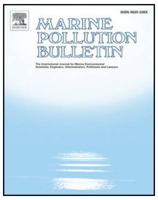
Marine Pollution Bulletin xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul



Baseline

Potential bioavailability assessment, source apportionment and ecological risk of heavy metals in the sediment of Brisbane River estuary, Australia

Godfred Odame Duodu [a], Ashantha Goonetilleke [b], Godwin A. Ayoko [a],*

[a] Queensland University of Technology (QUT), Science and Engineering Faculty, School of Chemistry, Physics and Mechanical Engineering, 2 George St, QLD 4001, Australia
[b] Queensland University of Technology (QUT), Science and Engineering Faculty, School of Civil Engineering and Built Environment, 2 George St, QLD 4001, Australia

ARTICLE INFO

Article history:
Received 3 November 2016
Received in revised form 2 February 2017
Accepted 5 February 2017
Available online xxxx

Keywords:
Heavy metal
Brisbane River sediment
PCA/APCS
Modified pollution index
Modified ecological risk index
PROMETHEE

ABSTRACT

A weak acid extraction was used to mobilize the loosely bound metals in estuary sediment samples. More than 30% of Ag, As, Ca, Cd, Co, Cu, Hg, Mn Ni, Pb and Zn were leached from the sediment showing that these metals are significantly present in the bioavailable form. PCA/APCS identified three sources of the metals, namely: lithogenic accounting for 72%, shipping related contributing 15% and traffic related representing 13% of the total load. Application of pollution index (PI) and modified pollution index (MPI) revealed that the sediment range from unpolluted to heavily polluted while ecological risk index (RI) classifies the sediment as posing low ecological risk modified ecological risk index (MRI) suggests considerable to very high ecological risk. To provide holistic insights into the ecological risks posed by metals, enrichment factor, MPI and MRI are recommended for the assessment of sediment in complex environments such as estuaries.

The growing public and environmental health concerns of heavy metals in the environment have led many countries to implement various programs and regulations to monitor, control or restrict their release into the environment (Laidlaw & Taylor 2011). Anthropogenic activities have been found to be culpable for the elevation of heavy metal concentrations in the environment (Saleem et al., 2015; Mummullage, 2015; Brady et al., 2014a). However, heavy metals are also found naturally in the earth crust. Therefore, it is very important for any monitoring program to distinguish between anthropogenic and natural sources of metals. Interestingly, most studies on sediment quality use the total metal concentration, which does not reflect the actual risk posed by the metal (Brady et al., 2014a). The chemical form or binding behaviour of metals in sediments is essential for assessing both, the source and potential risk they pose to aquatic species. The binding behaviour together with changes in environmental conditions such as pH, redox potential or organic matter can cause metals to be transferred or mobilised between sediment and overlying water. These factors in turn influence processes that are important for evaluating the potential impact on aquatic biota such as mobility as well as the bioavailability of the metals in sediment (Peijnenburg et al., 2007). Therefore, the total concentration is generally not considered to be a good indicator when determining the toxic effects and remobilisation potential of metals in sediments (Brady 2015; Ahdy and Youssef, 2011; Quevauviller et al., 1997).

A number of methods have been developed for determining mobility and readily available metals in sediment. Such methods range from simple leaching with dilute (~1 M) hydrochloric acid (Hu et al., 2011) to elaborate procedures such as sequential extraction methods by Tessier et al. (1979) and the Community Bureau of Reference (Bureau Communautaire de Référence or BCR) (Davidson et al., 1999; Quevauviller et al., 1997). Other methods for metal mobility studies require the use of strong chelating agents (such as EDTA) (Peijnenburg et al., 2007). However, the use of sequential methods (Tessier or BCR protocols) presents potential re-adsorption and non-specificity problems, complex chemistry and are relatively long (Ure & Davidson, 2008; Nirel & Morel, 1990). The use of EDTA has also been limited since dilute HCl is reported to be more efficient for partial extraction of metals (Malo, 1977). Nonetheless, some insoluble metal chlorides (most notably Pb and Hg) are encountered when dilute HCl is used (Brady et al., 2014a). Therefore, in assessing the weakly bound metals, dilute nitric acid (HNO_3) is employed, which in some cases, is more efficient than the use of sequential extraction and other weak acid extraction methodologies as shown in the comparison of partial extraction reagents for assessing potential bioavailability of heavy metals in sediments (Brady et al., 2016; Brady et al., 2014a).

