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Queensland Alliance for
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# Catchment and Drinking Water Quality Micro Pollutant Monitoring Program – Passive Sampling

## Report 18 – Summer 2023

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**Title**
Catchment and Drinking Water Quality Micro Pollutant Monitoring program – Passive Sampling.
Report 18 – Summer 2023.

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# Executive Summary

The *Catchment and Drinking Water Quality Micro Pollutant Monitoring Program* was launched in mid-2014 with the aim of improving the characterisation and understanding of the micro pollutant risk profile in source water reservoirs through bi-annual summer and winter sampling campaigns. The monitoring program utilising passive samplers was continued in reservoirs in South East Queensland (SEQ) during the first quarter of 2023. Results presented provide a continued insight into the water quality of the target catchments and drinking water reservoirs. While deployment dates in this report are consistent, at some sites, multiple samplers required redeployment due to unforeseen events resulting in samplers being compromised.

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

Chemical analyses of the passive sampler extracts reported 72 different chemicals including 18 OCPs, 14 PAHs, 31 polar pesticides and 9 PPCPs. OCPs were detected at 100% of sites, with trans-Chlordane (95%) and Dieldrin (87%) the most frequently reported. Total ∑OCP water concentrations across sites ranged between 0.005 – 5.95 ng $L^{-1}$ where concentrations were reportable. PAHs were detected at 100% of sites, with Chrysene/Triphenylene (97%) and Fluoranthene (95%) reported at the highest abundance across all sites. Total ∑PAH water concentrations across sites ranged between 0.005 – 3.35 ng $L^{-1}$. In total, 31 different polar pesticides were reported in 37 sites (97%), with Terbuthylazine desethyl (87%) and Atrazine (87%) reported at highest abundance across all sites. Total ∑polar pesticides ranged between 0.340 – 412 ng $L^{-1}$. Additionally, 9 PPCPs were detected across sites with highest detection frequencies observed for DEET (100%) and Carbamazepine (16%). Total estimated ∑PPCP water concentrations ranged between 1.68 – 440 ng $L^{-1}$ across sites.

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

# Introduction

As the bulk supplier of drinking water to South East Queensland, Seqwater maintains a Catchment and Drinking Water Quality Micro Pollutant Monitoring Program to ensure safe and reliable supply of the region’s drinking water source reservoirs. The aim of this program is to identify and understand the presence of micro pollutants in the source water reservoirs as well as to recognise any spatial and temporal trends of micro pollutants. The first campaigns ran between 2014 and 2020 and an extension of the program has been introduced to extend the use of passive sampling technologies in the monitoring of source water reservoirs over the three-year period (2020 – 2023; summer and winter sampling campaigns). The recent campaign aims to continue to assess the risk from micro pollutants posed to drinking water quality as well as add to a longitudinal dataset to aid catchment management. Additional passive samplers may be deployed at sites when required during high rainfall or event periods.

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

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

# Methodology

Passive water samplers were deployed in periods between January and March 2023 at 38 sites of SEQ reservoirs/waterways (Table 1). Samplers from Site 30 were lost and no redeployment was made. Sites 2, 28 and 36 were redeployed due to either sampler loss or samplers being compromised. Due to PFM lids accidentally being left on for the sampler at site 29, water flow was estimated from previous campaigns. One of the replicate passive flow monitors (PFMs) was damaged at Site 31, therefore the water flow velocity at the site was calculated using the undamaged PFM data only.

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

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

In this campaign, the following sites were not sampled:

SEQ03 (Borumba Dam)

SEQ22 (North Pine River at Petrie Offtake)

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

| Site | Site Code | Date Deployed | Date Retrieved | Days Deployed | Flow Velocity (cm/s) | Comments |
|---|---|---|---|---|---|---|
| **SEQ01 : Mary River @ Coles X ing** | **MRS-SP012.PAS** | **10/01/2023** | **7/02/2023** | **28** | **4.8** | |
| **SEQ02 : Lake Macdonald Intake** | **LMD-SP001.PAS** | **3/03/2023** | **31/03/2023** | **28** | **8.4** | **ORIGINAL SAMPLER LOST - REDEPLOYED** |
| **SEQ04 : Mary River @ Kenilworth** | **MRS-SP013.PAS** | **13/01/2023** | **10/02/2023** | **28** | **8.2** | |
| **SEQ05 : Poona Dam** | **POD-SP001.PAS** | **17/01/2023** | **15/02/2023** | **29** | **4.9** | |
| **SEQ06 : South Maroochy Intake Weir** | **SOR-SP001.PAS** | **17/01/2023** | **15/02/2023** | **29** | **4.1** | |
| **SEQ07 : Yabba Creek @ Jimna** | **YAC-SP001.PAS** | **13/01/2023** | **10/02/2023** | **28** | **3.4** | |
| **SEQ08 : Baroon Pocket Dam** | **BPD-SP001.PAS** | **24/01/2023** | **28/02/2023** | **35** | **7** | |
| **SEQ09 : Ewen Maddock** | **EMD-SP001.PAS** | **4/01/2023** | **3/02/2023** | **30** | **5.6** | |
| **SEQ10 : Kilcoy WTP offtake** | **SOD-SP010.PAS** | **12/01/2023** | **14/02/2023** | **33** | **10** | |
| **SEQ11 : Kirkleagh** | **SOD-SP011.PAS** | **12/01/2023** | **14/02/2023** | **33** | **10.1** | |
| **SEQ12 : Somerset Dam Wall** | **SOD-SP001.PAS** | **12/01/2023** | **14/02/2023** | **33** | **6.7** | |
| **SEQ13 : Wivenhoe Dam @ Esk** | **WID-SP004.PAS** | **17/01/2023** | **17/02/2023** | **31** | **7.9** | |
| **SEQ14 : Wivenhoe Dam Wall** | **WID-SP001.PAS** | **17/01/2023** | **17/02/2023** | **31** | **25.6** | **EMPTY PFM** |
| **SEQ15 : Central Lockyer Creek @ Lake Clarendon Way** | **LOC-SP034.PAS** | **6/01/2023** | **2/02/2023** | **27** | **5.8** | |

