

Queensland Alliance for Environmental Health Sciences



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

Report 12 – Summer 2020

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#### Title

Catchment and Drinking Water Quality Micro Pollutant Monitoring program – Passive Sampling. Report 12 – Summer 2020.

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### **Executive Summary**

The Catchment and Drinking Water Quality Micro Pollutant Monitoring Program was launched in mid-2014 with the aim of improving the characterisation and understanding of the micro pollutant risk profile in source water reservoirs through 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 2020. These sampling events represent the twelfth such campaign and the final one in a 6-year monitoring study (encompassing seasonal winter/summer sampling from 2014 – 2020). Results presented provide a continued insight into the water quality of the target catchments and drinking water reservoirs. The staggered deployment times in this report were due to challenging weather conditions, logistical issues, and possibly in part to the movement restrictions raised in response to the COVID-19 pandemic.

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 detected 85 different chemicals including 22 OCPs, 10 PAHs, 37 herbicides and insecticides and 16 PPCPs. OCPs were detected at 35 out of 36 sampled sites (97% detection), with pp-DDD, pp-DDE, dieldrin and endosulfan sulfate the most frequently detected, and chlorpyrifos showing the highest individual concentration. Total  $\sum$ OCP water concentrations across sites ranged between 0.018 - 2.73 ng L<sup>-1</sup>. PAHs were detected at 34 out of 36 sampled sites (94%), with chrysene, benzo[b,j,k]fluoranthene and benzo[e]pyrene at the highest abundance across all sites. Total  $\sum$ PAH water concentrations across sites ranged between 0.006 - 2.26 ng L<sup>-1</sup>. Thirty-seven different herbicides/insecticides were detected, with at least one compound detected at every site. Fifteen of the 37 compounds detected were present in over 50% of sites sampled. The most frequently detected compounds were diuron (97%), metsulfuron-methyl (89%) and metolachlor and desisopropyl-atrazine (both at 86%). The highest single concentration was observed for atrazine at 21.9 ng L<sup>-1</sup>. Total  $\sum$  herbicides/insecticides ranged between 0.29 - 45.9 ng L<sup>-1</sup>. Sixteen PPCPs were detected across sites with highest detection frequencies observed for DEET (47%), carbamazepine (44%) and hydroxycotinine (36%). Total estimated  $\sum$ PPCP water concentrations ranged between 0.02 - 59.1 ng L<sup>-1</sup> 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 and diazinon were consistently 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 six year period (2014 – 2020; 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 not only analytical challenges, but further challenges in obtaining appropriate and representative samples. Grab samples may not offer enough volume to allow sufficient concentration factors for detection of micro pollutants. Grab samples may also miss episodic contamination events, comprised as they are, of water representing 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. Some of the benefits of passive sampling tools include; *in-situ* concentration of chemical pollutants, increased sensitivity and 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.

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 twelfth monitoring campaign.

### Methodology

Passive water samplers were deployed in periods between January 2020 to April 2020 at 36 sites of SEQ reservoirs/waterways (Table 1). Most deployments were for periods of between 27 and 33 days. Some sites, like Little Nerang Dam (SEQ33), were affected by flood or other events and could not be retrieved on schedule. At other sites, such as Lowood intake & Canungra Creek (SEQ17 & SEQ32), samplers were lost, unable to be retrieved, or were compromised by periods taken out of the water. In instances where sample integrity was in doubt, only the replacement samplers were processed for reporting. Replicate samplers were deployed at six randomly selected sites (Table 1, highlighted in green), and supplemented with further replicates where replacements were required (Table 1, highlighted in orange).

All sampling and laboratory analysis for this report was undertaken during the global COVID-19 pandemic, and as such staffing levels and access to sites and laboratory facilities were disrupted. This contributed to the staggered sampling periods rather than a single synchronised deployment and some delays returning samples to QAEHS for analysis. The deployment of samplers was conducted in alignment with the "Drinking and Catchment Water Quality Micro Pollutant Passive Sampling Procedure" (27 May 2014). Table 1 below lists the deployment site locations, site numbers, site codes, dates and lengths of deployment periods, as well as the water velocity (cm s<sup>-1</sup>) 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) SEQ22 (North Pine River at Petrie Offtake)

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Table I Deblovment locations date	S IPNATAS AT APNIAVMPAT	nerina ana water velocit	v mensuren at ench site
Tuble 1. Deployment locations, date	, icingtino of acproyincine	period and water verocit	y measured at each site.

