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Signatures of Urbanization in Temperate Highland Peat Swamps on Sandstone (THPSS) of the Blue Mountains World Heritage Area

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Abstract: Urban freshwater ecosystems exhibit distinct patterns of elevated major ions (calcium, potassium and bicarbonate) and metals, referred to as the 'urban geochemical signature'. However, the implications of this urban fingerprint at the water-sediment interface within sensitive freshwater systems are not well-known. Temperate Highland Peat Swamps on Sandstone are unique freshwater wetlands found within and surrounding the high-conservation value Greater Blue Mountains World Heritage Area and are a listed 'endangered ecological community' in Australia. Water and sediment chemistry were assessed within four urban and four naturally vegetated swamp catchments, through field monitoring and novel laboratory techniques (including X-ray diffraction). Urban swamps had distinct elemental signatures compared to naturally vegetated swamps. Urban swamp water displayed increased pH, elevated ionic strength, major ions (calcium and bicarbonate) and metals (strontium, barium, manganese and iron). Urban swamp sediment had higher calcium, with calcium hydroxide detected at two urban sites. Urban development and concrete drainage infrastructure in swamp catchments modify natural hydrology and water chemistry. Findings suggest swamp sediments may act as sinks of metals and alkalinity, with urbanization remaining a potential source. However, the consequences for high-conservation value systems are not well understood. As urbanization continues to expand, this has implications for fragile freshwater environments worldwide.

Keywords: upland swamps; concrete contamination; water chemistry; sediment chemistry

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1. Introduction

Urbanization is a significant anthropogenic issue that is expanding on a global scale and placing increasing pressure on freshwater and terrestrial ecosystems [1]. Urban waterways exhibit key characteristics, including altered natural hydrology, modified water chemistry, elevated nutrient levels and alkalinization, termed 'urban stream syndrome' [2,3]. High coverage of impervious surfaces, such as concrete, building materials and stormwater infrastructure, contribute to increased surface runoff and are commonly associated with the degradation of water quality in urban areas [4,5]. Urban waterways worldwide are increasingly being recognized as exhibiting a distinct 'urban geochemical signature' [6], as urban inputs such as stormwater and weathering of urban infrastructure contribute to enhanced inputs of elements and nutrients, including elevated calcium, bicarbonate, potassium, magnesium and sulfate [7–10].

Sediments collected from urbanized catchments worldwide can be strongly impacted by urban development, with elevated metals and nutrient enrichment compared to sediment in non-urban catchments [11–14]. The sediment acts as a sink, particularly in urban ecosystems, as elements accumulate over time [15,16]. The transport and availability of sediment in urban waterways can be reduced by urban pavements, as measured by catchment imperviousness [11]. Increasing metal loads may drive structural breakdown [17] and result in increased elemental export [18]. This is particularly the case for peat swamps and wetland systems, with the sediment record indicating evidence of anthropogenic markers correlated with increasing human activities [19,20]. Sediment provides a temporal record of changes and can be used to understand changes to ecosystem function due to urbanization.

Increasingly, research has linked the weathering of urban derived materials, particularly the dissolution and weathering of concrete, with modified water chemistry including elevated calcium and modified pH [4,21–24]. The urban alkalinization process can be characterized as the dissolution of calcium hydroxide (lime; $Ca(OH)_2$), a common component of concrete, which dissociates in the presence of water to increase pH to a potential maximum of 12.5 [25] Reaction 1. This can react with atmospheric carbon dioxide (CO_2) and if this exceeds solubility precipitation of calcium carbonate (or calcite; $CaCO_3$) can occur [25] Reaction 2. Previous research has also observed increased calcium concentrations in urban riparian sediment [12,14,26], which suggests that excess calcium may be accumulating in urban sediments.

$$Ca(OH)_{2(S)} = Ca^{2+} + 2OH^{-} \quad (1)$$

$$Ca^{2+} + HCO_3^{-} \rightarrow CaCO_{3(S)} + H^{+} \quad (2)$$

The Greater Blue Mountains Area (GBMA) was listed as a World Heritage Area in 2000 due to its exceptional biodiversity values that reflect unique evolutionary adaptations occurring within Australia since the post-Gondwana period [27,28]. Covering 1.04 million hectares, this region incorporates eight protected reserves, and areas of urban and agricultural land use in New South Wales (NSW), south-eastern Australia [29]. The ecological, cultural, and economic value of this region is significant within Australia and reflects Outstanding Universal Value (OUV), which emphasizes the importance of conserving the natural condition of this area [27,30]. The GBMA is managed under Federal and State legislation, including the Environment Protection and Biodiversity Conservation Act 1999 (Commonwealth; EPBC Act), the Biodiversity Conservation Act 2016 (NSW; BC Act), National Parks and Wildlife Act 1974 (NSW; NPW Act) and Wilderness Act 1987 (NSW) [27], and the Greater Blue Mountains World Heritage Area Strategic Plan [31]. This region is recognized to be vulnerable to the effects of climate change, bushfires and human activities such as mining [29,30]. Urban development is also a key concern, and as the population of Greater Sydney continues to expand this places increasing pressure on the fringing ecosystems of the GBMA [30,31]. The Blue Mountains, with a population of approximately 80,000, is one of two cities worldwide that is encompassed within a World Heritage National Park [32]. Management of the region and national parks seeks to protect natural environments from human degradation. However, urban development still occurs within the Blue Mountains, particularly along major highway corridors, which poses a threat to fragile natural environments within and along the national park boundaries in this region [29,30].

Temperate Highland Peat Swamps on Sandstone (THPSS) are unique peat swamps overlaying sandstone geology across the Blue Mountains and Southern Highlands regions that contain distinct vegetation communities dominated by sedges and shrubs [33,34]. They are listed as an 'endangered ecological community' under the EPBC Act 1999 (criterion two), as they have a limited geographic distribution and are at risk of ongoing threats [35]. They are also recognized as having important biodiversity value within the GBMA [30]. Many THPSS are found within the Blue Mountains region of NSW, west of Sydney, at altitudes of 500–1000 m and their distribution is restricted to a combined area of less than 2000 ha [36]. Urban encroachment within this region poses a threat to THPSS, including urban runoff, water pollution, weeds, and invasive species [30]. It is estimated that almost one third of THPSS are impacted by urbanization [37], and many swamp catchments occur along the fringe or fall outside the World Heritage boundary in urban centers of the Blue Mountains, making them vulnerable to habitat loss and degradation.

The effects of urban development on sediment structure, geomorphology and carbon storage [33,38,39], water chemistry [34,40] and potential differences in surface sediment elemental composition within urban swamp catchments in the Blue Mountains has been identified [40]. However, the potential influence of catchment urbanization on water chemistry and sediment mineralogy interactions has not been previously studied in these systems. This study aimed to further enhance knowledge of possible links between urban development, concrete materials, and physical and chemical properties of THPSS. The key questions addressed were: (i). Do urban swamps have modified water chemistry relative to naturally vegetated catchments; and (ii). Does sediment from urban swamps exhibit altered chemical composition and mineralogy compared to naturally vegetated catchments? The dilute, low nutrient and acidic nature of THPSS makes them a model system to investigate how urban inputs alter the natural geochemical signature of sensitive freshwater wetlands. As urbanization continues to expand globally, learnings from THPSS contribute to our understanding of how fragile freshwater environments might be impacted by urban geochemical modification.

2. Materials and Methods

2.1. Study Area

The geology of the Blue Mountains region is dominated by Permo-Triassic quartz sandstone and inter-bedded claystone [41,42]. THPSS are considered stable systems, with carbon dating of sediment cores dated to approximately 9000 to over 15,000 years [33,43]. THPSS in the Blue Mountains region experiences a temperate climate, with a mean annual rainfall of 1399.6 mm at Katoomba [44], however, during the sampling period conditions were dry and rainfall was below average. Water quality within THPSS is typically acidic, dilute, poorly buffered, and dominated by sodium and chloride [34,40].