| | | | | | | |
|---|---|---|---|---|---|---|
| **SEQ16 : Central Lockyer Creek @ O'Reilly's Weir** | **LOC-SP033.PAS** | **6/01/2023** | **3/02/2023** | **28** | **5.2** | |
| **SEQ17 : Lowood Intake** | **MBR-SP016.PAS** | **4/01/2023** | **31/01/2023** | **27** | **4.1** | |
| **SEQ18 : Mt Crosby Westbank Offtake Tower** | **MBR-SP001.PAS** | **4/01/2023** | **31/01/2023** | **27** | **8.3** | |
| **SEQ19 : North Pine River @ Dayboro Well** | **NOD-SP091.PAS** | **17/01/2023** | **21/02/2023** | **35** | **3.9** | |
| **SEQ20 : North Pine VPS** | **NOD-SP001.PAS** | **17/01/2023** | **21/02/2023** | **35** | **5.7** | |
| **SEQ21 : Lake Kurwongbah** | **LAK-SP001.PAS** | **18/01/2023** | **22/02/2023** | **35** | **8.4** | |
| **SEQ23 : Herring Lagoon** | **NSC-SP001.PAS** | **17/01/2023** | **21/02/2023** | **35** | **3.6** | |
| **SEQ24 : Leslie Harrison Dam** | **LHD-SP005.PAS** | **19/01/2023** | **22/02/2023** | **34** | **6.7** | |
| **SEQ25 : Wyaralong Dam Wall** | **WYD-SP001.PAS** | **5/01/2023** | **7/02/2023** | **33** | **6.4** | |
| **SEQ26 : Reynolds Creek @ Boonah** | **MOD-SP027.PAS** | **18/01/2023** | **21/02/2023** | **34** | **4.2** | |
| **SEQ27 : Moogerah Dam** | **MOD-SP002.PAS** | **18/01/2023** | **21/02/2023** | **34** | **10.9** | |
| **SEQ28 : Logan River @ Kooralbyn Offtake** | **LRS-SP017.PAS** | **1/02/2023** | **1/03/2023** | **28** | **16.8** | **ORIGINAL SAMPLER LOST - REDEPLOYED** |
| **SEQ29 : Maroon Dam Wall** | **MAD-SP004.PAS** | **12/01/2023** | **9/02/2023** | **28** | **15.8** | **LIDS LEFT ON PFMs - FLOW ESTIMATE USED** |
| **SEQ30 : Logan River @ Helen St** | **LRS-SP013.PAS** | **3/01/2023** | **8/02/2023** | **36** | **3.4** | **ORIGINAL SAMPLER LOST - NOT REDEPLOYED** |
| **SEQ31 : Rathdowney Weir** | **LRS-SP016.PAS** | **3/01/2023** | **1/02/2023** | **29** | **4.7** | **1/2 PFM DAMAGED - INTACT PFM DATA USED** |
| **SEQ32 : Canungra Creek @ Offtake** | **CAC-SP001.PAS** | **16/01/2023** | **20/02/2023** | **35** | **4.8** | |
| **SEQ33 : Little Nerang Dam** | **LND-SP014.PAS** | **25/01/2023** | **28/02/2023** | **34** | **7** | |
| **SEQ34 : Hinze Upper Intake** | **HID-SP001.PAS** | **24/01/2023** | **23/02/2023** | **30** | **5.4** | |
| **SEQ35 : Hinze Lower Intake** | **HID-SP002.PAS** | **24/01/2023** | **23/02/2023** | **30** | **6.4** | |
| **SEQ36 : Fernvale STP @ Savages Crossing** | **MBR-SP013.PAS** | **3/02/2023** | **3/03/2023** | **28** | **5.9** | **ORIGINAL SAMPLER LOST - REDEPLOYED** |
| **SEQ37 : Logan River @ Cedar Grove** | **LRS-SP012.PAS** | **3/01/2023** | **1/02/2023** | **29** | **9.9** | |
| **SEQ38 : Wappa Dam** | **WAD-SP001.PAS** | **17/01/2023** | **15/02/2023** | **29** | **3.4** | |
| **SEQ39 : Cooloolabin Dam** | **COD-SP001.PAS** | **5/01/2023** | **7/02/2023** | **33** | **5.6** | |
| **SEQ40 : Wivenhoe Dam @ Logans Inlet PRW** | **WID-SP061.PAS** | **17/01/2023** | **17/02/2023** | **31** | **21.9** | |
| **SEQ43 : Enoggera Reservoir** | **END-SP001.PAS** | **10/01/2023** | **15/02/2023** | **36** | **5.6** | |

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

## Passive sampler preparation and extraction

In this campaign, two types of passive samplers were deployed at each site. Empore Disk$^{TM}$ (3M; ED) samplers were deployed to detect and quantify the presence of polar organic pollutants such as herbicides, pharmaceuticals and personal care products (PPCPs). Polydimethylsiloxane (PDMS) strips in stainless steel cages (Figure 1) were deployed to quantify the presence of more hydrophobic organic pollutants (non-polar chemicals) such as certain organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs). Passive flow monitors (PFMs) were co-deployed in duplicate with the passive samplers at each site to estimate the water flow conditions during the deployment period. ED and PDMS passive samplers were all prepared and extracted according to previously published procedures and methods described in Kaserzon *et al.* (2017).

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

## Analytical methods

Chemical analysis was performed at QAEHS using established standard operating procedures (SOPs). ED extracts were analysed by LC-QQQ MS/MS for polar herbicides and PPCPs (85 chemicals) as well as on LC-QToF MS/MS with detect/non-detect screening conducted for an additional >45 chemicals. PDMS extracts were analysed for non-polar chemicals comprising of 30 OCPs, 16 PAHs and 1 other Herbicide/Pesticide compounds via GC-HRMS (Appendix 1). The analytical methods for herbicides and PPCPs (LC-QQQ MS/MS), OCPs and PAHs (GC-HRMS), and suspect screening of herbicides and PPCPs (LC-QToF MS/MS) are detailed in previously published reports (Kaserzon *et al.* 2017) and in *Quality Protocol: Contract 03944 Micro-Pollutant and Passive Sampler Monitoring program*.

## Data modelling and reporting of results

Data were modelled and reported according to previously published procedures and methods described in Kaserzon *et al.* (2017).

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

Quality control was also carried out in accordance with *Quality Protocol: Contract 03944 Micro-Pollutant and Passive Sampler Monitoring program*.

# Results

## Passive flow monitors (PFM) results

Two passive flow monitors (PFMs) were deployed at each site to allow for flow rate calculations. Under very low flow conditions the change in mass loss rates from the PFM are too small to provide a reliable measure of flow, and therefore cannot accurately provide flow data for the chemical sampling rate ($R_s$) calculation (i.e. below a threshold flow of 3.40 cm $s^{-1}$ or PFM loss rate equal to 0.58 g $d^{-1}$; O'Brien *et al.* 2009; 2011b). Therefore, to remain within the accurate mathematical modelling range for PFM-based flow velocity prediction, we applied a minimum flow rate of 3.40 cm $s^{-1}$ for the sites showing flow below this threshold and the minimum atrazine equivalence $R_s$. This may result in a slight over-estimation of $R_s$ and under-estimation of water concentration estimates ($C_w$), though we do not expect this to be significant (Kaserzon *et al.* 2014; O'Brien *et al.* 2011b). Average flow velocities estimated from PFMs over the deployment period ranged between 3.4 cm $s^{-1}$ (SEQ38 : Wappa Dam) to 25.6 cm $s^{-1}$ (SEQ14 : Wivenhoe Dam Wall) (Figure 2).

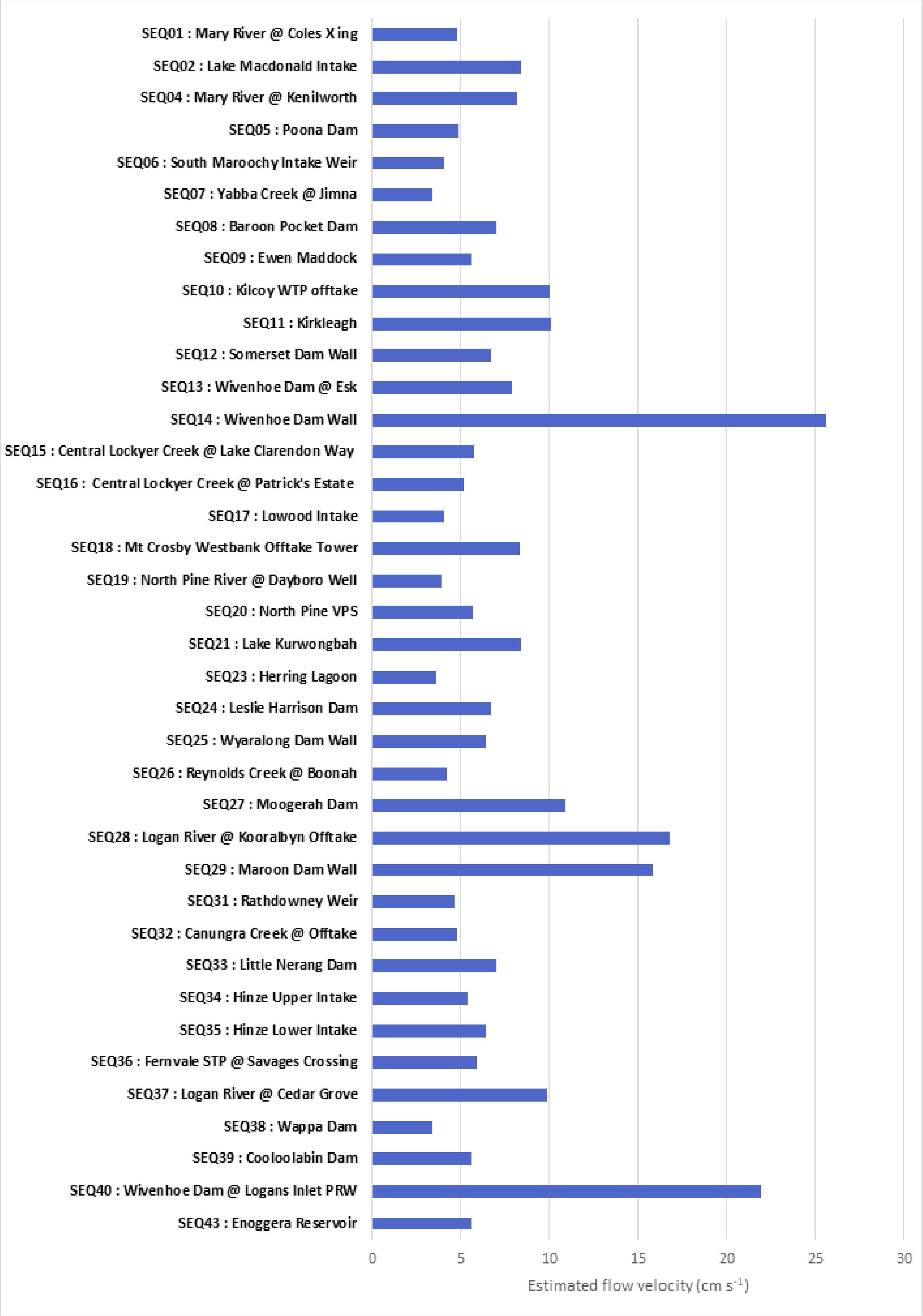

*Figure 2. Passive flow monitor (PFM) based water flow velocity estimations (cm s$^{-1}$) at the deployment sites (n=38).*