Site#	Site code	Site Name	Date Deployed	Date Retrieved	Days Deployed	Flow velocity (cm/s)	Comments
SEQ01	MRS-SP012	SEQ-MARY RIVER @ COLES CROSSING	20/02/2020	20/03/2020	29	4.53	Replicate samplers deployed
SEQ02	LMD-SP001	SEQ-LAKE MACDONALD INTAKE	10/03/2020	7/04/2020	28	5.51	
SEQ04	MRS-SP013	SEQ-MARY RIVER @ KENILWORTH	20/02/2020	20/03/2020	29	17.5	
SEQ05	POD-SP001	SEQ-POONA DAM	4/02/2020	3/03/2020	28	4.70	
SEQ06	SOR-SP001	SEQ-SOUTH MAROOCHY INTAKE WEIR	4/02/2020	3/03/2020	28	4.70	
SEQ07	YAC-SP001	SEQ-YABBA CREEK @ JIMNA WEIR	18/03/2020	15/04/2020	28	3.40	
SEQ08	BPD-SP001	SEQ-BAROON POCKET DAM	18/02/2020	18/03/2020	29	7.18	
SEQ09	EMD-SP001	SEQ-EWEN MADDOCK INTAKE	5/03/2020	2/04/2020	28	8.23	
SEQ10	SOD-SP010	SEQ-KILCOY WTP OFFTAKE	16/01/2020	14/02/2020	29	4.82	
SEQ11	SOD-SP011	SEQ-KIRKLEAGH	16/01/2020	14/02/2020	29	8.32	
SEQ12	SOD-SP001	SEQ-SOMERSET DAM WALL	16/01/2020	14/02/2020	29	5.43	
SEQ13	WID-SP004	SEQ-WIVENHOE DAM @ ESK PROFILER	21/01/2020	18/02/2020	28	7.56	
SEQ14	WID-SP001	SEQ-WIVENHOE DAM WALL @ PROFILER	21/01/2020	18/02/2020	28	8.56	
SEQ17	MBR-SP016	SEQ-LOWOOD INTAKE	19/02/2020	18/03/2020	28	5.00	Original kit lost. Sampled with a replacement kit Duplicate PDMS samplers provided in replacement
SEQ18	MBR-SP001	SEQ-MID BRIS RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER	22/01/2020	19/02/2020	28	12.8	Replicate samplers deployed
SEQ19	NOD-SP091	SEQ-NORTH PINE RIVER @ DAYBORO WELL	28/01/2020	25/02/2020	28	7.15	Flooding moved sampling site by 15 m
SEQ20	NOD-SP001	SEQ-NORTH PINE VPS	17/01/2020	13/02/2020	27	5.71	
SEQ21	LAK-SP001	SEQ-LAKE KURWONGBAH	17/01/2020	17/02/2020	31	10.8	Replicate samplers deployed
SEQ23	NSC-SP001	SEQ-HERRING LAGOON	21/01/2020	18/02/2020	28	4.05	
SEQ24	LHD-SP005	SEQ-LESLIE HARRISON DAM	16/01/2020	13/02/2020	28	5.99	
SEQ25	WYD-SP001	SEQ-WYARALONG DAM WALL	8/01/2020	5/02/2020	28	6.70	
SEQ26	MOD-SP027	SEQ-REYNOLDS CREEK @ BOONAH	29/01/2020	26/02/2020	28	4.97	Replicate samplers deployed
SEQ27	MOD-SP002	SEQ-MOOGERAH DAM @ OFFTAKE	29/01/2020	26/02/2020	28	9.42	

