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

Report 17 – Winter 2022

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Title
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Executive Summary

The *Catchment and Drinking Water Quality Micro Pollutant Monitoring Program* was launched in mid-2014 with the aim of improving the characterisation and understanding of the micro pollutant risk profile in source water reservoirs through bi-annual summer and winter sampling campaigns. The monitoring program utilising passive samplers was continued in reservoirs in South East Queensland (SEQ) during the third quarter of 2022. 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, multiple samplers required redeployment due to unforeseen events resulting in sampler compromise.

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

Chemical analyses of the passive sampler extracts reported 75 different chemicals including 21 OCPs, 14 PAHs, 32 polar pesticides and 8 PPCPs. OCPs were detected at 95% of sites, with Chlorpyrifos (74%) and Dieldrin (85%) the most frequently reported. Total ∑OCP water concentrations across sites ranged between 0.01 – 47 ng L^{-1} where concentrations were reportable. PAHs were detected at 97% of sites, with Benzo[b,j,k]fluoranthene (92%) and Chrysene/Triphenylene (95%) reported at the highest abundance across all sites. Total ∑PAH water concentrations across sites ranged between 0.004 – 4.3 ng L^{-1}. In total, 32 different polar pesticides were reported in 31 sites (82%), with Metsulfuron methyl (76%) and Metalaxyl (58%) reported at highest abundance across all sites. Total ∑polar pesticides ranged between 0.47 – 90 ng L^{-1}. Additionally, 8 PPCPs were detected across sites with highest detection frequencies observed for DEET (100%) and Sulfamethoxazole (8%). Total estimated ∑PPCP water concentrations ranged between 0.64 – 84 ng L^{-1} across sites.

Australian and New Zealand Guidelines for Drinking Water (ADWG) as well as Fresh and Marine Water Quality values are available for some of these chemicals (ANZECC & ANCANZ 2018) for comparison. No chemicals were present in concentrations that exceeded the ADWG values. In the ecotoxicological setting, Diazinon, Metolachlor, Tebuthiuron and Chlorpyrifos were often above the thresholds set for 99% species protection, and in one instance (SEQ15 - Central Lockyer Creek @ Lake Clarendon Way) Diazinon and Chlorpyrifos were both 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 monitoring program 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 several weeks, 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 or exclusion of target analytes based on on-going risk assessment and detection frequency.

Methodology

Passive water samplers were deployed in periods between July 2022 to September 2022 at 39 sites in SEQ reservoirs and waterways (Table 1). Deployments were for periods of 27 to 36 days in duration. A replicate sampler was deployed at nine randomly selected sites (Table 1, highlighted in green). At some sites samplers required redeployment due to losses as indicated in Table 1 comments.

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)

In addition to the baseline monitoring program, an additional event ED sampler was deployed at site 24 for 28 days between June and July (Table 1). This event sampler data is included in this report as "SEQ24 : Leslie Harrison Dam - Event".

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

Site	Site Code	Date Deployed	Date Retrieved	Days Deployed	Flow Velocity (cm/s)	Comments
SEQ01 : Mary River @ Coles crossing	**MRS-SP012.PAS**	**22/08/2022**	**19/09/2022**	**28**	**3.4**	**Samplers were redeployed due to either sampler loss or samplers being compromised**
SEQ02 : Lake Macdonald Intake	**LMD-SP001.PAS**	**27/07/2022**	**29/08/2022**	**33**	**3.4**	**lids left on PFM. Flow estimate used**
SEQ04 : Mary River @ Kenilworth	**MRS-SP013.PAS**	**20/07/2022**	**18/08/2022**	**29**	**18.5**	
SEQ05 : Poona Dam	**POD-SP001.PAS**	**19/07/2022**	**17/08/2022**	**29**	**3.9**	
SEQ06 : South Maroochy Intake Weir	**SOR-SP001.PAS**	**19/07/2022**	**19/08/2022**	**31**	**3.4**	
SEQ07 : Yabba Creek @ Jimna	**YAC-SP001.PAS**	**20/07/2022**	**19/08/2022**	**30**	**3.4**	
SEQ08 : Baroon Pocket Dam	**BPD-SP001.PAS**	**2/08/2022**	**31/08/2022**	**29**	**3.6**	**lids left on PFM. Flow estimate used**
SEQ09 : Ewen Maddock	**EMD-SP001.PAS**	**5/07/2022**	**3/08/2022**	**29**	**6.1**	
SEQ10 : Kilcoy WTP offtake	**SOD-SP010.PAS**	**11/07/2022**	**8/08/2022**	**28**	**3.4**	
SEQ11 : Kirkleagh	**SOD-SP011.PAS**	**11/07/2022**	**8/08/2022**	**28**	**3.4**	
SEQ12 : Somerset Dam Wall	**SOD-SP001.PAS**	**11/07/2022**	**8/08/2022**	**28**	**3.4**	
SEQ13 : Wivenhoe Dam @ Esk	**WID-SP004.PAS**	**2/08/2022**	**30/08/2022**	**28**	**12.3**	
SEQ14 : Wivenhoe Dam Wall	**WID-SP001.PAS**	**2/08/2022**	**30/08/2022**	**28**	**11**	
SEQ15 : Central Lockyer Creek @ Lake Clarendon Way	**LOC-SP034.PAS**	**26/07/2022**	**23/08/2022**	**28**	**3.4**	