This study was conducted at swamps from four urban and four naturally vegetated catchments across the Blue Mountains region, west of Sydney, NSW within the Hawkesbury-Nepean catchment (Table 1; Figure 1). These eight swamps do not represent swamps across the entire study area but were chosen to provide a broad assessment of urban land uses on a small number of THPSS. Urban (located on the national park fringe) and naturally vegetated (located within the GBMA) classifications were determined using satellite images to calculate the total percentage of impervious area (IA%) and the percentage of Directly Connected Impervious Area (DCIA%) of each catchment. This approach followed the methods outlined by [45], using the conservative assumption of low-density residential land use in each swamp catchment. All sites had vegetation communities consistent with the THPSS listing, however, urban sites were observed to have greater disturbance and a higher presence of exotic species.

Table 1. The location and details of the eight Temperate Highland Peat Swamps on Sandstone (THPSS) study sites from which water and sediment were collected.

Swamp Name	Catchment Type	Latitude and Longitude	Elevation above Sea Level at Sampling Location (m)	Swamp Area (ha)	Total Impervious Area within Catchment (IA%)	Percentage Directly Connected Impervious Area (DCIA%)
(1). Bullaburra	Urban	−33.727319, 150.412928	755	0.68	25.03	9.54
(2). Wentworth Falls	Urban	−33.707627, 150.361313	880	9.93	22.41	7.90
(3). North Lawson	Urban	−33.713851, 150.427195	695	1.15	23.15	8.35
(4). Popes Glen	Urban	−33.633639, 150.292336	1010	0.82	34.30	16.30
(5). Mt Hay	Naturally vegetated	−33.668644, 150.346508	920	3.92	0.00	0.00
(6). Hat Hill	Naturally vegetated	−33.599941, 150.328782	967	4.10	0.00	0.00
(7). Lawson	Naturally vegetated	−33.696739, 150.444027	665	9.10	0.00	0.00
(8). Kings Tableland	Naturally vegetated	−33.76210, 150.38373	780	6.06	0.18	0.002

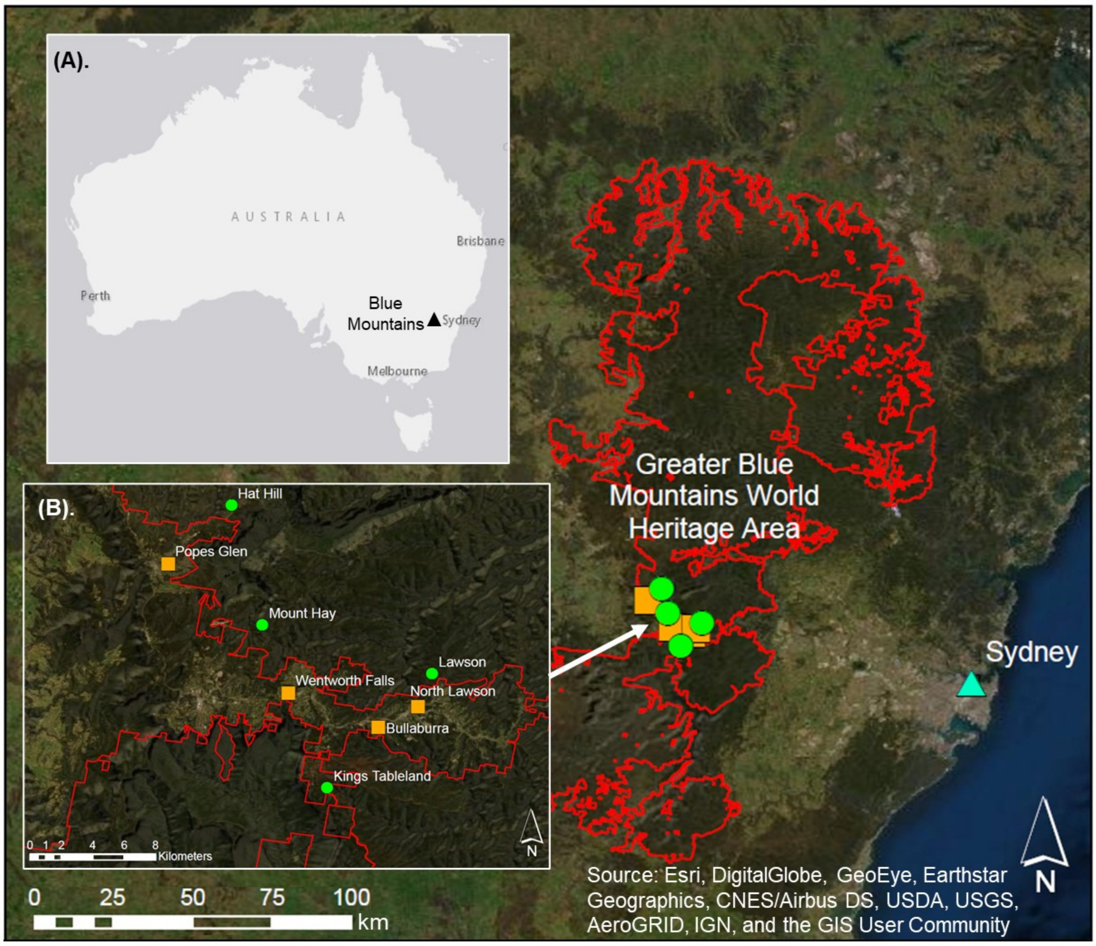

Figure 1. The location of the study region in the Blue Mountains (inset (**A**)), west of Sydney (blue triangle), NSW, Australia, with the boundary of the Greater Blue Mountains World Heritage Area shown in red [46]; Creative Commons Attribution 4.0]. Inset (**B**) outlines the Temperate Highland Peat Swamps on Sandstone (THPSS) sites, including urban (orange squares) and naturally vegetated (green circles) THPSS catchments.

2.2. Monitoring of Water Chemistry

Surface water was collected from the exit stream at each swamp on three occasions between April and June 2018. This study was the first of its kind in THPSS and did not aim to conduct a seasonal or multi-year investigation. The study included parameters that were shown to be important in contrasting water and sediment quality in urban and non-urban catchments in previous studies of THPSS [34,36–40]. This current study included more a detailed examination of several parameters, including nutrients, a more extensive suite of metals and conducted the first minerology examination of urban and non-urban THPSS sediment cores.

Water physiochemical properties (five repeated measures once the meter had stabilized) were tested in the field, including pH (pH units) and electrical conductivity (EC; µS cm^{-1}) using a calibrated TPS AQUA-Cond-pH meter, and dissolved oxygen (DO; percentage (%)) and temperature (°C) using a calibrated YSI ProODO meter. Turbidity was tested using a HACH 2100P Turbidimeter (five replicates per swamp). Due to dry conditions, surface water at Mount Hay was only sampled in April 2018. Nutrients (nitrates (mg L^{-1} NO_3^-) and reactive phosphates (mg L^{-1} PO_4^{3-})) were tested using a HACH Drel Spectro-photometer (DR/2400; cadmium reduction method 8171, calibrated as per manufacturer's instructions), each with five replicates per swamp.

Duplicate 500 mL grab water samples were collected (unfiltered) from surface water in sterilized plastic containers, stored at 4 °C and acidified (0.1 mL of nitric acid) to preserve samples for cation and metal analysis. Determination of major ions and metals followed standard methods (APHA method 4110 and APHA method 2320-B, analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) [47]). The major ions that were assessed included cations calcium, magnesium, potassium, sodium, and anions sulfate, chloride, bicarbonate and carbonate. Trace elements included aluminium, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, lithium, manganese, molybdenum, nickel, strontium, titanium, uranium and zinc. As molybdenum and uranium were not detected at either catchment type, they were excluded from subsequent analysis.

