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Geochemical impact of urban development on fragile freshwater wetlands

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Abstract. Urbanization is associated with increased cover of impervious surfaces, which poses significant challenges to freshwater ecosystems globally. Implications of catchment urbanization include altered natural hydrology, erosion, weed invasions and modified water chemistry. Blue Mountains Upland Swamps are sensitive freshwater ecosystems located in the Blue Mountains region in south-eastern Australia. They have high conservation value as they are located within a World Heritage Area, are a listed 'endangered ecological community' in Australia and contain endemic and endangered flora and fauna. Water chemistry was assessed in four naturally vegetated and four urban swamps. Urban swamps had higher impervious cover and modified water chemistry, with elevated pH, electrical conductivity and major ions compared to non-urban swamps. Water in urban swamps had elevated calcium, potassium and bicarbonate compared to non-urban catchments, by 19.8, 5.2 and 10.3 times respectively. Although further research is needed, we hypothesize that common concrete materials, particularly drainage infrastructure, strongly influenced differences between urban and non-urban catchments. This adds to growing international research highlighting the potential role of concrete in modifying urban water chemistry due to gradual dissolution and mobilization of ions. In an increasingly urban world, consideration of the ecological consequences of urbanization is required to guide future management approaches.

1. Introduction

Urbanization is increasing on a global scale, resulting in altered land use and increasing cover of impervious surfaces in urban areas [1]. This places growing pressure on freshwater ecosystems, referred to as "urban stream syndrome" [2]. Key issues of concern associated with urban aquatic ecosystems include altered hydrology, modified water chemistry, increased erosion and weed invasions [3,4].

Catchment imperviousness, which refers to the coverage of impermeable materials such as buildings, roads, stormwater infrastructure and concrete, is recognized as a key factor linked with degradation of urban freshwater systems [3,5]. High imperviousness alters natural flow regimes by reducing infiltration and increasing the volume and flow energy of surface runoff [6]. High impervious cover has also been linked with chemical modification of freshwater ecosystems, as increased stormwater and the weathering of urban materials have been identified as potential sources of major ions to freshwater systems [5,7]. This is suggested to contribute to urban waterways exhibiting a distinct 'urban geochemical signature', with elevated major ions such as calcium, bicarbonate and potassium [8].

Concrete is a widely used, chemically complex material that is prominent in urban landscapes. Whilst concrete provides many benefits within urban ecosystems, environmental impacts of high

concrete use have also been recognized, including contributions to carbon dioxide emissions and landfill [9]. However, there is increasing evidence that identifies concrete as a potential source of urban geochemical modification within freshwater environments, due to increased mobilization of major ions, such as calcium, bicarbonate and potassium, associated with leaching and dissolution of concrete [5,10-13]. The Greater Blue Mountains World Heritage Area in south-eastern Australia covers 1.03 million ha and is recognised as being a pristine, high conservation value ecosystem [14]. Within this region, Blue Mountains Upland Swamps (BMUS) are fragile freshwater wetlands of which there are less than 3,000 ha in existence [15]. Whilst the ecosystem function of BMUS is understood, there is a paucity in information into their degradation in response to urbanization. This study aimed to explore the potential implications of catchment urbanization and impervious surfaces such as concrete on water chemistry within a sensitive freshwater wetland, BMUS.

2. Case study: Blue Mountains Upland Swamps (BMUS)

BMUS refers to peat swamps formed on sandstone geology at altitudes of 500 - 1000 m in the Blue Mountains region of south-eastern Australia [16]. They lack karst features in the underlying geology and water quality is naturally acidic (less than 5 pH units), dilute (less than 30 μS/cm) and sodium and chloride dominated, resulting in poor buffering capacity [15]. Found nowhere else on Earth, BMUS have high conservation value as their distribution covers less than 3000 ha [15]. These swamps are listed as an 'endangered ecological community' under the Australian Environment Protection and Biodiversity Conservation Act 1999 (Commonwealth) and Threatened Species Conservation Act 1995 (New South Wales) [16]. They provide valuable ecosystem services, have high biodiversity and are home to endemic and endangered species of flora and fauna, including the Blue Mountains Water Skink (*Eulamprus leuranensis*) and Giant Dragonfly (*Petalura gigangtea*) [17]. Many swamps are located within the Greater Blue Mountains region, a recognized UNESCO World Heritage Area [14], however urban development also occurs within sections of this region. Urban impacts are recognized to negatively affect natural hydrology and geomorphology in BMUS [15,18], however geochemical implications are not well-known. It was hypothesized that urban BMUS water would exhibit a modified ionic signature compared to non-urban catchments.