SEQ16 : Central Lockyer Creek @ Patrick's Estate	**LOC-SP033.PAS**	**26/07/2022**	**23/08/2022**	**28**	**3.6**	
SEQ17 : Lowood Intake	**MBR-SP016.PAS**	**21/07/2022**	**18/08/2022**	**28**	**7.5**	
SEQ18 : Mt Crosby Westbank Offtake Tower	**MBR-SP001.PAS**	**22/07/2022**	**19/08/2022**	**28**	**6**	
SEQ19 : North Pine River @ Dayboro Well	**NOD-SP091.PAS**	**18/07/2022**	**15/08/2022**	**28**	**4.7**	
SEQ20 : North Pine VPS	**NOD-SP001.PAS**	**18/07/2022**	**15/08/2022**	**28**	**4**	
SEQ21 : Lake Kurwongbah	**LAK-SP001.PAS**	**19/07/2022**	**16/08/2022**	**28**	**3.4**	
SEQ23 : Herring Lagoon	**NSC-SP001.PAS**	**19/07/2022**	**23/08/2022**	**35**	**3.4**	
SEQ24 : Leslie Harrison Dam	**LHD-SP005.PAS**	**21/07/2022**	**17/08/2022**	**27**	**3.4**	
SEQ25 : Wyaralong Dam Wall	**WYD-SP001.PAS**	**20/07/2022**	**23/08/2022**	**34**	**3.4**	
SEQ26 : Reynolds Creek @ Boonah	**MOD-SP027.PAS**	**20/07/2022**	**18/08/2022**	**29**	**3.4**	
SEQ27 : Moogerah Dam	**MOD-SP002.PAS**	**24/08/2022**	**29/09/2022**	**36**	**8.6**	**Samplers were redeployed due to either sampler loss or samplers being compromised**
SEQ28 : Logan River @ Kooralbyn Offtake	**LRS-SP017.PAS**	**16/08/2022**	**15/09/2022**	**30**	**18.2**	**Samplers were redeployed due to either sampler loss or samplers being compromised**
SEQ29 : Maroon Dam Wall	**MAD-SP004.PAS**	**3/08/2022**	**6/09/2022**	**34**	**10.1**	**Samplers were redeployed due to either sampler loss or samplers being compromised**
SEQ30 : Logan River @ Helen St	**LRS-SP013.PAS**	**4/08/2022**	**31/08/2022**	**27**	**14.7**	**ED lost due to flooding**
SEQ31 : Rathdowney Weir	**LRS-SP016.PAS**	**7/07/2022**	**4/08/2022**	**28**	**10.6**	
SEQ32 : Canungra Creek @ Offtake	**CAC-SP001.PAS**	**18/07/2022**	**15/08/2022**	**28**	**5**	
SEQ33 : Little Nerang Dam	**LND-SP014.PAS**	**2/09/2022**	**30/09/2022**	**28**	**3.5**	**Samplers were redeployed due to either sampler loss or samplers being compromised**
SEQ34 : Hinze Upper Intake	**HID-SP001.PAS**	**28/07/2022**	**25/08/2022**	**28**	**3.4**	
SEQ35 : Hinze Lower Intake	**HID-SP002.PAS**	**28/07/2022**	**25/08/2022**	**28**	**4.5**	
SEQ36 : Fernvale STP @ Savages Crossing	**MBR-SP013.PAS**	**21/07/2022**	**18/08/2022**	**28**	**22.2**	**1 PFM lost**
SEQ37 : Logan River @ Cedar Grove	**LRS-SP012.PAS**	**7/07/2022**	**4/08/2022**	**28**	**3.4**	
SEQ38 : Wappa Dam	**WAD-SP001.PAS**	**19/07/2022**	**17/08/2022**	**29**	**3.4**	
SEQ39 : Cooloolabin Dam	**COD-SP001.PAS**	**6/07/2022**	**4/08/2022**	**29**	**3.6**	
SEQ40 : Wivenhoe Dam @ Logans Inlet PRW	**WID-SP061.PAS**	**2/08/2022**	**30/08/2022**	**28**	**3.8**	
SEQ43 : Enoggera Reservoir	**END-SP001.PAS**	**14/07/2022**	**11/08/2022**	**28**	**3.6**	
SEQ24 : Leslie Harrison Dam - Event	**LHD-SP005.PAS**	**14/06/2022**	**12/07/2022**	**28**	**3.4**	**Event sampler**

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 Pesticide compounds via GC-HRMS (Appendix 1). The analytical methods for herbicides and PPCPs (LC-QQQ MS/MS), OCPs and PAHs (GC-HRMS), and suspect screening of herbicides and PPCPs (LC-QToF MS/MS) are detailed in previously published reports (Kaserzon *et al.* 2017) and in Quality Protocol: Contract 03944 Micro-Pollutant and Passive Sampler Monitoring program.

Data modelling and reporting of results

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

Quality control and assurance (QC/QA) procedures

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

Results

Passive flow monitors (PFM) results

Two passive flow monitors (PFMs) were deployed at each site to allow for flow rate calculations. Under very low flow conditions the change in mass loss rates from the PFM are too small to provide a reliable measure of flow, and therefore cannot accurately provide flow data for the chemical sampling rate (R_s) calculation (i.e. below a threshold flow of 3.40 cm s^{-1} or PFM loss rate equal to 0.58 g d^{-1}; O'Brien *et al.* 2009; 2011b). Therefore, to remain within the accurate mathematical modelling range for PFM-based flow velocity prediction, a minimum flow rate of 3.40 cm s^{-1} is applied for the sites showing flow below this threshold and the minimum atrazine equivalence R_s. This may result in a slight over-estimation of R_s and under-estimation of water concentration estimates (C_w), though it is not expected 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 22 cm s^{-1} (SEQ36 : Fernvale STP @ Savages Crossing) (Figure 2).