2.3. Sediment Sample Collection and Testing

2.3.1. Sample Collection

Sediment cores were collected from each site over the course of two days using cleaned polyvinyl chloride (PVC) pipe (55 mm × 500 mm). All cores were collected in close proximity (5–20 m) to the swamp exit stream and main drainage channel. The top layer of vegetation was moved aside, and the pipe was eased in approximately 40 cm or until it hit the resistant layer. After extraction, cores were immediately wrapped in clingfilm and frozen (−18 °C) until analysis.

Frozen cores were thawed and the outer layer was cleaned away using a scalpel. The sediment color of each layer was determined using a Munsell Soil Color chart. A subsample (approximately 5–10 g) was collected from each layer from the center of the left-hand side of the core and placed in sterile PTFE tubes (50 mL). Once thawed, readings for pH (pH units; using a TPS Aqua-CP Conductivity/pH meter) and redox (Eh; measured in millivolts (mV) using a TPS WP-80D Dual pH-mV meter) were taken at 5 cm intervals along the right-hand side of the core. Samples from each core were dried in the PTFE tubes (with lid removed) in a Labec laboratory incubator S4218 (Laboratory Equipment Pty Ltd., Marrickville, Australia) for up to 48 h at 30 °C.

2.3.2. Mineralogy

The elemental composition and mineralogy of sediment samples from each layer per core was analyzed using a Bruker D8 Advance X-ray Diffractometer (XRD) with a copper K-alpha radiation source and LynxEye detector. All sediment samples were ground into a fine powder using a mortar and pestle. The analysis included a 5–80 degree 2θ scan (duration 4 h) with a step rate of 0.02 degrees, 3.5 s time per step and rotation off. A divergence and anti-scattering slit size of 12.0 mm and a generator voltage of 40 kV were used. Analysis of all XRD results was undertaken using Bruker's EVA software [48], with spectra compared with $CaCO_3$ and $Ca(OH)_2$ standards using the Powder Diffraction File (PDF) database from the International Centre for Diffraction Data (ICDD).

2.4. Data Analysis

2.4.1. Statistical Analysis

Water quality data were analyzed using IBM SPSS Statistics version 22. Water physiochemical attributes, major anions and cations were averaged for each site. EC results from Lawson in June 2018 were excluded due to suspected equipment error and no water samples were obtained from Mount Hay from May-June 2018 due to dry conditions. Each water quality parameter was analysed using a mixed linear model, where the fixed factor was the catchment type and the random variable was the sampling event (to incorporate variability over time). For all analyses conducted, statistical significance was established at the 0.05 level. Any values that were below detection limits were attributed as half of the minimum detection value for analysis [7,49], however, were indicated as below detection in the figures shown. Principal Component Analysis (PCA) was conducted across all sites and sampling events using the 'PCA' function in the *FactoMineR* package in R v4.1.1 [50,51]. EC for Lawson for the second sampling event was averaged from the first and third sampling events for the purpose of the PCA analysis due to missing data. Mo and U were excluded from the PCA analysis as they were not detected at any sites.

2.4.2. Water Quality Modelling

The PHREEQC software program (version 3.1.7.9213) with the LLNL database package was used to calculate ionic activities and determine the ionic strength of water [52]. Phases considered included atmospheric carbon dioxide ($pCO_2 = -3.5$), portlandite ($\log K = 22.55$) and calcite ($\log K = 1.84$). Solution speciation was calculated, and saturation index (SI) was determined based on $SI = \log IAP/Ks$, where IAP indicates the ion activity product and Ks refers to the thermodynamic solubility product of the relevant phase.

3. Results

3.1. Water Chemistry

3.1.1. Physiochemical Properties

Urban swamps had significantly higher pH (mean 6.20 pH units), compared to the naturally vegetated catchments (mean 4.87 pH units), and the range of values did not overlap ($p < 0.001$; Table 2). EC in urban swamps (mean 116.30 µS cm^{-1}) was 2.55 times greater than the non-urban catchments (mean 45.57 µS cm^{-1}; $p < 0.01$). Mean DO was also 33.50% higher in the non-urban catchments compared to the urban sites ($p < 0.01$).

Table 2. Summary of water physiochemical properties for Temperate Highland Peat Swamps on Sandstone (THPSS) in urban ($n = 4$) and naturally vegetated ($n = 4$) catchments from April–June 2018 sampling.

Attributes	*F* Statistic	d.f	*p* Value	Urban Catchments			Naturally Vegetated Catchments		
				Range	Mean	Median	Range	Mean	Median
pH	50.38	1, 20	0.000 **	5.56–7.09	6.20	6.08	4.56–5.40	4.87	4.81
Electrical Conductivity (µS cm^{-1})	18.80	1, 19	0.000 **	45.10–169.90	116.30	137.45	25.30–79.10	45.57	49.70
Dissolved Oxygen (% saturation)	11.98	1, 20	0.002 *	3.20–91.40	51.52	50.05	75.00–102.50	85.02	83.45
Temperature (°C)	0.51	1, 18.01	0.483 (ns)	6.60–16.90	10.59	8.95	6.20–24.70	11.85	9.40
Turbidity (NTU)	2.92	1, 20	0.103 (ns)	1.57–88.50	13.52	7.04	0.73–19.80	3.00	2.18
Nitrates (mg L^{-1} NO_3^-)	0.02	1, 18.12	0.890 (ns)	0.10–0.80	0.38	0.40	0.00–1.10	0.37	0.35
Reactive Phosphates (mg L^{-1} PO_4^{3-})	1.71	1, 18.01	0.207 (ns)	0.02–1.35	0.27	0.20	0.04–2.39	0.32	0.20

Notes: Significance is indicated as * = $p < 0.01$, ** = $p < 0.001$ and ns = not significant. d.f. denotes the degrees of freedom (numerator, denominator).

Nitrate and reactive phosphates concentrations showed no significant differences between urban and non-urban swamps (Table 2). Additionally, median reactive phosphate values were equal (0.20 mg L^{-1} PO_4^{3-}) for each catchment type. Turbidity was not observed to significantly differ between catchment types, and there was variability between sampling events.

3.1.2. Water Ionic Composition of Major Cations and Anions

Urban swamp water exhibited differences in ionic composition compared to the naturally vegetated swamps (Table 3; Figure 2). Calcium was below detection in the naturally vegetated swamp catchments (excluding at Kings Tableland) and 19.82 times higher (mean

10.90 mg L^{-1}) in the urban swamps ($p < 0.001$). Bicarbonate was below detection in all naturally vegetated swamps, however, was present in significantly higher quantities in the urban swamps (mean 25.67 mg L^{-1}; $p < 0.001$). The ratio of Ca: HCO_3^- was 1:2 in naturally vegetated swamps and 1:1 in urban swamps (Table 3). Urban catchments also had significantly higher potassium, magnesium, chloride and sulfate concentrations compared to the non-urban swamps (Table 3). Sodium was naturally present at all sites, however, was significantly higher within the urban catchments (mean 8.19 mg L^{-1}) compared to the non-urban swamps (mean 5.87 mg L^{-1}; $p < 0.001$).

Table 3. Summary of water chemistry results from urban and non-urban Temperate Highland Peat Swamps on Sandstone (THPSS) between April–June 2018.

