and Drinking Water Quality Micro Pollutant Monitoring program – Passive Sampling. Report 19 – Winter 2023, prepared for Seqwater, December 2023.

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.

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.

Xiao, F. (2017). Emerging poly- and perfluoroalkyl substances in the aquatic environment: A review of current literature. Water Research 124: 482-495.

# Appendix 1

See enclosed excel file 'SEQW24\_Client\_Report FINAL\_combined\_with UV.xlsx'

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