3. Methodology

Eight BMUS sites were examined in the Blue Mountains region in NSW, Australia, with four urban and four naturally vegetated catchments (figure 1; table 1). Impervious Area (IA%) and Directly Connected Impervious Area (DCIA%) was calculated from satellite images, based on methods of US EPA [19] assuming low-density residential land use. Water chemistry was assessed at each site on three occasions between April and June 2018. Surface water samples were collected from the exit stream (where surface water emerged at the end of the swamp) at each site. Electrical conductivity (EC) and pH were tested in the field using a calibrated TPS AQUA-Cond-pH meter and five repeated measures were taken per sampling event after the meter had stabilized [15]. Duplicate 500 mL samples were collected from surface water in sterile plastic containers and analysed for major cations and anions using standard methods at a commercial National Association of Testing Authorities (NATA) accredited laboratory. This study focused on ions with the highest enrichment factor (EF), including calcium and potassium measured using ICP-MS and bicarbonate alkalinity measured using titration (APHA method 2320-B) [20]. Data was analyzed in IBM SPSS Statistics version 22 using a mixed linear model, and values below detection were attributed as half of the minimum detection value [12].

Figure 1. Locations of Blue Mountains Upland Swamps (BMUS) study sites. Sites are located within the Blue Mountains region (indicated in dark green), containing the Blue Mountains World Heritage area, which is located to the west of Sydney, NSW, Australia and the urban Sydney catchment area (grey). Urban swamp catchments are indicated using orange squares and naturally vegetated catchments are shown using light green circles. Image sourced from ArcGIS version 10.6.1.

Table 1. Characteristics and locations of BMUS study sites.

| Swamp Location	Catchment Type	Latitude and Longitude	Altitude (m)	Impervious Area (IA%)	Directly Connected Impervious Area (DCIA%)
Bullaburra	Urban	-33.727319, 150.412928	755	25.03	9.54
Wentworth Falls	Urban	-33.707627, 150.361313	880	22.41	7.90
North Lawson	Urban	-33.713851, 150.427195	695	23.15	8.35
Popes Glen	Urban	-33.633639, 150.292336	1010	34.30	16.30
Mount Hay	Naturally vegetated	-33.668644, 150.346508	920	0	0
Hat Hill	Naturally vegetated	-33.599941, 150.328782	967	0	0
Lawson	Naturally vegetated	-33.696739, 150.444027	665	0	0
Kings Tableland	Naturally vegetated	-33.76210, 150.38373	780	0.18	0.002

4. Results

Urban swamps had higher impervious cover (table 1), with mean IA of 26% and DCIA of 11% in urban compared to 0.045% and 0.0005% respectively in naturally vegetated swamps. Water chemistry differed significantly between urbanized and the naturally vegetated catchment types (table 2). Water pH was elevated by 1.33 pH units in the urban (mean 6.20 pH units) compared to the naturally vegetated swamps (mean 4.87 pH units; $p<0.05$). Mean EC within urban BMUS (116.30 µS/cm) was more than double that of the non-urban swamps (45.57 µS/cm; $p<0.05$). Water in urban BMUS had an

altered ionic profile compared to naturally vegetated BMUS. In urban swamps, mean calcium levels were elevated by 19.8 times (10.99 mg/L), compared to 0.55 mg/L in naturally vegetated BMUS (table 2; figure 2). Potassium was below the detection limit in the non-urban swamps, however, was enriched by 5.2 times in urban BMUS (mean 1.29 mg/L). Bicarbonate was also 10.3 times greater in urban swamps (mean 25.67 mg/L), compared to being below detection limits in non-urban swamps.

Table 2. Summary of water chemistry from urban and naturally vegetated BMUS between April-June 2018. Significance was established at the 0.05 level and * denotes values set to half the detection limit. EF refers to Enrichment Factor and d.f. indicates degrees of freedom.

