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Comparison of Pollution Indices for the Assessment of Heavy Metal in Brisbane River Sediment

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ABSTRACT

Estuarine environment is complex and receives different contaminants from numerous sources that are persistent, bioaccumulative and toxic. The distribution, source, contamination and ecological risk status of heavy metals in sediment of Brisbane River, Australia were investigated. Sediment samples were analysed for major and minor elements using LA-ICP-MS. Principal component analysis and cluster analysis identified three main sources of metals in the samples: marine sand intrusion, mixed lithogenic and sand intrusion as well as transport related. To overcome inherent deficiencies in using a single index, a range of sediment quality indices, including contamination factor, enrichment factor, index of geo-accumulation, modified degree of contamination, pollution index and modified pollution index were utilised to ascertain the sediment quality. Generally, the sediment is deemed to be slightly to heavily polluted. A further comparison with the Australian Sediment Quality Guidelines indicated that Ag, Cr, Cu, Ni, Pb and Zn had the potential to rarely cause biological effects while Hg could frequently cause biological effects. Application of potential ecological risk index (RI) revealed that the sediment poses moderate to considerable ecological risk. However, RI could not account for the complex sediment behaviour because it uses a simple contamination factor. Consequently, a modified ecological risk index (MRI) employing enrichment factor is proposed. This provides a more reliable understanding of whole sediment behaviour and classified the ecological risk of the sediment as moderate to very high. The results demonstrate the need for further investigation into heavy metal speciation and bioavailability in the sediment to ascertain the degree of toxicity.

Capsule

A modified ecological risk index is proposed based on in-depth investigation of Brisbane River sediment

Keywords

Heavy metal; Surface sediment quality; PCA; Pollution indices; Modified ecological risk index.

Highlights

- In-depth investigation of heavy metal pollution of river sediments
- Current pollution indices found to provide poor indication of risk
- A modified ecological Index (MRI) is proposed.
- MRI provides an improved method for assessing ecological risk.

1. Introduction

Globally, disproportionately large human populations live near waterways and they extensively modify riparian zones, resulting in significant threat to water quality and river health. Worldwide deterioration of water quality arises from both natural and anthropogenic processes including soil erosion, mining, agricultural, industrial, transportation and energy production related activities (Chung, 2015, Li, 2014). These activities generate pollutants such as heavy metals, which eventually find their way into rivers and streams through weathering, disposal of effluents, runoff and leachates, as well as atmospheric deposition (Mucha et al., 2003). After their introduction into the aquatic ecosystem, most metals are attached to fine-grained particulates and, as a result of settling, accumulate in bottom sediments (Farkas, 2007), where they may cause adverse biological effects even though water quality criteria are not exceeded (NRC 1989, Bibi et al., 2007). Heavy metals are ubiquitous environmental pollutants, which are persistent, non-biodegradable, toxic and bio-accumulate in the aquatic ecosystem (Arnason and Fletcher, 2003, Li, 2014). They have drawn wide attention due to their negative effects on human and ecosystem health (Brady et al., 2014a). Consequently, their concentrations, distribution, fate, impact and sources in the environment have attracted global interest and are areas of ongoing research (Brady et al., 2014a & b, Iqbal and Shah, 2014, Sekabira et al., 2012, Singovszka, 2015, Vaezi, 2015).

The accumulation of metals in the sediment poses a long term threat to water bodies and other parts of the environment. Therefore, there is a need for sediment quality indicators to assess the risks of contamination and toxicity posed by metals in the aquatic environment. This has led to the development of many sediment quality indicators such as contamination factor, enrichment factor, index of geo-accumulation (I-geo), (modified) degree of contamination (Cd or mCd), (modified) pollution index (PI or MPI) and sediment quality guidelines (Muller, 1969, Tomlinson et al., 1980, Qingjie et al., 2008, Brady et al., 2015, Vidal and Bay, 2005). However, these sediment quality indicators either define a qualitative threshold or focus on ecological risk assessment of a single metal. Yet heavy metal pollution in the environment generally occurs in the form of complex mixtures. The synergistic effects of metal pollution rather than an individual metal effect may be of greater concern. The potential adverse risks due to hazardous chemicals (such as heavy metals) in the same medium can be assumed to be cumulative in worse case scenarios (Neff et al., 2005). Consequently, the potential ecological risk index (RI) developed by Hakanson (1980), which evaluates the combined pollution risk of an aquatic system through a toxic-response factor is well suited for assessing ecological risk posed by heavy metals in the environment. Nonetheless, RI is computed using a simple contamination factor. This could possibly introduce error in the assessment of risk pose by a complex environment like an estuary where sedimentation with significant input from creeks is a common occurrence (Brady et al., 2015). Contamination factor does not take the lithogenic and sedimentary inputs of the element of interest into account. In contrast, enrichment factor, which can normalise the impact of terrestrial sedimentary inputs, could provide more useful information and offer a more realistic estimate of the real ecological risk.

The area under study, the Brisbane River estuary, is the largest and most highly urbanised river system in south east of Queensland. The river catchment supports a large population (in excess of one million) and is currently experiencing rapid population growth (ABS, 2015). The catchment is characterised by sub-tropical weather with discrete wet summer (November to May) and dry winter (April to October) seasons (Eyre et al., 1998). The area is also categorised by a physio-geographic stratification along a hydrological gradient from lower to upper catchment, varying urbanization and distinct land uses.

Historically, the river has received large amounts of treated sewage effluent with the lower reaches receiving effluent from eight wastewater treatment plants. The area is tidal and flood prone with eleven (11) major floods recorded since 1840. Elevated concentrations of metals in the sediment have been documented (Cox and Preda, 2005, Mackey and Mackey, 1996 and Mackey et al., 1992). However, there is lack of information on the quality of the sediment after the recent significant floods in January 2011 and 2013.

The aim of the study was to use sediment quality indicators, including contamination factor, enrichment factor, index of geo-accumulation, modified degree of contamination, modified pollution index, Australian New Zealand sediment quality guidelines and potential ecological risk index to assess the ecological state of the river sediment. This will provide a tool for key stakeholders, including catchment managers, government, and the public in relation to action to protect aquatic biota and wildlife. Also, we propose a modified potential ecological risk index (MRI) which uses enrichment factor instead of contamination factor. This should account for the non-conservative sediment behaviour and natural variations in the sediment resulting in proper identification of anthropogenic contamination. Moreover, the generic outcomes of this study are expected to provide essential guidance for monitoring and regulation of heavy metals in urban waterways.

2. Materials and methods

2.1. Sample collection

The study was conducted in 2014-2015 to cover the different land-use types and various urbanization levels of the river. Twenty two sites spanning Latitude 27°32'20.81"S to 27°22'39.37"S and Longitude 152°51'1.55"E to 153° 9'40.86"E were sampled (Fig. 1). The sites can be grouped into four physio-geographical strata namely: rural (SP1-SP3, which is mostly forestland), residential (SP4-SP12, moderately to highly residential, park and bushlands), commercial (SP13-SP18, highly urbanized, commercial area, parklands and marinas) and industrial (SP19-SP22, mouth of the river, highly industrialised and marinas). Grab (0-3 cm depth) sediments were collected using a ponar stainless-steel grab sampler (Envco, Auckland) in the months of June, September, December, 2014, and May, 2015. Samples were collected into clean labelled polyethylene bags, kept and transported on ice to the laboratory and stored at -20 °C until further analysis. Frozen samples were lyophilised with Alpha 1-4 LDplus freeze dryer (John Morris Scientific, Australia) and sieved (<106 µm grain size). A background sample was taken from the upper reaches of the river at Latitude 27°33'54.54"S and Longitude 152°44'50.37"E where there is little or no anthropogenic activities. This sample was treated the same way as the other samples.

2.2. Reagents and standards

Germanium (IV) oxide (99.99%, Aldrich) powder was used as the internal standard. Certified sediment reference materials (CRMs): (a) Drainage sediment reference material, GBW07312 (IGGE, IRMA, China); (b) Marine sediment reference materials, MESS-3 (National Research Council of Canada, Ottawa, Canada) and (c) Stream sediment reference material, STSD-1 (National Research Council of Canada, Ottawa, Canada) were used for calibration while PACS-2 (National Research Council of Canada, Ottawa, Canada) was employed for the optimization and evaluation of the analytical performance. Ethanol undenatured 100% AR (Chem-Supply Pty Ltd, Australia) was used as solvent for milling.