**Note:** A minimum flow velocity of 3.4 cm s$^{-1}$ is used to assess flow velocity using Passive Flow Monitors (PFMs).

## Chemical analysis results

A summary of the number of chemicals quantified at the sampling sites, the percent detection of each chemical and mass accumulation (ng sampler$^{-1}$) is presented in Tables 2 and 3 below. Table 2 summarises the non-polar chemicals detected via PDMS (OCPs and PAHs). A total of 18 OCPs and 14 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% – 95% for OCPs and 5% – 97% for PAHs. Table 3 summarises the polar chemicals quantified via ED (pesticides and PPCPs). A total of 31 pesticides (predominantly herbicides) and 9 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3% - 87% for pesticides and 3% - 100% for PPCPs.

*Table 2. Summary of the number of chemicals accumulated in PDMS passive samplers, percentage of detection at the sites and the range of mass accumulated over the deployment periods (ng PDMS$^{-1}$).*

| Analyte | Number of sites detected | % Detection | Min reported (ng/PDMS) | Max reported (ng/PDMS) |
|---|---|---|---|---|
| **OCP** | | | | |
| **Aldrin** | **0** | **0%** | **0.00** | **0.00** |
| **Azinphos methyl** | **0** | **0%** | **0.00** | **0.00** |
| **Bifenthrin** | **17** | **45%** | **0.564** | **4.54** |
| **Chlorpyrifos** | **29** | **76%** | **2.59** | **177** |
| **cis-Chlordane** | **15** | **39%** | **0.723** | **7.28** |
| **Cypermethrin** | **1** | **3%** | **3.22** | **3.22** |
| **Dacthal** | **16** | **42%** | **2.66** | **155** |
| **Deltamethrin** | **0** | **0%** | **0.00** | **0.00** |
| **Dieldrin** | **33** | **87%** | **2.72** | **29.9** |
| **Endosulfan sulfate** | **9** | **24%** | **1.12** | **6.69** |
| **Endrin** | **2** | **5%** | **1.61** | **4.12** |
| **Endrin ketone** | **1** | **3%** | **2.16** | **2.16** |
| **HCB** | **1** | **3%** | **1.65** | **1.65** |
| **Heptachlor** | **0** | **0%** | **0.00** | **0.00** |
| **Heptachlor epoxide a** | **0** | **0%** | **0.00** | **0.00** |
| **Heptachlor epoxide b** | **6** | **16%** | **1.55** | **16.1** |
| **Methoxychlor** | **0** | **0%** | **0.00** | **0.00** |
| **Mirex** | **0** | **0%** | **0.00** | **0.00** |
| **o,p-DDD** | **4** | **11%** | **1.09** | **2.09** |
| **o,p-DDE** | **0** | **0%** | **0.00** | **0.00** |
| **o,p-DDT** | **0** | **0%** | **0.00** | **0.00** |
| **p,p-DDD** | **11** | **29%** | **1.45** | **6.48** |
| **p,p-DDE** | **15** | **39%** | **1.23** | **41.6** |
| **p,p-DDT** | **1** | **3%** | **4.77** | **4.77** |
| **Pendimethalin** | **5** | **13%** | **5.79** | **109** |
| **Permethrin** | **8** | **21%** | **1.50** | **5.52** |
| **trans-Chlordane** | **36** | **95%** | **1.63** | **12.6** |
| **α-Endosulfan** | **0** | **0%** | **0.00** | **0.00** |
| **α-HCH** | **0** | **0%** | **0.00** | **0.00** |
| **β-endosulfan** | **0** | **0%** | **0.00** | **0.00** |
| **β-HCH** | **0** | **0%** | **0.00** | **0.00** |
| **γ-HCH (Lindane)** | **0** | **0%** | **0.00** | **0.00** |

| | | | | |
|---|---|---|---|---|
| **PAH** | | | | |
| **Acenaphthene** | **2** | **5%** | **18.6** | **119** |
| **Acenaphthylene** | **5** | **13%** | **5.69** | **8.35** |
| **Anthracene** | **6** | **16%** | **5.72** | **21.4** |
| **Benzo[a]anthracene** | **7** | **18%** | **1.26** | **11.3** |
| **Benzo[a]pyrene** | **2** | **5%** | **2.33** | **2.48** |
| **Benzo[b,j,k]fluoranthene** | **33** | **87%** | **0.509** | **5.12** |
| **Benzo[e]pyrene** | **17** | **45%** | **1.08** | **5.46** |
| **Benzo[g,h,i]perylene** | **12** | **32%** | **1.06** | **5.85** |
| **Chrysene/Triphenylene** | **37** | **97%** | **0.51** | **20.1** |
| **Dibenz[a,h]anthracene** | **0** | **0%** | **0.00** | **0.00** |
| **Fluoranthene** | **36** | **95%** | **5.72** | **203** |
| **Fluorene** | **2** | **5%** | **45.9** | **55.5** |
| **Indeno[1,2,3-c,d]pyrene** | **7** | **18%** | **1.02** | **2.95** |
| **Naphthalene** | **0** | **0%** | **0** | **0** |
| **Phenanthrene** | **8** | **21%** | **43.5** | **62.8** |
| **Pyrene** | **21** | **55%** | **8.15** | **125** |

Table 3. Summary of the number of chemicals accumulated in ED passive samplers, percentage of detection at the sites and the range of mass accumulated over the deployment periods (ng ED$^{-1}$).

| Analyte | Number of sites detected | % Detection | Min reported (ng/ED) | Max reported (ng/ED) |
|---|---|---|---|---|
| **Herbicides and Pesticides** | | | | |
| **2,4,5-T** | **0** | **0%** | **0.00** | **0.00** |
| **2,4-D** | **5** | **13%** | **7.54** | **20.9** |
| **3,4 Dichloroaniline** | **0** | **0%** | **0.00** | **0.00** |
| **Ametryn** | **0** | **0%** | **0.00** | **0.00** |
| **Ametryn hydroxy** | **2** | **5%** | **1.11** | **3.45** |
| **Aminocarb** | **0** | **0%** | **0.00** | **0.00** |
| **Atrazine** | **33** | **87%** | **1.07** | **426** |
| **Atrazine desethyl** | **26** | **68%** | **1.00** | **11.9** |
| **Atrazine desisopropyl** | **25** | **66%** | **1.01** | **5.70** |
| **Bendiocarb** | **0** | **0%** | **0.00** | **0.00** |
| **Bromacil** | **0** | **0%** | **0.00** | **0.00** |
| **Bromoxynil** | **0** | **0%** | **0.00** | **0.00** |
| **Carbaryl** | **0** | **0%** | **0.00** | **0.00** |
| **Carbendazim** | **9** | **24%** | **2.12** | **20.3** |
| **DCPMU** | **1** | **3%** | **0.930** | **0.930** |
| **DCPU** | **0** | **0%** | **0.00** | **0.00** |
| **Diazinon** | **12** | **32%** | **0.140** | **0.760** |
| **Difenoconazole** | **0** | **0%** | **0.00** | **0.00** |
| **Diketonitrile** | **1** | **3%** | **0.110** | **0.110** |
| **Diuron** | **26** | **68%** | **0.500** | **27.3** |
| **Fenuron** | **0** | **0%** | **0.00** | **0.00** |
| **Fipronil** | **2** | **5%** | **0.660** | **3.23** |
| **Fluazifop** | **3** | **8%** | **0.390** | **2.15** |

