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Detecting long-term temporal trends in sediment-bound trace metals from urbanised catchments ☆

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A B S T R A C T

The shift from rural lifestyles to urban living has dramatically altered the way humans interact and live across the globe. With over 50% of the world's populations living within cities, and significant increases expected over the next 50 years, it is critical that changes to social, economic and environmental sustainability of cities globally be implicit. Protecting and enhancing aquatic ecosystems, which provide important ecosystem services, is challenging. A number of factors influence pollutants in urban waterways including changes in land-use, impervious area and stormwater discharges, with sediment-bound pollution a major issue worldwide. This work aimed to investigate the spatial and temporal distribution of trace metals in freshwater sediments from six urbanised catchment over a 30-year period. It provides an estimate of pollution using a geoaccumulation index and examines possible toxicity using a probable effect concentration quotient (mPECq). Results showed significant temporal changes in metal concentrations over time, with lead generally decreasing in all but one of the sites, attributed to significant changes in environmental policies and the active elimination of lead products. Temporal changes in other metals were variable and likely dependent on site-specific factors. While it is likely that diffuse pollution is driving changes in zinc, for metals such as lead, chromium and copper, it is likely that watershed landuse and/or point sources are more important. The results clearly indicated that changes to watershed landuse, environmental policy and pollution abatement programs are all driving changes in sediment quality, highlighting the utility of long-term sediment monitoring for assessment of urban watershed condition. While this study has demonstrated the utility of detecting long-term changes in metal concentrations, this approach could easily be adapted to detect and assess future trends in other hydrophobic contaminants and emerging chemicals of concern, such as synthetic pyrethroids, providing essential information for the protection of catchment.

1. Introduction

Watershed urbanisation significantly alters natural water flows and aquatic ecosystem condition. Under natural conditions, rainfall typically seeps into soils and is absorbed by plants, or moves through soil profiles and into groundwater or river systems (Heath, 1983). In urbanised areas however, the change in hydrology is often dramatic (Walsh et al., 2012), with waters rapidly flowing off impervious surfaces such as roads, roofs and footpaths, which are directed through stormwater pipes into local running waters. In some instances, construction of wetlands redirect stormwater flows, treating waters before it re-enters the receiving environment. Nonetheless, changes in hydraulic regimes (i.e. timing and rate of streamflow) can influence the ecological condition of streams and creeks, while the addition of urban contaminants via stormwaters into receiving environments are known to cause aquatic pollution and biological degradation (Förstner and Wittmann, 2012).

Over the last century, metal production has increased in line with growth in the world population, gross domestic production and the exploitation of natural resources (Nriagu, 1990). Metals are utilised in a large number of products and services worldwide, which has been accompanied by growth in metallic wastes from the production, usage, degradation and discards of these products. These metallic wastes can enter waterways through various

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pathways including stormwater and road run-off, licenced and unlicensed discharges, and atmospheric emissions, where they can persist for a considerable extent of time (Brown and Peake, 2006). Sediments are a major sink for hydrophobic toxicants such as trace metals and other organic chemicals that bind to sediments particles and deposit in waterways (Sharley et al., 2012). Sediments can adversely affect the overlying water column and can be resuspended during storm events and facilitate entry of contaminants into the food chain (Simpson et al., 2005). Trace metals in particular, due to their highly toxic effect, long residence time and bioavailability, pose a risk to benthic organisms, and potentially to human health (Bryan and Langston, 1992). Long-term monitoring of surface sediments provides critical information on temporal trends of trace metal pollution in waterways, thereby improving the risk assessment process (OSPAR, 2009; Partridge et al., 2005).

Urban landscapes are a mosaic of different land uses that are continually in flux. Numerous studies have shown that as urbanisation increases, pollution levels also increase (Brown and Peake, 2006; Carew et al., 2007; Davis and Birch, 2010; Pettigrove and Hoffmann, 2003). In highly urbanised catchments or downstream of major point sources, metal pollution can pose a risk to aquatic communities. With over 50% of the world's populations living within cities, and significant increases expected over the next 50 years, it is critical that changes to social, economic and environmental sustainability of cities globally be implicit. To reduce pollution caused by urban development, waterway managers are adopting a host of stormwater treatment measures to reduce contaminants from entering receiving waters. The type of treatment used depends on the pollutant being targeted. For instance, it is recognised that there is a relationship between pollutant size and the treatment process required to retain the pollutant (CSIRO, 1999), and often a treatment train involving numerous treatment processes is required to remove the majority of pollutants. Monitoring trends in sediment quality in downstream receiving environments provides an ideal approach to measure and assess the efficacy of treatment programs or Water Sensitive Urban Design (WSUD) initiatives that aim to reduce the impacts of contaminated stormwater on local ecological communities.