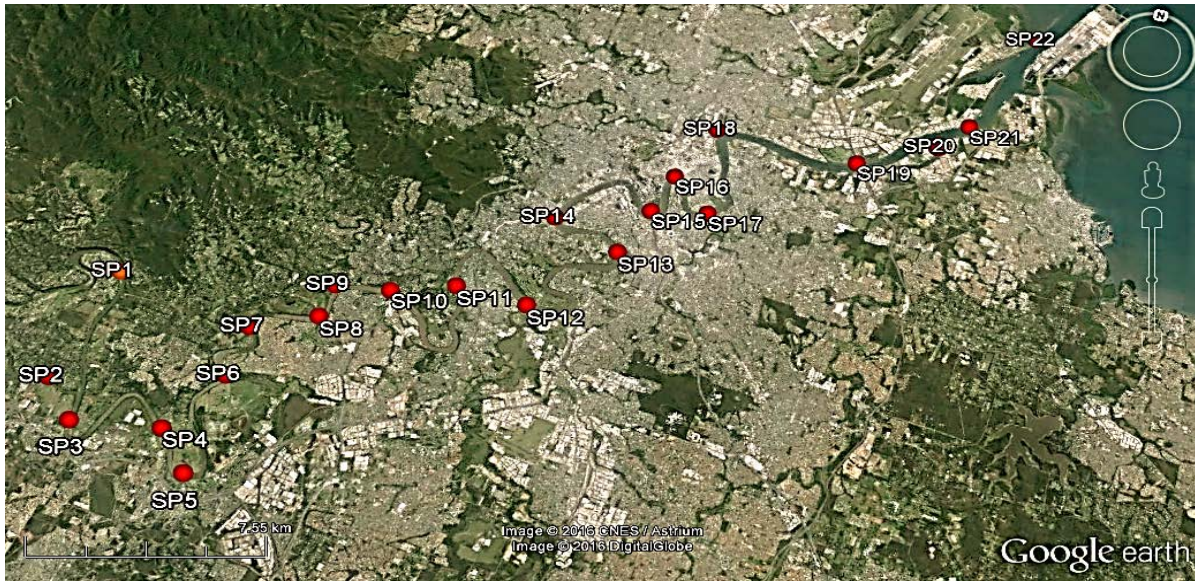


Fig. 1: Map of study area with sampling point locations (adapted from Google earth).

2.3. *Sample preparation and analysis*

Details of method for sample preparation and analysis had been published elsewhere (Duodu et al., 2015). The only change is the use of 10 Hz laser pulse frequency instead of 8 Hz to enhance count rates and precision. In summary, about 40 mg of germanium (IV) oxide was added to a known mass of sediment samples such that the mass of Ge ~ 1%. The mixture was milled and homogenized using a vibratory McCrone Micronizing mill after the addition of ethanol. The slurry sample was completely dried in a sealed oven at 40 °C in a petri dish for about 5 h and 1 g of the dried homogenized sediment pressed into a pellet of about 12 mm diameter and 2 mm thick using SPECAC Manual Hydraulic Press.

A 193 nm ArF excimer laser ablation system (Electro Scientific Industries, New Wave Research Division, Tokyo, Japan) coupled to an Agilent 8800 Triple Quad ICP-MS (Agilent Technologies Australia Pty Ltd) were used for the measurements. Instrument parameters of both laser and ICP-MS are summarized in Duodu et al. (2015). The data generated by the instrument were subsequently processed with Igor Pro version 6.34 coupled to Iolite 2.5 software using external calibration with GBW07312, MESS-3 and STSD-1, and Ge as internal standard. Before analysis, the ICP-MS was calibrated to low oxide production rates ($\text{ThO}^+/\text{Th}^+ < 0.5\%$, using NIST 610, and 612), which was monitored throughout batch acquisition. All data were background corrected and four replicate measurements were taken for each sample (Duodu et al., 2015). For quality control, randomly selected duplicate samples, field blanks and CRM PACS-2 were analysed along with the samples during the analysis procedure.

2.4. *Data analysis*

The average and standard deviation of metal concentrations were calculated. These provided an insight into trends and patterns of variation with land use and season at various physio-geographic strata and sampling locations. The data were subsequently analysed using the multivariate statistical tools: principal component analysis (PCA), and hierarchical clustering analysis (HCA) to group sites and variables based on similarities and their sources. Finally, single and multiple sediment quality indices as well as Australian New Zealand sediment quality guidelines and ecological risk indices were employed to assess the ecological state of the sediment.

2.4.1. Source identification

The possible sources of heavy metals in the sediment were identified with multivariate data analysis techniques PCA and HCA. Both PCA and HCA are common unsupervised pattern recognition procedures that are employed to group different objects and variables based on their similarities or dissimilarities. Detailed descriptions of both procedures and their applications can be found in a number of texts (e.g. Goonetilleke et al., 2014 and Brereton, 2003). The multivariate data analyses were performed with the statistical package SPSS 23. For PCA, variables were mean centred and only PCs with eigenvalue >1 were retained (Kaiser, 1960). Varimax rotation was applied to component loadings to facilitate the interpretation of the outcomes and loadings greater than 0.5 were considered and interpreted (Loska and Wiechula, 2003). The HCA was performed on mean centred data set using average linkage with correlation coefficient between samples for similarity groupings and the results were reported in the form of a dendrogram.

2.4.2. Contamination factor CF

Contamination factor is a simple and single index indicator used to evaluate metal contamination. It provides a ratio between an element at the sampling site and the same element at a background site, reference value or a national criterion for that metal (Eq. 1) (Qingjie et al., 2008). This gives information about how an element has been concentrated at the site of interest relative to a background site. The calculation of CF does not take into account the lithogenic and sedimentary inputs of the element of interest, which is a limitation considering sedimentation and metal input from the terrestrial environment in waterways (Brady et al., 2015).

$$Cf = \frac{C_i}{C_b} \quad Eq. 1$$

Where C_f is contamination factor, C_i is the concentration of metal of interest at a site and C_b is the concentration of the same metal at a background or reference site. Four qualitative terminologies are used to describe the contamination factor (Qingjie et al., 2008): $C_f < 1$, low contamination; $1 \leq C_f < 3$, moderate contamination; $3 \leq C_f < 6$, considerable contamination and $C_f \geq 6$, very high contamination.

2.4.3. Enrichment factor EF

This is another single element index, which compares the ratio of the element of interest to a “conservative element” (assumed to have no anthropogenic input and little or not affected by weathering) (e.g., Fe, Al and Li) in a given sample to the same ratio in a local background (Eq. 2) (Sucharovà et al, 2012). The normalisation against a conservative element accounts for the lithogenic and sedimentary inputs of the element of interest enhancing the prediction of anthropogenic pollution with enrichment factor. Enrichment factor > 1 is an indication of anthropogenic source of the element of interest (Çevik et al., 2009). Factors to be considered for choice of normalization element as well as the limitations are detailed in Brady et al. (2015). For this study, Al was used as the normalization element.

$$Ef = \frac{\left(\frac{C_i}{C_{ref}} \right)_{sample}}{\left(\frac{C_i}{C_{ref}} \right)_{background}} \quad Eq. 2$$

Where C_i is the concentration of element of interest and C_{ref} is the concentration of normalization element. Generally, five contamination categories are associated with enrichment factor (Qingjie et al., 2008): $Ef < 2$, depletion to minimum enrichment; $2 \leq Ef < 5$, moderate enrichment; $5 \leq Ef < 20$, significant enrichment; $20 \leq Ef < 40$, very high enrichment; and $Ef > 40$, extremely high enrichment.

2.4.4. Index of geo-accumulation (I-geo)

Similar to the two above, index of geo-accumulation (I-geo) is also a single element index proposed by Müller (1969) and is used to describe metal contamination in sediments by comparing current concentrations with pre-industrial levels. It can be calculated by the using (Eq. 3) and the comparison is based on seven classes of qualification (Qingjie et al., 2008).

$$I_{-geo} = \log_2 \left(\frac{C_i}{1.5 \times B_i} \right) \quad Eq. 3$$

Where C_i is the measured concentration of the examined metal in the sediment, and B_i is the geochemical background concentration or reference value of the metal. The factor 1.5 is used to account for the possible variations in background values for a given metal in the environment as well as very small anthropogenic influences. Seven grades of qualification were distinguished by Müller (Duodu et al., 2011): I-geo ≤ 0 (grade 0), unpolluted; $0 < I\text{-geo} \leq 1$ (grade 1), slightly polluted; $1 < I\text{-geo} \leq 2$ (grade 2), moderately polluted; $2 < I\text{-geo} \leq 3$ (grade 3), moderately severely polluted; $3 < I\text{-geo} \leq 4$ (grade 4), severely polluted; $4 < I\text{-geo} \leq 5$ (grade 5), severely extremely polluted; I-geo > 5 (grade 6), extremely polluted.