| | | | | |
|---|---|---|---|---|
| **Fluometuron** | **0** | **0%** | **0.00** | **0.00** |
| **Fluroxypyr** | **1** | **3%** | **1.19** | **1.19** |
| **Haloxyfop** | **2** | **5%** | **1.43** | **4.73** |
| **Hexazinone** | **11** | **29%** | **1.01** | **8.73** |
| **Imazapyr** | **0** | **0%** | **0.00** | **0.00** |
| **Imazethapyr** | **0** | **0%** | **0.00** | **0.00** |
| **Imidacloprid** | **11** | **29%** | **1.02** | **24.6** |
| **Malathion** | **0** | **0%** | **0.00** | **0.00** |
| **MCPA** | **2** | **5%** | **5.60** | **6.01** |
| **Metalaxyl** | **13** | **34%** | **0.140** | **3.30** |
| **Methidathion** | **0** | **0%** | **0.00** | **0.00** |
| **Methomyl** | **2** | **5%** | **6.49** | **18.6** |
| **Metolachlor (S+R)** | **26** | **68%** | **1.01** | **317** |
| **Metolcarb** | **0** | **0%** | **0.00** | **0.00** |
| **Metribuzin** | **0** | **0%** | **0.00** | **0.00** |
| **Metsulfuron methyl** | **32** | **84%** | **1.23** | **25.0** |
| **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** | **2** | **5%** | **1.23** | **1.73** |
| **Propachlor** | **0** | **0%** | **0.00** | **0.00** |
| **Propazine** | **2** | **5%** | **1.03** | **5.28** |
| **Propiconazole** | **7** | **18%** | **1.04** | **3.41** |
| **Propoxur** | **0** | **0%** | **0.00** | **0.00** |
| **Simazine** | **13** | **34%** | **1.02** | **10.0** |
| **Simazine hydroxy** | **0** | **0%** | **0.00** | **0.00** |
| **Tebuconazole** | **4** | **11%** | **1.00** | **1.79** |
| **Tebuthiuron** | **18** | **47%** | **1.05** | **226** |
| **Terbuthylazine** | **20** | **53%** | **1.11** | **4.95** |
| **Terbuthylazine desethyl** | **33** | **87%** | **1.12** | **10.7** |
| **Thiamethoxam** | **2** | **5%** | **0.960** | **6.48** |
| **Triclopyr** | **3** | **8%** | **5.68** | **20.5** |
| **Pharmaceuticals and personal care products (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%** | **146** | **146** |
| **Carbamazepine** | **6** | **16%** | **1.28** | **3.70** |
| **Codeine** | **0** | **0%** | **0.00** | **0.00** |
| **DEET** | **38** | **100%** | **3.52** | **1081** |
| **Diclofenac** | **1** | **3%** | **0.480** | **0.480** |
| **Gabapentin** | **0** | **0%** | **0.00** | **0.00** |
| **Hydrochlorthiazide** | **0** | **0%** | **0.00** | **0.00** |
| **Iopromide** | **0** | **0%** | **0.00** | **0.00** |

| | | | | |
|---|---|---|---|---|
| **Naproxen** | **0** | **0%** | **0.00** | **0.00** |
| **Oxazepam** | **1** | **3%** | **1.72** | **1.72** |
| **Paracetamol** | **1** | **3%** | **1.36** | **1.36** |
| **Paraxanthine** | **1** | **3%** | **74.2** | **74.2** |
| **Salicyclic acid** | **0** | **0%** | **0.00** | **0.00** |
| **Sulfadiazine** | **2** | **5%** | **0.520** | **0.560** |
| **Sulfamethoxazole** | **4** | **11%** | **0.180** | **0.530** |
| **Tadalafil** | **0** | **0%** | **0.00** | **0.00** |
| **Temazepam** | **0** | **0%** | **0.00** | **0.00** |
| **Verapamil** | **0** | **0%** | **0.00** | **0.00** |

## Organochlorine pesticides (OCPs)

In total, 18 OCPs were accumulated in PDMS samplers over the deployment period (Table 2, Figure 3, Appendix 1), with the amount of ∑OCPs accumulated ranging from below reporting limits to 442 ng PDMS$^{-1}$ (SEQ15 - Central Lockyer Creek @ Lake Clarendon Way ).

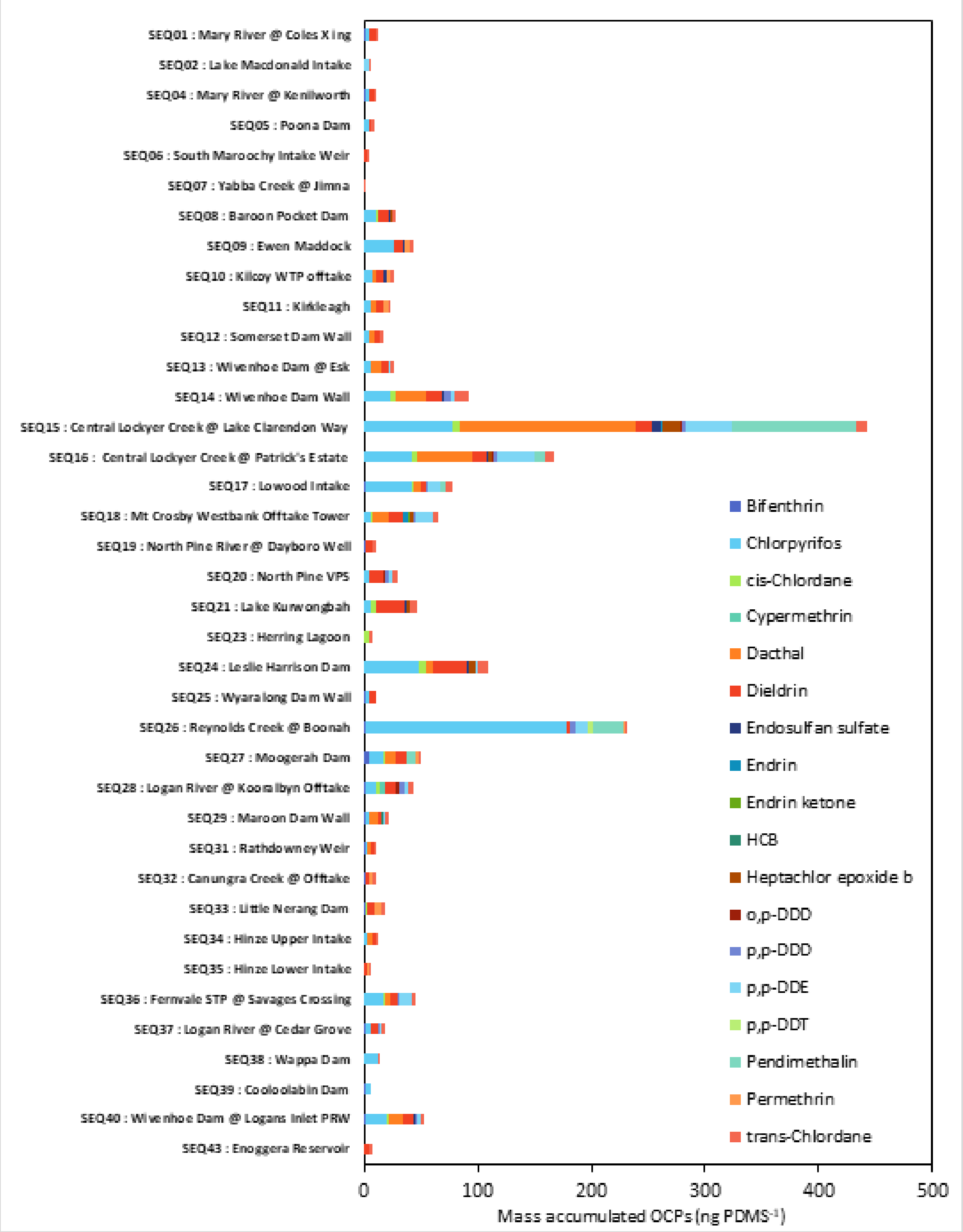

*Figure 3. Total mass of 18 ΣOCPs (ng PDMS$^{-1}$) accumulated in PDMS passive samplers at each site.*

Discounting the sites below reporting limits, the conversion of ∑OCP masses accumulated in passive samplers to time-weighted average water concentrations revealed an estimated water concentration range of 0.005 to 5.95 ng L$^{-1}$ (SEQ07 - Yabba Creek @ Jimna and SEQ15 - Central Lockyer Creek @ Lake Clarendon Way , respectively; Figure 4).

