



NSW Environment Protection Authority *and*
NSW Department of Climate Change, Energy, the Environment and Water

Lake Illawarra snapshot contamination assessment

Metals and pesticides in the lake, tributaries
and surrounding groundwater

November 2024



A vertical decorative bar on the left side of the page, featuring intricate Aboriginal patterns in shades of blue and white. The patterns include concentric circles, wavy lines, and geometric shapes, typical of traditional Indigenous art.

Acknowledgement of Country

The NSW Environment Protection Authority acknowledges the Traditional Custodians of the land on which we live and work, honours the ancestors and the Elders both past and present and extends that respect to all Aboriginal people.

We recognise Aboriginal peoples' spiritual and cultural connection and inherent right to protect the land, waters, skies and natural resources of NSW. This connection goes deep and has since the Dreaming.

We also acknowledge our Aboriginal and Torres Strait Islander employees who are an integral part of our diverse workforce and recognise the knowledge embedded forever in Aboriginal and Torres Strait Islander custodianship of Country and culture.

Aboriginal artwork by Worimi artist Gerard Black

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This report presents water and sediment quality data collected during a one-off sampling event around Lake Illawarra, conducted in January and February 2024. The investigation involved analysing metals and pesticides in three types of water samples: surface water and sediments collected from six locations within Lake Illawarra and from passive samplers deployed at the same six locations; stormwater collected from 11 tributaries leading into the lake; and groundwater from two monitoring bores located near the lake.

For all samples collected within the lake, the water and sediment quality parameters assessed were within the recommended range of relevant Australian guideline values (or third-party guideline values where no relevant Australian value was available). Analysis of the stormwater samples identified that the main contaminant inputs were the metals cobalt, copper, manganese, lead and zinc, and the pesticides diuron and diphenylamine. Within the groundwater, elevated concentrations of dissolved iron and manganese were detected at one of the bores.

1 Introduction

1.1 Project overview

Lake Illawarra is a barrier estuary system located 80 km south of Sydney and 10 km south of Wollongong City (Figure 1). The Lake Illawarra catchment covers an area of approximately 240 km and is fed by several watercourses, including Macquarie Rivulet and Mullet Creek. The lake remains permanently open to the ocean via the entrance channel. The catchment for Lake Illawarra spans suburbs in both Wollongong and Shellharbour and is managed by Wollongong and Shellharbour local councils in partnership with the NSW Government. Land uses in the catchment range from grazing land to residential and industrial urban land to natural bushland.

Lake Illawarra is used recreationally but also has significant environmental value as the lake and its surrounds provide habitat for protected plant communities, such as saltmarsh, as well as other important communities supporting human and estuarine health, such as mangroves, seagrass, and swamp oak floodplain forest. The lake and its surrounds are also of strong cultural significance to Aboriginal people.

Wollongong and Shellharbour local councils are implementing a coastal management program (CMP) for Lake Illawarra to maintain and enhance the quality of the lake and estuaries. The program provides nine strategies to improve water quality in the lake and estuaries, including strategy WQ9: 'Investigate and manage potential pollution sources including contaminated sites that contribute to poor water quality in the lake'.



Figure 1 Lake Illawarra, NSW, Australia

DCCEEW-Ecotoxicology and the NSW EPA undertook a snapshot (single point in time) health check of Lake Illawarra and its estuaries by investigating common urban, industrial and agricultural contaminants in the water body. The contaminants investigated were metals and metalloids (hereafter referred to as metals for simplicity); pesticides; and microplastics in groundwater. Microplastics were excluded from the surface water and stormwater elements of the program due to a recent and comprehensive investigation of this contaminant by the DCCEEW's Coastal and Marine team.

1.2 Aims and objectives

The objective of this sampling program was to investigate the presence of key urban and industrial metal contaminants and agricultural pesticides in:

- passive samplers (a bioaccumulation modelling approach to assess the potential for accumulation by aquatic fauna)
- water and sediments from major Lake Illawarra tributary in-flow points
- water at stormwater ingress points
- water in nearby groundwater wells.

2 General methodology

2.1 Study sites

Figure 2 shows the sampling locations for the lake water grab samples, sediment samples, passive sampler deployments, stormwater grab samples, and groundwater grab samples. The sampling locations for the lake water grab samples, sediment samples and the passive sampler deployments were selected to provide a representative understanding of contaminant distribution in various areas of the lake, including near major tributary entry points. The stormwater grab samples were collected from strategically chosen locations to provide an accurate representation of the contaminant profile entering the lake and its tributaries through stormwater channels. Groundwater sampling locations were selected to provide a representation of the contaminant distribution within the groundwater surrounding the lake. Site selection was limited by available bores, both on public land and on EPA-licensed premises.

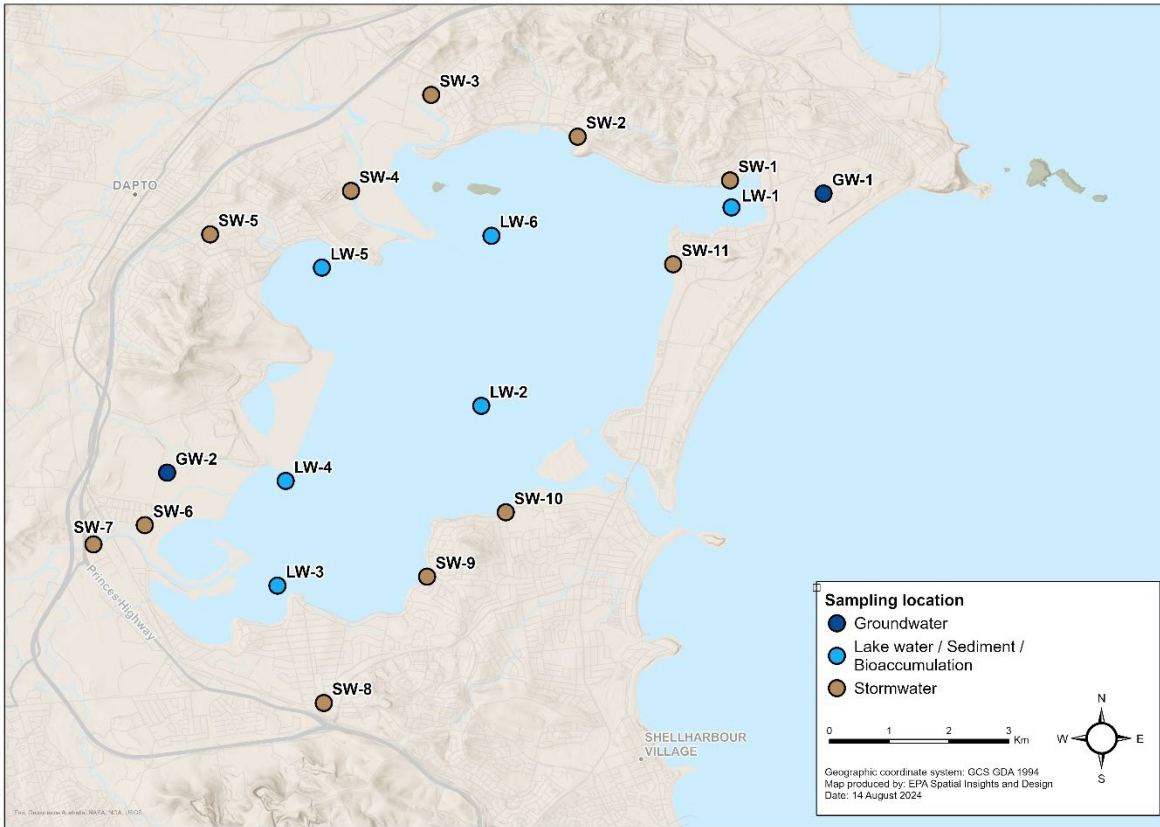


Figure 2 Lake water, sediment, passive sampler, stormwater and groundwater sample collection locations (Lake Illawarra, NSW, Australia)