Application of sediment quality indicators (including enrichment factor (Ef), pollution index (PI), modified pollution index (MPI), potential ecological risk index (RI) and modified potential ecological risk index (MRI)) on the weak acid extractable metals (WE-M) can thus provide a true assessment of contamination and give a real indication of the ecological state of sediment in complex environments (Duodu et al.,

---

* Corresponding author.
E-mail address: g.ayoko@qut.edu.au (G.A. Ayoko).

http://dx.doi.org/10.1016/j.marpolbul.2017.02.017
0025-326X/

Please cite this article as: Duodu, G.O., et al., Potential bioavailability assessment, source apportionment and ecological risk of heavy metals in the sediment of Brisbane River e..., Marine Pollution Bulletin (2017), http://dx.doi.org/10.1016/j.marpolbul.2017.02.017

2016; Brady et al., 2015; Manoj and Padhy, 2014; Qingjie et al., 2008). Sources of WE-M can also be identified with the help of multivariate techniques such as Principal component analysis (PCA) and Hierarchical Cluster Analysis (HCA) (Brady et al., 2014b). However, they are unable to quantitatively determine the contribution of each source to the total pollution load. This can be achieved with Principal Component Analysis/Absolute Principal Component Scores (PCA/APCS) (Brady et al., 2014a).

The case study area (the Brisbane River Estuary) is the largest urbanised river in South-East coast of Queensland with an estimated catchment area of 13,560 km^2. The city of Brisbane, located along the river, is the second fastest growing city in Australia (ABS, 2011). The increasing population density is accompanied by heightened environmental stress on the river. There are influxes of effluent from a variety of anthropogenic activities (including chemical and petrochemical industries, sewage treatment facilities, boat building and repair yards, paper recycling plant, and heavy vehicular and maritime traffic) into the river. A recent data on sediment quality which employed total metal concentrations revealed that the sediment is slightly to heavily polluted with the potential to pose moderate to very high ecological risk (Duodu et al., 2016). However, bioavailability and source apportionment of the metals, which could provide valuable information for mitigation action have not been undertaken.

The aim of this present study was to determine the readily available form of metals and employ a range of sediment quality indices to provide insights into the risk posed by the sediment. In addition, the sources of metals are quantified to provide valuable information for the formulation of effective mitigation strategies. The generic outcomes of this study are expected to provide essential guidance for monitoring and regulation of heavy metal contamination of urban waterways worldwide.

Samples were taken from twenty two sites (Fig. 1), which can be grouped into four physio-geographical strata to cover the different urbanisation and land-use activities along the river. The four strata are: rural (SP1-SP3 mostly forestland), residential (SP4-SP12, moderately to highly residential, park and bushlands), commercial (SP13-SP18, highly urbanised, commercial area, parklands and marinas) and industrial (SP19-SP22, mouth of the river, highly industrialised and marinas). Sediment samples to a depth of 0–3 cm were collected using a ponar stainless-steel grab sampler (Envco, Auckland) in the months of June, September, December 2014, and May 2015 covering different climatic seasons. Samples were collected into cleaned plastic bags, stored on ice, transported to the laboratory and stored at -20°C until further analysis. The frozen samples were freeze-dried with Alpha 1-4 LDplus freeze dryer (John Morris Scientific, Australia) and sieved to $<$106 μm grain size to remove coarse materials and shells prior to analysis. A sample was taken at Latitude 27°33′54.54″S and Longitude 152°44′50.37″E for geochemical background concentration of metals (Duodu et al., 2016). This is because there are little or no anthropogenic activities around this area.