*Figure 4. Total estimated water concentrations (ng L$^{-1}$) of 18 ΣOCPs at each site derived from PDMS passive samplers.*

## Polycyclic aromatic hydrocarbons (PAHs)

In total, 14 PAHs were accumulated in PDMS samplers over the deployment period (Table 2, Figure 5, Appendix 1), with the amount of ∑PAHs accumulated ranging from below reporting limits to 444 ng PDMS$^{-1}$ (SEQ12 - Somerset Dam Wall).

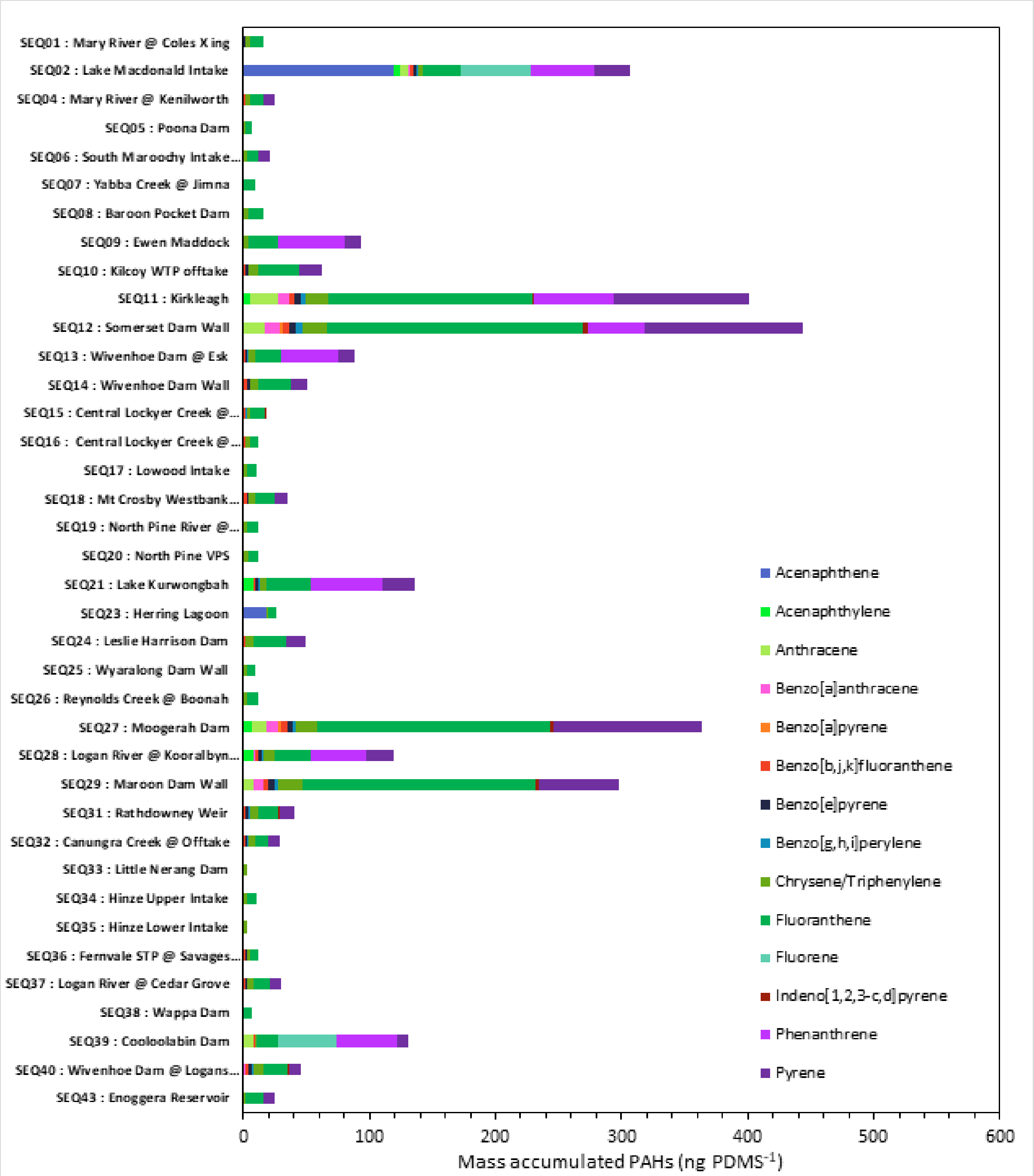

*Figure 5. Total mass of 14 ΣPAHs (ng PDMS$^{-1}$) accumulated in PDMS passive samplers at each site.*

Discounting the sites below reporting limits, the conversion of ∑PAH masses accumulated in passive samplers to time-weighted average water concentrations revealed an estimated water concentration range of 0.005 to 3.35 ng L$^{-1}$ (SEQ33 - Little Nerang Dam and SEQ02 - Lake Macdonald Intake, respectively; Figure 6).

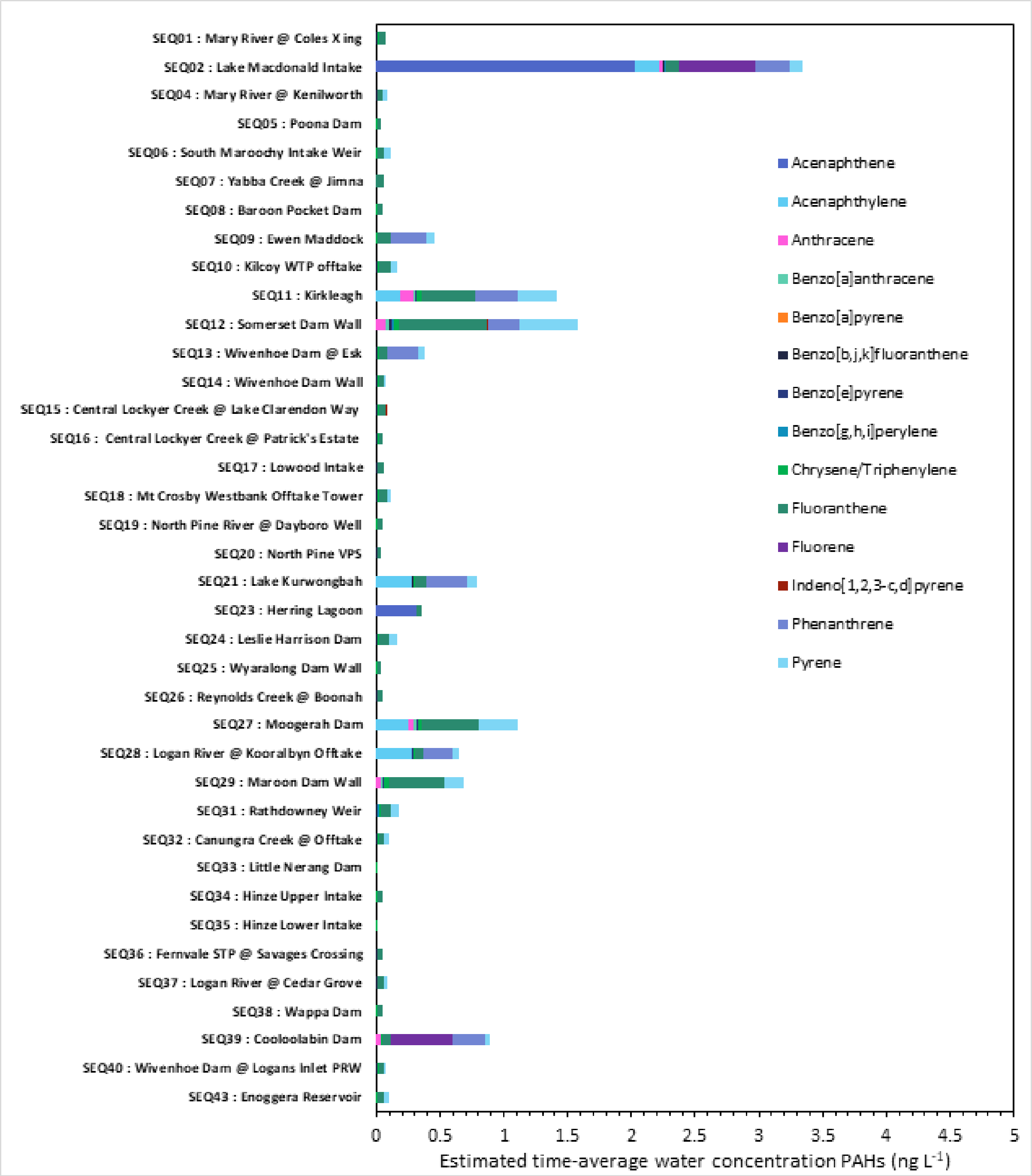

*Figure 6. Total estimated water concentrations (ng L$^{-1}$) of 14 ΣPAHs at each site derived from PDMS passive samplers.*

## Pesticides

Over the deployment period, 31 polar pesticides (including herbicides, fungicides and insecticides) accumulated in ED passive samplers (Table 3, Figure 7, Appendix 1). The ∑polar pesticides accumulated ranged from below reporting limits (SEQ23 - Herring Lagoon) to 735 ng ED$^{-1}$(SEQ26 - Reynolds Creek @ Boonah).