3 Sample collection

The water quality monitoring program was carried out between 22 January and 19 February 2024. The program included a one-off collection of grab water samples from the lake (via boat), stormwater, and groundwater, as well as surface sediment from the lake (via boat). In addition, passive samplers were deployed to collect data on potential contaminants in the lake over an extended period (approximately 20 days).

3.1 Lake and stormwater sampling

At each site, physicochemical parameters were recorded using a multi-parameter water quality probe (YSI ProDSS, USA). For the lake sites, the measurements were taken at a depth of approximately 20–40 cm below the surface.

From the lake and stormwater, water grab samples were collected using a sampling pole that was rinsed with site water. The sampling pole was submerged to a depth of approximately 30 cm below the surface of the water, and the samples were collected directly into laboratory-prepared containers to minimise the potential for introducing contamination to the samples. Samples for pesticide analysis were collected into 1 L amber glass hexane-rinsed bottles. Samples for total metal analysis were collected into 300 mL acid-washed plastic containers. From the total metals sample, an aliquot was passed through a 0.45 µm polyethersulfone (PES) syringe filter (Microscience – SF35PS045, Australia) using a 50 mL syringe (Terumo – SS50LE, Japan) into a 30 mL plastic vial for dissolved metal analysis. All containers, syringes and filters were rinsed with the site water before the sample was collected. All samples were kept on ice during sampling. Samples for total and dissolved metal analyses were acidified upon return to the laboratory, and all samples were stored at 4°C until analysis. A field duplicate sample (for intra-laboratory analysis) was collected for each sampling event (one each for the lake water and stormwater sample collections).

3.1.1 Passive sampling

Passive samplers were deployed at the same sites as the lake water grab samples were collected. Three types of passive water samplers were deployed to detect a broad range of contaminants in surface waters. Empore samplers and the polar organic chemical integrative sampler (POCIS) were used to measure polar to moderately nonpolar pesticides. Diffusive gradients in thin films (DGT) were used to measure cationic and anionic metals.

The Empore samplers consisted of an SDB-XC (polystyrenedivinylbenzene) Empore™ disc (47 mm diameter, Phenomenex, USA) as the receiving phase covered with a polyethersulfone (PES) diffusion limiting membrane (0.45 µm, 47 mm diameter, Sartorius, Germany). The Empore samplers were pre-conditioned and assembled in the laboratory before deployment. This was done by pre-conditioning the SDB-XC receiving disc in a vacuum manifold with the sequential addition of acetone, isopropanol, methanol and high-purity water (18 MΩ.cm, Milli-Q, Millipore, Australia). The PES membrane was soaked in methanol (≥2 h) followed by high-purity water (≥2 h). The discs were then assembled into polytetrafluoroethylene housings that had been soaked in a 5% liquid detergent (≥12 h, Decon 90) followed by ultrasonication in acetone (10 mins), capped, placed in zip-lock bags, and kept at 4°C until deployment. All solvents used were of high-performance liquid chromatography (HPLC) grade. The POCIS consisted of 235 mg of AttractSPE® HLB sorbent as the

receiving phase enclosed between two PES diffusion limiting membranes (0.1 μm , 90 mm diameter) (Affinisep, France). POCIS were supplied ready for deployment and were stored at room temperature until deployment.

DGT samplers were purchased from DGT Research Limited (Lancaster UK). The LSNX-NP variety was selected which consists of a PES filter membrane, a 0.8 mm agarose crosslinked polyacrylamide (APA) diffusive gel, and a mixed receiving layer of Chelex and titanium oxide (Metsorb). The DGT samplers were supplied ready for deployment and were stored in zip-lock bags at 4°C until deployment.

At each sampling site, triplicate DGT samplers, a single Empore sampler, and a single POCIS sampler were secured inside a protective plastic mesh cage with zip ties. The cage was then attached to a rope that was weighted at one end with a concrete weight and a solid styrene float at the other. As a part of the quality control process, a duplicate Empore and POCIS sampler was deployed at Site 5. The variation between the results of the duplicates was used to indicate the reproducibility of the analysis.

All passive samplers were deployed on 30 January 2024. The DGT samplers were retrieved after three days, on 2 February 2024. Upon retrieval of the DGT samplers, the Empore and POCIS samplers were checked and rinsed with high-purity water from a squeeze bottle to remove particulates and biofouling. The Empore and the POCIS samplers were retrieved after 20 days, on 19 February 2024. Upon retrieval, all samplers (i.e. DGT, Empore and POCIS) were rinsed thoroughly with high-purity water. The Empore samplers were capped with their transport lid. All samplers were then placed into zip-lock bags and were kept on ice during sampling and transport. As a part of the quality control process, DGT (n=3), Empore (n=1), and POCIS (n=1) field blanks were included and used to identify any instances of contamination caused by handling and exposure in the field. The field blanks were briefly exposed at one site while the samplers were being retrieved. They were then rinsed with high-purity water, placed in a zip-lock bag, and transported back to the laboratory with the exposed samplers.

All samplers were stored at 4°C upon return to the laboratory. The Empore and POCIS samplers were disassembled for preservation. The receiving phase of the Empore samplers was recovered using clean tweezers and placed into individual 15 mL centrifuge vials. Each POCIS was carefully opened, and the sorbent was transferred by washing with high-purity water into a 6 mL polypropylene SPE cartridge containing a polyethylene frit (Affinisep). The sorbent was then capped by placing a second frit into the SPE cartridge and dried under vacuum in an SPE manifold. The SPE cartridge was then placed into a 50 mL centrifuge tube. The centrifuge vials containing the receiving phases of the Empore and POCIS samplers were stored at -20°C until analysis.