Details of methods for sample preparation and analysis are similar to those published elsewhere (Brady et al., 2016; Brady et al., 2014a; Duodu et al., 2015). Generally, the readily available metals (WE-metals) were extracted as follows: A 0.05 g sample was weighed into in a clean 50 mL centrifuge tube and 20 mL of ultra-pure (18 MΩ resistivity) water added. A 3.7 mL aliquot of double distilled, concentrated nitric acid was added and diluted to 50 mL before placing in an end-over-end tumbler and tumbled at 100 rpm for 6 h. The samples were then centrifuged at 3500 rpm for 10 min before a 10 mL sub sample was taken and analysed via ICP-MS/MS using an Agilent 8800 ICP- Triple Quad MS (ICP-QQQ) (Brady et al., 2016; Brady et al., 2014a,b). As part of the quality control (QC) procedure, two sediment Certified Reference Materials (CRMs) MESS-3 and STSD-1 were treated and analysed as samples in every 20 WE-metal samples, in accordance with NATA guidelines (NATA, 2012).

The average and standard deviation of the WE-M concentrations estimated formed the basis for further data analyses using Ef, PI, MPI, RI and MRI to assess the sediment quality. Analysis of Variance (ANOVA), a statistical method used to test differences between two or more means and their associated characteristics (such as "variation" among and between means), was employed to compare the average metal concentration among the different strata. Subsequently, the data was analysed using multivariate statistical tools: principal component analysis/absolute principal component scores (PCA/APCS) and PROMETHEE for source apportionment and ranking of sites from the most to the least polluted based on metal concentrations and enrichment, respectively. Details of the theories behind the data analysis techniques can be found in the literature, including (Duodu et al., 2016; Brady et al., 2015; Sucharovà et al., 2012; Qingjie et al., 2008; Çevik et al., 2008; Bruno et al., 2001; Mostert et al., 2012; 2010; Brady et al., 2014b; Friend et al. 2011; Ayoko et al., 2004; Ayoko et al. 2007 and Hakanson, 1980) while equations used for their calculation together with sediment grading systems are provided in the Supplementary Material (SM). Aluminium (Al) was used for normalisation in this study. Metal concentration of background sample is also given in SM. The weak acid soluble concentrations were used for fraction analysis to determine the potential bioavailability of an element (Chaudhary et al., 2016; Brady et al., 2014a,b). Fraction analysis compares the weak acid soluble concentration of an element against its total concentration (Eq. 1). It mimics the effects of an acidic input into the sediment and removes species held at ion-exchange, as carbonate and organically bound fractions expected to contain the easily mobile and bioavailable fractions of metals in sediments (Chaudhary et al., 2016). The total metal (T-metal) data is

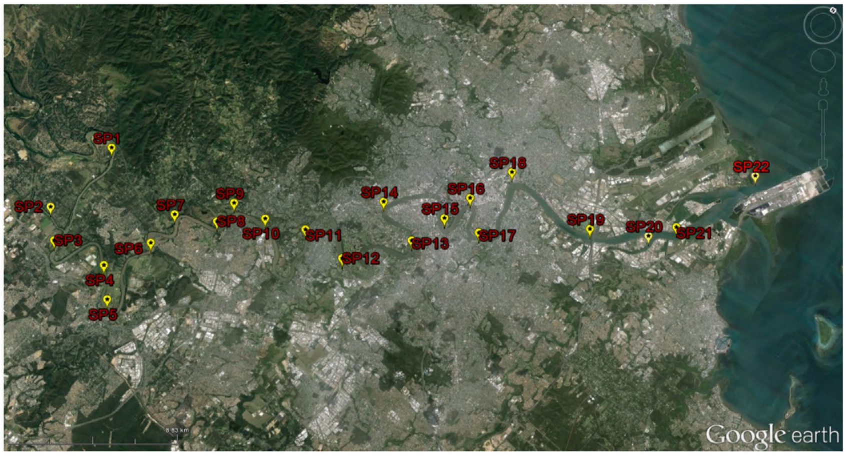


Fig. 1. Location of sampling points (adapted from Google earth).

Please cite this article as: Duodu, G.O., et al., Potential bioavailability assessment, source apportionment and ecological risk of heavy metals in the sediment of Brisbane River e..., Marine Pollution Bulletin (2017), http://dx.doi.org/10.1016/j.marpolbul.2017.02.017