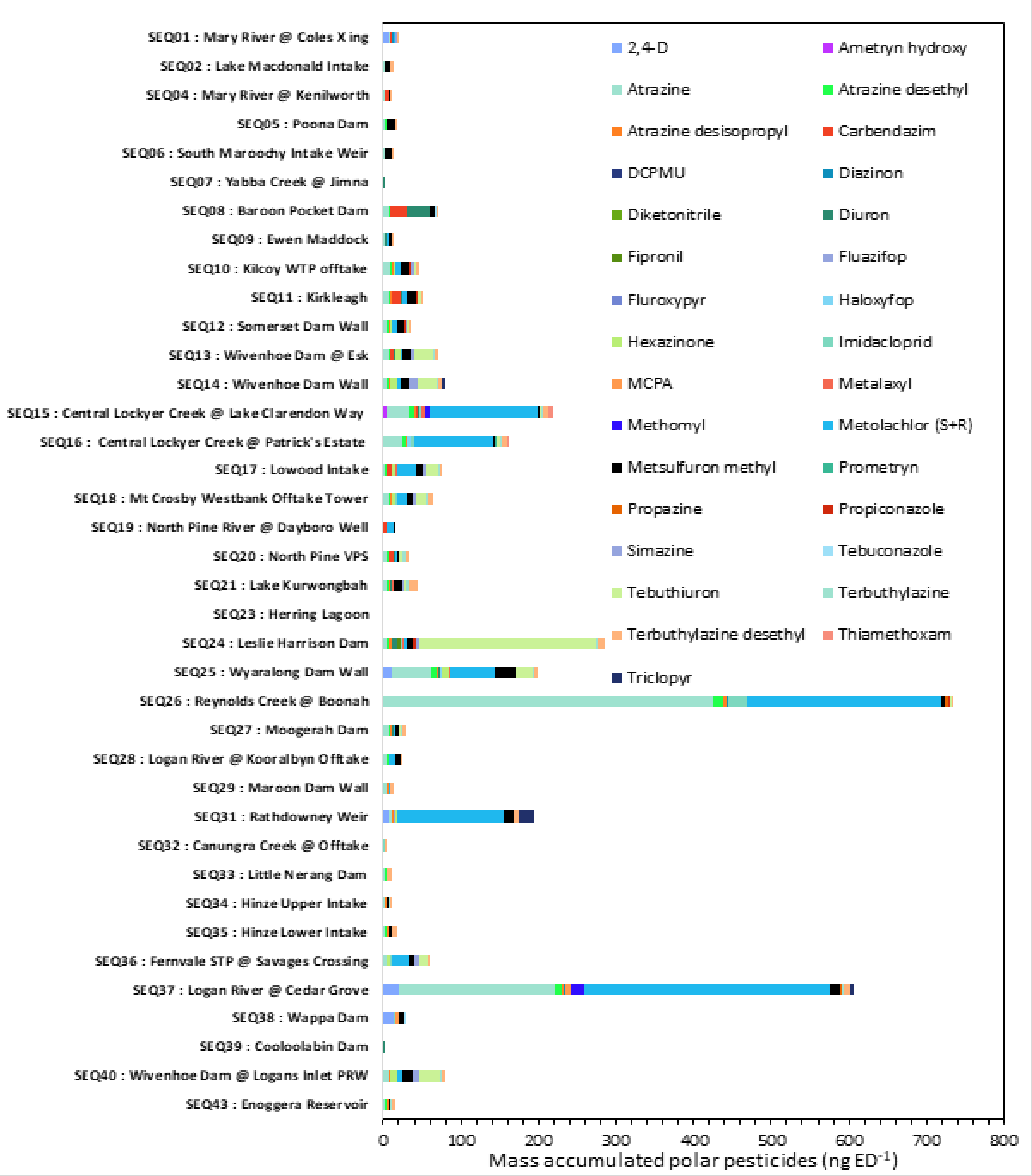

*Figure 7. Total mass of 31 Σpolar pesticides (ng ED$^{-1}$) accumulated in ED passive samplers at each site.*

Water concentrations were estimated for the polar pesticides accumulated where sampling rates have been previously calibrated. From the 31 chemicals reported, 16 were converted to time-weighted average water ∑concentrations. Discounting the sites below reporting limits, these water concentrations ranged between 0.340 and 412 ng L$^{-1}$ (SEQ39 - Cooloolabin Dam and SEQ26 - Reynolds Creek @ Boonah, respectively; Figure 8).

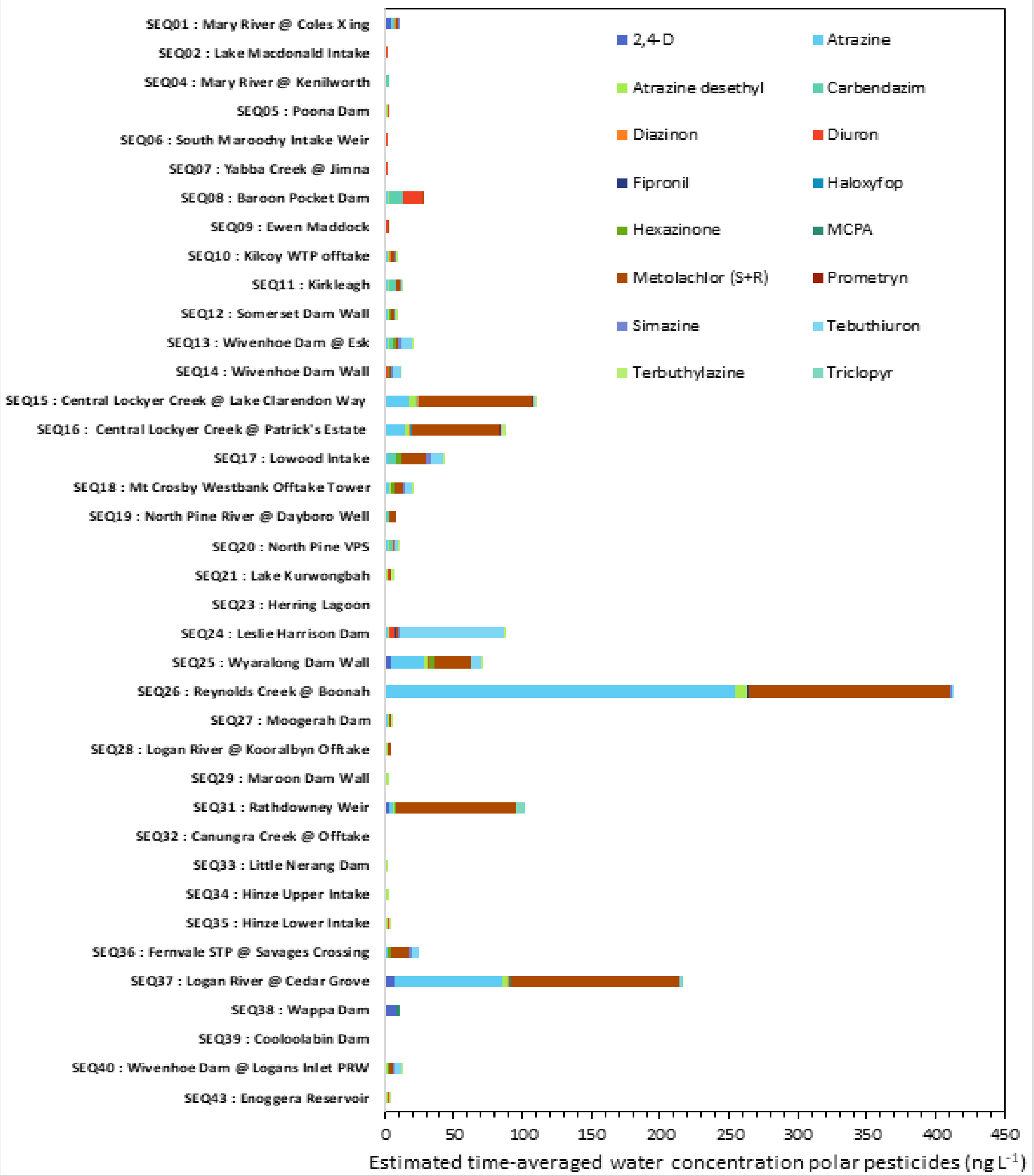

*Figure 8. Total estimated water concentrations (ng L$^{-1}$) of 16 Σpolar pesticides at each site derived from ED passive samplers.*