4 Sediment sampling

All sediment samples were collected using a handheld piston corer with a polyvinylchloride tube (approximately 400 mm long x 70 mm wide) attached. After being plunged vertically into the sediment, the core was gently lifted to the surface and while still in the water the base of the core was plugged with a foam stopper. The top 10 cm of the core was extruded onboard the boat by slowly pushing the core down a wooden plunger and collecting the extruded sediment into a new glass jar with a plastic spoon. Unrepresentative materials (such as litter, twigs, and large stones and shells) were removed by hand-picking. A field duplicate sample (for intra-laboratory analysis) was

collected from a single site. All samples were kept on ice during sampling. Upon return to the laboratory, they were stored at 4°C until analysis.

4.1 Groundwater sampling

Groundwater samples were taken from licensee-owned groundwater bores, maintained as part of their Environment Protection Licence (EPL) conditions. To sample groundwater, an interface probe was lowered to the depth of the groundwater interface in the bore, and then a peristaltic pump was used to draw up water through silicone tubing for several minutes until a pumping speed was determined that matched the speed at which water in the bore refilled (i.e. the groundwater interface height remained stable). The physicochemical parameters were recorded using a multi-parameter water quality probe (YSI ProDSS, USA). The measurements were taken within a flow cell with water drawn through using the peristaltic pump and silicon tubing.

Once pH on the water quality probe had stabilised, containers were rinsed with bore water before samples were pumped into laboratory-prepared containers. Samples for pesticide analysis were collected into 1 L amber glass hexane-rinsed bottles. Samples for total metal analysis were collected into 300 mL acid-washed plastic containers. From the total metals sample, an aliquot was passed through a 0.45 µm polyethersulfone (PES) syringe filter (Microscience – SF35PS045, Australia) using a 50 mL syringe (Terumo – SS50LE, Japan) into a 30 mL plastic vial for dissolved metal analysis.

A field duplicate sample (for intra-laboratory analysis) was collected from a single site. All samples were kept on ice during sampling and stored at 4°C until delivered to the laboratory for analysis.

4.1.1 Microplastic sampling

Microplastics were sampled at the two groundwater bores, following the procedure outlined in Section 4.1. After samples were collected for pesticides, total metals and dissolved metals, groundwater was pumped directly into 1 L glass pre-prepared bottles from Eurofins. A field duplicate sample (for intra-laboratory analysis) was collected from a single site. All samples were kept on ice during sampling and stored at 4°C until delivered to the laboratory for analysis.

4.2 Chemical analyses

4.2.1 Water and sediment samples

The lake grab and sediment samples, stormwater grab samples and groundwater grab samples were analysed by the National Measurement Institute (NMI) – Analytical Services Branch (North Ryde, NSW) according to standard operating procedures. All water and sediment samples were quantitatively analysed for 109 pesticides by gas chromatography-tandem mass spectrometry (GC-MSMS) and 38 pesticides by liquid chromatography-tandem mass spectrometry (LC-MSMS) with some overlap of analytes.

All water samples were quantitatively analysed for both total and dissolved metals by inductively coupled plasma mass spectrometry (ICP-MS). All sediment samples were quantitatively analysed for total recoverable metals by ICP-MS. Twelve metals were investigated (arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), vanadium (V) and zinc (Zn)). All sediment samples were also quantitatively analysed for dilute-acid-extractable Ni (1M HCl extraction method).

4.2.2 Passive samplers

The Empore and POCIS samplers were extracted and analysed by the National Measurement Institute – Analytical Services Branch (Port Melbourne, VIC) according to standard operating procedures. The Empore extracts were quantitatively analysed for a total of 99 pesticides by gas chromatography–tandem mass spectrometry (GC–MS/MS) and 102 pesticides by liquid chromatography–tandem mass spectrometry (LC–MS/MS). The POCIS extracts were analysed for 102 pesticides by LC–MS/MS.

The DGT samplers were extracted and analysed by the Environmental Research Facility (Griffith University, Australia) according to standard operating procedures. They were analysed for the same suite of metals as the water grab samples, except Hg, which is not retained by the DGT device used in this study.

As a part of the quality control, DGT (n=3), Empore (n=1) and POCIS (n=1) laboratory blanks were included and used to identify instances of laboratory contamination. The laboratory blanks remained unexposed at the laboratory for the duration of the deployment. The laboratory and field blanks were extracted and analysed in parallel with the exposed samplers.

Appendix A gives further details of the passive sampling technique and calculations for converting the reported analyte concentration within the passive sampler receiving phase to an estimated time-weighted average concentration within the i.e. lake water.

4.2.3 Groundwater samples

Samples for microplastic analysis were collected from the groundwater wells and analysed by Eurofins Scientific (Dandenong South, VIC) according to standard operating procedures.

4.3 Quality assurance and quality control

Quality assurance (QA) procedures were established for this project to maximise sample integrity. Quality control (QC) procedures were implemented to assess the effectiveness of QA and to determine the validity of the data. The QC process involved the use of laboratory blanks, field blanks and triplicate or duplicate samplers, as previously described. Details of the QA and QC measures implemented during the current study are provided in Appendix B.

All analyses were performed by a NATA-accredited laboratory using established standard operating procedures. Laboratory QA/QC procedures included the use of reagent blanks, matrix-matched standards, laboratory duplicates, and matrix-matched spikes which had to comply with the laboratory's established criteria of acceptance for reporting.

4.4 Identifying key contaminants of potential concern

4.4.1 Lake water

The physicochemical data were compared to the ANZECC/ARMCANZ (2000) default trigger values for estuaries. The concentrations of metals and pesticides were compared with the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZG, 2018). ANZG (2018) provides Default Guideline Values (DGVs), which represent estimates of the concentration of chemicals below which there is a low risk of significant adverse effects on the aquatic ecosystem, to assist in identifying where further investigation or consideration of potential risks may be required.

Lake Illawarra is best described as a slightly to moderately disturbed system. Where available, marine DGVs for slightly to moderately disturbed systems (95% species protection) were adopted. For Cd and Hg, which are known to bioaccumulate in the marine environment, the DGV for high conservation or ecological value systems (99% species protection) was used. For Ni, the DGV for high conservation or ecological value systems (99% species protection) was also used, to protect key species from chronic toxicity. In the absence of a DGV for As in marine waters, the proposed third-party guideline value derived by Golding et al. (2022) for As(V) of 12 µg/L (95% species protection) has been used as the screening criterion. No marine DGV was available for diuron. However, an indicative interim working level of 200 ng/L (unknown reliability) for diuron in freshwater was available. Indicative interim working levels are considered interim as they should be revised when more data becomes available. To improve the reliability of the screening criteria value for diuron in marine ecosystems, a third-party proposed guideline value for the protection of aquatic ecosystems (95% species protection) was derived by King et al. (2018). The value was 670 ng/L and met the classification criteria to be considered of very high reliability (King et al., 2018). This value was used as the screening criterion for diuron in the current study.