2.4.5. Modified degree of contamination (mC_d) and modified pollution index (MPI)

The limitations of the single element indices have led to the development of multi-element pollution indices for the assessment of sediment quality (Hakanson, 1980, Nemerow, 1991 and Brady et al., 2015). The two most common and widely used are the modified degree of contamination (mCd) and pollution index (PI) developed by Hakanson (1980) and Nemerow (1991), respectively. More recently, Brady et al (2015) proposed a modified pollution index (MPI), which is an improvement of the pollution index and uses enrichment factors instead of contamination factors in its calculation. This takes into account the background concentrations and the complex, non-conservative behaviour of sediments. Another advantage is that the sediment qualification threshold was adjusted to give a more accurate qualification of sediment contamination. This is unlikely to overstate sediment contamination unlike the low trigger value of 3 used for PI (Brady et al., 2015). Equations 4, 5 and 6 show how the modified degree of contamination, pollution index and the modified pollution index are calculated. Thresholds for sediment quality classification using the three integrated indices are presented in Table 1.

$$mC_d = \frac{\sum_{i=1}^n Cf^i}{n} \quad Eq. 4$$

$$PI = \sqrt{\frac{(Cf_{average})^2 + (Cf_{max})^2}{2}} \quad Eq. 5$$

$$MPI = \sqrt{\frac{(Ef_{average})^2 + (Ef_{max})^2}{2}} \quad Eq. 6$$

Where Cf^i , $Cf_{average}$, $Ef_{average}$, Cf_{max} and Ef_{max} represent contamination factor for individual element, average of contamination factors, average of enrichment factors, maximum contamination factor and maximum enrichment factor, respectively.

Table 1: Thresholds for sediment quality classification for multi-element indices (adapted from Brady et al., 2015).

Class	Sediment qualification	mC_d	PI	MPI
0	Unpolluted	$mC_d < 1.5$	$PI < 0.7$	$MPI < 1$
1	Slightly Polluted	$1.5 < mC_d < 2$	$0.7 < PI < 1$	$1 < MPI < 2$
2	Moderately polluted	$2 \leq mC_d < 4$	$1 < PI < 2$	$2 < MPI < 3$
3	Moderately-heavily polluted	$4 \leq mC_d < 8$	-	$3 < MPI < 5$
4	Severely polluted	$8 \leq mC_d < 16$	$2 < PI < 3$	$5 < MPI < 10$
5	Heavily polluted	$16 \leq mC_d < 32$	$PI > 3$	$MPI > 10$
6	Extremely polluted	$mC_d > 32$	-	-

2.4.6. Sediment quality guidelines (SQGS) and potential ecological risk index (RI)

Though sediment pollution indices are good starting points for assessing sediment quality, they offer only qualitative description of the status of sediment. A more realistic approach would be guidelines that give some quantitative measures of the potential to cause impairment to aquatic animals and the water body as a whole. Consequently, sediment quality guidelines (SQGs) (Burton, 2002) and potential ecological risk index (RI) (Hakanson, 1980) are used to quantitatively evaluate ecological risk posed by pollutants in sediments.

The Australia and New Zealand SQG provides two values for each pollutant: Interim Sediment Quality Guidelines -Low (ISQG-L) and -High (ISQG-H) (Long et al., 1995). Three concentration ranges delineate the use of this scheme. Concentrations below ISQG-L values identify conditions where adverse biological effects are rarely observed; concentrations at or above ISQG-H values represent a range above which adverse biological effects frequently occur; and concentrations equal to or greater than ISQG-L, but below ISQG-H represent a range within which biological effects occur occasionally (ANZECC/ ARMCANZ, 2000).

Potential ecological risk index (RI) also measures the sensitivity of biological community to the overall contamination at a site (Hakanson, 1980). It takes into account contamination factor of elements, their potential ecological risk factors (Er), and the sedimentological toxic response factors (Tr) (Manoj & Padhy, 2014). The equation for calculating the RI as proposed by Hakanson (1980) is presented below (Eq. 7):

$$RI = \sum_{i=1}^n Er^i = \sum_{i=1}^n Tr^i \times Cf^i \quad Eq. 7$$

Where Er^i is the potential ecological risk index of an individual element, Tr^i is the biological toxic response factor of an individual element and Cf^i is contamination factor for each single element.

2.4.7. Modified ecological risk index (MRI)

The RI is widely used and universally accepted for quantitative ecological risk assessment. It uses contamination factor (Eq. 1) in its calculation, which does not take into

consideration lithogenic and sedimentary inputs of the element of interest. This is a source of concern especially in estuarine environments, where sedimentation with significant input from creeks is a common phenomenon. Therefore, to account for the effect of terrestrial sedimentary input, we propose the use of enrichment factor (Eq. 2) instead of contamination factor in the calculation of RI in order to account for the impact of terrestrial sedimentary inputs. Also supporting this argument is the fact that from a large complex data set, the use of enrichment factors was determined to be the preferred single element index for assessing contamination at a site (Brady et al., 2015). In addition, it accounted for lithogenic sources of heavy metals and changes in the background concentration as well as the non-conservative behaviour of sediments that frequently occur in estuarine environments (Brady et al., 2015). Equation 7 therefore becomes:

$$MRI = \sum_{i=1}^n Er^i = \sum_{i=1}^n Tr^i \times Ef^i \quad Eq. 8$$

Where MRI is the modified potential ecological risk index and Ef^i is the enrichment factor for each single element. The grading standards of MRI are maintained as that of RI (Table 2).

Table 2: Grading standards of potential and modified ecological risk index (adapted from Suresh et al., 2012).

Er^i	Ecological grade	<i>RI or MRI</i>	Ecological grade
<40	Low risk	<150	Low risk
40–80	Moderate risk	150–300	Moderate risk
80–160	Considerable risk	300–600	Considerable risk
160–320	High risk	-	
>320	Very high risk	>600	Very high risk

3. Results and discussion

3.1. Analytical performance of the method of analysis

The performance of the LA-ICP-MS method had been detailed in Duodu et al. (2015). However, due to the initial poor recovery of Cr, a simple excel equation was developed from the average Cr concentration of PACS-2 using GBW07312, MESS-3 and STSD-1 as calibration standards. This gave Cr recovery of 100.3%. Table 3 gives the measured against certified values of some metals in PACS-2 employing GBW07312, MESS-3 and STSD-1 as calibration standards. There was good agreement between the measured and certified value for each metal reported. Recoveries between 94.4% (Ni) and 106.7% (Ag) were observed, which are comparable to published data by Brady et al. (2014a) where recoveries between 93.1% for Mn and 100.9% for Al were obtained using aqua regia digestion. This signifies that the method is good for the analysis of heavy metals in sediment.

3.2. Variations of metals in sediment

The box and whisker plot (Fig. 2) shows the concentrations of both major and trace elements in $\mu\text{g/g}$. Generally, the concentration of most elements (52% of elements analysed including Al, Fe, As, Cd, Co, Hg, Li, Ni, Sb, Se, Tl and Zn) in the sediment varied by a factor < 2. The widest concentration variations (> 5) were observed for Ag and Sn. This indicates that the concentration of most metals analysed remain fairly stable across the sampling sites

and either Al or Fe would be a good choice for normalization (Brady et al., 2015). Aluminium (Al) was therefore used as the normalisation element in this study.

Table 3: Measured and certified values of some metals in PACS-2 using GBW07312, MESS-3 and STSD-1 as calibration standards.