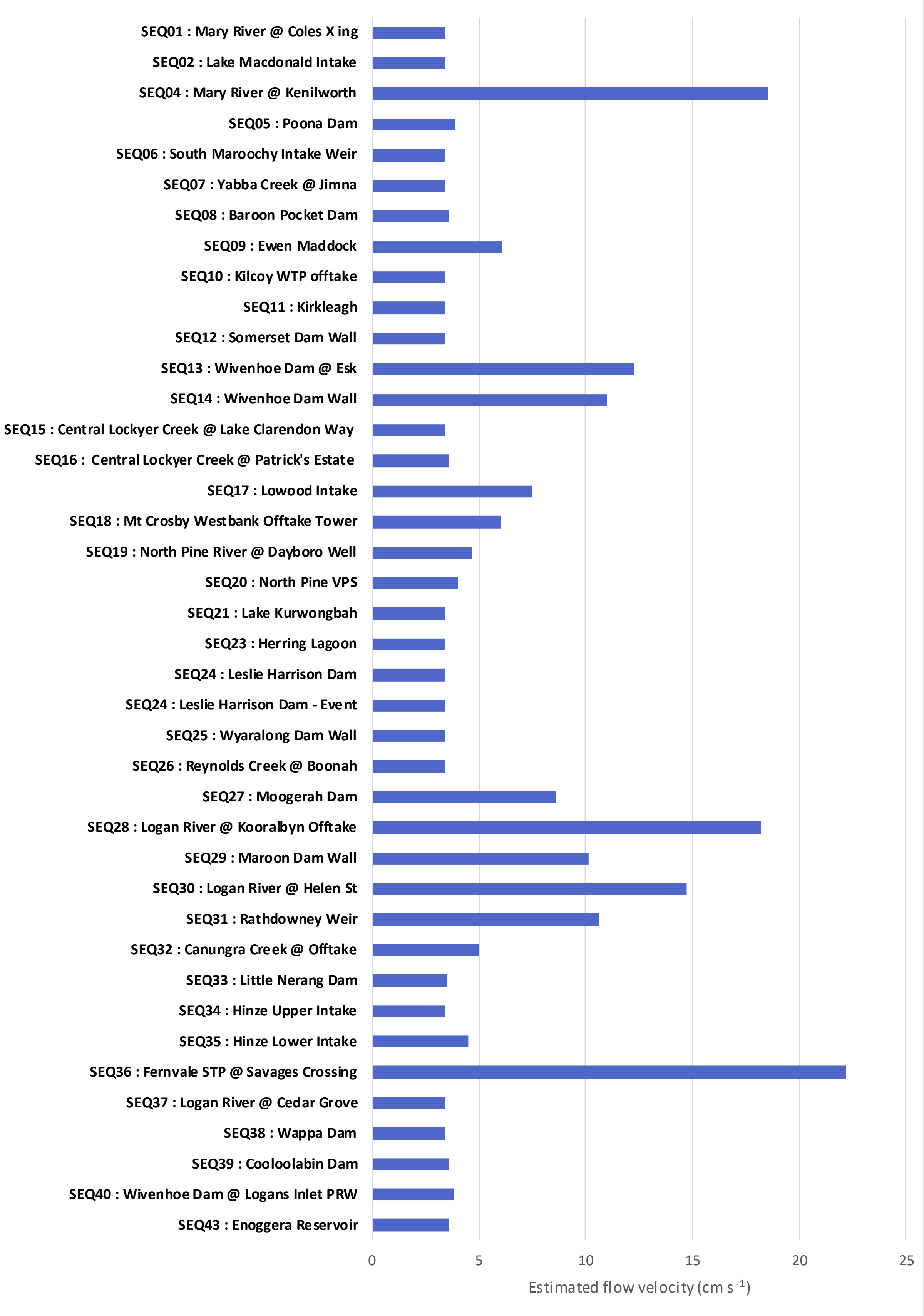

Figure 2. Passive flow monitor (PFM) based water flow velocity estimations (cm s^{-1}) at the deployment sites (n=40).

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 21 OCPs and 14 PAHs were accumulated in samplers with percent detection at sampling sites ranging from 3% – 85% for OCPs and 5% – 95% for PAHs. Table 3 summarises the polar chemicals quantified via ED (pesticides and PPCPs). A total of 32 pesticides (predominantly herbicides) and 8 PPCPs accumulated in samplers with percent detection at sampling sites ranging from 3% - 76% for pesticides and 3% - 100% for PPCPs.

Table 2. Summary of the number of chemicals accumulated in PDMS passive samplers, percentage of detection across the sites and the range (minimum and maximum) 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	**1**	**3%**	**1.09**	**1.09**
Bifenthrin	**19**	**49%**	**1.07**	**2.80**
Chlorpyrifos	**29**	**74%**	**5.87**	**1381**
cis-Chlordane	**16**	**41%**	**4.73**	**13.7**
Cypermethrin	**1**	**3%**	**4.78**	**4.8**
Dacthal	**20**	**51%**	**2.63**	**1271**
Dieldrin	**33**	**85%**	**3.87**	**95.3**
Endosulfan sulfate	**17**	**44%**	**1.06**	**11.8**
Endrin	**2**	**5%**	**1.46**	**2.73**
Endrin ketone	**2**	**5%**	**1.91**	**4.87**
HCB	**16**	**41%**	**2.26**	**6.69**
Heptachlor	**12**	**31%**	**1.92**	**3.78**
Heptachlor epoxide b	**18**	**46%**	**1.51**	**39.4**
o,p-DDD	**3**	**8%**	**1.78**	**2.86**
p,p-DDD	**12**	**31%**	**1.07**	**6.49**
p,p-DDE	**15**	**38%**	**1.03**	**20.5**
p,p-DDT	**2**	**5%**	**2.73**	**3.34**
Permethrin	**6**	**15%**	**2.30**	**5.11**
trans-Chlordane	**16**	**41%**	**9.79**	**28.3**
α-Endosulfan	**6**	**15%**	**1.56**	**2.29**
β-HCH	**4**	**10%**	**0.535**	**0.635**
PAH				
Acenaphthene	**2**	**5%**	**11.7**	**15.4**
Acenaphthylene	**13**	**33%**	**6.08**	**34.5**
Anthracene	**8**	**21%**	**9.17**	**16.5**
Benzo[a]anthracene	**9**	**23%**	**2.63**	**10.6**
Benzo[a]pyrene	**9**	**23%**	**1.01**	**2.10**
Benzo[b,j,k]fluoranthene	**36**	**92%**	**0.996**	**6.57**
Benzo[e]pyrene	**9**	**23%**	**1.88**	**6.37**
Benzo[g,h,i]perylene	**10**	**26%**	**1.27**	**2.47**

Chrysene/Triphenylene	**37**	**95%**	**2.47**	**23.7**
Fluoranthene	**28**	**72%**	**19.9**	**122**
Fluorene	**4**	**10%**	**51.8**	**74.9**
Indeno[1,2,3-c,d]pyrene	**7**	**18%**	**1.01**	**1.94**
Phenanthrene	**8**	**21%**	**139**	**376**
Pyrene	**27**	**69%**	**20.8**	**107**

Table 3. Summary of the number of chemicals accumulated in ED passive samplers, percentage of detection across the sites and the range (minimum and maximum) 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-D	**6**	**16%**	**5.29**	**19.3**
Ametryn hydroxy	**2**	**5%**	**1.13**	**1.19**
Atrazine	**9**	**24%**	**1.04**	**3.50**
Atrazine desethyl	**2**	**5%**	**1.02**	**1.13**
Atrazine desisopropyl	**4**	**11%**	**1.06**	**1.26**
Bromacil	**3**	**8%**	**1.36**	**1.62**
Bromoxynil	**1**	**3%**	**1.03**	**1.03**
Carbendazim	**3**	**8%**	**2.42**	**11.5**
DCPMU	**2**	**5%**	**0.121**	**0.266**
Diazinon	**8**	**21%**	**0.119**	**22.4**
Diuron	**7**	**18%**	**1.18**	**16.2**
Fipronil	**10**	**26%**	**0.570**	**11.8**
Fluazifop	**3**	**8%**	**0.196**	**1.01**
Haloxyfop	**1**	**3%**	**1.34**	**1.34**
Hexazinone	**7**	**18%**	**2.21**	**6.59**
Imidacloprid	**9**	**24%**	**1.01**	**176**
MCPA	**1**	**3%**	**5.04**	**5.04**
Metalaxyl	**22**	**58%**	**0.119**	**5.59**
Methomyl	**2**	**5%**	**4.67**	**37.9**
Metolachlor (S+R)	**17**	**45%**	**1.74**	**41.5**
Metribuzin	**1**	**3%**	**1.87**	**1.87**
Metsulfuron methyl	**29**	**76%**	**1.01**	**32.1**
Prometryn	**2**	**5%**	**1.48**	**2.99**
Propachlor	**2**	**5%**	**1.86**	**2.22**
Propiconazole	**7**	**18%**	**1.21**	**4.10**
Simazine	**10**	**26%**	**1.07**	**13.9**
Tebuconazole	**6**	**16%**	**1.66**	**4.97**
Tebuthiuron	**16**	**42%**	**1.50**	**97.4**
Terbuthylazine	**2**	**5%**	**1.02**	**1.43**
Terbuthylazine desethyl	**1**	**3%**	**1.24**	**1.24**
Thiamethoxam	**5**	**13%**	**2.08**	**66.5**
Triclopyr	**13**	**34%**	**5.24**	**70.9**

Pharmaceuticals and personal care products (PPCPs)				
Carbamazepine	**1**	**3%**	**1.06**	**1.06**
DEET	**38**	**100%**	**1.69**	**136**
Iopromide	**2**	**5%**	**1.10**	**2.30**
Naproxen	**1**	**3%**	**1.66**	**1.66**
Oxazepam	**1**	**3%**	**1.13**	**1.13**
Paraxanthine	**1**	**3%**	**1.75**	**1.75**
Sulfadiazine	**1**	**3%**	**0.556**	**0.556**
Sulfamethoxazole	**3**	**8%**	**0.146**	**0.415**

Organochlorine pesticides (OCPs)

Accumulation of OCPs in PDMS samplers over the deployment period show the mass per sampler of total ∑OCPs ranging from below reporting limits (SEQ32 - Canungra Creek @ Offtake) to 2727 ng PDMS^{-1} (SEQ15 - Central Lockyer Creek @ Lake Clarendon Way) (Table 2, Figure 3, Appendix 1).