4.4.2 Sediment

The concentration of metals and pesticides reported for the sediment samples were compared with the sediment quality guideline values (SQGVs) (ANZECC/ARMCANZ, 2000; ANZG, 2018). The SQGVs are indicative of concentrations below which adverse effects rarely occur, whilst the SQGV-high represents concentrations above which effects frequently occur in exposed macrofauna. The application of the SQGVs involves a tiered (or decision tree) assessment framework. As outlined in ANZG (2018), the first tier is to compare the SQGV with the measured value for the total recoverable contaminant concentration in the sediment. If the SQGV is exceeded (and above the background concentration for the area), then the next tier of the assessment considers the fraction of the contaminant that is likely to be bioavailable or can be transformed and mobilised in a bioavailable form (based on chemical measurements). The dilute acid-extractable (1 M HCl) metal concentration provides a useful measure of the potentially bioavailable fraction of metals.

4.4.3 Stormwater

The DGVs are not intended for the screening of contaminant concentrations in stormwater. The guideline values are typically derived from toxicity tests which utilise continuous contaminant concentrations over a defined period. Contaminants in stormwater, however, generally occur as intermittent or short-term inputs to aquatic systems. Therefore, the guideline values may not provide environmentally relevant assessments for stormwater run-off, where such guidelines may be quite conservative. In the present study, the concentrations of contaminants in the stormwater were compared against the DGVs (ANZG, 2018) to identify possible input sources of contaminants to the lake system.

4.4.4 Groundwater

National guidance for groundwater quality protection is provided in the *Guidelines for groundwater quality protection in Australia* (Australian Government, 2013). This document does not provide guidelines for toxicants in groundwater but instead provides guidance on how existing DGVs for other community values (e.g. aquatic ecosystems, drinking water, livestock drinking water, irrigation water) might be applied. For this study, the environmental value classification selected for the groundwater body was aquatic ecosystem protection. Therefore, the concentrations of metals and pesticides reported for the groundwater samples were compared to the DGVs (ANZG, 2018).

4.4.5 Microplastics

There are no Australian standards or guidelines on microplastic exposure limits or acceptable levels of microplastics in water against which to compare the findings in the present study. Instead of attempting to ascertain a hazardous level of microplastics, the analyses for microplastics in groundwater were treated as exploratory in this study.

5 Results and discussion

5.1 Rainfall

In the two weeks leading up to the sampling event, the Bellambi AWS weather station (68228) in Wollongong observed 29.4 mm of rain (Table A2), suggesting that the stormwater system was flushing and minimal stagnant water would be collected as part of the program. During the DGT deployment, 5.4 mm of rain was recorded, while during the Empore and POCIS deployment, 56.4 mm of rain was recorded.

5.2 The lake

5.2.1 Water

The physicochemical properties of the lake were recorded on two occasions during the monitoring program and are summarised in Table 1. In brief, temperature was relatively consistent across all sites, with values between 25 and 27°C. All sites were saline with salinity values between 33 and 35 PSU and specific conductance between 50 and 53 mS/cm. Dissolved oxygen was high across all sites with values $\geq 92\%$. Turbidity was low across all sites with values ≤ 9.0 FNU.

No pesticides were detected above the limit of reporting (LOR) in any of the water grab samples collected within Lake Illawarra (supplementary information, available upon request).

The concentrations of total and dissolved metals in water grab samples collected from Lake Illawarra are summarised in Table 2. Total copper exceeded the marine DGV (95% species protection) of 1.3 $\mu\text{g/L}$ at a single site, LW-1 (2.2 $\mu\text{g/L}$). However, the concentration of dissolved copper at LW-1 (<1 $\mu\text{g/L}$), which is more reflective of the potentially bioavailable form of the metal, was below the marine DGV. While the results only represent a single sampling occasion within representative regions of the lake, they suggest that the metals investigated as part of the current study present a low risk of significant adverse effects on the aquatic ecosystem within Lake Illawarra.

Table 1 Physicochemical properties of surface water within Lake Illawarra at sites LW-1 to LW-6

Water quality parameter	DTV	LW-1	LW-2	LW-3	LW-4	LW-5	LW-6
Measured on 30/01/2024							
Temperature (°C)	-	26	25	26	26	26	25
Salinity (PSU)	-	33	34	33	33	34	35
Specific conductance (mS/cm)	-	51	51	51	50	52	52
Dissolved oxygen (%)	80–110	93	92	96	106	101	101
Turbidity (FNU)	0.5–10	9.0	2.8	8.7	3.4	5.9	6.3
Measured on 02/02/2024							
Temperature (°C)	-	26	25	27	27	26	25
Salinity (PSU)	-	35	35	34	34	34	34
Specific conductance (mS/cm)	-	53	53	51	51	52	52
Dissolved oxygen (%)	80–110	107	95	105	103	98	93
Turbidity (FNU)	0.5–10	6.7	2.8	7.8	2.5	5.0	1.7

* ANZECC/ARMCANZ (2000) default trigger values (DTVs) for estuaries

Table 2 Total and dissolved metal concentrations ($\mu\text{g/L}$) of surface water collected within Lake Illawarra at sites LW-1 to LW-6. The ANZG (2018) default guideline values (DGVs) for 95% species protection have been applied as screening criteria unless otherwise specified. Values that exceed the DGV are indicated by bold font.

Metal/metalloid	DGV	LW-1	LW-2	LW-3	LW-4	LW-5 (n=2)*	LW-6
Total metal concentrations ($\mu\text{g/L}$)							
As	12 [†]	1.8	1.6	1.8	1.5	1.8	1.7
Cd	0.7 [‡]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cr	4.4	1.0	<1	<1	<1	1.1	<1
Co	1	<1	<1	<1	<1	<1	<1
Cu	1.3	2.2	<1	1.3	<1	1.0	<1
Fe	NA	800	250	670	250	560	520
Pb	4.4	1.5	<1	<1	<1	<1	<1
Mn	80 [§]	44	17	47	23	36	24
Hg	0.1 [‡]	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ni	7 [‡]	<1	<1	<1	<1	<1	<1
V	100	5.4	3.1	4.5	3.5	3.9	3.5
Zn	8	6.7	1.1	2.9	2.9	3.8	3.1
Dissolved (filtered <0.45 μm) metal concentrations ($\mu\text{g/L}$)							
As	12 [†]	1.3	1.5	1.4	1.4	1.4	1.4
Cd	0.7 [‡]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cr	4.4	<1	<1	<1	<1	<1	<1
Co	1	<1	<1	<1	<1	<1	<1
Cu	1.3	<1	<1	<1	<1	<1	<1
Fe	NA	<5	<5	<5	<5	<5	<5
Pb	4.4	<1	<1	<1	<1	<1	<1
Mn	80 [§]	6.6	3.1	3.6	3.7	3.7	2.5
Hg	0.1 [‡]	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ni	7 [‡]	<1	<1	<1	<1	<1	<1
V	100	2.7	2.4	2.6	2.6	2.5	2.0
Zn	8	<1	<1	<1	1.7	<1	<1

NA = not available

* A duplicate sample was collected at Site 5. The mean of the two measurements is presented.