Element	Certified value ($\mu\text{g/g}$)	\pm	Measured value ($\mu\text{g/g}$)	\pm	% Recovery	LOD (ng/g) (Duodu et al., 2015)
Si	280000		287122	2932	102.5	19390
Al	66200	3200	65252	1466	98.6	80
Fe	40900	600	41373	761	101.2	1170
Ca	19600	1800	19842	270	101.2	100
Mn	440	19	441	3.9	100.2	50
Sr	276	30	277	1.1	100.4	2.5
Ag	1.2	0.1	1.28	0.11	106.7	3.8
As	26.2	1.5	26.4	0.1	100.8	0.9
Cd	2.1	0.2	2.1	0.03	100.0	0.2
Co	11.5	0.3	11.3	0.3	98.3	1.9
Cr	90.7	4.6	91	6.1	100.3	10.9
Cu	310	12	307	22.2	99.0	3.1
Hg	3	0.2	3.1	0.05	103.3	2.4
Li	32.2	2	31.4	0.6	97.5	2.3
Ni	39.5	2.3	37.3	0.2	94.4	1.5
Pb	183	8	181	1	98.9	3
Sb	11.3	2.6	11.3	0.05	100.0	9.8
Se	0.9	0.2	0.9	0.2	100.0	6.3
Sn	19.8	2.5	18.8	0.2	94.9	1
Tl	0.6		0.6	0.01	100.0	1
U	3		3.1	0.08	103.3	6.5
V	133	5	133	1.6	100.0	10.3
Zn	364	23	364	0.8	100.0	7.4

Based on their Pearson correlation coefficients ($r \geq 0.5$) (Table S1 in Supplementary Material (SM)) the elements could be grouped into three in terms their spatial distribution. The first group consist of Li, Al, Mn, Fe, Co, Ni, Se and Tl with related average spatial variation patterns within the physio-geographical strata (Fig. 3a). The average concentrations of these elements tend to be relatively high or equal in the rural (37 ± 1.4 , 103134 ± 12066 , 1006 ± 78 , 67728 ± 8876 , 25 ± 4 , 26 ± 4 , 0.7 ± 0.04 and 0.4 ± 0.02 $\mu\text{g/g}$, respectively) and residential (41 ± 4 , 100768 ± 11138 , 916 ± 199 , 66808 ± 8341 , 23 ± 3 , 25 ± 3 , 0.7 ± 0.05 , 0.4 ± 0.02 $\mu\text{g/g}$, respectively) strata compared to the commercial (35 ± 3 , 81480 ± 5465 , 558 ± 124 , 56748 ± 5249 , 19 ± 1.5 , 24 ± 3 , 0.7 ± 0.02 , 0.4 ± 0.02 $\mu\text{g/g}$, respectively) and industrial (34 ± 3 , 91484 ± 8385 , 456 ± 135 , 60099 ± 6512 , 20 ± 4 , 24 ± 7 , 0.7 ± 0.07 and 0.4 ± 0.05 $\mu\text{g/g}$, respectively) strata. However, ANOVA analysis revealed that the differences in the mean concentrations of these elements among the strata are not statistically different to exclude the possibility that the difference is due to random sampling variability ($P = 0.808, 0.982, 0.833, 0.066, 0.731, 0.818, 0.625$ and 0.343 for Li, Al, Mn, Fe, Co, Ni, Se and Tl, respectively). The elements in this group are of terrestrial origin and can be attributed to the geology of the area (Cox and Preda, 2005). This explains their even spatial distribution among the different strata. The

relatively low concentrations of these elements in the commercial and industrial strata could be as a result of dilution by marine sand. Marine sediment had been identified to be trapped in the navigational section of the estuary due to dredging (Eyre et al., 1998). The average concentrations of Al, Fe, Mn and Ni were higher in the present study than those recorded previously in the river by Cox and Preda (2005) (Table 4). The low concentrations registered by Cox and Preda (2005) could be as a result of the aqua regia digestion used, which cannot completely recover elements in refractory minerals such as rutile and zircon (Duodu et al., 2015). Comparatively, Al, Fe, Mn, Co and Tl concentrations recorded in this study were also higher than that of South Bramble Bay (a section of Moreton Bay), where the river empties into the ocean (Brady et al., 2015b; Morelli and Gasparon, 2014) (Table 4). This is expected as dilution of terrestrial sediment with marine sand occurs in the bay. More than 90% of the sediment composition in the bay is sand (Brady et al., 2015b; Morelli and Gasparon, 2014). Conversely, the concentration of Ni in Bramble Bay was higher than registered for this work. (It is worth noting that the Bramble Bay work by Brady et al (2015b) was on weak acid recoverable metals using ~1% HNO₃). It has been reported that background concentration of Ni around the bay is elevated (Morelli and Gasparon, 2014). Also, the concentrations of Al, Fe and Tl in this study were higher than those in average sediments and soils in South East Queensland (De Caritat and Cooper, 2011), when aqua regia digestion on < 2mm fraction was used. Digestion methods under recover elements compared to total elemental determination by LA-ICP-MS (Duodu et al., 2015). However, the average Mn, Co and Ni concentrations were lower in this study than in average sediments and soils in South East Queensland (SEQ) (De Caritat and Cooper, 2011). This could be attributed to high background concentrations of these elements in the sampled area compared to the Brisbane River sediment.

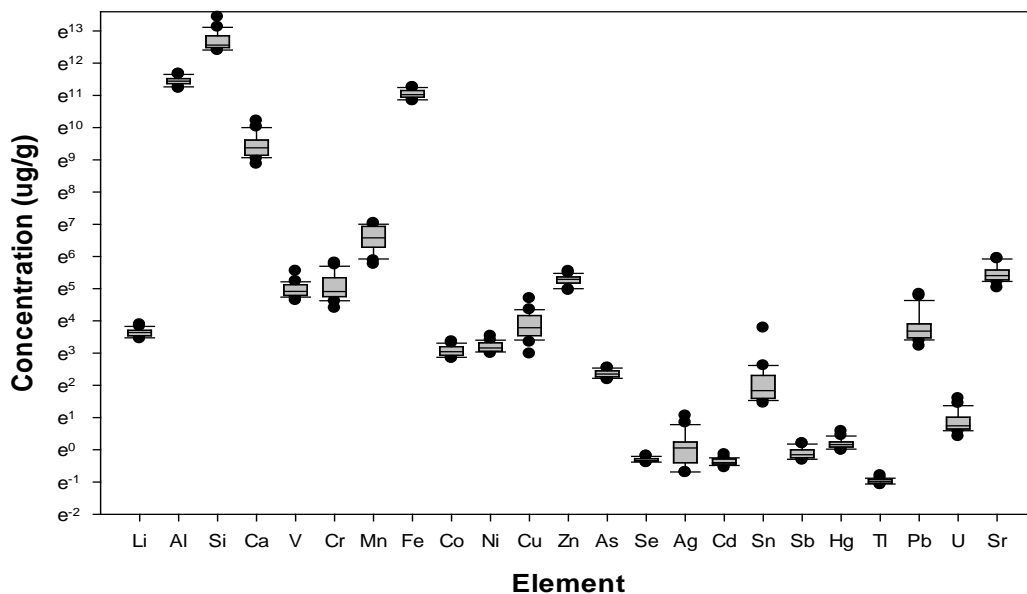


Fig. 2: Box and whisker plot of concentrations of metals in surface sediment from Brisbane River (µg/g).

The second group of elements, which correlated together, comprise of Si, Ca, V, Cr, As, Sn, Sb, U and Sr (Fig. 3b). Their average spatial concentrations were fairly stable from the rural to the commercial strata but increased slightly at the industrial stratum (Fig. 3b). These elements are of marine origin (Brady et al., 2015b). The industrial stratum is close to

the mouth of the river where marine sediment is a dominant source of sediment deposited in the estuary (Eyre et al., 1998). This explains the elevation of these elements in the industrial stratum. ANOVA analysis on the average concentrations of these elements within the different strata did not reveal any significant difference among the strata ($P = 0.412, 0.207, 0.425, 0.064, 0.396, 0.340, 0.756, 0.704$ and 0.095 for Si, Ca, V, Cr, As, Sn, Sb, U and Sr, respectively). The Brisbane River estuary is a micro-tidal estuary with significant sediment inputs (about 450,000 tonnes/yr) from Moreton Bay where tides and tidal currents supply energy for mixing and circulation of the estuarine sediment about 75 km from the mouth (Hossain et al., 2004). Generally, the mean concentration of V was higher in the present study than that recorded previously in the river (Cox and Preda, 2005). Similarly, the average concentrations of V, Cr, As, Sb and U were all higher in the present study than in Moreton Bay and average sediment and soil concentrations in SEQ (with only Sb being higher in average SEQ sediments and soils than this study (Brady et al., 2015b; Morelli and Gasparon, 2014; De Caritat and Cooper, 2011) (Table 4). All the four studies (Cox and Preda, 2005; Morelli and Gasparon, 2014; Brady et al., 2015b; De Caritat and Cooper, 2011) used digestion methods, which under recover elements in sediments compared to total elemental determination by LA-ICP-MS (Duodu et al., 2015). The low Sb concentration in the present study compared to average SEQ sediments and soils could be as a result of mixing and dilution of marine sediment with terrestrial sediment (Brady et al., 2015b).