SEQ28	LRS-SP017	SEQ-LOGAN RIVER @ KOORALBYN OFFTAKE	23/01/2020	20/02/2020	28	36.2	Samplers reported to have been out of water. Not replaced.
SEQ29	MAD-SP004	SEQ-MAROON DAM WALL @ OFFTAKE W2 BUOY	6/01/2020	3/02/2020	28	6.64	Partial biofouling of ED sampling disc observed on retrieval
SEQ30	LRS-SP013	SEQ-LOGAN RIVER @ HELEN ST	23/01/2020	25/02/2020	33	21.4	
SEQ31	LRS-SP016	SEQ-RATHDOWNEY WEIR	23/01/2020	25/02/2020	33	9.56	Replicate samplers deployed. ED replicate not deployed.
SEQ32	CAC-SP001	SEQ-CANUNGRA CREEK @ OFFTAKE	20/01/2020	17/02/2020	28	6.16	Original samplers had been out of water for >3 days. Replaced.
SEQ32r	CAC-SP001r	SEQ-CANUNGRA CREEK @ OFFTAKE	19/02/2020	18/03/2020	28	3.82	Replacements for above. Duplicate PDMS samplers provided in replacement kit
SEQ33	LND-SP014	SEQ-LITTLE NERANG DAM	15/01/2020	24/04/2020	100	3.40	Over-deployed, original samplers could not be retrieved due to limited access
							Replacement samplers
SEQ33r	LND- NR001.PAS	SEQ-LITTLE NERANG DAM	25/02/2020	24/03/2020	28	36.4	deployed in different location at site. Duplicate PDMS samplers provided in replacement kit
SEQ33r SEQ34	LND- NR001.PAS HID-SP001	SEQ-LITTLE NERANG DAM SEQ-HINZE DAM UPPER INTAKE	25/02/2020 15/01/2020	24/03/2020 12/02/2020	28 28	36.4 4.79	deployed in different location at site. Duplicate PDMS samplers provided in replacement kit
SEQ33r SEQ34 SEQ35	LND- NR001.PAS HID-SP001 HID-SP002	SEQ-LITTLE NERANG DAM SEQ-HINZE DAM UPPER INTAKE SEQ-HINZE DAM LOWER INTAKE	25/02/2020 15/01/2020 15/01/2020	24/03/2020 12/02/2020 12/02/2020	28 28 28	36.4 4.79 6.38	deployed in different location at site. Duplicate PDMS samplers provided in replacement kit
SEQ33r SEQ34 SEQ35 SEQ36	LND- NR001.PAS HID-SP001 HID-SP002 MBR-SP013	SEQ-LITTLE NERANG DAM   SEQ-HINZE DAM UPPER INTAKE   SEQ-HINZE DAM LOWER INTAKE   SEQ-HINZE DAM SEQ-HINZE DAM COMER INTAKE   SEQ-HINZE DAM SEQ-HINZE DAM COMER INTAKE   SEQ-HINZE DAM SEQ-HINZE DAM COMER INTAKE   SEQ-HINZE DAM SEQ-HINZE DAM SEQ-HINZE DAM SEQ-HINZE DAM SEQ-HINZE DAM SEQ-HINZE DAM SEQ	25/02/2020 15/01/2020 15/01/2020 22/01/2020	24/03/2020 12/02/2020 12/02/2020 19/02/2020	28 28 28 28 28	36.4 4.79 6.38 6.85	deployed in different location at site. Duplicate PDMS samplers provided in replacement kit
SEQ33r SEQ34 SEQ35 SEQ36 SEQ37	LND- NR001.PAS HID-SP001 HID-SP002 MBR-SP013 LRS-SP012	SEQ-LITTLE NERANG DAM   SEQ-HINZE DAM UPPER INTAKE   SEQ-HINZE DAM LOWER INTAKE   SEQ-DOWNSTREAM OF FERNVALE STP @ SAVAGES CRC   SEQ-LOGAN RIVER @CEDAR GROVE	25/02/2020 15/01/2020 15/01/2020 22/01/2020 5/03/2020	24/03/2020 12/02/2020 12/02/2020 19/02/2020 2/04/2020	28 28 28 28 28 28	36.4 4.79 6.38 6.85 4.34	deployed in different location at site. Duplicate PDMS samplers provided in replacement kit
SEQ33r SEQ34 SEQ35 SEQ36 SEQ37 SEQ38	LND- NR001.PAS HID-SP001 HID-SP002 MBR-SP013 LRS-SP012 WAD-SP001	SEQ-LITTLE NERANG DAM   SEQ-HINZE DAM UPPER INTAKE   SEQ-HINZE DAM LOWER INTAKE   SEQ-DOWNSTREAM OF FERNVALE STP @ SAVAGES CRC   SEQ-LOGAN RIVER @CEDAR GROVE   SEQ-WAPPA DAM	25/02/2020 15/01/2020 15/01/2020 22/01/2020 5/03/2020 4/02/2020	24/03/2020 12/02/2020 12/02/2020 19/02/2020 2/04/2020 3/03/2020	28 28 28 28 28 28 28 28	36.4 4.79 6.38 6.85 4.34 3.40	deployed in different location at site. Duplicate PDMS samplers provided in replacement kit
SEQ33r SEQ34 SEQ35 SEQ36 SEQ37 SEQ38 SEQ39	LND- NR001.PAS HID-SP001 HID-SP002 MBR-SP013 LRS-SP012 WAD-SP001 COD-SP001	SEQ-LITTLE NERANG DAM   SEQ-HINZE DAM UPPER INTAKE   SEQ-HINZE DAM LOWER INTAKE   SEQ-DOWNSTREAM OF FERNVALE STP @ SAVAGES CRC   SEQ-LOGAN RIVER @CEDAR GROVE   SEQ-WAPPA DAM   SEQ-COOLOOLABIN DAM   SEQ-COOLOOLABIN DAM	25/02/2020 15/01/2020 22/01/2020 5/03/2020 4/02/2020 5/03/2020	24/03/2020 12/02/2020 12/02/2020 19/02/2020 2/04/2020 3/03/2020 2/04/2020	28 28 28 28 28 28 28 28 28	36.4 4.79 6.38 6.85 4.34 3.40 3.74	deployed in different location at site. Duplicate PDMS samplers provided in replacement kit

**Note:-** Flow velocity of 3.4 cm s<sup>-1</sup> was used for calculation where the flow velocity falls below 3.4 cm s<sup>-1</sup>

Sites with replicate samplers deployed for QA/QC purposes are highlighted green.

Sites where the original sampling kit was replaced due to unforeseen circumstances are listed twice with the details of both the original (grey) and replacement samplers (orange) (where both were able to be retreived).

#### Passive sampler preparation and extraction

For this campaign, two types of passive samplers were deployed at each site. Empore Disk<sup>™</sup> (3M)(ED) samplers were deployed to detect the presence of polar organic pollutants such as herbicides, pharmaceuticals and personal care products (PPCPs). Polydimethylsiloxane (PDMS) strips in stainless steel cages were deployed to detect 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 (86 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 29 OCPs and 16 PAHs 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) have all been detailed in previously published reports (Kaserzon *et al.* 2017) and SOPs.