† Proposed third-party guideline value from Golding et al. (2022)

‡ The 99% species protection level DGV is used for slightly to moderately disturbed systems for Cd and Hg (to account for its bioaccumulating nature) and Ni (to protect key species from chronic toxicity)

§ Unknown species protection

5.2.2 Passive samplers

No pesticides were detected above the LOR in the Empore samples. A single pesticide, diuron, was detected above the LOR in the POCIS samplers deployed at all lake sites investigated. Table 3 provides the estimated TWA water concentration. Concentrations were low across the lake (1-2 ng/L) and were well below the third-party proposed guideline value for the protection of marine ecosystems (95% species protection) for diuron of 670 ng/L (King et al., 2018).

The results of the DGT technique, reported as the estimated time-weighted average concentration of metals (also known as the DGT-labile concentration), are presented in Table 4. The DGT-labile concentrations were found to be similar to or slightly lower than the measured dissolved

concentrations of the grab samples collected upon deployment of the DGT samplers. This observation suggests that there was no appreciable pulse of metal inputs to the lake during the deployment period. A comparison of all three measurements (total metals in the grabs, dissolved metals in the grabs, and the DGT-labile metals) suggests that most of the metals measured were present as colloids and/or non-labile complexes, which are generally not detected by DGT and are unlikely to be taken up by biota.

The DGT-labile concentrations across all sites were below their respective screening criteria for all metals. This provides further support that the metals investigated as part of the current study present a low risk of significant adverse effects on the aquatic ecosystem within Lake Illawarra.

Table 3 The mass accumulated (ng/sampler) within the POCIS samplers deployed at six sites within Lake Illawarra (LW-1 to LW-6) and the estimated time-weighted average (TWA) water concentrations (ng/L) of pesticides detected

Analyte	LOR	LW-1	LW-2	LW-3	LW-4	LW-5 (n=2)*	LW-6	Guideline value† (ng/L)
Mass accumulated by POCIS samplers (ng/POCIS sampler)								
Diuron	<5	7	6	7	7	6	7	-
Estimated TWA concentration based on the POCIS samplers (ng/L)‡								
Diuron	<1	2	1	2	2	1	2	670

LOR = limit of reporting

* A duplicate Empore and POCIS sampler was deployed at Site 5. The mean of the two measurements is presented.

† The third-party proposed aquatic ecosystem protection guideline value for the protection of marine ecosystems (95% species protection) was used as screening criteria for diuron (King et al., 2018)

‡ The mean sampling rate determined from data presented by Ibrahim et al. (2013) for the HLB sorbent receiving phase (pharm-POCIS) was used to calculate the estimated TWA water concentrations for diuron (0.209 L/day)

Table 4 The concentration of metals within Lake Illawarra (sites LW-1 to LW-6) between 30 January 30 and 2 February (2024), estimated using the diffusive gradients in thin films (DGT) technique and expressed as a time-weighted average ($\mu\text{g/L}$). The ANZG (2018) default guideline values (DGVs) have been applied as screening criteria unless otherwise specified.

Metal/metalloid	DGV	LW-1	LW-2	LW-3	LW-4	LW-5	LW-6
Estimated time-weighted average (DGT-labile) concentration (mean, n = 3, $\mu\text{g/L}$)							
As	12*	0.75	0.89	0.81	0.88	0.84	0.88
Cd	0.7 [†]	0.021	0.012	0.013	0.014	0.014	0.016
Cr	4.4	0.088	0.12	0.093	0.079	0.11	0.11
Co	1	0.075	0.011	0.023	<0.009	<0.009	0.012
Cu	1.3	0.15	0.17	0.20	0.19	0.21	0.22
Fe	NA	1.2	1.1	1.6	0.8	1.0	2.6
Pb	4.4	0.012	0.0012	0.0013	0.0041	0.0048	0.0079
Mn	80 [‡]	3.6	2.6	4.1	3.6	3.1	2.0
Ni	7 [†]	0.39	0.36	0.35	0.31	0.33	0.34
V	100	2.4	1.9	2.2	2.2	2.1	1.9
Zn	8	0.7	0.5	<0.3	<0.3	<0.3	1.2

NA = not available

* Proposed third-party guideline value from Golding et al. (2022)

† The 99% species protection level DGV is used for slightly to moderately disturbed systems for Cd (to account for its bioaccumulating nature) and Ni (to protect key species from chronic toxicity)

‡ Unknown species protection

5.2.3 Sediment

No pesticides were detected above the LOR in any of the surface sediment samples collected within Lake Illawarra (supplementary information, available upon request).

The metal concentrations in the surface sediments collected from Lake Illawarra have been compared against their respective SQGV (Table 5). All metals, except for Ni, were found to be below their respective SQGVs based on total recoverable metal concentrations. At a single site, LW-1, the concentration of total recoverable Ni exceeded the SQGV and the SQGV-high value. However, when the sediment samples were analysed to determine the estimated bioavailable fraction (using dilute-acid extraction/1M HCl), it was found that the estimated bioavailable fraction of Ni was below the SQGV for all sites, including LW-1. Based on these results, it can be concluded that the metals present in the sediments of Lake Illawarra are unlikely to have any harmful biological effect on benthic assemblages.

Table 5 Metal concentrations (mg/kg) within surface sediment collected within Lake Illawarra. The ANZG (2018) sediment quality guideline values (SQGVs) have been applied as screening criteria. Values that exceed the SQGV or the SQGV-high are indicated by bold font and bold purple font, respectively.

Metal/ metalloid	SQGV	SQGV-High	LW-1	LW-2	LW-3	LW-4	LW-5 (n = 2)*	LW-6
Total recoverable metal concentrations (mg/kg)								
As	20	70	5.9	14	8.5	4	11	12
Cd	1.5	10	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cr	80	370	8.6	31	25	3	28	31
Co	-	-	6	16	13	2	16	16
Cu	65	270	27	49	51	2.6	46	48
Fe	-	-	10,800	42,900	35,800	6,650	39,200	40,100
Pb	50	220	17	34	29	3	37	39
Mn	-	-	80	550	340	49	520	430
Hg	0.15	1.0	0.04	0.079	0.066	<0.01	0.075	0.079
Ni	21	52	102	17	15	1.6	15	17
V	-	-	22	84	72	18	78	84
Zn	200	410	96	150	110	11	150	170
Dilute acid-extractable metal concentrations (mg/kg)								
Ni	21	52	0.89	3.7	2.8	<0.5	3.3	3.4

* A duplicate sample was collected at Site 5. The mean of the two measurements is presented.

5.3 Stormwater

The physicochemical properties of the stormwater samples are summarised in Table 6. In brief, temperature (between 21 and 24°C) and pH (between 6.9 and 8.3) were relatively consistent across all sites. Sites with low levels of specific conductance (<1.5 mS) included SW-2, SW-3, SW-5, SW-6, SW-8, SW-9, and SW-10. The remaining sites (SW-1, SW-4, SW-7 and SW-11) were considerably more brackish (values between 4.8 and 47 mS/cm). Dissolved oxygen and turbidity varied across the stormwater sites, with the recorded values ranging between 42 and 99%, and 1.2 and 170 FNU, respectively. Dissolved oxygen levels below 5 mg/L (approximately 60%) may be stressful to aquatic species (Koehn and O'Connor, 1990). Sites with dissolved oxygen levels below 60% included SW-3, SW-9, and SW-11.