The third group of elements (Cu, Zn, Ag, Cd, Hg, and Pb) also showed some similar spatial variations at most strata (Fig. 3c). With the exception of Cu and Cd, the differences in the mean concentrations of these elements among the strata were statistically different ($P = 0.074, 0.029, 0.017, 0.057, < 0.001$ and < 0.001 for Cu, Zn, Ag, Cd, Hg, and Pb, respectively). The highest average concentrations of Ag ($1.5 \pm 0.9 \mu\text{g/g}$) and Cu ($76 \pm 31 \mu\text{g/g}$) were recorded at the industrial and rural strata, respectively. The remaining metals (Zn, Cd, Hg and Pb) registered their highest average concentrations at the commercial stratum ($215 \pm 25, 0.7 \pm 0.1, 1.4 \pm 0.03$ and $72 \pm 20 \mu\text{g/g}$, respectively). The strong correlation among Hg, Pb, Cd and Zn could be attributed to anthropogenic activities, specifically traffic related (Sun et al., 2014). The commercial stratum, which is highly urbanised with a lot of vehicular activity, receives much of these metals compared to the other strata. The proximity of sampling site SP1 (in the rural stratum) to a boat ramp could be the source of high Cu concentration in the rural stratum (Brady et al., 2015a). Also, antimicrobial paints used on bridges and wharves in the industrial stratum could be the source of high Ag in the industrial stratum. The average concentrations of Pb, Zn and Cu were higher in the present study than had been reported previously (Cox and Preda, 2005). Also, the mean value of Cd, Cu, Hg, Pb and Zn were all higher in the present study than in studies by Brady et al. (2015b) and De Caritat and Cooper (2011). These metals are of anthropogenic origin and with continuing anthropogenic activities within the study area, their concentration will be increasing with time. In addition, the digestion methods used in the previous studies could under recover the metals compared to the present LA-ICP-MS method (Duodu et al., 2015).

Figure 4 below shows the temporal variations of the different groups of elements among the four physio-geographical strata along the river. Two elements each were used to represent the variations pattern of the first (Al and Fe) and second (Ca and Cr) groups of elements. The concentrations of these two groups of elements were fairly stable during the four sampling periods across all the physio-geographical strata. ANOVA analysis confirmed that there is no significant difference in the means of these two groups of elements among the sampling periods in all the four strata (Al: $P = 0.404, 0.677, 0.685$ and 0.796 ; Fe: $P = 0.509, 0.709, 0.720$ and 0.432 ; Cr: $P = 0.125, 0.138, 0.075$ and 0.110 ; Ca: $P = 0.753, 0.936, 0.847$ and 0.931 , for rural, residential, commercial and industrial strata, respectively). The first group of

elements (Al and Fe) is attributed to the geology of the study area with even concentration distribution irrespective of time or season (Cox and Preda, 2005). Similarly, the second group of elements (Ca and Cr) is ascribed to marine sediment intrusion, which can travel all year to about 75 km upstream and evenly mix due to tidal influence (Hossain et al., 2004).

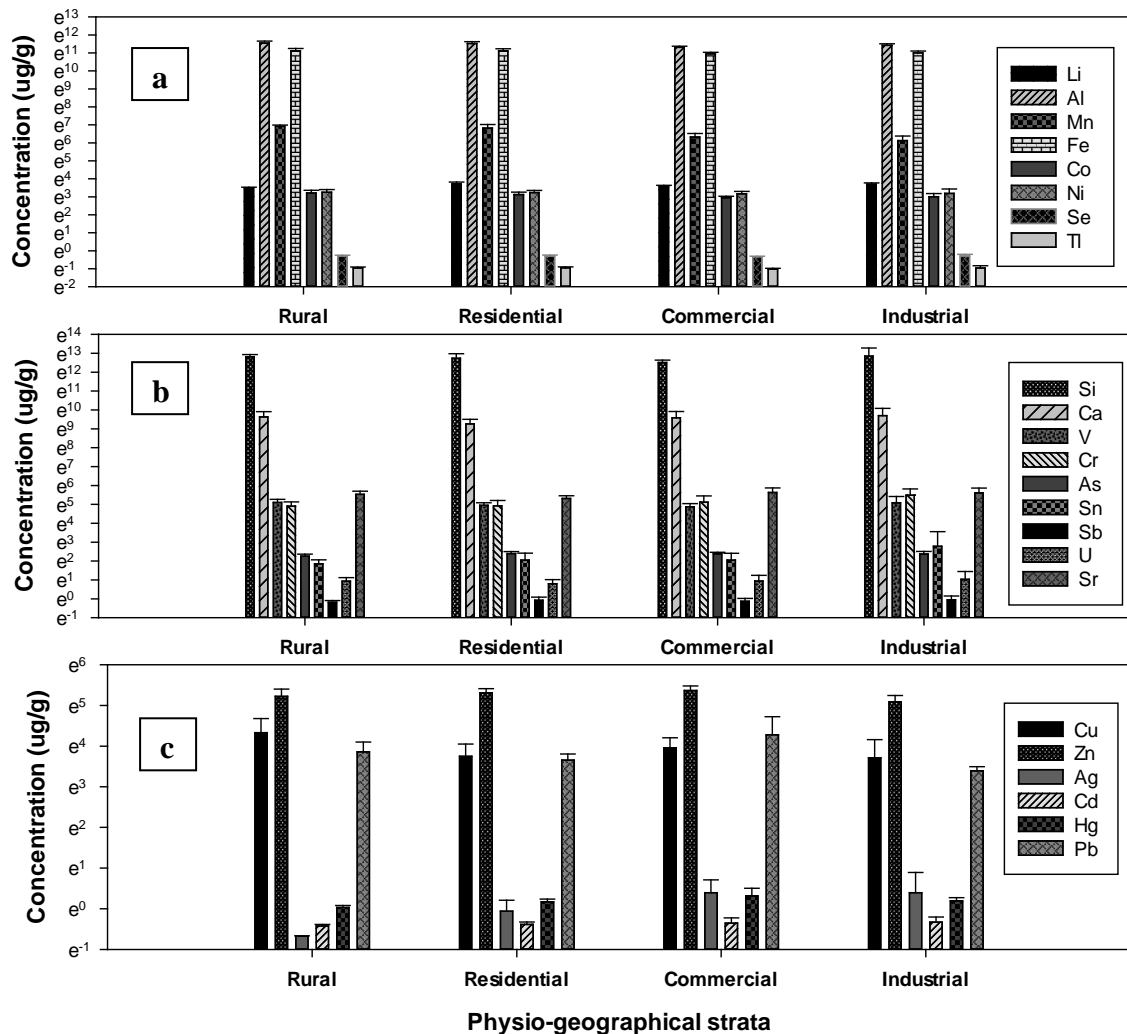


Fig. 3: Spatial variation of elements in the Brisbane River sediment among the physio-geographical strata

However, one or more elements in the third group (comprising of Cu, Zn, Ag, Cd Hg and Pb) showed some temporal variation in each stratum. In the rural stratum, all the elements in this group registered their highest and lowest concentrations in the December 2014 and September 2014 sampling regimes, respectively (Fig 4). There was statistical difference in the mean concentrations of Cu, Hg and Pb among the sampling periods (ANOVA $P = 0.023$, < 0.001 and 0.0424 , respectively). On the other hand, there was no significant difference in the mean concentrations of Zn, Ag and Cd among the different sampling regimes. SP1 and SP3 (both in the rural stratum) are near a boat ramp and a road leading to a vehicle ferry crossing on the river, respectively. Increase in the use of recreational boats and jetskis during the hot summers as well as a storm event three days before the sampling in December could be responsible for the elevated concentrations. Wet deposition of heavy metals originating from vehicle emission and component wear has been

found to be primarily associated with stormwater (Gunawardena et al., 2013). A similar temporal trend was observed for this third group of elements in the residential, commercial and industrial strata. With the exception of Ag (ANOVA $P < 0.001$ in all three strata), there was no significant variation in the concentrations of the remaining metals in this group among the sampling periods (Fig. 4). As observed in the rural stratum, Ag concentration in the December sampling period was highest in all three strata. Increase in exposure to antimicrobial paints on bridges and wharves as a result of rising water level during the wet season could be attributed to this observation. Sampling sites SP10 (in residential stratum), SP13, SP15 and SP16 (in the commercial stratum) and SP19 (in the industrial stratum) are all close to bridges while SP21 and SP22 are located near wharves. There was no significant differences in the concentrations of the traffic related metals (Cu, Zn, Cd and Pb) during the four sampling periods because diesel powered city ferries ply between SP11 (in the residential stratum) and SP20 (in the industrial stratum) every day. Coupled to this, similar vehicular traffic volume is observed on each bridge across the river all year round. Both dry and wet depositions of atmospheric vehicular emissions have been cited to contribute similar metal levels in the urban environment (Gunawardena et al., 2013).