## Pharmaceuticals and personal care products (PPCPs)

In total, 9 PPCPs were reported (Table 3, Figure 9, Appendix 1) with the average amount of ΣPPCPs accumulated ranging from 1.68 ng ED$^{-1}$ (SEQ23 - Herring Lagoon) to 1081 ng ED$^{-1}$ (SEQ09 - Ewen Maddock).

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

Of the 9 reported PPCPs, 5 were able to be converted into estimated time-weighted average water concentrations. Discounting the sites below reporting limits, these ∑PPCP water concentrations ranged between 1.68 and 440 ng L$^{-1}$ (sites SEQ23 - Herring Lagoon and SEQ09 - Ewen Maddock, respectively; Figure 10).

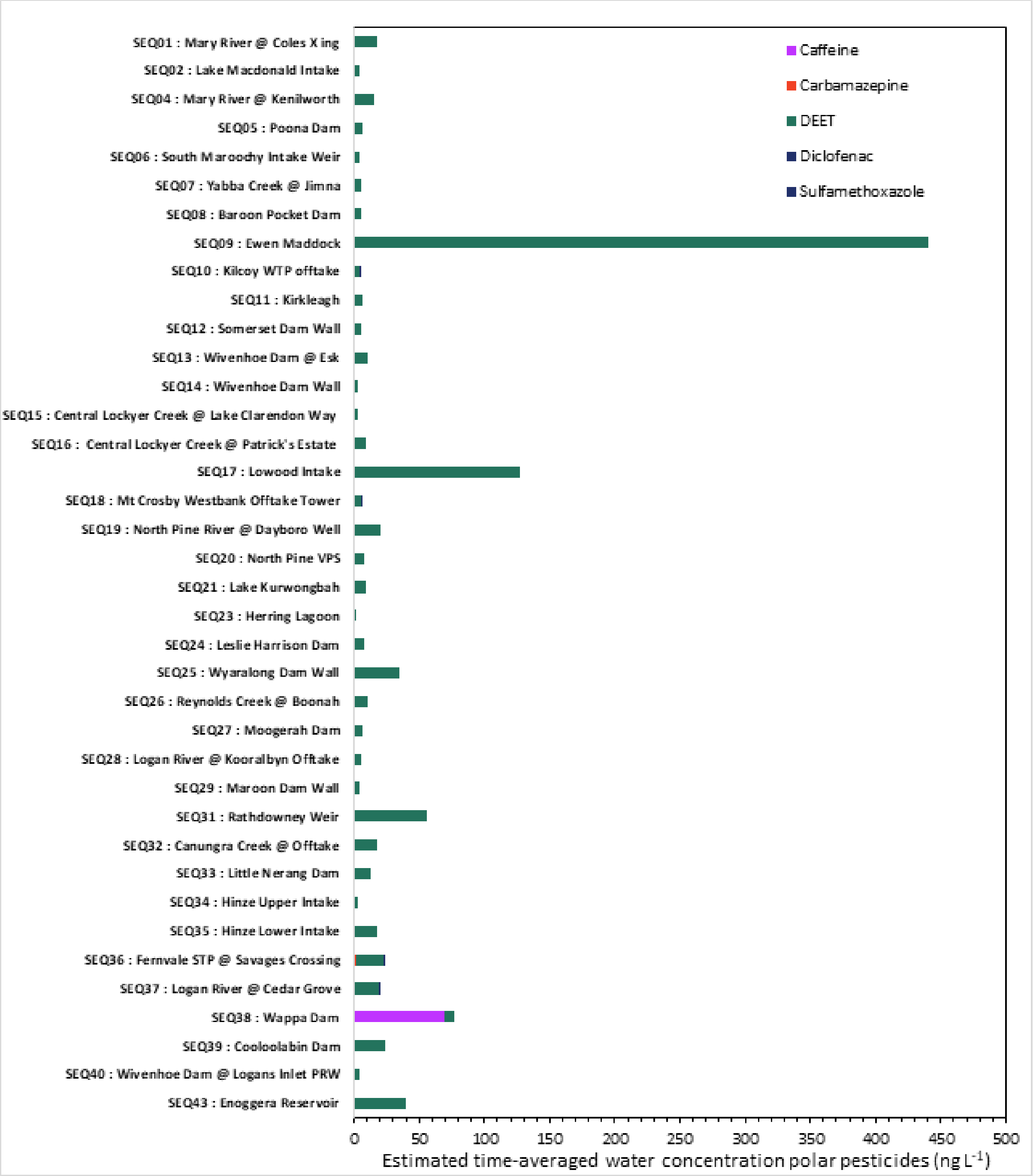

*Figure 10. Total estimated water concentrations (ng $L^{-1}$) of 5 ΣPPCPs.*

## Analysis of non-target polar chemicals

Along with the target list of polar chemicals identified for investigation, the screening for an additional 45 herbicides and PPCP chemicals that have the potential to transport to waterways has been performed to investigate their presence in the water systems. During this sampling season no compounds of interest were detected, however a larger screening through additional pesticide, pharmaceutical and personal care product libraries revealed tentative detection of 3 compounds (Table 4). The suspect screening provides tentative identification of the presence / absence of these chemicals. It is noted that in order to fully confirm the identification and quantification of these analytes, the use of appropriate chemical standards would be necessary. Tentative identifications are considered when the suspect spectra met strict criteria (strong signal/noise of >3, reverse dot product score >90%) and mass errors were <5 ppm.

*Table 4. List of tentatively identified non-target chemicals in EDs, and the sites in which they were detected.*

| Chemical Name | Description | Sites with tentative detects |
|---|---|---|
| Azoxystrobin acid | Azoxystrobin breakdown product | SEQ02 : Lake Macdonald Intake<br>SEQ05 : Poona Dam<br>SEQ06 : South Maroochy Intake Weir<br>SEQ15 : Central Lockyer Creek @ Lake Clarendon Way<br>SEQ16 : Central Lockyer Creek @ O'Reilly's Weir<br>SEQ17 : Lowood Intake<br>SEQ18 : Mt Crosby Westbank Offtake Tower<br>SEQ24 : Leslie Harrison Dam<br>SEQ26 : Reynolds Creek @ Boonah<br>SEQ36 : Fernvale STP @ Savages Crossing<br>SEQ38 : Wappa Dam |
| Boscalid | Fungicide | SEQ15 : Central Lockyer Creek @ Lake Clarendon Way<br>SEQ18 : Mt Crosby Westbank Offtake Tower<br>SEQ24 : Leslie Harrison Dam |
| Tylosin | Vetinary antibiotic - toxic to algae | SEQ02 : Lake Macdonald Intake<br>SEQ13 : Wivenhoe Dam @ Esk<br>SEQ14 : Wivenhoe Dam Wall<br>SEQ16 : Central Lockyer Creek @ O'Reilly's Weir<br>SEQ25 : Wyaralong Dam Wall<br>SEQ35 : Hinze Lower Intake<br>SEQ36 : Fernvale STP @ Savages Crossing<br>SEQ37 : Logan River @ Cedar Grove<br>SEQ38 : Wappa Dam<br>SEQ39 : Cooloolabin Dam<br>SEQ40 : Wivenhoe Dam @ Logans Inlet PRW<br>SEQ43 : Enoggera Reservoir |

## Comparison to water quality guideline values

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

Exceedances for eco-toxicological guidelines were observed in the estimated time-averaged water concentrations for diazinon, metolachlor, tebuthiuron and chlorpyrifos. ANZECC & ANCANZ have set diazinon freshwater guideline values of 0.03 and 10 ng $L^{-1}$ for 99% and 95% species protection levels, respectively. There were no sites with any detected in excess of the 95% species protection guideline for any chemical. Furthermore, totals of 14, 10, 1 and 33 sites exceeded the 99% species protection guidelines for diazinon, metolachlor, tebuthiuron and chlorpyrifos, respectively (Table 5).