Major Ions	*F* Statistic	d.f.	*p* Value	Urban Catchments			Naturally Vegetated Catchments		
				Range	Mean	Median	Range	Mean	Median
Calcium	61.72	1, 42	0.000 **	2.10–20.00	10.90	12.00	0.25 ×–1.30	0.55	0.25
Potassium	24.29	1, 42	0.000 **	0.25 ×–2.80	1.29	0.90	0.25 ×	0.25 ×	0.25 ×
Sodium	16.54	1, 40.25	0.00 **	4.80–13.00	8.19	7.55	4.00–7.40	5.87	6.00
Magnesium	46.74	1, 40.39	0.00 **	0.60–1.90	1.23	1.20	0.25 ×–0.80	0.54	0.70
Bicarbonate Alkalinity as $CaCO_3$	42.86	1, 40.35	0.000 **	5.00–56.00	25.67	22.50	0.00	2.50 ×	2.50 ×
Sulfate	6.73	1, 40.17	0.013 *	0.5 ×–11.00	4.46	3.00	0.5 ×–6.00	2.40	1.00
Chloride	16.69	1, 42	0.000 **	6.00–36.00	16.74	14.00	6.00–11.00	8.62	9.00
Calculated Ionic Strength (M)	-	-	-	0.0005–0.0020	0.0015	0.0016	0.0002–0.0006	0.0004	0.0004
Ratio Ca:HCO_3^-	-	-	-	0.75:1–1.4:1	1:1	0.95:1	0.3:1–1:1	1:2	0.3:1

Notes: Significance is indicated as * = $p < 0.05$, ** = $p < 0.001$. Data is presented as mg L^{-1}, unless otherwise specified. × denotes values that were below the detection limit. d.f. refers to degrees of freedom (numerator, denominator) and—indicates that statistical analysis was not required for the attribute. Units for ionic strength are in Moles (M).

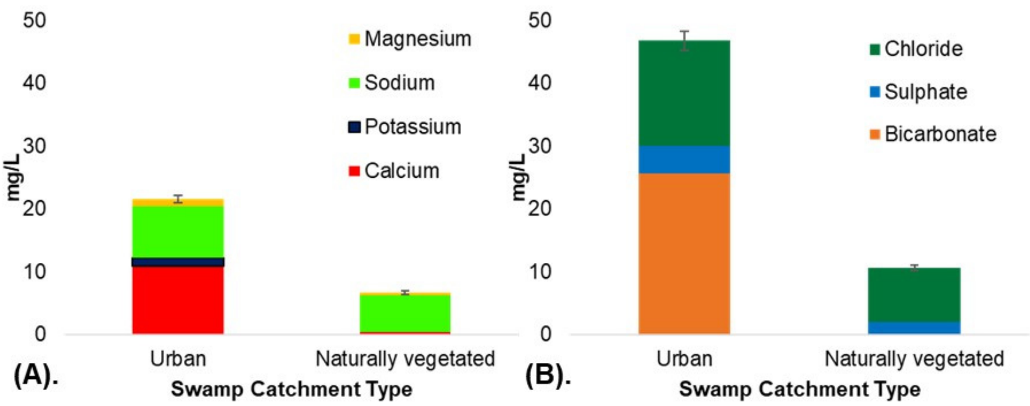

Figure 2. Comparison of the mean (+/− standard error) ionic signature of water in urban ($n = 4$) and naturally vegetated ($n = 4$) Temperate Highland Peat Swamps on Sandstone (THPSS) catchments from April to June 2018, including (**A**) major cations and (**B**) major anions.

Ionic strength (IS) was greater in the urban swamp catchments (mean 0.0015 M) compared to the naturally vegetated catchments (mean 0.0004 M; Table 3). There was a strong correlation between IS and EC ($R^2 = 0.91$; see Supplementary data Figure S1a). When calcium alone (converted to Moles) was compared with EC, the correlation was 0.82 (see Supplementary data Figure S1b), suggesting that calcium is contributing to the overall EC and ionic strength.

3.1.3. Elemental Loads

Urban swamps exhibited statistically significant differences in strontium, barium, manganese and iron, suggesting that the metal signature of the urban THPSS differs from naturally vegetated catchments (Table 4; Figure 3). A suite of metals not detected in the non-urban swamps were present in the urban catchments, however, these were not statistically significant. This included nickel, chromium, cobalt, arsenic and lithium (Table 4).

Table 4. Summary of metals in water between urban (n = 4) and naturally vegetated (n = 4) Temperate Highland Peat Swamps on Sandstone (THPSS) catchment types (mean from the three sampling events).

Major ions	*F* Statistic	d.f.	*p* Value	Urban Catchments			Naturally Vegetated Catchments		
				Range	Mean	Median	Range	Mean	Median
Aluminium	0.06	1, 40.14	0.81 (ns)	5 ×–1200.00	214.44	70.00	80.00–290.00	159.55	120.00
Manganese	7.57	1, 42	0.009 *	2.5 ×–260.00	68.93	17.00	2.5 ×–31.00	9.95	9.00
Iron	15.40	1, 40.13	0.00 **	250.00–7100.00	2288.15	1300.00	58.00–630.00	281.73	270.00
Nickel	1.73	1, 42	0.20 (ns)	0.5 ×–1.00	0.56	0.50	0.5 ×	0.5 ×	0.5 ×
Zinc	2.63	1, 42	0.11 (ns)	0.5 ×–25.00	8.70	6.00	0.5 ×–34.00	13.14	6.50
Barium	27.73	1, 42	0.00 **	3.00–36.00	18.63	18.00	4.00–9.00	5.77	5.00
Cadmium	0.47	1, 40.13	0.50 (ns)	0.05 ×–48.00	3.64	0.30	0.05 ×–22.00	1.93	0.35
Chromium	1.73	1, 40.14	0.20 (ns)	0.5 ×–2.00	0.67	0.50	0.5 ×	0.5 ×	0.5 ×
Lead	0.74	1, 40.41	0.40 (ns)	0.5 ×–8.00	1.37	0.50	0.5 ×–2.00	0.75	0.50
Strontium	55.84	1, 40.13	0.00 **	11.00–75.00	37.26	38.00	1.40–7.90	3.85	2.65
Cobalt	1.73	1, 40.010	0.20 (ns)	0.5 ×–2.00	0.67	0.50	0.5 ×	0.5 ×	0.5 ×
Copper	0.18	1, 40.13	0.674	0.5 ×–94.00	15.17	3.00	0.5 ×–60.00	17.00	3.50
Arsenic	1.73	1, 40.25	(ns)	0.5 ×–3.00	0.78	0.50	0.5 ×	0.5 ×	0.5 ×
Lithium	2.04	1, 40.11	0.20 (ns)	0.5 ×–1.00	0.54	0.50	0.5 ×	0.5 ×	0.5 ×
Titanium	2.30	1, 40.13	0.16 (ns)	0.5 ×–12.00	1.96	0.50	0.5 ×–1.70	0.62	0.50

Notes: Significance is indicated as * = $p < 0.01$, ** = $p < 0.001$ and ns = not significant. Data is presented as µg L^{-1}. × denotes values that were below the detection limit. d.f. denotes the degrees of freedom (numerator, denominator).

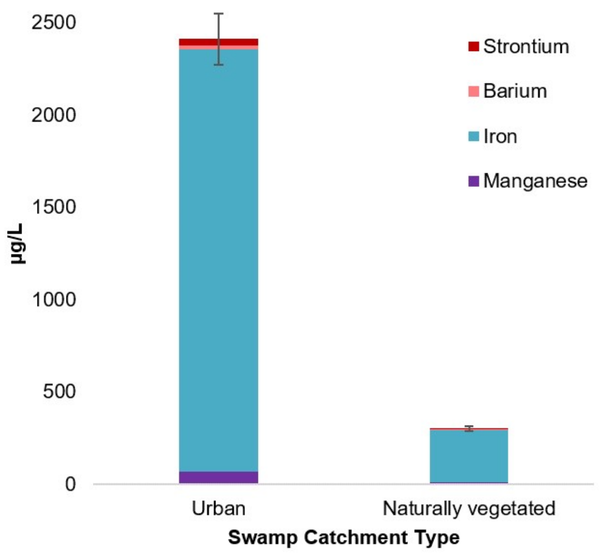

Figure 3. Comparison of mean (+/− standard error) concentrations of statistically significant metals in water between urban (n = 4) and naturally vegetated (n = 4) Temperate Highland Peat Swamps on Sandstone (THPSS) catchments over the course of the study (April–June 2018).