Pollution indices and quotients provide powerful tools in processing, analysing and assessing trace metal contamination and ecological risk (Caeiro et al., 2005; Gong et al., 2008). Sediment quality guidelines were developed to protect the aquatic fauna from stress associated with sediment-bound contaminants (ANZECC, 2000; MacDonald et al., 2000), prioritise chemicals of concern (Birch and Taylor, 2002) and allow evaluation of aquatic ecosystems for long-term risk through adaptive management frameworks (Florsheim et al., 2006). To assist in assessing sediment quality, mean probable effect concentration quotients (mPECq) have been developed, and analysis has shown that as the mean quotient increases, so does the probability of toxicity (MacDonald et al., 2000). The mPECq also provides a basis for assessing the potential effects of sediment associated contaminants when they occur in complex mixtures. Furthermore, an index of geo-accumulation (I_{geo}) first described by Müller in 1969 (Muller, 1969), is used to ascribe metal contamination in sediments, by comparing pre-industrial with present day concentrations, and can be used to indicate changes in sediment-bound toxicants over time (Martínez and Poleto, 2014).

Our objective in this study was to improve understanding of temporal changes in sediment quality by assessing six urban catchments in Melbourne, south-eastern Australia over a 30-year period, and provide an approach that can be adapted globally to assess long-term trends in sediment-bound contaminants. Other studies have assessed long-term trends in metal pollution in estuarine or coastal areas (Chandia and Salamanca, 2012; Gredilla et al., 2013), and freshwater environments (Clements et al., 2010; Dang et al., 2010; Kohušová et al., 2011), these studies focus on one catchment or river system. The outcomes from this study provide an approach to detect and assess long-term trends in other hydrophobic contaminants such as hydrocarbons and emerging chemicals of concern such as synthetic pyrethroids.

2. Material and methods

2.1. Study area and sampling design

Sediment samples were collected from six freshwater sites within the Greater Melbourne Area between 1981 and 2012. The Greater Melbourne metropolitan area (GMA) supports a population of approximately 4.3 million people and encompasses a watershed area of approximately 12,800 km^2. The six sites were located on 6 urban waterways; Merri Creek, Gardiners Creek, Maribyrnong River, Kororoit Creek, Plenty River and Dandenong Creek, all draining catchments with a myriad of different land-uses (Fig. 1). Sediment in riverine systems is highly dynamic, often moving large distances over time, especially after storm events.

To determine long-term trends in sediment quality within the six waterways, it was most appropriate to analyse newly deposited sediments collected over the 30-year period, rather than the analysis of sediment cores, which are more widely used in lentic systems such as lakes, estuaries and marine environments to determine long-term trends. The upper 2 cm sediment surface layer was collected using a shallow scoop from multiple locations at each site and composited to form one sample for analysis. Between 15 and 38 samples were collected at irregularly spaced temporal intervals (typically 6 months for 3 years every 5–10 years) between January 1981 and December 2012. Data was sourced from a number of environmental surveys conducted by the Environmental Protection Agency Victoria and Melbourne Water Corporation in the 1980s and 1990s (Pettigrove, 1999), in addition to data collected by the authors after 2005. On some occasions, more than one sample was collected at each site. When this occurred, the averaged data was used. Sediment samples were wet sieved in the field using a 63 μm net, with this fine fraction retained for analysis. This reduces inherent variability associated with site differences, grain size, organic carbon and laboratory methods (ANZECC, 2000), and to allows comparisons of the sediment fraction most often associated with sediment-ingesting biota (Tessier et al., 1984).

2.2. Chemical analysis

All samples were transferred into cleaned glass jars and stored at 4 °C and transported to the laboratory on ice for analysis. Chemical analyses were carried out by commercial laboratories accredited to ISO 17025 and 9001 for trace metals. From these analyses, four metals were comparable across the three temporal time periods, namely Cu, Cr, Pb and Zn. For total metal digestion, 1 g of loose air-dried sediments (<50% moisture content) were refluxed and digested with hot nitric (4 ml; 50% HNO_3) and hydrochloric (10 ml; 20% HCl) acids for 2 h or until the volume was sufficiently reduced (USEPA, 1991; Method 200.2). The solution was then cooled and hydrogen peroxide (30% H_2O_2) was added. Samples were heated and cooled again before bulked to a volume of 50 ml using de-ionised water and settled prior to extraction for analysis.

Standard U.S. EPA recommended methods were used for analysis of metals in sediments using either atomic adsorption spectroscopy (FAAS) (Method 200.9) or Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES; Method 200.7) (USEPA, 1994). Trace metals prior to 2000 were extracted using strong acid digest and analysed by FAAS (Pettigrove, 1999). From 2000

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