Only two pesticides were detected above the LOR at a single site each during the sampling program within stormwater (supplementary information, available upon request). Diuron was detected at SW-5 at a concentration of 0.15 µg/L and diphenylamine was detected at SW-11 at a concentration of 0.18 µg/L (Table 7). The concentration of diuron was below the screening criterion (King et al., 2018). No guideline value was available to screen the concentration of diphenylamine against.

Elevated concentrations of particulate Co, Cu, Mn, Pb and Zn and dissolved Cu, Mn, and Zn were observed at some stormwater sites (Table 8). Heavy metals are commonly present in urban run-off, particularly roadway run-off, which has been shown to accumulate metals from building materials, automobile brakes, and tyres (Davis and Shubei Ni, 2001).

Table 6 Physicochemical properties of stormwater inputs entering Lake Illawarra – sites SW-1 to SW-11

Water quality parameter	DTV*	SW-1	SW-2	SW-3	SW-4	SW-5	SW-6	SW-7	SW-8	SW-9	SW-10	SW-11
Temperature (°C)	-	22	22	23	23	21	24	23	22	22	22	22
pH (pH units)	-	7.6	8.3	7.7	7.8	7.6	7.3	7.3	7.5	7.5	7.5	6.9
Specific conductance (mS/cm)	-	47	0.72	1.2	21	0.92	0.49	4.8	0.51	0.85	1.1	16
Dissolved oxygen (%)	80–110	60	96	44	99	67	72	85	78	52	77	42
Turbidity (FNU)	0.5–10	4.7	3.4	1.2	3.7	170	17	8.0	2.2	4.1	1.9	2.5

* ANZECC/ARMCANZ (2000) default trigger values (*DTVs) for estuaries

Table 7 Pesticides detected in the stormwater entering Lake Illawarra (µg/L) – sites SW-1 to SW-11

Analyte	Guideline value (µg/L)	SW-1	SW-2	SW-3	SW-4	SW-5	SW-6	SW-7 (n = 2)*	SW-8	SW-9	SW-10	SW-11
Diuron	0.670†	<0.1	<0.1	<0.1	<0.1	0.15	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Diphenylamine	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.18

* A duplicate sample was collected at Site 7. Both measurements were less than the LOR.

† The third-party proposed aquatic ecosystem protection guideline value for the protection of marine ecosystems (95% species protection) for diuron (King et al., 2018)

Table 8 Total and dissolved metal concentrations (µg/L) of stormwater entering Lake Illawarra – sites SW-1 to SW-11

Metal/ metalloid	DGV [¶]	SW-1	SW-2	SW-3	SW-4	SW-5	SW-6	SW-7 (n = 2)*	SW-8	SW-9	SW-10	SW-11
Total metal concentrations (µg/L)												
As	12 [†]	1.7	<1	1.1	1.1	<1	<1	1.2	<1	<1	<1	<1
Cd	0.7 [‡]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cr	4.4	1.8	<1	<1	<1	<1	<1	1.5	<1	<1	<1	<1
Co	1	<1	<1	<1	<1	<1	1.2	1.8	<1	<1	<1	<1
Cu	1.3	4.1	5.6	1.2	1.4	2.9	1.7	4.4	5.0	15	4.2	<1
Fe	NA	1,470	230	320	470	300	4,560	2,210	340	130	700	650
Pb	4.4	2.9	<1	<1	1.1	<1	<1	4.5	<1	<1	<1	<1
Mn	80 [§]	57	47	390	130	85	140	190	50	38	160	270
Hg	0.1 [‡]	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ni	7 [‡]	1.1	<1	<1	1.4	<1	1.4	1.5	<1	<1	<1	<1
V	100	7.2	11	8	1.8	5.6	1.6	4.7	2.8	6.5	8.4	1.1
Zn	8	17	5.6	4.9	4.9	25	9.5	12	3.2	22	14	<1
Dissolved (filtered <0.45 µm) metal concentrations (µg/L)												
As	12 [†]	1.2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cd	0.7 [‡]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cr	4.4	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Co	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cu	1.3	<1	4.2	<1	<1	2.1	<1	<1	3.7	6.7	1.4	<1
Fe	NA	16	21	79	17	120	290	140	120	31	65	530
Pb	4.4	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Mn	80 [§]	35	8.1	370	73	60	51	120	65	31	110	270
Hg	0.1 [‡]	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ni	7 [‡]	<1	<1	<1	1.1	<1	<1	1.0	<1	<1	<1	<1
V	100	2.4	9.7	7.2	1	4.6	<1	<1	2.2	5.9	4.9	1.1
Zn	8	5.4	1.8	3.2	<1	20	1.3	<1	2.2	13	2.6	1.2

NA = not available (footnotes continue on the next page)

¶ ANZG (2018) default guideline values (DGVs) for 95% species protection unless otherwise specified. Values greater than the DGV are indicated by bold font.

* A duplicate sample was collected at Site 7. The mean of the two measurements is presented.

† Proposed third-party guideline value from Golding et al (2022)

‡ The 99% species protection level DGV is used for slightly to moderately disturbed systems for Cd and Hg (to account for its bioaccumulating nature) and Ni (to protect key species from chronic toxicity)

§ Unknown species protection

5.4 Groundwater

The physicochemical properties of the two groundwater samples differed and are summarised in Table 9. GW-1 was alkaline (pH 12) and only slightly brackish (specific conductance was 1.4 mS/cm). GW-2 was neutral (pH 7.1) and brackish (specific conductance was 21 mS/cm). Both samples were low in dissolved oxygen (<15%).

No pesticides were detected above the limit of reporting (LOR) in either of the groundwater samples collected near Lake Illawarra (supplementary information, available upon request).

Total and dissolved metal concentrations within the groundwater samples are presented in Table 10. All dissolved metal concentrations in the GW-1 sample were below their respective screening criteria for the protection of freshwater and marine ecosystems. The high alkalinity (pH 12) of GW-1 would predict a decrease in the solubility for cationic metals and the formation of precipitates (US EPA, 1992), and this was observed for Cd, which was present in the total concentration but not the dissolved concentration. In the GW-2 sample, dissolved Fe and Mn concentrations exceeded the screening criteria for the protection of freshwater and marine ecosystems. Fe and Mn are naturally occurring minerals that are ubiquitous in soils and groundwater. They are redox-active metals, meaning their release into groundwater is primarily due to microbially-mediated reductive dissolution of naturally occurring minerals, which is controlled by local biogeochemical conditions (Davison, 1993). Under anoxic conditions, Fe and Mn are released into dissolved forms, whereas under oxic conditions they tend to precipitation into particulate form (Davison, 1993).

