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Tracing metals through urban wetland food webs

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ABSTRACT

Constructed wetlands are commonly used to remove contaminants such as heavy metals from stormwater. However, metals can become bioavailable and be transferred into and along wetland food chains. Our study sought to establish whether urbanisation affected concentrations of metals in water, wetland sediments, freshwater crayfish and fish tissues. Samples were taken from constructed wetlands in western Melbourne. There was no relationship between catchment total imperviousness (TI, an index of urbanisation) and water column and sediment concentrations of metals with the exception of Zn, which was higher in more urbanised catchments. Concentrations of metals in fish tissues were highest in benthic species but declined with increasing body size and trophic level. This suggests that metals are not bioaccumulating or biomagnifying along food chains in these systems. Metabolic activity can differ between smaller and larger fish, or smaller fish may also be feeding on different food sources. Our results suggest that there is not a major human health risk associated with accumulation of metals in large-bodied fish in these wetlands, and that most of the metal load is retained in sediments, or the lowest trophic levels.

1. Introduction

By 2050, it is predicted that 66% of the world's population will be living in urban areas (United Nations, 2014), mostly adjacent to freshwater ecosystems (Miller and Boulton, 2005; Catford et al., 2007; Hughes et al., 2014). Urbanisation increases impervious area, the amount of a catchment that is covered by surfaces such as roads, roofs and sealed areas (Morse et al., 2003; Walsh et al., 2005; Cuffney et al., 2010). Total imperviousness (TI) is the proportion of a catchment cover in impervious surfaces and can be used as an indication of how much stormwater is entering aquatic systems (Morse et al., 2003; Walsh et al., 2005; Cuffney et al., 2010). Stormwater is of concern because it can contain pollutants including heavy metals such as Cr, Cu, Cd, Pb, Ni, Zn, Hg and As (Scholz, 2006; Yang et al., 2006). Although metals can be present due to the presence of naturally occurring deposits, the main source of metals in the aquatic environment is through anthropogenic activities (Ekeanyanwu et al., 2010; Merciai et al., 2014). These can come from fuel additives, vehicle corrosion, and tyre and brake wear, and can pose a threat to both humans and wildlife (Scholz, 2006; Yang et al., 2006). Unlike organic contaminants, metals do not degrade, therefore they persist in nature and elimination is slow (Ekeanyanwu et al., 2010; Nasirian et al., 2013; Merciai et al., 2014).

One method of removing contaminants, such as heavy metals, from stormwater is the use of 'constructed wetlands'. These are engineered systems designed to mimic the processes which occur in natural wetlands, with the aim of removing contaminants and pollutants from stormwater through physical, chemical and biological processes (Nuttall et al., 1997; Chavan et al., 2007). However, as constructed wetlands are designed to act as a sink for metals, they are a potential source of uptake by aquatic organisms (Rainbow, 2007; Santoro et al., 2009). Where rates of intake exceed excretion, metals bioaccumulate in an organism. Top predators in food webs can also be subject to biomagnification of metals through the food chain. Large-bodied predators in contaminated systems can have high metal loads as a consequence of being long lived (high potential for bioaccumulation) and high in food chains (high potential for biomagnification) (Mays and Edwards, 2001; Lemly and Ohlendorf, 2002; Zeng et al., 2012). Where humans use these organisms as a source of food, high metal loads can present a substantive public health risk (Campbell, 1994).

Heavy metals in the aquatic environment can be monitored by recording concentrations in water, sediment and biota (Ekeanyanwu et al., 2010). There has been a major focus on heavy metals in rivers and lakes (Watanabe and Omura, 2008; Santoro

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et al., 2009; Ekeanyanwu et al., 2010), with less attention on the passage of metals through food webs in constructed wetlands. Those studies that have been published have shown that contaminated sediments can act as a significant source of metals to the aquatic environment as metals which are dissolved in the sediment solution or weakly adsorbed to sediment particles can become released into the water column (Dunbabin and Bowmer, 1992; Allinson et al., 2015). These metals are then available for uptake by biota and continuous inputs of contaminated stormwater can lead to sediment contamination and degradation of native vegetation and ecosystems (Dunbabin and Bowmer, 1992; Sheoran and Sheoran, 2006; Rouff et al., 2013).

The mobilization of heavy metals from sediments means they can be transferred through aquatic food webs to fish, piscivorous animals and humans (Mazej et al., 2010; Alhashemi et al., 2011). However, the uptake of metals begins at the base of the food chain with biological removal of metals through phytoplankton and aquatic plants such as *Typha latifolia* and *Phragmites australis* (Ellis et al., 1994; Scholes et al., 1998; Rouff et al., 2013). To produce adverse effects, metals must bioaccumulate and this processes is widely accepted as fundamental in understanding environmental risk (Mcgeer et al., 2003; Mazej et al., 2010). Metals may accumulate in fish either directly through the food web or from exposure due to resuspended sediment (Campbell, 1994; Kirby et al., 2001). Species at relatively low trophic levels are exposed to comparatively lower levels of contamination, whilst animals at higher trophic levels are prone to accumulate metals (Weber et al., 2013; Mazej et al., 2010). However, this response can vary, for example Cardwell et al. (2013) report biomagnification of certain metals in macroinvertebrates but not fish, whilst Mazej et al. (2010) conclude that concentrations of metals are more likely to be associated with feeding strategy than trophic position, but suggest some metals (Hg and Zn) may be influenced by the number of trophic transfers involved.