#### Data modelling and reporting of results

Passive sampling enables estimation of time-integrated water concentrations ( $C_w$ ) based on the amounts of chemicals accumulated in the sampler within a given exposure period (Vrana *et al.* 2005; Kot *et al.* 2000). The uptake of these chemicals into the sampler is initially linear but eventually reaches steady state whereby equilibrium of the concentration in the sampler and the concentration in the water is reached. The size and polarity of the contaminant and other environmental factors such as water flow, turbulence and temperature can affect the rate of uptake or sampling rate ( $R_s$ ) which is measured as volume of water sampled per day (L day<sup>-1</sup>). The duration of the deployment period is another critical factor determining whether time-integrated sampling or equilibrium phase sampling is occurring for a given analyte in a sampler. Equations 1 and 2 describe the estimation of water concentration based on linear or equilibrium phase sampling, respectively.

Equation 1. Estimation of water concentration based on linear phase sampling.

$$C_W = \frac{C_S x M_S}{R_S x t} = \frac{N_S}{R_S x t}$$

Equation 2. Estimation of water concentration based on equilibrium phase sampling.

$$C_W = \frac{C_S}{K_{SW}}$$

Where:

 $C_{\rm W}$  = the concentration of the compound in water (ng L<sup>-1</sup>)  $C_{\rm S}$  = the concentration of the compound in the sampler (ng g<sup>-1</sup>)  $M_{\rm S}$  = the mass of the sampler (g)  $N_{\rm S}$  = the amount of compound accumulated by the sampler (ng)  $R_{\rm S}$  = the sampling rate (L day<sup>-1</sup>) t = the time deployed (days)  $K_{\rm SW}$  = the sampler –water partition coefficient (L g<sup>-1</sup>)

Calibration data (such as sampling rates or sampler-water partition coefficients) obtained in laboratory or field studies were used to derive these concentration estimates. Together with the sampling rates derived from calibration data, deployment-specific PFM data are used to correct for site-specific effects of water flow velocity on the sampling rates of chemicals (O'Brien *et al.* 2009). For chemicals detected where no calibration data was available, results were reported as ng sampler<sup>-1</sup>. Methodologies used to calculate site-specific sampling rates during the deployment periods are fully described in Kaserzon *et al.* (2017).

#### Quality control and assurance (QC/QA) procedures

QAEHS laboratory procedures are performed by fully trained staff in accordance with established Standard Operating Procedures (SOPs) (Table 2). In order to ensure quality control and to prevent false positives, blank passive samplers were prepared, extracted and analysed in parallel with exposed samplers for each deployment period. Laboratory blanks (n = 5 each, PDMS & ED) were prepared before each deployment and were retained at QAEHS for the duration of the deployment. These samplers were included with each batch to provide insight into any contamination arising in the laboratory from preparation or extraction. Travel/field blank samplers (n = 2 each, PDMS & ED) were also prepared and transported to and from the field without deployment. These provide measures of contamination arising from the transport, storage and handling processes.

For chemicals detected in both blank and deployed samplers, the concentration in the exposed sample was only reported if it: a) exceed three times the standard deviation of the blanks plus the average sum of the blanks, or b) exceed three times the average blank concentration. Results were not subtracted for detections in blank samples. Any blank levels are reported in Appendix 1.

Despite being sent to 6 sites, replicate ED samplers were only deployed at 5 sites. Furthermore, due to a laboratory issue, only 4 were able to be analysed (a vial was inadvertently dropped during sample loading and broke on impact). These originated from sites SEQ01 (Mary River at Coles Crossing), SEQ18 (Brisbane River at Mt. Crosby), SEQ21 (Lake Kurwongbah) & SEQ26 (Reynold's Creek at Boonah). Replicate PDMS samplers were analysed from the same sites, including the fifth missed in the ED analysis, SEQ40 (Wivenhoe dam at Logan's inlet PRW). In addition, at several sites where replacement samplers were required, replicate PDMS were deployed. These included SEQ17 (Lowood intake), SEQ31 (Rathdowney Weir), SEQ32 (Canungra Creek at offtake), SEQ33 (Little Nerang Dam), and SEQ37 (Cedar Grove Weir), bringing the total replicates for PDMS samplers to n = 10.

For most analytes acceptable replicate values were obtained with relative percent differences (RPD) of < 30 %. In some cases, the compounds that occurred in blanks, such as DEET, caffeine, paraxanthine, were observed above the blank thresholds described above in one rather than both replicates.

Code	Description
NTX-A-003	GC-HRMS Method for Pesticide and PAH Analysis
NTX-A-004	Target and Non-target Polar Herbicides and PPCP Analysis by LC-ESI-QTOF-MS/MS
NTX-A-005	LC-MS/MS/QQQ method for herbicide and PPCP analysis
NTX-P-001	Extraction of PDMS from water
NTX-P-004	Preparation of Empore Disks (EDs)
NTX-P-005	Extraction of EDs
NTX-P-008	Pre-cleaning and preparation of PDMS samplers
NTX-P-009	Preparation of Flow Monitoring Devices (PFMs) for use with Water Passive Samplers
NTX-S-001	Deployment and Retrieval of Passive Samplers-Empore Disks, Sampling Cages, Passive
	Flow Monitors

Table 2. List of established standard operating procedures (SOPs) used in relation to this campaign.