Figure 3. Total mass of 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 0.013 to 46.7 ng L^{-1} (for sites SEQ23 - Herring Lagoon and SEQ15 and Central Lockyer Creek @ Lake Clarendon Way, respectively; Figure 4).

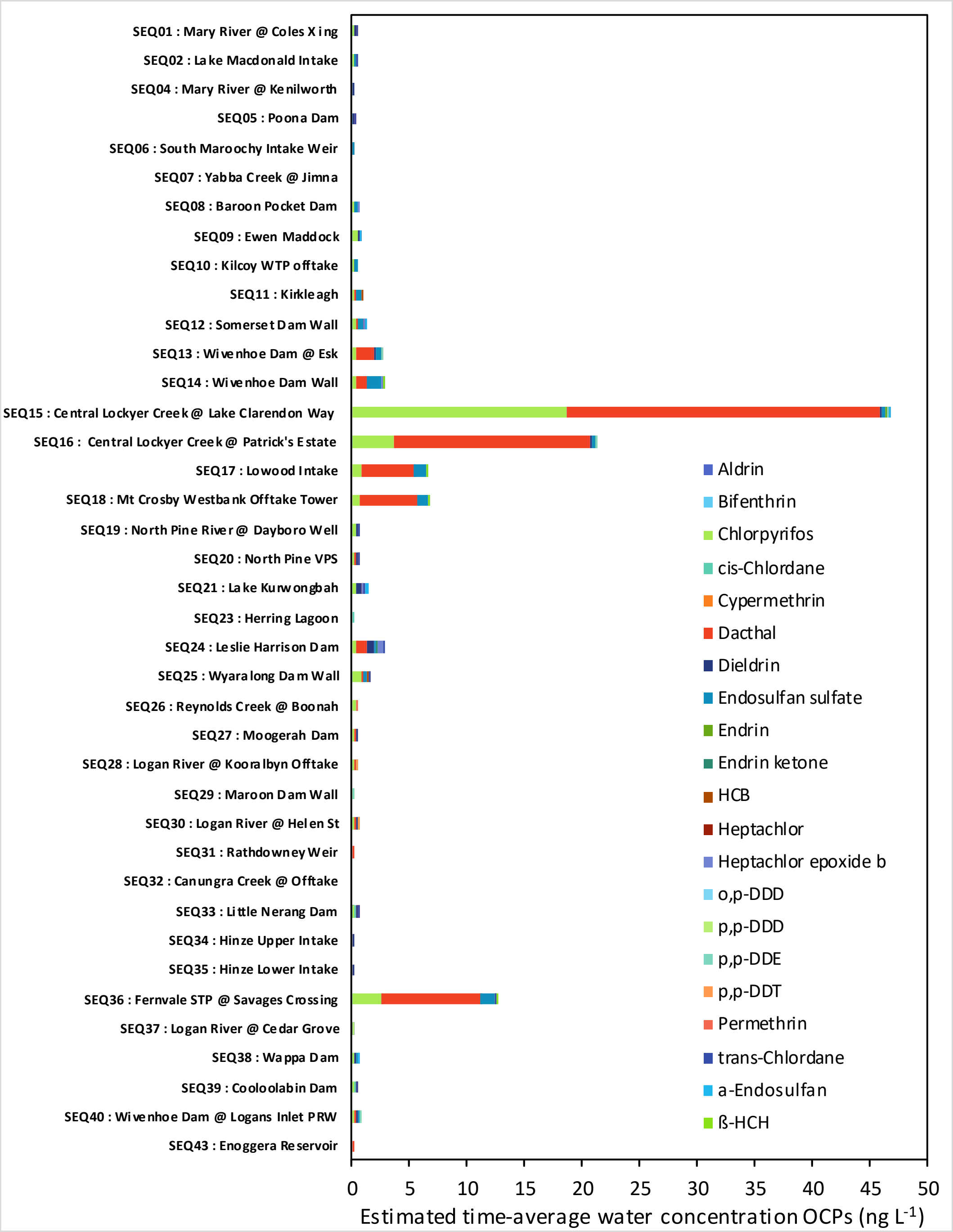

Figure 4. Total estimated water concentrations (ng L^{-1}) of ΣOCPs at each site derived from PDMS passive samplers.

Polycyclic aromatic hydrocarbons (PAHs)

Accumulation of PAHs in PDMS samplers over the deployment period show the mass per sampler of total ∑PAHs accumulated ranging from below reporting limits (SEQ26 - Reynolds Creek @ Boonah) to 719 ng $PDMS^{-1}$ (SEQ13 - Wivenhoe Dam @ Esk) (Table 2, Figure 5, Appendix 1).