Strontium concentrations in urban swamps were 9.68 times higher than in naturally vegetated swamps (mean 37.26 µg L^{-1}; $p < 0.001$). Urban swamps had significantly higher levels of barium, by 3.23 times, compared to the non-urban swamps ($p < 0.001$). Manganese was significantly higher within the urban (mean 68.93 μg L^{-1}) compared to the naturally vegetated swamps (mean 9.73 μg L^{-1}; $p < 0.01$). Iron was one of the most abundant elements detected across all sites, however, there was more than an eight-fold difference in iron concentrations between urban (mean 2288.10 μg L^{-1}) and naturally vegetated (mean 281.73 μg L^{-1}) catchments (Table 4; $p < 0.001$).

The PCA highlighted that there were differences between catchment types, with the first and second principal components reflecting approximately 63% of variance (PC1 41.3% and PC2 21.4%; see Supplementary data Tables S1–S3). Urban sites (1–3, 7–12) and naturally vegetated sites (numbered 13–22) showed distinct groups (Figure 4). The urban site at Wentworth Falls (numbered 4–6) was separate from the other three urban sites, being closer to the naturally vegetated sites. There was also consistency within sites over time. Impervious area (IA) showed an association with pH, electrical conductivity, calcium, magnesium, bicarbonate, strontium, potassium and barium (Figure 4).

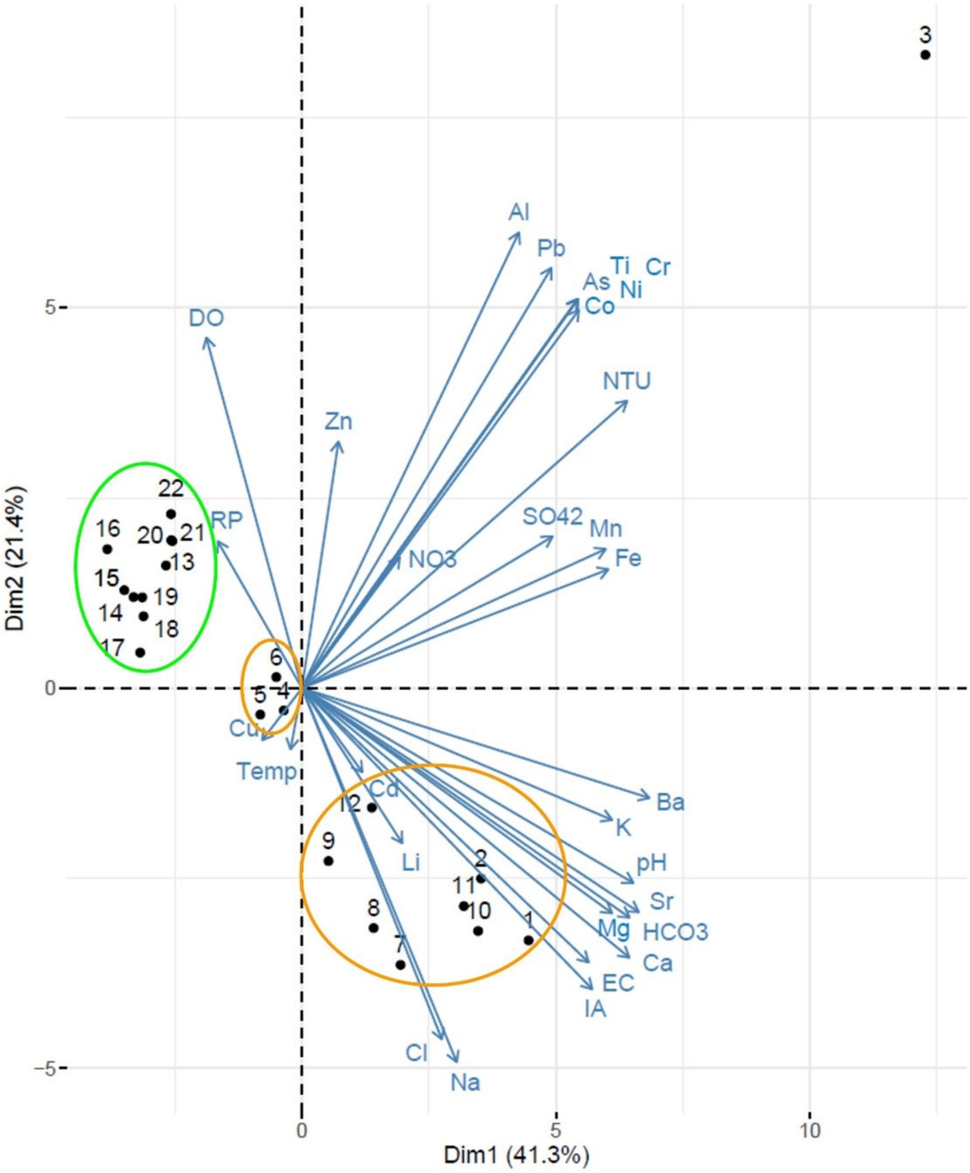

Figure 4. Principal Components Analysis (PCA) of water quality parameters and impervious area from four urban (outlined in orange) and four naturally vegetated (outlined in green) Temperate Highland Peat Swamps on Sandstone (THPSS) from April–June 2018 (excluding Mount Hay). Sites are numbered as urban Bullaburra (1–3), Wentworth Falls (4–6), North Lawson (7–9), and Popes Glen

(10–12), and naturally vegetated Mount Hay (13), Hat Hill (14–16), Lawson (17–19), and Kings Tableland (20–22). Variables are indicated as impervious area (IA), pH, electrical conductivity (EC), dissolved oxygen (DO), temperature (Temp), turbidity (NTU), nitrates (NO3), reactive phosphates (RP), calcium (Ca), bicarbonate alkalinity as $CaCO_3$ (referred to as HCO3), magnesium (Mg), potassium (K), aluminium (Al), strontium (Sr), barium (Ba), iron (Fe), manganese (Mn), sulfate (SO42), cobalt (Co), arsenic (As), nickel (Ni), chromium (Cr), titanium (Ti), lead (Pb), zinc (Zn), copper (Cu), cadmium (Cd) and lithium (Li).

3.2. Sediment Chemistry

3.2.1. Physical and Chemical Characterization of Sediment

All eight sediment cores can be broadly classified as having a peat/organic rich layer of 5–10 cm in depth overlaying clay or sandy-clay (see Supplementary data Figure S2). The peat/organic layers contained variable amounts of dark black (10YR 2/1) material primarily as decomposed detrital materials, mixed with more structured brown root material (5YR 3/2), which combines to the reported 10YR 2/2 for the majority of samples at 0–10 cm depths. Below this organic-rich layer, each core (excluding Hat Hill where the clay layer was lost during extraction due to suction) contained a dark brown (7.5YR 3/2) to black (10YR 2/1) fine clay layer with variable amounts of coarse, unsorted sand grains (up to 5%). There was limited evidence of redoximorphic features within the clay layers, which were field moist at the time of sampling but were not saturated.

There was no clear difference in pH and Eh between the catchment types (see Supplementary data Figure S2). Surface layer pH ranged from 5 to 6 pH units for the majority of cores, which is in line with the anticipated pH of water at equilibrium with atmospheric CO_2 and humic acid. The exception was naturally vegetated Hat Hill, which was slightly more acidic at 4.31 pH units. Conversely, urban Lawson and Bullaburra had surface pH that was approaching neutral at 6.40 and 6.96 pH units, respectively. All sediment cores generally exhibited a decrease in pH (increasing acidity) between the organic/peat-rich surface materials and clay layer at depths (excluding Hat Hill). The Eh results also showed a decreasing trend with depth, with the highest readings within the surface layers and the lowest readings at depth. The mixing and exposure to atmospheric conditions within the surface layers are evident and persist through the peat layers that readily allow mixing with surface water. At depth, the permeability is lower due to the clay (and to a lesser extent sandy-clay), which would not readily facilitate mixing with oxygenated surface water conditions.