No microplastics were detected in the GW-1 sample (supplementary information, available upon request). In the GW-2 sample, polyethylene terephthalate (PET) was the only plastic-type detected (9 microplastics per litre (MPs/L)). Of these microplastics, four particles had a diameter between 20 and 100 µm and the remaining five were between 100 and 200 µm.

Table 9 Physicochemical properties of groundwater near Lake Illawarra

Water quality parameter	GW-1	GW-2
Depth to groundwater (m)	1.4	1.6
Temperature (°C)	24	23
pH (pH units)	12	7.1
Specific conductance (mS/cm)	1.4	21
Dissolved oxygen (%)	4.2	15
Turbidity (FNU)	2.1	14

Table 10 Total and dissolved metal concentrations (µg/L) of groundwater near Lake Illawarra. The ANZG (2018) default guideline values (DGVs) for 95% species protection have been applied as screening criteria unless otherwise specified. Values that exceed either the freshwater or marine DGV are indicated by bold font.

Metal/metalloid	Freshwater DGV	Marine DGV	Site GW-1 (n = 2)*	Site GW-2
Total metal concentrations (µg/L)				
As	13	12 [†]	<1	<1
Cd	0.2	0.7 [‡]	0.39	<0.1
Cr	1	4.4	<1	1.8
Co	-	1	<1	<1
Cu	1.4	1.3	<1	<1
Fe	300 [¶]	NA	51	10,200
Pb	3.4	4.4	<1	9.3
Mn	1900	80 [§]	2.2	2,620
Hg	0.06	0.1 [‡]	<0.05	<0.05
Ni	11	7 [‡]	<1	1.6
V	-	100	48	4.6
Zn	8	8	21	39
Dissolved (filtered <0.45 µm) metal concentrations (µg/L)				
As	13	12 [†]	<1	<1

Metal/metalloid	Freshwater DGV	Marine DGV	Site GW-1 (n = 2)*	Site GW-2
Cd	0.2	0.7 [‡]	<0.1	<0.1
Cr	1	4.4	<1	<1
Co	-	1	<1	<1
Cu	1.4	1.3	<1	<1
Fe	300 [¶]	NA	28	3,730
Pb	3.4	4.4	<1	<1
Mn	1900	80 [§]	<1	2,170
Hg	0.06	0.1 [‡]	<0.05	<0.05
Ni	11	7 [‡]	<1	<1
V	-	100	46	2
Zn	8	8	4.2	<1

NA = not available

* A duplicate sample was collected at LI-GW-1. The mean of the two measurements is presented except when one of those values was less than the LOR, in which case the detected value is presented.

† Proposed third-party guideline value from Golding et al. (2022)

‡ The 99% species protection level DGV is used for slightly to moderately disturbed systems for Cd and Hg (to account for its bioaccumulating nature) and Ni (to protect key species from chronic toxicity).

§ Unknown species protection

¶ Interim indicative working level based on the Canadian guideline (CCREM, 1987)

6 Conclusion

The current study provides a snapshot look at the presence of contaminants within Lake Illawarra and its surrounding tributaries and groundwater. Elevated concentrations of particulate Co, Cu, Mn, Pb, and Zn and dissolved Cu, Mn, and Zn were observed at some stormwater sites. However, the concentrations of metals within the lake were all low and below their respective screening criteria, suggesting a low risk of significant adverse effects on the aquatic ecosystem within Lake Illawarra. Diuron and diphenylamine were also detected at a single stormwater site each. Diuron was detected in trace amounts at all of the lake sites using passive samplers. Diuron concentrations were below the screening criterion for the protection of aquatic ecosystems. No guideline value was available for screening diphenylamine. Within the sediment, elevated Ni was identified at a single site, but based on the estimated bioavailable fraction, the concentration presents a low risk of significant adverse effects on the aquatic ecosystem within Lake Illawarra. Within the groundwater, only Fe and Mn exceeded the screening criteria.

7 References

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8 Limitations

This snapshot contaminant assessment of Lake Illawarra was an analysis at a single point in time, not accounting for potential seasonal changes in water quality or in pollutant input or biological uptake. The snapshot methodology allowed the NSW Government to conduct a broad examination of pollutants not routinely tested for in this catchment, and which are important to forming a picture of catchment health. However, due to the breadth of analytes and sample locations, using duplicates to confirm findings at each site was not possible. Despite this limitation, the wide span of testing employed meant that this project was able to give us a landscape-scale baseline picture of some key contaminants in the catchment, which could easily be repeated in the future to compare changes over time. The results of this study are not intended to be used in lieu of water quality testing, where deemed necessary.

9 Acknowledgements

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Appendix A: Supporting information for the passive samplers

Estimating the environmental concentration from the Empore and POCIS sampler results

Results for the Empore samplers were supplied as the mass of each analyte accumulated within the Empore receiving phase (reported as µg/filter and equivalent to µg/Empore). Whereas results for the POCIS samplers were supplied as the concentration of each analyte within the extraction medium (i.e. dissolved in 5 mL of solvent) (reported as µg/L). Subsequently, all POCIS results were multiplied by 0.005 L to determine the mass of each analyte within the POCIS receiving phase (reported as µg/POCIS and equivalent to the mass accumulated in the 5 mL extract) before any further calculations were undertaken. For presentation purposes, all results were converted to nanograms (ng).

The mass of the analyte accumulated in the Empore and/or POCIS sampler (ng/Empore and ng/POCIS, respectively) was then used to determine an estimated time-weighted average (TWA) water concentration of the analyte in the deployment media (i.e. the environment) over the deployment period. No pesticides were detected by the Empore samplers, and only diuron was detected by the POCIS samplers. Estimated TWA water concentrations for diuron were calculated using the mean of sampling rates for diuron and the POCIS HLB receiving phase provided by Ibrahim et al. (2013) and *Equation 1*:

$$\textbf{Equation 1: } C_w = \frac{M}{R_s t}$$

where C_w is the estimated time-weighted average (TWA) water concentration (ng/L), M is the mass of the analyte in the sampler receiving phase (ng), R_s is the sampling rate of the analyte (L/day), and t is the sampler deployment period (days). A mean R_s was determined and used to address the challenge of variations between laboratory calibration studies and field exposure studies. The mean R_s is considered generic and is not specific to any particular deployment conditions. Consequently, the time-weighted average (TWA) water concentrations are approximations and offer an estimate of environmental concentrations during the deployment period.