Table 4: comparison of metal concentration ($\mu\text{g/g}$) in the Brisbane River sediment with similar studies around the study area.

Metal	This study		Brady et al., 2015b and Morelli & Gasparon, 2014		De Caritat and Cooper, 2011		Cox and Preda, 2005	
	MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX
Al	75311	116930	5900	62000	6000	39500	72	13425
Si	244383	685536						
Mn	319	1143	126.3	862	232	3260	3	322
Fe	51201	77263	8940	48180	11500	62800	1264	113925
Ca	7157	27303	14000	17000				
Sr	154	386						
Li	32	49						
Ag	0.5	8						
As	8.9	13	1.5	7.7	0.5	5.7	BD	16.9
Cd	0.6	0.9	0.01	0.1	0.02	0.16	BD	0.14
Co	17	29	4.5	25.4	3.2	38.6		
Cr	82	332	26.6	159.5	8.3	118	1	331
Cu	20	110	3.5	39.3	6.3	55.6	1	31
Hg	1	2	BD	0.0002	0.01	0.11	BD	0.73
Ni	20	34	8.9	39.2	4.5	92.9	1	20
Pb	25	126	2.2	22.5	2.8	18.7	2	59
Sb	0.7	1.2	0.07	0.2	0.07	4.4		
Se	0.7	0.8						
Sn	4	44						
Tl	0.3	0.5						
U	1.5	5	0.3	1.1	0.3	2.3		
V	104	258	11	73.58	15	93		
Zn	142	257	12.4	212.8	26.4	100	5	89

*BD- below detection

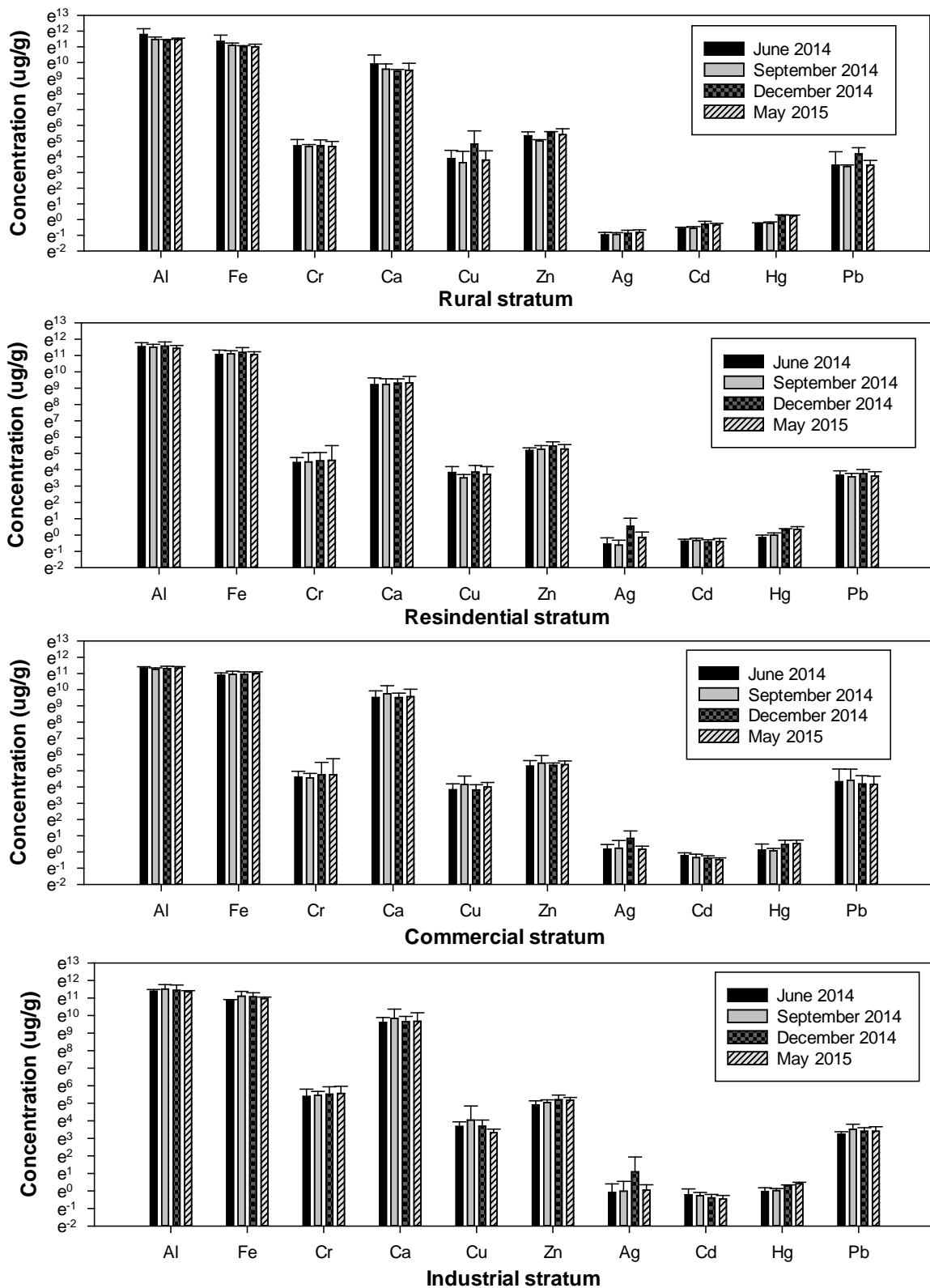


Fig. 4: Temporal variation of elements in the Brisbane River sediment among the physio-geographical strata

3.3. Source of elements in the sediment

Both PCA and HCA differentiated the samples according to the source of their metals. The elements were grouped into three clusters by HCA (Fig. 5), which also correlated with the three principal components (PCs) in the PCA results (Table 5). The three PCs explained 67.5% of the total variance in the data set and allowed the tentative assignment of sources.

The first PCA factor (Table 5) explained 28.5% of the data variance and correlated with the first cluster in HCA (Fig. 5, comprising of Si, Ca, Sr, Cr, V, U, Sn, Sb and As).

Table 4: Varimax rotated factor loadings of metals in sediment samples

Element	Factor 1	Factor 2	Factor 3
Li	-0.181	0.466	0.006
Al	-0.043	0.938	0.186
Si	0.623	0.698	-0.231
Ca	0.87	0.014	0.031
V	0.691	0.611	-0.138
Cr	0.769	-0.119	-0.027
Mn	-0.199	0.805	0.292
Fe	0.161	0.912	0.292
Co	0.29	0.862	0.187
Ni	0.01	0.411	0.528
Cu	-0.126	0.174	0.509
Zn	0.125	-0.048	0.835
As	0.569	0.208	0.018
Se	0.288	0.551	-0.216
Ag	0.119	-0.666	0.157
Cd	0.705	-0.17	0.181
Sn	0.801	0.253	-0.441
Sb	0.542	0.386	-0.052
Hg	0.672	-0.241	0.408
Tl	0.271	0.808	-0.209
Pb	0.5	-0.33	0.734
U	0.88	0.301	0.008
Sr	0.85	-0.134	0.149
% of variance	28.5	27.6	11.4
Cumulative %	28.5	56.1	67.5

This cluster has two sub groups with Ca, Sr and Cr forming one group and Si, V, U, Sn, Sb and As making up the other group. The grouping of Si and U can be attributed to the intrusion of mineral sand of marine origin (Brady et al., 2014a). The separation of Ca and Sr from the lithogenic group can be related to their biogenic origin (Zeng & Wu, 2013; Rubio et al., 2000; Cardoso et al., 2001; Álvarez-Iglesias et al., 2006). This sub-cluster was attributed to biogenic carbonates of marine origin. The first factor was therefore assigned to marine sand intrusion. Site SP22 at the mouth of the river was the major contributor to this source (Fig. 6). Eyre et al. (1998) identified marine sand to be the dominant source of sediment deposited in the estuary. Due to dredging at the mouth of the river, this area traps most of the marine sand (Eyre et al., 1998). The impact of this factor could be seen around sampling sites

close to the mouth of the river (SP22 and SP21) and depositional areas (SP10 and SP7) (Fig. 6, cluster 3).