3.2.2. Mineralogy

Surface sediment samples (top 3–5 cm) of the cores for all sites showed a mix of quartz, organics, and trace amounts of aluminosilicate materials. Multiple peaks throughout all samples show high crystallinity quartz, which is indicative of the dominant geology of the region, Hawkesbury sandstone (Figures 5 and 6). Results suggested the presence of $Ca(OH)_2$ in the surface sediment of two of the urban swamps, Bullaburra and Popes Glen, which was not present in any of the naturally vegetated swamps (Figure 5). This was particularly evident at 18 degrees 2θ and 71.5 degrees 2θ. However, the peaks for $Ca(OH)_2$ were not clearly visible in the other two urban swamps (North Lawson and Wentworth Falls). There was also no clear evidence of $CaCO_3$ in surface sediment from either catchment type (Figures 5 and 6). It cannot be concluded that $CaCO_3$ was not present (at a very low amount), due to the high crystallinity quartz in each sample, as this may have masked the presence of other elements and mineral structures. Spectra for surface samples from the naturally vegetated catchments remained consistent and did not exhibit any presence of $Ca(OH)_2$ or $CaCO_3$. Instead, all samples from the naturally vegetated THPSS were dominated by aluminosilicate materials (clay) and quartz (Figure 6).

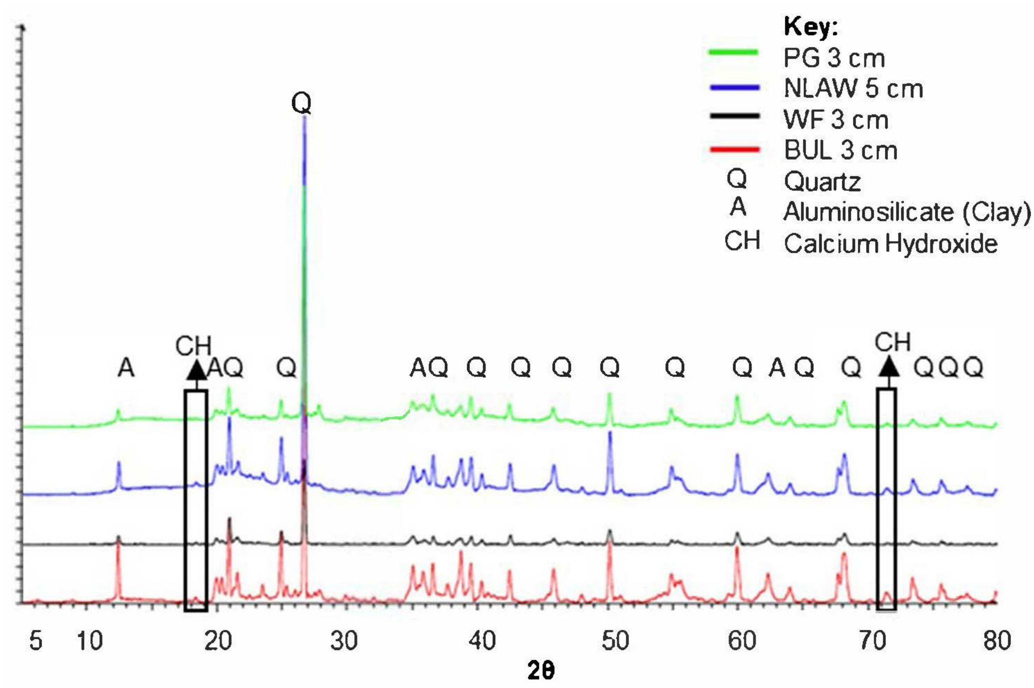

Figure 5. XRD spectra for surface sediment samples (0–5 cm) from urban (n = 4) Temperate Highland Peat Swamps on Sandstone (THPSS) catchments (from 5–80 degrees 2θ). Sites are indicated as Bullaburra (BUL; red), Wentworth Falls (WF; black), North Lawson (NLAW; dark blue) and Popes Glen (PG; light green). The y axis refers to intensity. Quartz is indicated as Q, aluminosilicate as A and calcium hydroxide as CH. Peaks at 18 degrees 2θ and 71.5 degrees 2θ are indicative of calcium hydroxide.

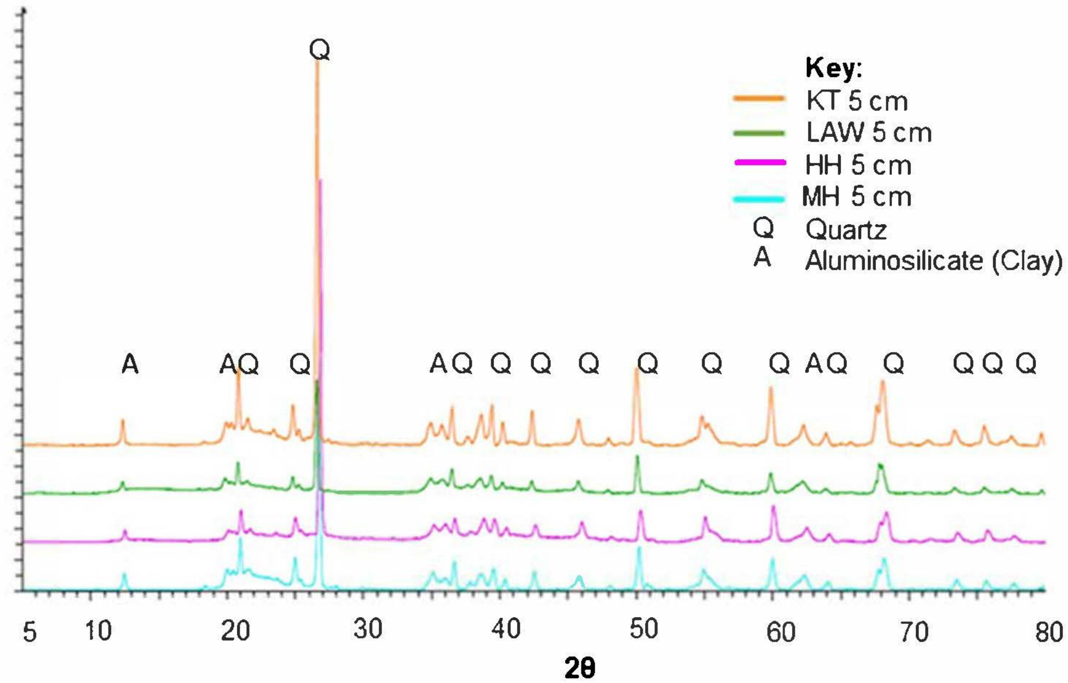

Figure 6. XRD spectra for surface sediment samples (0–5 cm) from naturally vegetated (n = 4) Temperate Highland Peat Swamps on Sandstone (THPSS) catchments (from 5–80 degrees 2θ). Sites are indicated as Mount Hay (MH; light blue), Hat Hill (HH; pink), Lawson (LAW; dark green) and Kings Tableland (KT; orange). The y axis refers to intensity. Quartz is indicated as Q and aluminosilicate as A.

There was variability in mineralogy by depth, as the surface layer of all cores contained more organic matter, resulting in the XRD samples being more amorphous, and quartz remained the dominant structure detected across all sites. A comparison by the depth of the two urban sites which exhibited the presence of $Ca(OH)_2$ in the surface sediment (Bullaburra and Popes Glen) revealed that $Ca(OH)_2$ was present at the positions of 18 degrees 2θ and 71.5 degrees 2θ throughout the soil profiles (see Supplementary data Figures S3 and S4). For the urban Bullaburra core, $Ca(OH)_2$ exhibited the largest peak in the surface layer (3 cm) and this decreased with depth (see Supplementary data Figure S3). However, this trend was reversed in the urban Popes Glen core, with the largest peak for $Ca(OH)_2$ observed in the deepest layer (19 cm) and decreasing in the higher layers (see Supplementary data Figure S4).