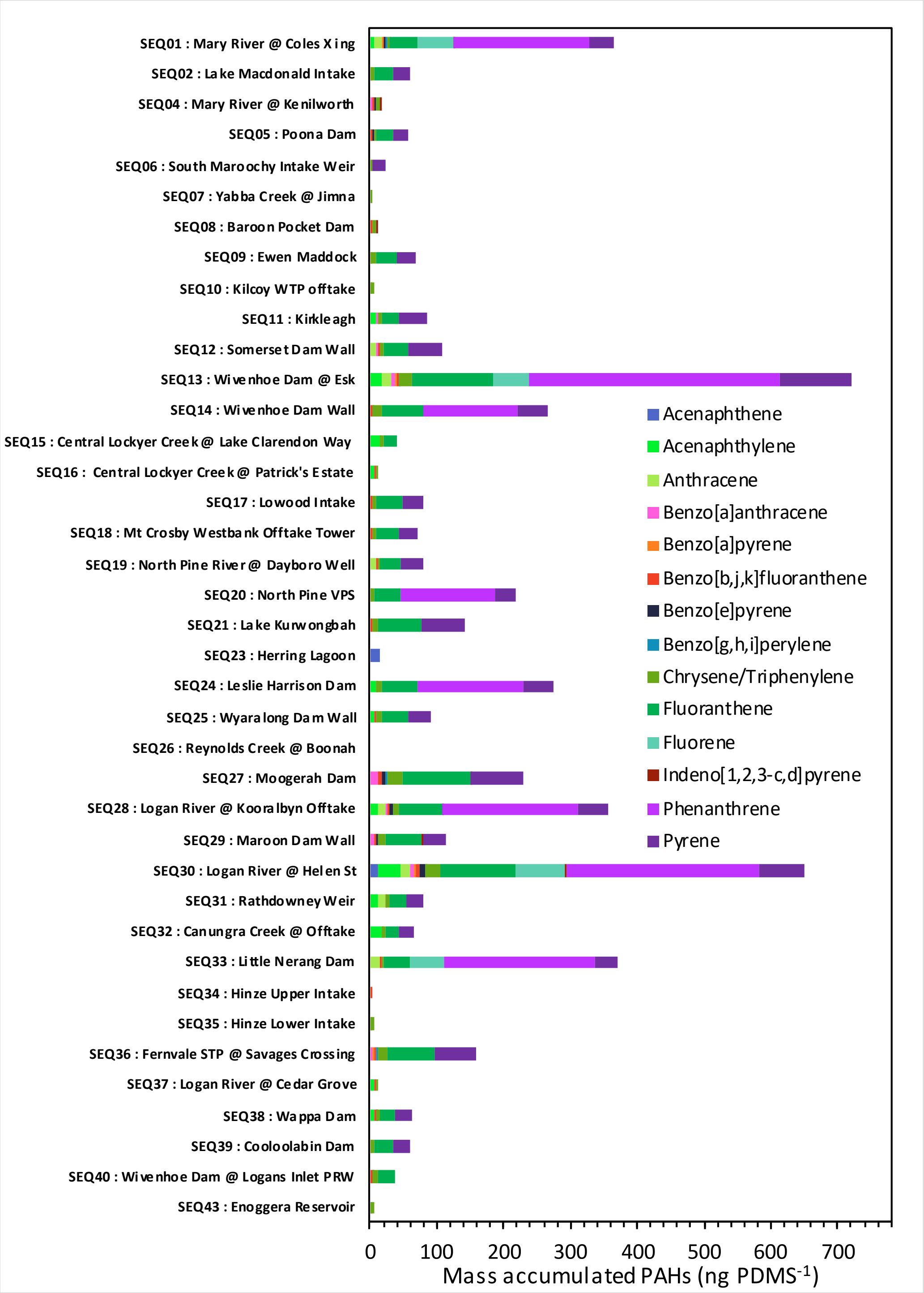

Figure 5. Total mass of ΣPAHs (ng PDMS^{-1}) accumulated in PDMS passive samplers at each site.

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 0.004 to 4.32 ng L^{-1} (for SEQ34 - Hinze Upper Intake and SEQ30 - Logan River @ Helen St, respectively; Figure 6).

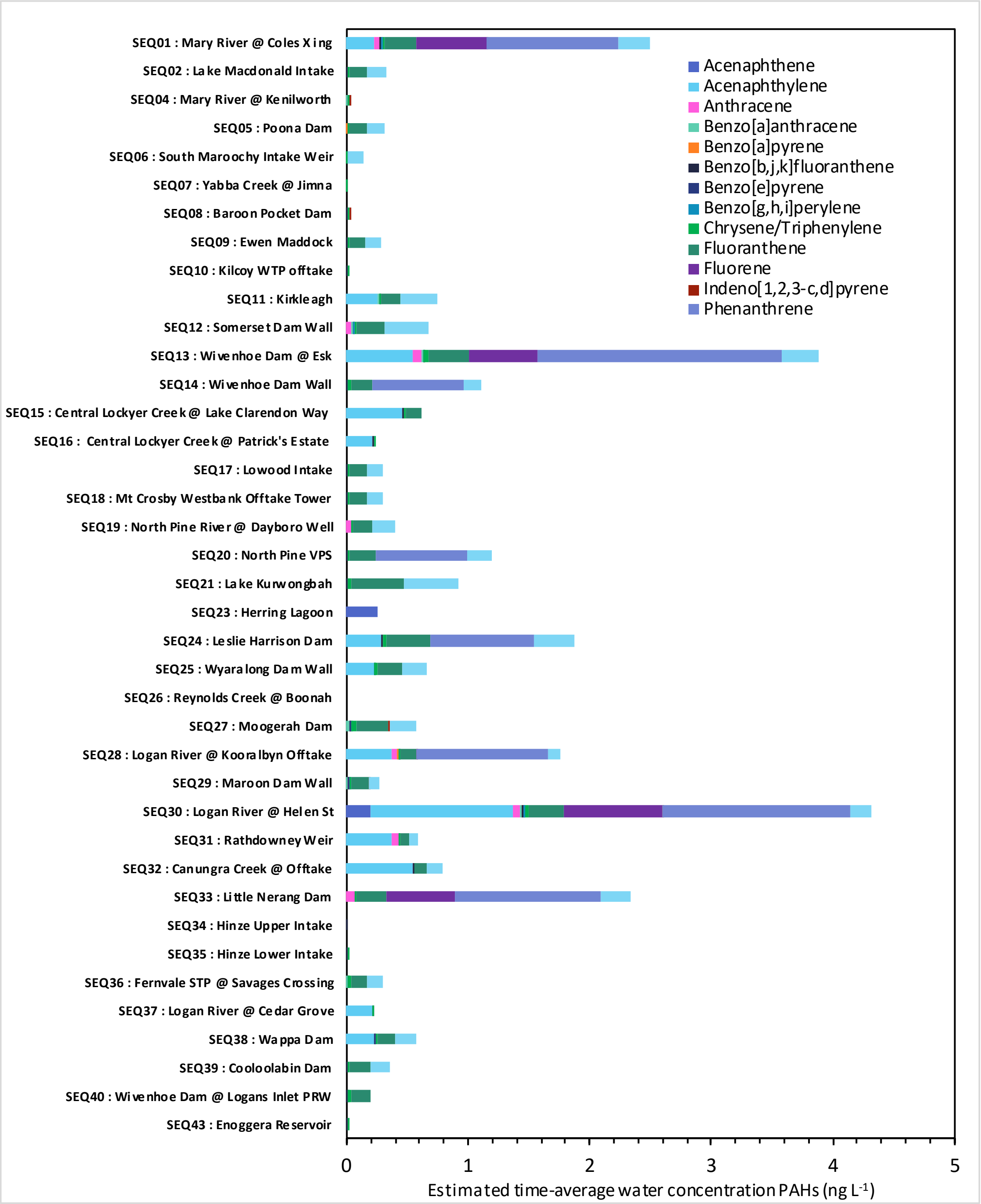

Figure 6. Total estimated water concentrations (ng L^{-1}) of ΣPAHs at each site derived from PDMS passive samplers.

Pesticides

Accumulation of Pesticides (including herbicides, fungicides and insecticides) in ED passive samplers over the deployment period show the mass per sampler of total ∑Pesticides accumulated ranging from below reporting limits (SEQ07 - Yabba Creek @ Jimna; SEQ32 - Canungra Creek @ Offtake; SEQ33 - Little Nerang Dam; SEQ39 - Cooloolabin Dam; SEQ43 - Enoggera Reservoir; SEQ01 - Mary River @ Coles X ing; SEQ23 - Herring Lagoon) to 354 ng ED^{-1} (SEQ15 - Central Lockyer Creek @ Lake Clarendon Way) (Table 3, Figure 7, Appendix 1).