	F	d.f.	*p*	Urban BMUS			Naturally vegetated BMUS			
				Mean	Median	Range	Mean	Median	Range	EF
pH (pH units)	50.38	1, 20	0.00	6.20	6.08	5.56 – 7.09	4.87	4.81	4.56 – 5.40	-
Electrical Conductivity (μS/cm)	18.80	1, 19	0.00	116.30	137.45	45.10 – 164.90	45.57	49.70	25.30 – 79.10	2.6
Calcium (mg/L)	61.72	1, 42	0.00	10.90	12.00	2.10 – 20.00	0.55	0.25*	0.25* – 1.30	19.8
Potassium (mg/L)	24.29	1, 42	0.00	1.29	0.90	0.25* - 2.80	0.25*	0.25*	0.25*- 0.25*	5.2
Bicarbonate (mg/L)	42.86	1,40.35	0.00	25.67	22.50	5.00 – 56.00	2.5*	2.5*	2.5* - 2.5*	10.3
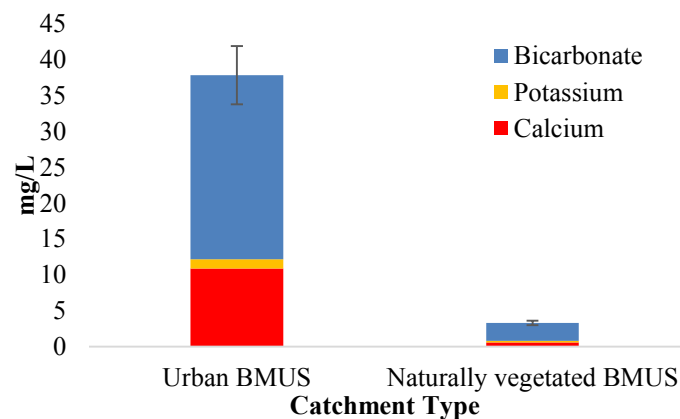
Figure 2. Mean calcium, potassium and bicarbonate concentrations in mg/L from collected waters in urban and naturally vegetated BMUS catchments.

5. Discussion

This study found that urban swamps had greater impervious area and modified water chemistry compared to naturally vegetated BMUS catchments. Urban swamps had elevated pH, EC, and concentrations of calcium (EF of 19.8), bicarbonate (EF of 10.3) and potassium (EF of 5.2) compared to water from non-urban swamps. This is consistent with previous research comparing urban and non-urban BMUS [15]. However, this work highlights that calcium, potassium, and bicarbonate may serve as a fingerprint for urbanization in these fragile ecosystems, which has not previously been reported in BMUS. This altered ionic profile of water in urban BMUS also reflects characteristics of urban stream

syndrome and the typical urban geochemical signature, which has been recorded in urban streams across the globe, including within Australia [21,22], the USA [5,8] and Asia [23,24].

Findings from this study suggest that catchment urbanization and high impervious cover has the potential to contribute to chemical modification of sensitive freshwater environments. In particular, the weathering and dissolution of concrete is suspected to contribute to the alteration of the natural ionic signature of freshwater ecosystems [5,10,13]. As urbanization expands across the globe, particularly in developing regions, this may have widespread implications for freshwater systems. This study highlights the impact this altered chemical signature may have on pristine, high conservation value environments across the globe. Further research is required to explore potential management approaches to address these emerging issues.