### **Results**

#### **PFM results**

Two passive flow monitors (PFMs) were deployed at each sampling site with good agreement observed between duplicate PFMs for most sites (RPD 0 – 20%) with the exception of PFMs deployed at Mary River at Kenilworth (RPD 49%) and Poona Dam (RPD 38%) (Figure 2). Average flow velocities estimated from PFMs over the deployment period ranged between 2.9 cm s<sup>-1</sup> (SEQ38; Wappa Dam) to 36 cm s<sup>-1</sup> (SEQ33; Little Nerang Dam & SEQ28; Logan River @ Kooralbyn Offtake). Some sites were below the linearity loss rate range of the PFM (i.e. < 3.4 cm s<sup>-1</sup>; O'Brien *et al.* 2009) (Table 1, Figure 3).

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, in order 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 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).



Figure 2. Passive flow monitors (PFMs) loss rate (g per day) of duplicate PFMs per site.

Note: - Error bars are standard deviation derived from two co-deployed PFMs.



Figure 3. Passive flow monitor (PFM) based water flow rate estimations 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 detected at the sampling sites, the percent detection of each chemical and mass accumulation (ng sampler<sup>-1</sup>) is presented in Tables 3 and 4 below. Table 3 summarises the non-polar chemicals detected with PDMS (OCPs and PAHs). A total of 22 OCPs and 10 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% - 89% (for OCPs) and 3% - 94% (for PAHs). Table 4 summarises the polar chemicals detected with EDs (pesticides and PPCPs). A total of 37 pesticides (predominantly herbicides) and 16 PPCPs accumulated in samplers with percent detection at sampling from 3% - 97% (for pesticides) and 3% - 47% (for PPCPs).

Number of sites Min detect Max detect Analyte % Detection detected (n = 36) (ng PDMS<sup>-1</sup>) (ng PDMS<sup>-1</sup>) Organochlorine pesticides (OCPs) Aldrin 13 36% 0.14 0.42 Chlorpyrifos 6 78 170 17% cis-Chlordane (a) 12 33% 0.27 1.6 Dacthal 25 69% 1.1 36 o,p-DDD 2 6% 0.38 0.9 0.06 p,p-DDD 32 89% 10 5 0.09 o,p-DDE 14% 0.27 p,p-DDE 0.27 31 86% 14 o,p-DDT 8 22% 0.05 1.3 p,p-DDT 11 31% 0.29 12 Dieldrin 30 83% 3.1 11 Endosulfan sulfate 27 75% 0.07 1.7  $\alpha$ -Endosulfan 5 14% 0.29 1 β-Endosulfan 0.57 1 3% 0.71 Endrin 6 17% 0.07 0.49 Endrin ketone 4 11% 0.33 0.81 HCB 4 6.1 11 11% α-HCH 7 19% 0.06 0.99 β-ΗCΗ 1 3% 0.66 0.74 Heptachlor epoxide B 17 47% 0.61 9.6 PeCB 3 2 8% 2.9 9 25% trans-Chlordane (y) 0.9 2.9 Polycyclic aromatic hydrocarbons (PAHs) Acenaphthylene 1 3% 16 16 Benzo (a) anthrancene 21 58% 0.7 13 0.35 Benzo (a) pyrene 10 28% 2.4 Benzo (bjk) fluoranthene 29 81% 0.56 5.8 7 Benzo (e) pyrene 27 75% 0.89 39% 0.58 6.1 Benzo (g,h,i) perylene 14 Chrysene 34 94% 2 23 Fluoranthene 15 42% 16 140 Indeno (1,2,3-cd) pyrene 14 39% 0.35 3.7 13 Pyrene 36% 16 91

Table 3. 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>).

Analyte	Numbers of site detected (n = 36)	% Detection	Min detect (ng ED <sup>-1</sup> )	Max detect (ng ED <sup>-1</sup> )
	Herbicides and	d Insecticides		
2,4,5-T	1	3%	0.61	0.61
2,4-D	25	69%	0.3	7.4
3,4 Dichloro Aniline	14	39%	0.46	1.7
Ametryn/Atrazine-hydroxy	22	61%	0.10	4.0
Atrazine	34	94%	0.24	34
Bromacil	5	14%	0.68	16
DCPMU	7	19%	0.12	0.5
DCPU	3	8%	0.26	0.57
Desethyl Atrazine	23	64%	0.34	7.9
Desisopropyl Atrazine	31	86%	0.26	6.4
Diazinon	16	44%	0.09	6.6
Diketonitrile	15	42%	0.01	0.08
Diuron	35	97%	0.37	16
Fluazifop	1	3%	0.86	0.86
Flumeturon	1	3%	0.14	0.14
Haloxyfop	12	33%	0.21	3.3
Hexazinone	22	61%	0.14	22
Imidacloprid	14	39%	0.43	7.6
МСРА	11	31%	0.41	13
Metalaxyl	29	81%	0.02	4.1
Methomyl	3	8%	0.02	1.8
Metolachlor	31	86%	0.18	28
Metribuzin	1	3%	1.5	1.5
Metsulfuron-Methyl	32	89%	0.46	15
Picloram	6	17%	0.24	0.7
Prometryn	3	8%	0.05	5
Propazine	6	17%	0.23	0.42
Propiconazole	19	53%	0.05	1.9
Propoxur	5	14%	0.19	0.6
Pyrimethanil	1	3%	0.04	0.04
Simazine	23	64%	0.37	23
Simazine-hydroxy	14	39%	0.11	1.6
Tebuconazole	22	61%	0.04	0.48
Tebuthiuron	26	72%	0.06	15
Terbuthylazine	7	19%	0.22	0.7
Terbuthylazine des ethyl	15	42%	0.02	2.2
Triclopyr	21	58%	0.24	14
Pharmaceut	icals and perso	nal care products (PPCP	rs)	
Acesulfame	3	8%	0.15	0.18
Atorvastatin	2	6%	0.46	0.67
Caffeine*	1	3%	43	43