The Saturation Index (SI) for $CaCO_3$ in the naturally vegetated swamps had a mean of $10^{-6.4}$ for all sites (Table 5). This low value observed in naturally vegetated THPSS suggests that $CaCO_3$ is unlikely to be present as a precipitate in the sediment profile. However, the urban sites had higher and more variable $CaCO_3$ SI values. Bullaburra (at $10^{-1.69}$) and Popes Glen ($10^{-2.88}$) had values approaching equilibrium for $CaCO_3$, suggesting that $CaCO_3$ precipitation is more likely. North Lawson ($10^{-3.23}$) and Wentworth Falls ($10^{-4.66}$) also had higher SI values compared to the non-urban swamps, however to a lesser extent than Bullaburra and Popes Glen. Wentworth Falls did not appear to be as impacted as the other urban sites, with an SI value that was closer to those of the naturally vegetated catchments. The SI for $Ca(OH)_2$ exhibited low values for all sites, which suggests the $Ca(OH)_2$ is not thermodynamically favored, however values were slightly higher in the urban catchments (mean of 10^{-15} compared to $10^{-18.7}$ in the naturally vegetated catchments). Goethite (αFeOOH) values were positive, indicating that iron oxide precipitate is forming within the THPSS sites, and values were slightly higher in urban swamps due to elevated pH.

Table 5. Saturation Index (SI) in log for calcite ($CaCO_3$), portlandite ($Ca(OH)_2$) and goethite (αFeOOH) in water from urban (n = 4) and naturally vegetated (n = 4) Temperate Highland Peat Swamps on Sandstone (THPSS) catchments.

Swamp Name	Catchment Type	Log SI		
		$CaCO_3$	$Ca(OH)_2$	αFeOOH
(1). Bullaburra	Urban	−1.69	−12.94	6.66
(2). Wentworth Falls	Urban	−4.66	−16.70	5.54
(3). North Lawson	Urban	−3.23	−15.28	5.69
(4). Popes Glen	Urban	−2.88	−15.13	6.21
(5). Mt Hay	Naturally vegetated	−6.46	−17.89	5.06
(6). Hat Hill	Naturally vegetated	−6.57	−18.83	4.37
(7). Lawson	Naturally vegetated	−6.38	−19.17	3.79
(8). Kings Tableland	Naturally vegetated	−6.20	−19.02	3.91

4. Discussion

The GBMA is a high conservation value region, however, urbanization and encroachment have the potential to place increasing pressure on fragile natural environments, such as THPSS, despite their legislative listings and heritage status. Findings from this study demonstrated that water in urban swamps had modified water chemistry, with elevated pH, EC, concentrations of major ions (particularly calcium and bicarbonate) and metals (including strontium, barium, manganese and iron) compared to non-urban catchments. The current study provides the first detailed examination yet conducted on THPSS mineralogy. This revealed that sediment from urban swamps had altered mineralogy, with a greater presence of calcium, particularly in the form of $Ca(OH)_2$, compared to non-urban sites. This is in line with typical characteristics of urbanized catchments worldwide [8,10,13,53], previous findings from swamps within the GBMA [34,36,38], and patterns of evidence that strongly suggest that urban materials and impervious surfaces such as concrete remain a potential source of elevated calcium and alkalinity within sensitive freshwater systems [4,6,8]. However, this research is the first to investigate links between catchment urbanization, water chemistry and mineralogy of sediment within a sensitive freshwater wetland. The degree of modification identified within urban THPSS is lower relative to geochemical changes seen in other higher density urban catchments (such as [10,14,24]). However, findings are in line with concerns raised regarding the high threat of water pollution and urban development to the GBMA [30]. Whilst urban waterways typically have elevated nitrogen and phosphorus concentrations [2], this study revealed that nitrate and phosphate concentrations were not significantly enriched in urban THPSS. This study reinforces the potential impact that urbanization can have on fragile, acidic, dilute freshwater ecosystems, particularly in lands surrounding and within a recognized World Heritage Area. It is acknowledged that the study was conducted over a relatively short period of time and further longer-term studies are recommended.

4.1. Calcium and Urban Development

Calcium levels were elevated in urban swamp water and were associated with overall EC and greater ionic strength. This trend corresponds with global findings of higher calcium in urban waterways [7,10,24], and previous research within THPSS [34,40]. There is also evidence worldwide of elevated calcium in urban sediment profiles [12,13]. An increase in calcium concentrations of over 2000 times in urban riparian sediment (classified as >18% impervious area; mean 1184.96 mg kg^{-1}) compared to non-urban catchments (<5% impervious area; mean 0.56 mg kg^{-1}) was observed in the Georges River catchment in south-eastern Australia [14]. Findings from THPSS reflect this trend of elevated calcium, being almost 20 times greater in urban swamp water compared to non-urban sites, and highlights how sediment can act as a key sink for metals and alkalinity in urban catchments.

At the sediment-water interface, extensive research has examined the legacy of urbanization on sediment (such as in streams and wetlands), particularly in Europe (see [49]). The ratio of Ca: HCO_3^- predicted that precipitation of calcium phases was more likely in urban sediment. This was supported by the results of the mineralogical investigation, where trace levels of $Ca(OH)_2$ were only observed to be present in two urban THPSS (Bullaburra and Popes Glen). Increased inputs of calcium and bicarbonate in urban catchments alters the equilibrium state and promotes $CaCO_3$ precipitation. It is important to note that $Ca(OH)_2$ is metastable in waters in equilibrium with atmospheric CO_2 and ultimately $CaCO_3$ will be formed. These reactions are mediated by acidity, alkalinity and the partial pressure of CO_2. There were differences in the pH of BMUS sediment between catchment types, with surface sediment from naturally vegetated BMUS being more acidic (mean 5.2 pH units) than the urban swamps (mean 5.8 pH units).

The low natural background levels of calcium and alkalinity in regional geology, coupled with increasing encroachment of urban infrastructure within THPSS catchments [34,42], suggests that impervious materials such as concrete and urban stormwater infrastructure (including gutters and pipes) may contribute to increasing calcium above background concentrations within these systems, with the potential to accumulate in the sediment. This is further highlighted by the associations shown between impervious area and key elements such as calcium, bicarbonate and pH in Figure 4. The detection of $Ca(OH)_2$ in sediment from two of the urban swamps is of interest, indicating the potential for urban modification within these poorly buffered systems, particularly as $Ca(OH)_2$ is a common component of concrete. Calcium levels also decreased with depth, suggesting that calcium is not sourced from groundwater, but rather is coming from surface inputs, which could include urban runoff [7,24]. However, further research is required to characterize sources of elements, interactions between sediment and water, and the ecological implications of these sinks of nutrients is poorly understood in these ecosystems.

4.2. Altered Chemical Signature of Urban Ecosystems

Globally, it is recognized that aquatic ecosystems, including rivers, lakes and wetlands, with urban catchments exhibit altered elemental composition, elevated concentrations of metals, greater ionic strength and higher pH compared to background conditions [2,12,13,24,53–56]. This is supported by findings from this study, as urban THPSS demonstrated a modified ionic signature compared to naturally vegetated catchments. Whilst elemental loading still occurred, the signature of urban Wentworth Falls was more similar to the non-urban catchments despite having higher impervious cover (as shown in Figure 4), however, this may be impacted by interactions with the adjacent Wentworth Falls Lake. Findings from this study reflect the trends of previous water quality monitoring at this site [57–59]. Wentworth Falls Lake is an artificial impoundment which has resulted to partial flooding of areas of the swamp [60]. This may contribute to elevating the depth of the water table in unflooded sections of the swamp, thereby modifying natural hydrology. Additionally, Wentworth Falls Lake has also received upgrades to stormwater infrastructure, such as biofiltration systems, to reduce urban runoff into the swamp area [61]. This highlights the need for further research and monitoring to investigate the role of stormwater mitigation on improving water quality in swamp systems.