The second PCA factor with 27.6% of variance comprises Al, Fe, Mn, Co and Tl with high loadings and Si, V, Se and Li with relatively low loadings. HCA Cluster 2 in Fig. 5 shows close resemblance to this factor (Al, Fe, Co, Mn, Tl, Se, Ni and Li). This was assigned to mixed lithogenic contribution and sand intrusion with the lithogenic contribution being the dominant source as evident by the high positive loadings for the lithogenic elements (Al, Fe, Mn) (Brady et al., 2014a; Saleem et al., 2015; Álvarez-Iglesias et al., 2006). The loading of Co and Tl to this factor might be due to clay and sulphide minerals acting as nucleation sites for the sorption of these metals (Duchesne et al., 1983; Takamatsu et al., 1985). The major contributions to this source are linked to sites SP1, SP2 and SP3 (for Al, Fe, Mn, Tl and Co) (Fig. 6, cluster 2, sub-cluster 1 and Table S2 in SM) and SP4, SP5, SP6 SP8 and SP9 (for mixed Al, Fe, Mn, Co, Tl, Si, V, Ni and Li) (Fig. 6, cluster 2, sub-cluster 2 and Table S2 in SM). All these sites can be found in the rural and residential strata of the river with mixed terrestrial and marine sediments due to tidal influence (Table S2 in SM) (Hossain et al., 2004; Cox and Preda, 2005).

The third PCA factor explained 11.4% of data variance and showed elevated loadings of Pb and Zn with moderate loadings of Cu and Ni. This can be linked to cluster 3 in the HCA comprising of Hg, Pb, Cd, Zn, Ag and Cu (Fig. 5). The strong correlation among Hg, Pb, Cd and Zn could be attributed to anthropogenic activities (Sun et al., 2014). The Pb and Hg could be linked to traffic emissions (Saleem et al., 2015; Pulles et al., 2012), while Zn, Ni and Cd are also markers for diesel and lubricant oil combustion, and tyre and brake abrasion (Pulles et al., 2012; Imperato et al. 2003; Wang et al., 2003). Also, the contribution of Cu to this factor can be attributed to antifouling paints from marina activities (Brady et al., 2014b), while the presence of Ag could be linked to the application of fertilizers, and pesticides or antimicrobial paints (Dumont et al., 2015; Schlich & Hund-Rinke, 2015 and Suresh, 2015). However, given the sites impacted by this factor, antimicrobial paints used on the bridges and wharves to prevent rusting and microbial attack in the water could be the possible source of Ag. This third factor was attributed to traffic-related sources. Samples from SP11 to SP20 contributed to this factor (Fig. 6, cluster 1). Sites SP15, SP16, SP19 and SP13 are located close to bridges, which carry vehicular traffic while SP14 is also close to one of the busiest roads in Brisbane (Congestion Reduction Unit, 2015). City ferries also ply along SP11 to SP20 with ferry terminals close to SP13, SP15, SP16 and SP19. Additionally, SP12, SP17, 18 and 20 are located close to the confluence of major creeks along the Brisbane River, with a lot of marina activity. SP20 is also close to a shipyard.

3.4. *Sediment quality assessment by single pollution indices*

Table S3 (in SM) gives the concentration of elements in the background sample used for the calculation of all pollution indices. Metals with high contamination factors are usually mobile (have low retention time) in sediment and pose high risk to the environment (Saleem et al., 2015). Table S4 (in SM) shows the contamination factors of metals in the sediment of Brisbane River. From the four contamination categories enumerated by Qingjie et al (2008), all the metals showed very low to moderate contamination with the exception of Cr (at commercial and industrial strata), Cu (rural, commercial and industrial strata), Ag (residential, commercial and industrial strata), Sn (industrial stratum) and Pb (commercial stratum), which showed considerable contamination along the river. The Cr contamination can be linked to tyre and break wear on one hand and shipping related activities (Mummullage, 2015; Brady et al., 2014b) as the impacted sites SP15, SP16 and SP20 are

close to bridges and a shipyard. The proximity of SP1 to a boat ramp, SP13 to a ferry terminal and SP20 to a shipyard indicates that Cu contamination is as a result of antifouling paints (Brady et al., 2014b). The Ag contamination at SP10, SP13, SP15, SP16 and SP19 (all close to bridges) confirms that antimicrobial paint on the bridges is responsible. Vehicle emissions are also responsible for the high Pb concentration (at SP15 and SP16) relative to background because of the proximity of these sites to bridges. The elevated Sn concentration at SP22 can be attributed to mixed marine intrusion and harbour sediments at the mouth of the river and closeness to a port.

Enrichment factor has also been used to assess the anthropogenic contributions of metals to sediments. The average enrichment factors computed for the metals at various sites are also presented in Table S5 (in SM). Most of the metals showed depletion to only mineral enrichment at various sites. However, Si, Ca, Cr, Mn, Cu, Zn, Ag, Sn, Hg, Pb, U and Sr showed moderate enrichment at (SP22), (SP16 and SP22), (SP2, SP7, SP10, SP13-SP16, SP19-SP22), (SP1-SP13, excluding SP2, SP11 and SP12), (SP2, SP3, SP6, SP8, SP11 and SP13-SP20), (SP16), (SP6-SP22 excluding SP13, SP15, SP16 and SP19), (SP15 and SP16), (SP14-SP17, SP19 and SP22), (SP13, SP15 and SP16), (SP15 and SP22) and (SP16) respectively (Table S5). The enrichment of Si and Ca could be attributed to marine sand intrusion and depletion of Al at sites SP22 and SP16 (Table S2). Enrichment of Cr at the residential and commercial strata could be associated with traffic such as tyre and break wear since impacted sites were close to bridges or roads (Mummullage, 2015). Conversely, Cr enrichment at the industrial strata could be linked to mixed marine sand and shipping related activities as marine sand intrusion is a dominant source of sediment at the river mouth (SP19-SP22), while SP20 and SP21-SP22 are close to a shipping yard and harbour, respectively (Brady et al., 2014b; Hossain et al., 2004). The slight elevation of Mn at the rural and residential strata could be linked to clay and sulphide minerals (Table S2 in SM) (Duchesne et al., 1983; Takamatsu et al., 1985). The moderate Cu enrichment at the rural stratum could be linked to abandoned boats around SP2 due to flooding and vehicle ferry crossing activity at SP3. In the residential to the industrial strata, Cu enrichment could be attributed to antifouling paints due to ferry activities from SP11 to SP20 and a shipping yard at SP20 (Brady et al., 2014b). Depletion of Al at SP6 could be the reason for the moderate Cu elevation at that site. However, no explanation could be offered for the elevation of Cu at SP8. The enrichment of Zn, Sn, Hg, Pb and Sr at the respective sites could be linked with traffic related activities (such as tyre wear, brake wear and vehicle exhaust) as the sites are close to bridges and roads (Mummullage, 2015). Uranium enrichment is as a result of mineral sand at SP15 and SP22 (Brady et al., 2014b). Antimicrobial paints used on structures and signage on the river could be ascribed to the moderate enrichment of Ag at SP6- SP22 excluding SP13, SP15, SP16 and SP19. In addition, three metals, Cu at SP1 and Ag at SP13, SP15, SP16 and SP19 and Sn at SP22 were significantly enriched in the sediment. This could be a result of marina activities at SP1 since it is close to a boat ramp, antimicrobial paint wear because SP13, SP15, SP16 and SP19 are all located near bridges and mixed marine and harbour sediments as SP22 is at the mouth of the river and close to a port.