pH was elevated in the urban swamps, which is characteristic of the described alkalinization of freshwater ecosystems in urban catchments and has been strongly linked with land use and cover of impervious surfaces [5,7]. Urban waterways across the globe have also been recognized to exhibit an altered ionic signature compared to naturally vegetated catchments [5,12,22,24]. Urban BMUS exhibited elevated calcium, bicarbonate and potassium levels. BMUS typically lack karst geological features [15], however calcium was significantly higher in urban swamps with an EF value of 19.8. This suggests that urban inputs may contribute to modifying natural geochemical cycles within urban swamps.
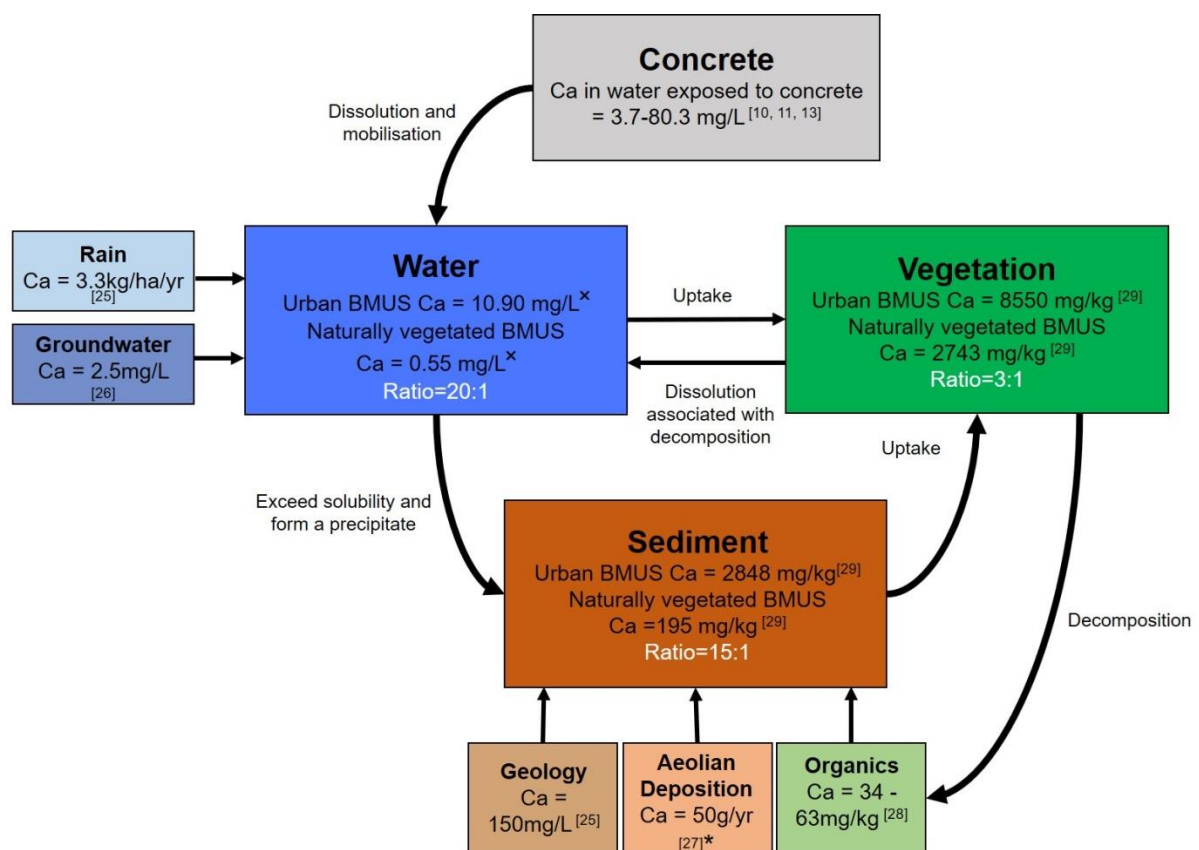
Figure 3. Conceptual model of the geochemical cycling of calcium in urban and naturally vegetated BMUS based on approximate mean values of inputs entering the system which were derived based on findings from the current study (×) and previous research from BMUS [29], Australian [10,11,13, 25-27] and international studies [28]. * The aeolian deposition value was derived from total salts (500g/ha), of which $CaCO_3$ type was assumed to represent 5% and the mean area of BMUS catchments was estimated at 5 ha. Ratio indicates the relationship between calcium in urban: naturally vegetated BMUS.

Here we have proposed a conceptual model to indicate how inputs from suspected urban sources of calcium, such as concrete, may alter geochemical cycling within urban BMUS (figure 3). Rainfall and groundwater are sources of calcium into surface water within BMUS [25,26]. However, urban swamps (mean 10.90 mg/L) have 20 times greater calcium levels compared to naturally vegetated BMUS catchments (mean 0.55 mg/L). Urban materials, particularly concrete, are recognized to contribute calcium to water [10,11,13], posing a potential source of calcium to these systems (figure 3). Sediment and vegetation can act as calcium sinks. Geology, aeolian deposition and organic material can be sources of calcium to sediment [25,27,28]. Previous research indicated that calcium levels were 15 times greater in sediment in urban compared to naturally vegetated BMUS [29]. Vegetation from urban swamps also had three times greater calcium levels compared to the non-urban catchments [29]. However, the implications of this magnitude of calcium enrichment within sediment and for biotic species within sensitive environments remains largely unclear. Excess calcium can have varied effects on plant species, such as impeding growth [30], however the consequences for species within fragile freshwater wetlands are not known and require further research.