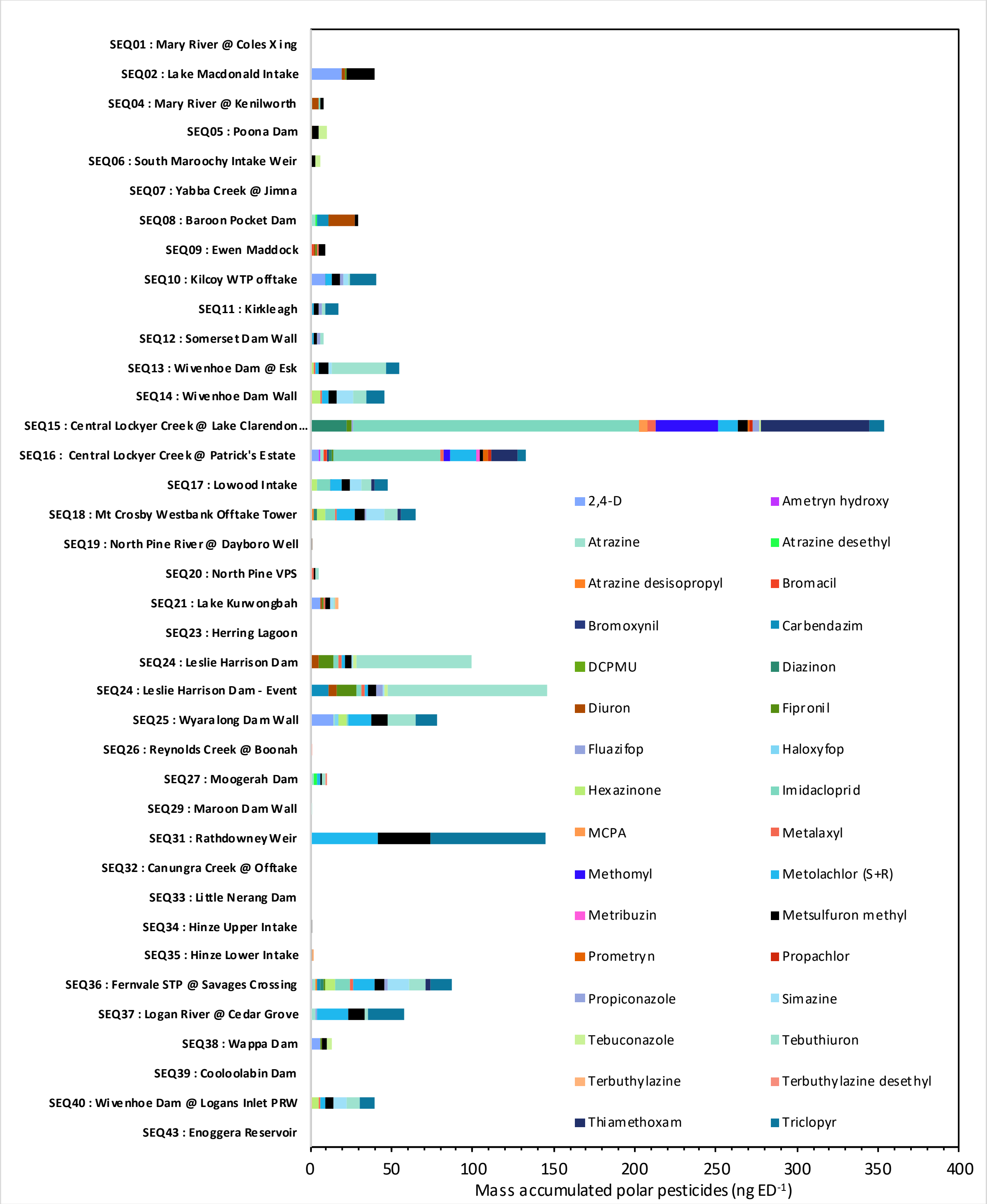

Figure 7. Total mass of ΣPesticides (ng ED^{-1}) accumulated in ED passive samplers at each site.

Water concentrations were estimated for the polar pesticides accumulated where sampling rates have been previously calibrated. From the 32 chemicals reported, 17 were converted to time-weighted average water ∑concentrations. Discounting the sites below reporting limits, these water concentrations ranged between 0.470 and 90.4 ng L^{-1} (for SEQ29 - Maroon Dam Wall and SEQ24 - Leslie Harrison Dam Event, respectively; Figure 8).

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

Pharmaceuticals and personal care products (PPCPs)

Accumulation of PPCPs in ED passive samplers over the deployment period show the mass per sampler of total ∑PPCPs accumulated ranging from 0.640 ng ED^{-1} (SEQ36 - Fernvale STP @ Savages Crossing) to 136 ng ED^{-1} (SEQ10 - Kilcoy WTP offtake) (Table 3, Figure 9, Appendix 1).