Elevated metals in water and sediment have previously been identified within urban areas [11,54,62,63]. This study builds on previous research to highlight that trace metals associated with urban development can accumulate in fragile, acidic and dilute wetlands. Iron, aluminium and manganese were dominant in THPSS, which is typical of undisturbed catchments in the Blue Mountains and reflect the influence of the sandstone geology [64] and ultimately the role of pH in regulating metal mobility. However, in urban swamp waters strontium and barium were significantly elevated compared to naturally vegetated catchments, whilst some trace metals (nickel, chromium, cobalt, arsenic and lithium) were only detected in urban swamps. Elevated strontium and barium have previously been associated with the weathering of urban materials, such as concrete and associated materials including fly ash [63,65–68]. These findings suggest that urban inputs may alter the elemental fingerprint of fragile freshwater ecosystems, however, the implications of elevated metals in these environments remain uncertain.

Contrary to global trends in urban waterways, nitrogen and phosphorus in water did not differ between catchment types [2,7,24,69]. The Blue Mountains region is naturally nutrient poor, however, highly urbanized waterways in the area have recorded nutrient enrichment [57,70]. Previous research by [71] suggested that ammonium was elevated in sediment in urban swamp catchments, however, found that nitrate levels were typically below detection methods across both urban and non-urban swamps, which reflects trends of this study. This suggests that elemental composition, along with pH and ionic strength, appear to be key factors driving differences between THPSS, not nutrient enrichment.

4.3. Relationships between Catchment Urbanization and Wetland Chemistry

There has been an increasing number of published studies making associations between the role of urban development, a high coverage of concrete surfaces in urban catchments and the modification of natural chemistry of water and sediment [4,6,7,10,24,53]. In particular, the dissolution of urban materials, such as concrete [25], poses a source of urban geochemical alteration for sensitive aquatic environments. Due to the global extent of urbanization and widespread documented sources of contamination such as stormwater runoff and weathering of urban materials, this has potential far-reaching implications for fragile, freshwater systems and the modification of natural wetland geochemistry. Findings from this study of THPSS suggest that urban swamps have elevated major anions, cations and trace metals in water, which can also accumulate in the sediment, and urban inputs are suspected as contributing to this modified elemental signature. Findings from the current study highlight the magnitude of the increased calcium content in both water and sediment of urban THPSS, compared to non-urban swamps. The current research also provides new insights into how the minerology of urban wetland sediment can act as a key sink for metals, calcium and other major ions. However, the ecological implications of this magnitude of change in water chemistry and accumulation within the sediment profile in fragile freshwater systems is not well-known.

Altering the chemical conditions of fragile freshwater wetlands may have significant implications for natural ecosystem functioning and biotic communities, such as leading to ecosystem shifts or weed invasions. This is a key suspected effect of urban geochemical modification of freshwater systems that requires further investigation. Urban runoff and stormwater are recognized to impact biotic communities through increased nutrient and pollutant levels, for example promoting weed species [72]. Weed invasion is recognized as a key threat within THPSS and the GBMA more broadly [29,30,35]. Recent research has suggested that modified physiochemical conditions, particularly elevated pH, in urban THPSS alters the abundance and composition of microbial communities, which has implications for nutrient cycling and decomposition rates [71]. The current study revealed that nitrogen and phosphorus concentrations were not significantly increased in urban THPSS, compared to non-urban swamps. This was in contrast to expectations, according to the global urban stream syndrome [2,3].

Links between catchment geological properties, chemical characteristics of the biotic community (such as aquatic plants), and urban land uses are increasingly being identified [73]. For example, [73] suggests that as carbon is a limiting factor for aquatic stream and lake vegetation, elevated bicarbonate concentrations (from geology and urban sources) can influence the distribution of species able to utilize bicarbonate under low CO_2 conditions for photosynthesis, thereby altering community composition. This highlights how urban development within the catchments of sensitive freshwater systems can contribute to a shift in natural conditions, thereby potentially altering the composition of the vegetation and biotic community adapted to those conditions. This is of particular concern in regions such as the GBMA, as many endemic and endangered species are found within these specialized habitats.

Management of freshwater systems impacted by catchment urbanization can be complex. Remediation and strategies to improve swamp condition and water quality are possible [37], such as using revegetation and soft engineering works to manage stormwater runoff and limit channelization. This current research shows that further investigation into the legacy effects of urbanization in the sediment profile of wetlands would be beneficial. The current research also suggests that it is unlikely that urban swamps will return to a pre-urban state after they become degraded. The long-term implications of catchment urbanization requires further investigation. It would be highly desirable to study wetland water and sediment chemistry over a longer time period, including before versus after a wetland catchment is modified by urban development [74]. For example, research indicates that urban development is associated with modifying the natural geomorphology, hydrology and functioning of swamps, which can lead to desiccation, shifts in vegetation communities or modified biogeochemical cycles and carbon storage [33,38,39]. This raises questions as to how to better manage or protect vulnerable freshwater ecosystems, such as THPSS that occur on the fringe of an important World Heritage Area, in the face of increasing future population growth and urban development.

5. Conclusions

This current study demonstrates that catchment urbanization has the potential to substantially alter the natural geochemistry of freshwater environments. Urban THPSS had modified water chemistry, with elevated pH, altered ionic strength and composition and higher concentrations of several metals (including strontium and barium). Sediment from urban swamps displayed higher calcium and the presence of $Ca(OH)_2$ was recorded at two of the urban swamps. These findings support previous research identifying that urban ecosystems exhibit altered water and sediment chemistry compared to non-urban catchments [8,14]. THPSS are poorly buffered, acidic, naturally dilute ecosystems that are vulnerable to degradation due to urban activities [34,36–40]. This study identifies novel interactions between water and sediment chemistry within a high-conservation value freshwater ecosystem, suggesting links between urban inputs, water chemistry and mineralogy of swamp sediments. It also highlights the potential for swamp sediments to be a sink for urban inputs, such as calcium, which may have long-lasting effects on the environment. However, the impact of urbanization on sediment is still poorly understood and further research is required to determine specific pathways and links between urban inputs, such as concrete sources, and the chemistry of urban freshwater environments. Further research should also investigate seasonal and multi-year studies. Urbanization is a global issue facing fragile, freshwater wetlands. Urban encroachment into natural ecosystems poses an increasing concern, particularly within a recognized World Heritage Area such as the GBMA which is at risk of further deterioration of conditions and biodiversity values. Examination of the water-sediment interface offers an important insight into changes to water chemistry and longer-term records within the sediment of urban inputs into sensitive freshwater systems. Lessons learnt from the effects of urban development on THPSS could be used to identify and target management strategies to better conserve these and other similar environments for the future.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14223724/s1; Figure S1: Electrical conductivity compared to (a). ionic strength (Moles; M) and (b). calcium (M); Figure S2: Summary of Redox (mV; indicated in green) and pH (pH units; indicated in blue) data for sediment cores from urban Temperate Highland Peat Swamps on Sandstone (THPSS) (a). Bullaburra, (b). Wentworth Falls, (c). North Lawson, (d). Popes Glen, and naturally vegetated THPSS catchments (e). Mount Hay, (f). Hat Hill, (g). Lawson and (h). Kings Tableland; Table S1: Eigenvalues for the Principal Component Analysis (PCA) conducted in R for the eight Temperate Highland Peat Swamps on Sandstone (THPSS) assessed in the Blue Mountains; Table S2: Summary of variables for the Principal Component Analysis (PCA) conducted in R for the eight Temperate Highland Peat Swamps on Sandstone (THPSS) assessed in the Blue Mountains; Table S3: Summary of individuals for the Principal Component Analysis (PCA) conducted in R for the eight Temperate Highland Peat Swamps on Sandstone (THPSS) assessed in the Blue Mountains; Figure S3: X-ray diffraction (XRD) spectra for sediment samples from the core collected from urban Bullaburra (BUL) Temperate Highland Peat Swamps on Sandstone (THPSS), where samples were collected at a depth of 3 cm (red), 10 cm (green) and 15 cm (blue); Figure S4: X-ray diffraction (XRD) spectra for sediment samples from the core collected from urban Popes Glen (PG) Temperate Highland Peat Swamps on Sandstone (THPSS), where samples were collected at a depth of 3 cm (light green), 10 cm (blue) and 19 cm (red).

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