The bioavailability of metals depends on whether they are in the dissolved phase or bound to organic matter, as well as water quality parameters such as dissolved and organic carbon, pH, hardness and alkalinity (Merciai et al., 2014). In addition, feeding behaviour, species, size and physiological condition are some of the parameters which can affect bioaccumulation in macroinvertebrates and fish beyond environmental concentrations (Cui et al., 2011; Merciai et al., 2014). Understanding the potential for metals to move through food chains requires an understanding of both local wetland conditions and the composition of the resident fish community. Knowledge of the effects of catchment urbanisation, local wetland factors and fish community composition is needed to develop an understanding of potential human health risk from metal accumulation in freshwater fish.

The objective of this study was to determine whether the amount of catchment urbanisation (estimated by total imperviousness) influences heavy metal concentrations in water, sediment and animal tissue in constructed wetlands. Specifically, we sought to answer the following questions:

1. Does catchment imperviousness affect concentrations of heavy metals in water and sediments?
2. Does catchment imperviousness affect concentrations of heavy metals in fish and freshwater crayfish tissue?

We hypothesised that an increase in catchment imperviousness would increase stormwater and pollutant inputs, increasing the concentrations of metals in water and sediment. We predicted that these higher levels would be reflected in heavy metal concentrations in fish and freshwater crayfish tissue. As many metals are known to bioaccumulate along food chains, concentrating in higher trophic levels (Zeng et al., 2012), we also predicted larger animals would have higher concentrations of metals.

2. Material and methods

2.1. Site selection and calculation of total imperviousness

This study was conducted in the Melbourne metropolitan region, an area of 9800 km^2 in south-east Australia with a population of 3.8 million people (73% of the inhabitants of the state of Victoria). Land use includes residential, industrial and commercial areas (ABS, 2013). The area comprises two distinct geological regions: basalt in the west and sedimentary material in the east and south (Pettigrove and Hoffmann, 2003).

Our study examined nine constructed wetlands located across the western basalt region. The wetlands were built between 1997 and 2004 and are managed by a single water utility (Melbourne Water). The design objectives for the construction of the wetlands were largely for the management of nitrogen (Melbourne Water, 2005). Wetlands are of a consistent design, with water flowing into an inlet zone, then through a gross pollutant trap, a ponding area, a vegetated zone and an outlet pond before returning to the stream. The constructed wetlands have been designed to be either 'online' or 'offline' (Table 1). Sites which are online have been built on an existing watercourse and all water in the watercourse is treated by the wetland. Where a site is offline, stream water will be diverted from an existing waterway into the wetland, essentially taking the 'first flush' while the remaining stream water bypasses the wetland (Melbourne Water, 2005).

The wetlands were all located in predominantly urban catchments and were chosen based on the availability of previous published studies (Pettigrove and Hoffmann, 2005; Carew et al., 2007). A gradient of TI for sub-catchments across the region was calculated using data supplied by Melbourne Water and applying the method of Walsh and Kunapo (2009). ArcGIS 10 (Environmental Systems Research Institute, Redlands, CA, USA) software was used to calculate the percentage of the catchment upstream of wetlands which comprised sealed surfaces including roads, paths and buildings.

Wetland area and distance of outlet from inlet were calculated using Google Earth Pro software (Map data: Google SKM, 2013). Annual total rainfall for the Melbourne region in 2011 was 862.8 mm, and in 2012 was 618.2 mm (AGBM, 2015).

2.2. Sampling

Turbidity, pH, conductivity, dissolved oxygen (DO) and temperature were recorded *in-situ* at each site using a Horiba U50 Water Quality Checker (Horiba Ltd., Japan), between December 2011 and January 2012. These were spot water measurements and sampling occurred between 10 am and 4 pm.

2.2.1. Water and sediment

Samples of water and sediment were collected at the same time from each wetland between December 2011 and January 2012. Six sediment cores were collected together with a single water sample. Our data suggests that in these small well-mixed waterbodies there is little spatial variation in water quality. Water samples for the measurement of metal concentrations in the water column were gathered using acid-washed 500 ml polyethylene sample bottles. Six sediment cores were collected from each wetland using a random sampling design for the measurement of metal concentrations in wetland sediments. Sampling coordinates were located using a random number table to generate sampling points on a spatial grid. If a point was inaccessible due to the depth of water (>1.5 m depth), the nearest accessible point was used.

Cores were extracted to a depth of 200 mm using a Universal Percussion Corer (comprising a clear polycarbonate core barrel (68 mm dia × 305 mm)) attached to a 'Universal Core Head'(Aquatic