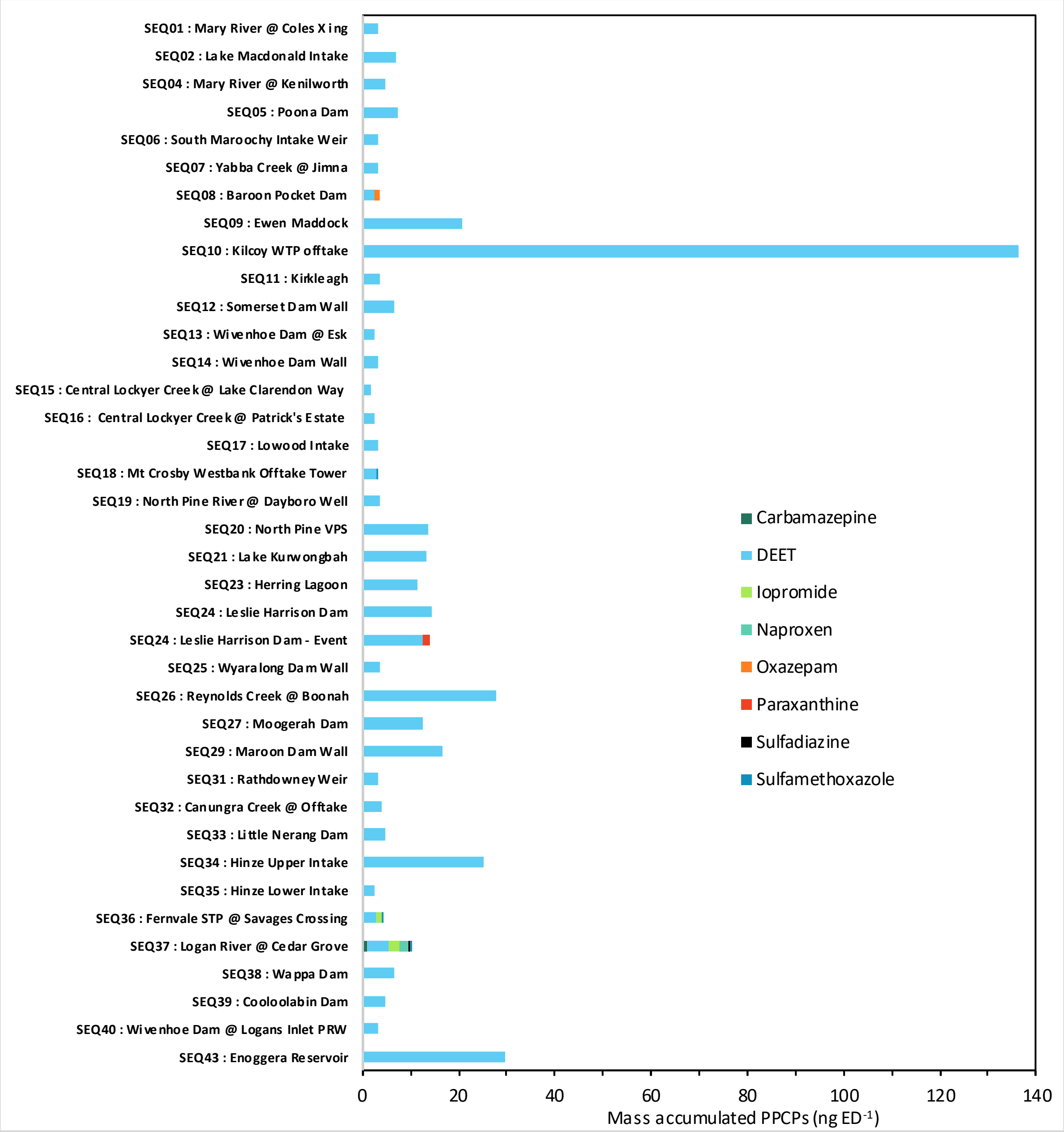

Figure 9. Total mass of ΣPPCPs (ng ED^{-1}) accumulated in ED passive samplers at each site.

Of the reported PPCPs, 3 were able to be converted into estimated time-weighted average water concentrations. Discounting the sites below reporting limits, these ∑PPCP water concentrations ranged between 0.64 and 83.8 ng L^{-1} (for sites SEQ36 - Fernvale STP @ Savages Crossing and SEQ10 - Kilcoy WTP offtake, respectively; Figure 10).

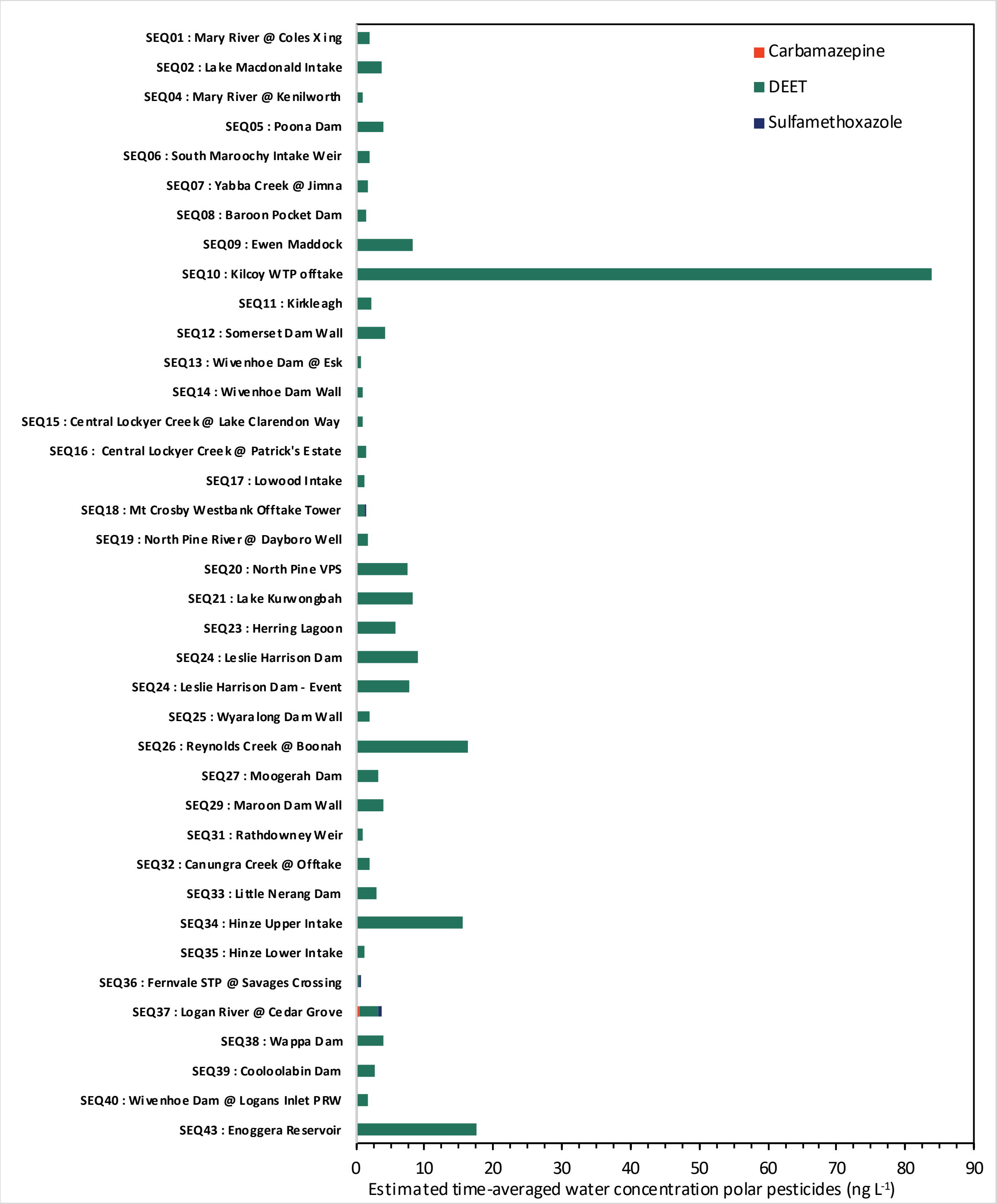

Figure 80. Total estimated water concentrations (ng L^{-1}) of ΣPPCPs.

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 10 compounds (Table 4). The suspect screening provides tentative identification of the presence or absence of these chemicals. We note that to fully confirm the identification and quantification of these analytes, the use of appropriate chemical standards would be necessary. Tentative identifications are considered when spectral library match scores exceed 99% and mass errors were <3 ppm.