Table 4. 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  $ED^{-1}$ ).

Carbamazepine	16	44%	0.1	6.8
Citalopram	1	3%	0.11	0.11
Codeine	3	8%	0.89	6.6
Cotinine	9	25%	0.27	4.1
DEET*	17	47%	7.4	113
desmethyl-citalopram	1	3%	0.07	0.07
Fluoxetine	3	8%	1.5	7.1
Hydrochlorothiazide	1	3%	0.89	0.89
Hydroxycotinine	12	33%	0.48	1.2
Ibuprofen	1	3%	0.23	0.23
Nicotine	7	19%	3.2	7
Paracetamol	3	8%	0.27	0.5
Temazepam	4	11%	0.16	1.9

\*Caffeine and DEET were detected consistently in the blanks, and taking a threshold of 3 times the average blank, values below 25 and 9 ng sampler<sup>-1</sup> were ignored. The frequency of detection does not include these samples

#### Organochlorine pesticides (OCPs)

In total, 22 OCPs were accumulated in PDMS samplers over the deployment period (Table 3, Figure 4, Appendix 1), with the amount of ∑OCPs accumulated ranging from below detection to 198 ng PDMS<sup>-1</sup> for sites SEQ05 (Poona Dam) and SEQ26 (Reynolds Creek at Boonah), respectively. The lowest measurable site was SEQ23 (Herring Lagoon) with 0.17 ng PDMS<sup>-1</sup> arising solely from endosulfan sulfate. The highest frequency of detection was observed for pp-DDD (89%) followed by pp-DDE (86%), dieldrin (83%) and endosulfan sulfate (75%).



Figure 4. Total mass of 22 ΣOCPs (ng PDMS<sup>-1</sup>) accumulated in PDMS passive samplers at each site.

The conversion of OCP masses accumulated in passive samplers to time averaged water concentrations revealed an estimated water concentration range of  $\Sigma$ OCPs 0.0178 – 2.73 ng L<sup>-1</sup> (sites SEQ23 (Herring Lagoon) and SEQ26 (Reynolds Creek @ Boonah), lowest and highest respectively). The second highest water concentration was found at SEQ09 (Ewen Maddock intake) at 2.59 ng L<sup>-1</sup> (Figure 5).



Figure 5. Total estimated water concentrations (ng L<sup>-1</sup>) of 22 ΣOCPs at each site derived from PDMS passive samplers.

#### Polycyclic aromatic hydrocarbons (PAHs)

In total, 10 PAHs were accumulated in PDMS samplers with amounts of  $\Sigma$ PAHs ranging from below detection at SEQ05 & 07 (Poona Dam and Yabba Creek), up to 285 ng PDMS<sup>-1</sup> at SEQ12 (Somerset Dam wall) (Table 3, Figure 6 and Appendix 1). The site with the lowest detectable  $\Sigma$ PAHs was SEQ34 (Hinze Dam upper intake) with 2.4 ng PDMS<sup>-1</sup> arising solely from chrysene. The highest frequency of detection was observed for chrysene (94%) followed by benzo[b,j,k]fluoranthene (81%), and benzo[e]pyrene (81%).



Figure 6. Total mass of  $10 \Sigma PAHs$  (ng PDMS<sup>-1</sup>) accumulated in PDMS passive samplers at each site.

Converted to average water concentrations the  $\Sigma$ PAHs ranged between 0.006 – 2.26 ng L<sup>-1</sup> (Figure 7), with lowest and highest concentrations at SEQ08 (Baroon Pocket Dam) and for SEQ12 (Somerset Dam wall), respectively.



Figure 7. Total estimated water concentrations (ng L<sup>-1</sup>) of 10 ΣPAHs at each site derived from PDMS passive samplers.

#### Herbicides and insecticides

Over the deployment period, 37 herbicides and insecticides accumulated in ED passive samplers (Table 4, Figure 8, Appendix 1), with at least one compound detected at every site. The amount of  $\sum$  polar pesticides accumulated ranged between 1.16 - 111 ng ED<sup>-1</sup> for sites SEQ04 (Mary River at Kenilworth) and SEQ28 (Logan River at Kooralbyn offtake), respectively. The highest frequency of detection was observed for diuron (97%), metsulfuron-methyl (89%) and metolachlor and desisopropyl-atrazine, both at 86%. 15 compounds in total were detected at over 50% of sites sampled.