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

| Australian Drinking Water Guidelines 6 (2011) Version 3.6 Updated December 2021 | | ANZECC & ANCANZ (2021) Trigger values for freshwater | | This campaign |
|---|---|---|---|---|
| **Herbicides & Insecticides** | **Guideline value (ng $L^{-1}$)** | **99% species protection value (ng $L^{-1}$)** | **95% species protection value (ng $L^{-1}$)** | **Highest Reported Value (ng $L^{-1}$)** |
| Atrazine | 20000 | 700 | 13000 | 255 |
| Ametryn | 70000 | N/A | N/A | N/A |
| Bromacil | 400000 | N/A | N/A | N/A |
| Bromoxynil | 10000 | N/A | N/A | N/A |
| Carbaryl | 30000 | N/A | N/A | N/A |
| Carbendazim | 90000 | N/A | N/A | 9.90 |
| Cypermethrin | 200000 | N/A | N/A | N/A |
| Diazinon | 4000 | 0.03 | 10 | 0.740 |
| Diuron | 20000 | N/A | N/A | 13.4 |
| Fipronil | 700 | N/A | N/A | 1.22 |
| Fluometuron | 70000 | N/A | N/A | N/A |
| Haloxyfop | 1000 | N/A | N/A | 1.54 |
| Hexazinone | 400000 | N/A | N/A | 3.93 |
| Imazapyr | 9000000 | N/A | N/A | N/A |
| MCPA | 40000 | N/A | N/A | 2.75 |
| Malathion | 70000 | 2 | 50 | N/A |
| Methomyl | 20000 | N/A | N/A | N/A |
| Metolachlor (S+R) | 300000 | 8.4 | 460 | 147 |
| Metribuzin | 70000 | N/A | N/A | N/A |
| Metsulfuron methyl | 40000 | 3.7 | 18 | N/A |
| Oryzalin | 400000 | N/A | N/A | N/A |
| Pendimethalin | 400000 | N/A | N/A | N/A |
| Picloram | 300000 | N/A | N/A | N/A |
| Propachlor | 70000 | N/A | N/A | N/A |
| Propazine | 50000 | N/A | N/A | N/A |
| Propiconazole | 100000 | N/A | N/A | N/A |
| Simazine | 20000 | 200 | 3200 | 3.10 |
| Tebuthiuron | N/A | 20 | 2200 | 75.2 |
| Terbuthylazine | 10000 | N/A | N/A | 1.80 |
| Triclopyr | 20000 | N/A | N/A | 6.65 |
| 2,4-D | 30000 | 140000 | 280000 | 8.44 |
| 2,4,5-T | 100000 | 3000 | 36000 | N/A |
| 3,4-Dichloroaniline | N/A | 1300 | 3000 | N/A |
| **OCPs** | | | | |
| Azinphos methyl | 30000 | 10 | 20 | N/A |
| Chlordane | 2000 | 30 | 80 | N/A |
| Chlorpyrifos | 10000 | 0.04 | 10 | 2.95 |
| Cypermethrin | 200000 | N/A | N/A | 0.005 |
| DDT | 9000 | 6 | 10 | 0.112 |
| Dieldrin | 300 | N/A | N/A | 0.081 |
| Aldrin | 300 | N/A | N/A | N/A |
| Endosulfan | 20000 | 30 | 200 | 0.716 |
| Endrin | N/A | 10 | 20 | 0.015 |
| Heptachlor | 300 | 10 | 90 | N/A |
| γ-HCH (Lindane) | 10000 | 70 | 200 | N/A |
| Methoxychlor | 300000 | N/A | N/A | N/A |
| **PAHs** | | | | |
| Anthracene | N/A | 10 | 400 | 0.091 |
| Benzo[a]pyrene | 10 | N/A | N/A | 0.005 |
| Fluoranthene | N/A | 1000 | 1400 | 0.698 |
| Naphthalene | 10 | 2500 | 16000 | N/A |
| Phenanthrene | N/A | 600 | 2000 | 0.337 |

# Discussion

OCPs were first introduced into Australia in the mid-1940s and were applied in many commercial products in different forms (such as powders and liquids). At one time up to 150 commercial products containing OCPs may have been registered in Australia. This followed a period of widespread use until the 1970s when recognition of risks related to OCPs resulted in reduced use and their ultimate ban in the 1980s. Since then, human biomonitoring studies in blood and breastmilk have showed the substantial decline of these chemicals from the early 1980s to the 1990s after which levels appear to plateau (Toms *et al.* 2012). Although OCPs were reported at 38 sites (100%), the concentrations were low (Total ∑OCPs <5.95 ng $L^{-1}$). Compounds still in use such as chlorpyrifos were reported at higher concentrations, consistent with ongoing inputs to the environment. Chlorpyrifos was introduced in 1965 and has been included in many products and formulations aimed at agricultural, urban, commercial and residential uses. Although regulation measures have been put in place in Australia (APVMA 2011b) the chemical has not been strictly banned. A search of the APVMA PubCris database reveals 72 currently registered or approved products containing chlorpyrifos. A continued review of chlorpyrifos is warranted to estimate any future risk. trans-Chlordane was the most frequently detected OCP, reported at 36 sites and Dieldrin was the second most frequent (87% of sites). Dieldrin has been used since the 1950's as an insecticide particularly as a termite treatment. It has been banned in Australia since 1987, though remains persistent in the environment due to its low breakdown rates.

PAHs are ubiquitous in the environment and are introduced via anthropogenic sources primarily as a result of incomplete combustion as well as via natural sources (i.e. forest fires and the transformation of biogenic precursors) (Nguyen *et al.* 2014). A number of PAHs have been included as chemicals of concern under the Stockholm Convention on Persistent Organic Pollutants (2011) due to their toxic and carcinogenic properties. They enter aquatic systems via storm water runoff from urban and industrial areas, roads and spills as well as via recreational activities such as boating. PAHs can undergo long-range atmospheric transport and deposition and are distributed in waterways during intense rainfall and flooding (Nguyen *et al.* 2014). The hydrophobic nature of PAHs typically results in low concentrations in water as they generally associate with particulate matter and sediment. Reportable concentrations of PAHs were detected at 100% of sites, including Chrysene/Triphenylene and Fluoranthene at low levels (<2.02 ng $L^{-1}$).

Polar pesticides (herbicides, insecticides and fungicides) were reported at 37 sites. The two most frequently reported pesticides were terbuthylazine desethyl and atrazine (both detected at 33 sites; 87%). Terbuthylazine and atrazine and 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 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). They can be used in conjunction with diuron and hexazinone, two herbicides also frequently observed.

Pharmaceuticals and personal care products have emerged as a major group of environmental contaminants over the past decade. Some polar organic chemicals persist through wastewater treatment processes resulting in their continuous release into the aquatic environment (Kaserzon *et al.* 2014). The most frequently reported PPCP was DEET (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 which contain DEET. The second most frequently reported PPCP was Carbamazepine (detected at 16% of sites). The persistence of carbamazepine to biodegradation has been previously noted, and it is frequently observed in wastewater influent and effluent as well as general aquatic environments (Andreozzi *et al.* 2002, Liu *et al.* 2020). The contribution of pharmaceuticals and personal care products can be an indicator of systems which are used for human recreational activities, or that receive some degree of treated effluent.

## Future recommendations

Recommendations for future work that build upon the findings in the current report.

- Continue temporal/ seasonal and spatial comparisons to investigate long term trends between sites and seasons.
- Review target compound lists to see if those frequently non-detected are better replaced with other targets.

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# Appendix 1

See enclosed excel file ‘SEQW results_Summer2023.xlsm’

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