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

Chemical name	Description	Sites with tentative detects
Acetaminophen	Pain medication	SEQ02: Lake Macdonald Intake SEQ08: Baroon Pocket Dam SEQ11: Kirkleagh
Aminocarb	Carbamate insecticide	SEQ01: Mary River @ Coles crossing SEQ10: Kilcoy WTP offtake SEQ16: Central Lockyer Creek @ Patrick's Estate SEQ23: Herring Lagoon SEQ37: Logan River @ Cedar Grove SEQ38: Wappa Dam SEQ43: Enoggera Reservoir
Carbaryl	Insecticide	SEQ27: Moogerah Dam
Carbofuran	Carbamate insecticide	SEQ07: Yabba Creek @ Jimna
Etofenprox	Insecticide	SEQ04: Mary River @ Kenilworth SEQ06: South Maroochy Intake Weir SEQ07: Yabba Creek @ Jimna SEQ12: Somerset Dam Wall SEQ13: Wivenhoe Dam @ Esk SEQ14: Wivenhoe Dam Wall SEQ20: North Pine VPS SEQ23: Herring Lagoon SEQ24: Leslie Harrison Dam SEQ25: Wyaralong Dam Wall SEQ26: Reynolds Creek @ Boonah SEQ31: Rathdowney Weir SEQ32: Canungra Creek @ Offtake SEQ37: Logan River @ Cedar Grove SEQ39: Cooloolabin Dam SEQ40: Wivenhoe Dam @ Logans Inlet PRW
Fenobucarb	Carbamate insecticide	SEQ38: Wappa Dam
Metronidazole	Antibiotic	SEQ02: Lake Macdonald Intake SEQ08: Baroon Pocket Dam SQE19: North Pine River @ Dayboro Well SEQ20: North Pine VPS
Mexacarbate	Carbamate insecticide	SEQ07: Yabba Creek @ Jimna SEQ16: Central Lockyer Creek @ Patrick's Estate SEQ18: Mt Crosby Westbank Offtake Tower SQE21: Lake Kurwongbah

		SEQ36: Fernvale STP @ Savages Crossing SEQ38: Wappa Dam SEQ43: Enoggera Reservoir
Promecarb	Insecticide	SEQ05: Poona Dam
Simetryn	Herbicide	SEQ01: Mary River @ Coles crossing SEQ38: Wappa Dam SEQ40: Wivenhoe Dam @ Logans Inlet PRW

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. The site SEQ15 - Central Lockyer Creek @ Lake Clarendon Way exceeded the 95% species protection guideline value for Diazinon and Chlorpyrifos with concentrations of 37.4 ng L^{-1} and 18.6 ng L-^{1}, respectively. Furthermore, totals of 8, 5, 1 and 29 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% or 99% species protection guideline.

Australian Drinking Water Guidelines 6 (2011) Version 3.6 Updated March 2021		ANZECC & ANCANZ (2021) Trigger values for freshwater		
Herbicides & Insecticides	**Guideline value (ng L^{-1})**	**99% species protection value (ng L^{-1})**	**95% species protection value (ng L^{-1})**	**This campaign Highest Reported Value (ng L^{-1})**
Atrazine	20000	700	13000	2.8
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	11.5
Cypermethrin	200000	N/A	N/A	N/A
Diazinon	4000	0.03	10	37.4
Diuron	20000	N/A	N/A	15.2
Fipronil	700	N/A	N/A	8.6
Fluometuron	70000	N/A	N/A	N/A
Haloxyfop	1000	N/A	N/A	N/A
Hexazinone	400000	N/A	N/A	3.5
Imazapyr	9000000	N/A	N/A	N/A
MCPA	40000	N/A	N/A	2.6
Malathion	70000	2	50	N/A
Methomyl	20000	N/A	N/A	N/A
Metolachlor (S+R)	300000	8.4	460	16.0
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	4.3
Tebuthiuron	N/A	20	2200	62.4
Terbuthylazine	10000	N/A	N/A	1.1
Triclopyr	20000	N/A	N/A	14.0
2,4-D	30000	140000	280000	11.5
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	18.6
Cypermethrin	200000	N/A	N/A	0.0
DDT	9000	6	10	0.048
Dieldrin	300	N/A	N/A	0.5
Aldrin	300	N/A	N/A	0.0
Endosulfan	20000	30	200	N/A
Endrin	N/A	10	20	0.0
Heptachlor	300	10	90	0.0
γ-HCH (Lindane)	10000	70	200	N/A
Methoxychlor	300000	N/A	N/A	N/A
PAHs				
Anthracene	N/A	10	400	0.1
Benzo[a]pyrene	10	N/A	N/A	0.0
Fluoranthene	N/A	1000	1400	0.4
Naphthalene	10	2500	16000	N/A
Phenanthrene	N/A	600	2000	2.0

Discussion

OCPs were first introduced into Australia in the mid-1940s and were applied in many commercial products in different forms (such as powders and liquids). At one time up to 150 commercial products containing OCPs may have been registered in Australia. This followed a period of widespread use until the 1970s when recognition of risks related to OCPs resulted in reduced use and their ultimate ban in the 1980s. Since then, human biomonitoring studies in blood and breastmilk have showed the substantial decline of these chemicals from the early 1980s to the 1990s after which levels appear to plateau (Toms *et al.* 2012). Although a few OCPs were reported, the concentrations were low (Total ∑OCPs <46.7 ng L^{-1}). The compound Chlorpyrifos, still in use today, was reported at higher concentrations, consistent with ongoing inputs to the environment. Chlorpyrifos was introduced in 1965 and has been included in many products and formulations aimed at agricultural, urban, commercial and residential uses. Although regulation measures have been put in place in Australia (APVMA 2011b) the chemical has not been strictly banned. A search of the APVMA PubCris database reveals 72 currently registered or approved products containing chlorpyrifos. A continued review of Chlorpyrifos is warranted to estimate any future risk. Dieldrin was the most frequently detected OCP, reported at 30 sites. Dieldrin has been used since the 1950s 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 sites at low levels (∑PAHs 4.32 ng L^{-1}).

Of the polar pesticides (herbicides, insecticides and fungicides) detected, the most frequently reported pesticide was Metsulfuron methyl (detected at 76% of sites). Metsulfuron methyl is a herbicide used in sugarcane and other farming crop as a broad spectrum pre- and early post-emergent control for various grass and broadleaf weeds. Contemporary herbicides can remain in soils for several months and can migrate from soil to groundwater or transport to waterways via runoff and flooding events. Some 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). Often, such herbicides are used in conjunction with Diuron and Hexazinone, two herbicides also frequently observed. Herbicides with some soil mobility are generally transported to the aquatic environment through runoff and/or percolation to groundwater. The second most frequently reported pesticide was Metalaxyl (detected at 58% of sites) which is a systemic fungicide used to control plant diseases caused by Oomycete fungi. Given its broad-spectrum activity, Metalaxyl is used world-wide on a variety of fruit and vegetable crops and its tolerance to a broad range of light, pH and temperature allow it to persist in the environment.

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 is often attributed to background contamination due to high DEET application by field staff, to combat insect bites. The second most frequently reported PPCP was Sulfamethoxazole (detected at 8% of sites). Sulfamethoxazole is a bacteriostatic antibiotic prescribed for human treatment of bacterial infections such as urinary tract infections. The contribution of pharmaceuticals and personal care products can be an indicator of systems which are used for human recreational activities, or which receive some degree of treated effluent.

Future recommendations

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

- Continue temporal/ seasonal and spatial comparisons to investigate long term trends and seasonal patterns of contaminants risk profiles in SEQ catchment areas.

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Appendix 1

See enclosed excel file 'SEQW results_Winter2022.xlsx'

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