Figure 8. Total mass of 37  $\Sigma$  polar 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 37 chemicals detected, 17 were converted to time integrated average water  $\sum$  concentrations. These ranged between 0.29 – 45.9 ng L<sup>-1</sup> for sites SEQ23 (Herring Lagoon) and SEQ10 (Kilcoy WTP offtake), respectively (Figure 9).



Figure 9. 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)

Sixteen PPCPs were detected with the average amount of  $\Sigma$ PPCPs accumulated ranging between below detection (SEQ38, 05 & 04; Wappa Dam, Poona Dam and Mary River at Kenilworth) up to 169 ng ED<sup>-1</sup> at site SEQ36 (Downstream of Fernvale STP @ Savages CRC), respectively (Figure 10) (Appendix 1). Unsurprisingly, the widest variety of PPCPs were detected downstream from the Fernvale water treatment facility. The highest frequency of detection was observed for DEET (47%), carbamazepine (44%) and hydroxycotinine (36%).

DEET and caffeine were common contaminants in the blank samplers, however for most sites DEET was detected in the samplers above the thresholds imposed by taking laboratory and field blanks into account. Realistically for each site a portion of this measured concentration is likely from the sources of DEET which impact the blanks. For caffeine only a single sample was greater than the blank thresholds. This gives a slightly misleading impression that a single site (SEQ36, downstream of Fernvale STP) is contaminated with a relatively high concentration, and there are total absences elsewhere. In fact, the more likely scenario is that there is a degree of environmental contamination at several sites, as well as fluctuating contamination arising from the everyday use of caffeinated products, and the handling of samplers in both the laboratory and the field.



Figure 10. Total mass of 16  $\Sigma$ PPCPs (ng ED<sup>-1</sup>) accumulated in ED passive samplers at each site.

Of the 16 detected PPCPs, five were able to be converted into estimated time-averaged water concentrations. Discounting the sites below detection, these  $\sum$ PPCP water concentrations ranged between 0.02 – 59.1 ng L<sup>-1</sup> for site SEQ40 (Wivenhoe Dam at Logan's Inlet PRW) and site SEQ36 (Downstream of Fernvale STP @ Savages CRC), respectively (Figure 11).



Figure 11. Total estimated water concentrations (ng  $L^{-1}$ ) of 5  $\Sigma$ PPCPs.

#### 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 chompounds of interest were detected, however a larger screening through additional pesticide, pharmaceutical and personal care product libraries revealed tentative detection of four compounds (Table 5). 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.

Chemical Name	Description	Sites with Tentative detects
		WIVENHOE DAM WALL @ PROFILER (SEQ14),
Mepiquat	plant growth regulator	HERRING LAGOON (SEQ23).
		KIRKLEAGH (SEQ11), SOMERSET DAM WALL (SEQ12),
		WIVENHOE DAM @ ESK PROFILER (SEQ13), MID BRIS
		RIVER @ MT CROSBY WESTBANK OFFTAKE TOWER
		(SEQ18), REYNOLDS CREEK @ BOONAH (SEQ26;
		SEQ26_Duplicate), MAROON DAM WALL @ OFFTAKE
Methcathinone	psychoactive stimulant	W2 BUOY (SEQ29)
		REYNOLDS CREEK @ BOONAH (SEQ6), MID BRIS RIVER
		@ MT CROSBY WESTBANK OFFTAKE TOWER (SEQ18),
		LAKE KURWONGBAH (SEQ21; SEQ21_Duplicate),
		LESLIE HARRISON DAM (SEQ24), MOOGERAH DAM @
	non-opioid central acting	OFFTAKE (SEQ27), LOGAN RIVER @ HELEN ST (SEQ30),
Pentoxyverine	antitussive with antimuscarinic	WAPPA DAM (SEQ38).
		LOGAN RIVER @ KOORALBYN OFFTAKE (SEQ28),
Nalbuphine	opioid analgesic	HINZE DAM UPPER INTAKE (SEQ34).

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

Tentative identifications are considered when spectral library match scores exceed >80%.

#### Comparison to water quality guideline values

A selection of water guideline values and species protection values are provided in Table 6. No compounds with an available Australian drinking water guideline (ADWG) value were detected with estimated average concentrations above the ADWG value. This analysis is somewhat limited in that not all detected compounds were able to be converted to a water concentration. However, given the levels observed, and the comparisons that were able to be made, it is highly 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 for two compounds, chlorpyrifos and diazinon. ANZECC & ANCANZ have set chlorpyrifos freshwater guideline values of 0.04 and 10 ng L<sup>-1</sup> for 99% and 95% level species protection, respectively. Six sites (ranging between 1.1 (SEQ28) – 2.4 ng L<sup>-1</sup> (SEQ09)) exceeded the 99% species protection guideline. No sites exceeded the 95% species protection guideline values. For diazinon, all 16 sites where it was detected, had estimated time averaged water concentrations exceeding the 99% level species protection value of 0.03 ng L<sup>-1</sup>. The concentrations at these sites ranged from 0.08 ng L<sup>-1</sup> to 3.02 ng L<sup>-1</sup> (SEQ14 & 30 – Wivenhoe Dam wall & Logan River at Helen Street, lowest and highest respectively). As with chlorpyrifos, diazinon did not exceed the 95% species protection level at any site.