Estimating the environmental concentration from the DGT sampler results

Results for the DGT devices were supplied as the concentration of each metal within the extraction medium (i.e. dissolved in 1 mL of acid) of micrograms per litre ($\mu\text{g/L}$). The time-average DGT-labile concentration of the metal in the deployment medium (i.e. the environment) over the deployment period was estimated according to *Equations 2 and 3* outlined below, provided by Davison (2016):

$$\textbf{Equation 2: } M = \textit{dilution factor} \times \frac{C_e(V_{\text{acid}} + V_{\text{gel}})}{f_e}$$

Variables for *Equation 2*

- C_e ($\mu\text{g/L}$) is the measured concentration of analyte in the acid eluent (determined by inductively coupled plasma mass spectrometry, ICP-MS).
- V_{acid} is the volume of the acid eluent.
- V_{gel} is the volume of the binding layer.
- f_e is the elution factor for the analyte (fraction of bound metal released) (DGT Research Limited, 2024b).

$$\textbf{Equation 3: } C_{\text{DGT}} = \frac{M\Delta_g}{D^{\text{dbl}}A_p t}$$

Variables for *Equation 3*:

- C_{DGT} ($\mu\text{g/L}$) is the time-averaged concentration of analyte in the deployment medium measured by DGT.
- M (μg) is the mass of analyte accumulated in the binding layer. Obtained from *Equation 2*.
- Δ_g (0.094 cm) is a constant for the LSNX-NP devices and represents the total thickness of the materials in the diffusion layer (diffusive gel and filter membrane).
- D^{dbl} (cm^2/s) is the diffusion coefficient of the analyte in the material diffusion layer for the deployment temperature (DGT Research Limited, 2024a).
- A_p (3.14 cm^2) is a constant for the LSNX-NP devices and represents the physical area of the exposed filter membrane.
- t (s) is the deployment time.

Appendix B: Data quality assessment

Quality assurance (QA) and quality control (QC) measures

QA procedures were established for this project to maximise sample integrity and included the use of:

- standard procedures for the collection and analysis of samples
- laboratory-supplied sampling containers and storage procedures appropriate for each analysis type
- appropriate equipment cleaning procedures between each sampling location.
- a new pair of disposable nitrile gloves for each sampling location
- the ‘clean hands/dirty hands’ technique for handling the passive samplers in the field
- sample collection undertaken by staff trained and experienced in taking surface water, groundwater, and sediment samples.

QC procedures were implemented to assess the effectiveness of QA and to determine the validity of the data. The QC process involved the use of the following measures:

- Water and sediment sampling
 - A field duplicate sample (for intra-laboratory analysis) was collected for each sampling event (that is one each for the lake water, stormwater, and groundwater sample collections). Duplicates were collected at Sites LW-5, SW-7, and GW-1.
- Passive sampling
 - Laboratory blanks: these were unexposed devices from the same batch of devices used for deployment. Four DGT laboratory blanks, and two Empore and POCIS laboratory blanks were analysed along with the sample batch (they were carried through the same measurement process from extraction to analysis).
 - Field blanks: these are used to detect any contamination from the passive sampler devices being handled and exposed in the field. Three DGT field blanks and one Empore and POCIS field blanks were taken to the monitoring site, briefly exposed when the devices were being retrieved, rinsed with high-purity water, returned to their zip-lock bags, and then transported back to the laboratory for analysis along with the sample batch.
 - DGT devices were deployed in triplicate to provide a measure of uncertainty.
 - Duplicate Empore and POCIS devices were included in the deployment at one site, LW-5.

The field duplicate samples were labelled to conceal their relationships to the primary sample. The field duplicate was used to identify variations in analyte concentrations between samples collected from the same sampling point. The data quality indicator (DQI) was for the primary and duplicated samples to be within the specified relative percentage difference (RPD) for the method. RPD is calculated as follows:

$$RPD (\%) = \frac{(\text{difference between sample duplicates})}{\text{average of sample duplicates}} \times 100$$

For the current study, the DQI for field duplicates (i.e. two separate samples taken at the same location) was as follows:

- For liquid samples – the field duplicates should agree within an RPD of $\pm 30\%$. Low levels of the analyte can exaggerate the RPD, therefore duplicate results with an RPD $> 30\%$ but $\leq 50\%$ were considered acceptable if the detected values were within 10 times of the LOR.
- For sediment samples, the field duplicates should agree within an RPD of $\pm 50\%$ (unless the sediment is very heterogeneous or greatly differs in grain size) (NADG, 2009).

Table A1 Summary of the intra-laboratory field duplicate data quality assessment. The data quality indicator (DQI) for this assessment is a relative percentage difference (%RPD) of duplicate results of $\leq 30\%$, or $\leq 50\%$ if the measured results were within 10 times the limit of reporting.

Parameter	Max % RPD	DQI assessment outcome
Lake water – Pesticides by GC-MSMS	NA*	DQI met
Lake water – Pesticides by LC-MSMS	NA*	DQI met
Lake water – Total metals	68	Total Zn had an RDP of 68%. No dissolved Zn was detected ($>$ LOR) in the filtered samples. The difference is most likely attributable to random sampling heterogeneity.
Lake water – Dissolved metals	47	DQI met
Sediment – Pesticides by GC-MSMS	NA*	DQI met
Sediment – Pesticides by LC-MSMS	NA*	DQI met
Sediment – Total recoverable metals	8	DQI met
Sediment – 1M HCl extractable Ni	6	DQI met
Stormwater – Pesticides by GC-MSMS	NA*	DQI met
Stormwater – Pesticides by LC-MSMS	NA*	DQI met
Stormwater – Total metals	93	Total Cu, Fe, Pb, V, and Zn had RPDs of 62, 52, 93, 68, and 60%, respectively. No dissolved Cu, Pb, V, or Zn was detected ($>$ LOR) in the filtered samples. Good agreement was observed for dissolved Fe (RPD of 7%). The difference is most likely attributable to random sampling heterogeneity.
Stormwater – Dissolved metals	7	DQI met
Groundwater – Pesticides by GC-MSMS	NA*	DQI met
Groundwater – Pesticides by LC-MSMS	NA*	DQI met
Groundwater – Total metals	55	Total Mn had an RDP of 55%. No dissolved Mn was detected ($>$ LOR) in the filtered samples. The difference is most likely attributable to random sampling heterogeneity.
Groundwater – Dissolved metals	29	DQI met

*Not applicable: all results (sample and its duplicate) were less than the limit of reporting.

Appendix C: Supplementary tables and figures

Table A2 Rainfall recorded in the lead-up to and during the sampling period at the Bellambi AWS weather station (68228)

Period	Date	Rainfall recorded (mm)
Pre-sampling	9/01/2024	3.6
	12/01/2024	1.2
	15/01/2024	5.2
	16/01/2024	19.4
Sampling	18/01/2024	19.2
	23/01/2024	0.4
	25/01/2024	0.2
Passive sampler deployment	30/01/2024	0.2
	31/01/2024	0.2
	01/02/2024	5.0
	06/02/2024	18.6
	07/02/2024	1.2
	11/02/2024	1.4
	14/02/2024	20.8
	15/02/2024	6.6
	16/02/2024	2.0
	17/02/2024	0.2
18/02/2024	0.2	



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Phone 133 677, then ask for 131 555

Speak and listen users:
Phone 1300 555 727, then ask for 131 555

Email:
info@epa.nsw.gov.au

Website:
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Report pollution and
environmental incidents

Environment Line:
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