High catchment imperviousness has been linked with modified water chemistry in urban streams [5]. Urban runoff and the weathering of urban materials, such as concrete drainage infrastructure and building materials, contribute nutrients and additional ions into freshwater environments [3,10,11]. There is also mounting evidence that identifies concrete as a potential source of ions, particularly calcium [8,10,11,13]. Concrete remains an integral component of modern urban environments, however there is limited knowledge of how urban inputs, such as chemical changes to water due to high concrete exposure and impervious surfaces, could impact geochemical cycling within sensitive freshwater wetlands. This indicates that there is a need to better understand how urban development may alter and effect nutrient cycling these ecosystems.

Modifying the chemical environment can also impact physical and biological components of freshwater systems, including enhancing erosion and sedimentation [3], and facilitating weed invasions via increased nutrients, which can contribute to altered community composition and biodiversity loss [4]. Weed invasions are a concern in urban BMUS and increased surface runoff contributes to altered geomorphology, removal of preferential drainage lines and channelization, which impairs swamp functioning [16]. For example, urban swamps were observed to have a distinct channel and be dominated by exotic species (figure 4), such as honeysuckle (*Lonicera japonica*), small-leaved privet (*Ligustrum sinese*) and blackberry (*Rubus fruticosus*), however weed species were not present in non-urban swamps (figure 5).

Figure 4. Urban BMUS dominated by weed species including blackberry.

Figure 5. Naturally vegetated BMUS dominated by native sedges and shrubs.

BMUS provide a unique case study to explore the effects of catchment urbanization and

imperviousness on a fragile freshwater wetland. These dilute, acidic and poorly buffered swamps have high conservation significance as they have biodiversity value and a restricted distribution that is located within a World Heritage area [15]. Key implications of urban development, including altered hydrology, modified water chemistry, erosion and weed invasions, occur within BMUS [15,18]. This study highlights the potential for urban development to contribute to modifying the ionic fingerprint of fragile, dilute and acidic freshwater ecosystems, in particular contributing to calcium enrichment. This BMUS case study serves to emphasize and raise awareness of the potential impacts of catchment urbanization and imperviousness on sensitive, pristine, high conservation value wetlands and waterways across the globe. Urban development continues to expand worldwide, highlighting the need for consideration of this issue to reduce degradation of fragile freshwater ecosystems.

Development and concrete use underpin urban environments; however, steps can be taken to seek to minimize these geochemical impacts. Consideration of strategies to manage influences of urban development are necessary at the planning stages and catchment scale to reduce risks of degradation to aquatic ecosystems. The establishment of baseline values and routine monitoring is key to understanding local conditions and identifying changes. Management of urban effects on sensitive, high conservation environments should seek to minimize urban runoff, stormwater and the degree of catchment imperviousness. The implementation of Water Sensitive Urban Design (WSUD) principles to promote the reduction of runoff entering pristine or sensitive environments, such as raingardens, swales, bioretention systems and soft engineering works (such as coir logs), is recommended [16,31]. Exploration of alternative materials to impervious surfaces such as concrete, including permeable pavement systems [31] and the potential to coat concrete to reduce leaching [11] also represent areas for further research.

6. Conclusions

Catchment urbanization and the effects of impervious surfaces, such as concrete, on the condition of freshwater ecosystems is a growing global issue that requires careful consideration, particularly in sensitive, poorly buffered wetland systems. Urban BMUS had elevated pH, EC, calcium, bicarbonate and potassium levels compared to non-urban catchments. Due to the magnitude of change in water chemistry between catchment types, urban development and concrete surfaces are suspected to pose a potential source of geochemical modification in urban freshwater systems. As urban development expands worldwide, this poses potential broader ecological implications for fragile freshwater wetlands and waterways across the globe. This study sought to raise awareness of the potential implications of high imperviousness and concrete use in sensitive, pristine environments, and promote consideration and further research of management strategies, such incorporating WSUD principles and exploring alternative materials to concrete, to reduce degradation of urban freshwater ecosystems.

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