	ANZECC & ANCANZ (2018)			
Australian Drinking Wat	Trigger values	This campaign		
Version 3.5 Updated August 2018 (ng L <sup>-1</sup> )		99% species	95% species	Highest
		protection value	protection value	Detected Value
		(ng L⁻¹)	(ng L <sup>-1</sup> )	(ng L <sup>-1</sup> )
Herbicides & Insecticides				
Atrazine	20000	700	13000	34
Ametryn	70000	N/A	N/A	N/A
Bromacil	400000	N/A	N/A	5.6
Carbaryl	30000	N/A	N/A	N/A
Carbendazim	90000	N/A	N/A	N/A
Carbofuran	10000	60	1200	N/A
Diazinon	4000	0.03	10	3.0
Dicamba	100000	N/A	N/A	N/A
Dichlorvos	5000	N/A	N/A	N/A
Diuron	20000	N/A	N/A	18
Fenamiphos	500	N/A	N/A	N/A
Fluometuron	70000	N/A	N/A	N/A
Haloxyfop	1000	N/A	N/A	1.0
Hexazinone	400000	N/A	N/A	9.0
MCPA	40000	N/A	N/A	4.1
Methiocarb	7000	N/A	N/A	N/A
Malathion	700000	2	50	N/A
Mathomyl	20000	N/A	N/A	N/A
Metolachlor	300000	N/A	N/A	9.8
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	14
Tebuthiuron	N/A	20	2200	8.9
Terbuthylazine	10000	N/A	N/A	N/A

Table 6. Threshold chemical guidelines for Australian Drinking Water and Freshwater Aquatic Ecosystems

Terbutryn	400000	N/A	N/A	N/A
Triclopyr	20000	N/A	N/A	2.4
2,4-D	30000	140000	280000	10.5
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	2.4
DDT	9000	6	10	0.019
Dieldrin and Aldrin	300	N/A	N/A	0.093
Endosulfan	20000	30	200	N/A
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 detected at almost all monitoring sites, the concentrations were very low. The legacy compounds (those now banned) such as endosulfan and DDT, were detected consistently, but at levels typically  $< 0.1 \text{ ng } L^{-1}$ , consistent with residual amounts still present after years of usage. Compounds still in use such as dacthal and chlorpyrifos were detected at higher concentrations, consistent with ongoing inputs to the environment. Dacthal is currently permitted for the use of controlling stinging nettle in lettuce crops (APVMA 2016) and may be in use close to these sites. The insecticide 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 both dacthal and chlorpyrifos is warranted to estimate any future risk.

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. Thirty-four sites showed reportable concentrations of PAHs including chrysene, benzo[b,j,k]fluoranthene, benzo[e] pyrene and indeno[1,2,3-cd] pyrene, at low levels (< 3 ng L<sup>-1</sup>). The increase in the frequency of PAHs detected this campaign compared to report 11 may be due to a combination of increased rainfall and subsequent runoff in summer, and at sites like Somerset Dam, increased recreational boating activities.

Herbicides were detected at every sampling site with total concentrations of  $\Sigma$ herbicides < 50 ng L<sup>-1</sup>. The most frequently detected herbicide diuron is used in sugarcane and other farming as a broad spectrum pre- and early post-emergent control for various grass and broadleaf weeds. It can be used in conjunction with atrazine and hexazinone, two herbicides also frequently detected at relatively high levels. 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 higher than average rainfall in January and February 2020 (BOM 2020 & 2020a), which may explain the increase in detections from Report 11. This increase may also be due to the seasonal nature of agriculture and pesticide applications. Triazine herbicides such as atrazine, simazine and hexazinone 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).

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). PPCPs that could be converted to water concentrations were found at 75% of sites with total

concentrations <60 ng L<sup>-1</sup>. The most frequently detected PPCP was DEET which is often attributed to background contamination due to high DEET application by field staff, to combat insect bites. If detection of DEET is ignored, then the frequency of detection drops to 47% of sites with measurable PPCP water concentrations. Of these, the primary contributor is carbamazepine, detected at 16 sites (44%) and the sole PPCP at 13 of these. 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). Site SEQ36, located downstream of a STP, had  $\sum$ PPCP concentrations four times higher than any other site, and provided detectable levels of seven PPCPs. 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. However, the low level and amount of compounds detected do not in themselves warrant any current concern.

### **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.
- Sampling devices should be placed strategically at high rainfall sites to better measure and account for any higher water flow velocities and increased runoff activity.
- 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 <u>AUGUST 2018</u>. 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 January 2020: second-warmest January on record; wet in the north.

url: <u>http://www.bom.gov.au/climate/current/month/qld/archive/202001.summary.shtml</u>. Accessed 20/06/2020. Australian Government

BOM (Bureau of Meteorology) (2020a). Web page: Australia in February 2020. url: <u>http://www.bom.gov.au/climate/current/month/aus/archive/202002.summary.shtml</u>. Accessed 20/06/2020. 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 'SEQW results\_Summer2020.xls'

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