Geo-accumulation index (I-geo) was similarly calculated (Table S6 in SM) to ascertain background metal enrichment. I-geo classified all sediments as either “unpolluted” or “unpolluted to slightly polluted” (I-geo value ≤ 1) with only sediments from SP20 (Cr), SP1 (Cu), SP13, SP15, SP16 and SP19 (Ag) and SP22 (Sn) being classified as “moderately polluted” ($1 < \text{I-geo} \leq 2$). This observation is very similar to the significant enrichment of the same metals above. Therefore the same reason can be ascribed to the I-geo classification. This suggests a moderate recent input of these metals (i.e. Cr, Cu, Ag and Sn) in the sediment.

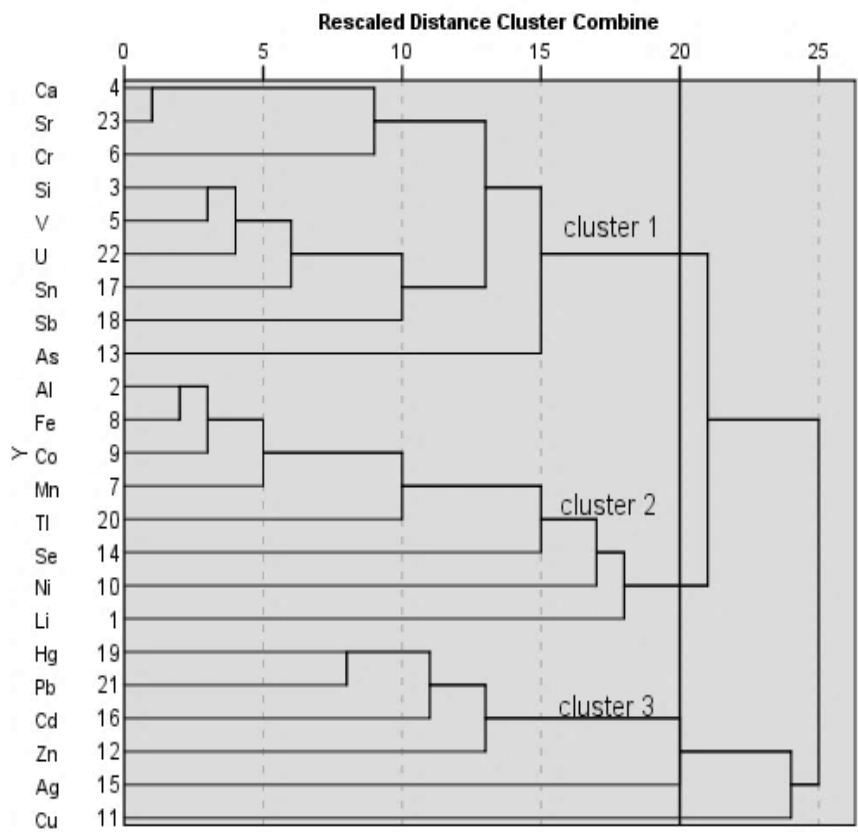


Fig. 5: Dendrogram showing clusterig of elements

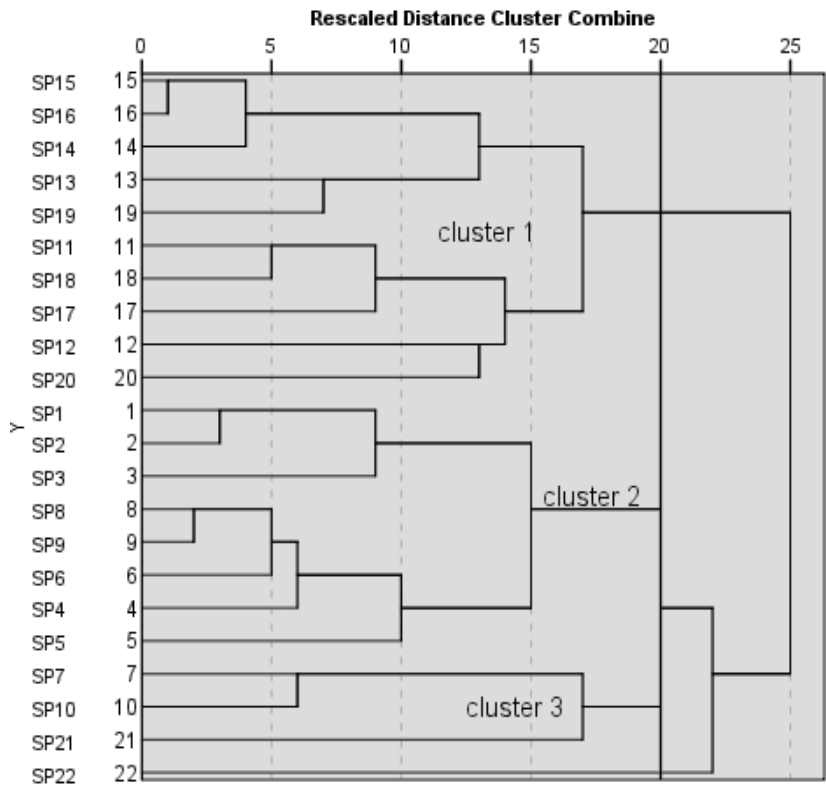


Fig. 6: Dendrogram showing clustering of sampling sites

Evaluation of all three indices suggests some contamination or anthropogenic inputs of Cr, Cu, Ag, Sn and to some extent Pb, Hg, Zn, Mn, Sr, Ca, U and Si in the sediment at specific sites. Though all three indices indicated some contamination, in the worst case scenario, enrichment factor appears to detect contamination (at more sites and of more metals) better than contamination factor and I-geo. This is due to the use of terrestrial element (Al in this study) for normalisation in the calculation of enrichment factor. It enables the detection of slight variation in the sedimentary composition at a site (Brady et al., 2015). Similar results were encountered in earlier studies (Brady et al., 2015; Çevik et al., 2008) where enrichment factor could detect terrestrial sedimentary inputs of metals due to the normalisation. This provides further evidence that the application of contamination factor and I-geo may be limited in complex environments such as estuarine.

3.5. *Multi-element indices for the assessment of sediment quality*

The use of multi-element indices can overcome some of the limitations of the single indices. They can assess the impact of multiple contamination species at a site. In this study, contamination was generally low as indicated by “modified degree of contamination” (Fig. 7) since none of the sites has an index (mCd) greater than 2. With the exception of SP6, SP15, SP16 and SP22, which were “slightly polluted” ($1.5 < \text{mCd} < 2$), the rest of the sites were virtually “unpolluted” ($\text{mCd} < 1.5$). However, both “pollution index” (PI) and “modified pollution index” (MPI) (Fig. 7) showed that Brisbane River sediment is “polluted”. For PI, only SP3, SP4 and SP9 were “moderately polluted” with the remaining sites being “severely polluted” (SP2, SP5, SP6, SP7, SP8, SP11, SP12, SP14, SP17, SP18 and SP21) or “heavily polluted” (SP1, SP10, SP13, SP15, SP16, SP19, SP20 and SP22). Similarly, MPI revealed that sites SP3, SP4, SP5 and SP9 were “slightly polluted” while SP7, SP8, SP11, SP12, SP14 and SP21 were “moderately polluted”. In addition, MPI discriminates between “moderately-heavily polluted” sites SP1, SP10, SP15, SP17, SP18 and SP120 and, “severely polluted” sites SP13, SP16, SP19 and SP22.

From Fig. 7, it could be observed that while mCd underestimate the risk posed by the sediment to the effect that none of the sites was found to be polluted, PI overestimates the risk at all sites except SP3, SP4 and SP9 being deemed to be “moderately” to “heavily polluted” due to the high and lower trigger values, respectively (Table 1). Thus, PI has an advantage over the other indices, as the low trigger values will ultimately lead to classifying sediments that pose high risk and most likely warrant further examination to identify the sources of contamination. However, MPI could clearly distinguish between “slightly polluted” (SP3, SP4, SP5 and SP9), “moderately polluted” (SP2, SP6, SP7, SP8, SP11, SP12, SP14, SP18 and SP21), “moderately-heavily polluted” (SP1, SP10, SP15, SP17 and SP20) and “severely polluted” (SP13, SP16, SP19 and SP22). However, none of the sites was heavily polluted. This makes MPI a potentially better index for sediment qualification because of its sensitivity in detecting successive graduation of sediment class (Table 1), especially because it uses enrichment factor which, takes into consideration diverse sediment behaviour that is likely to occur in complex environments due to the use of normalisation element.

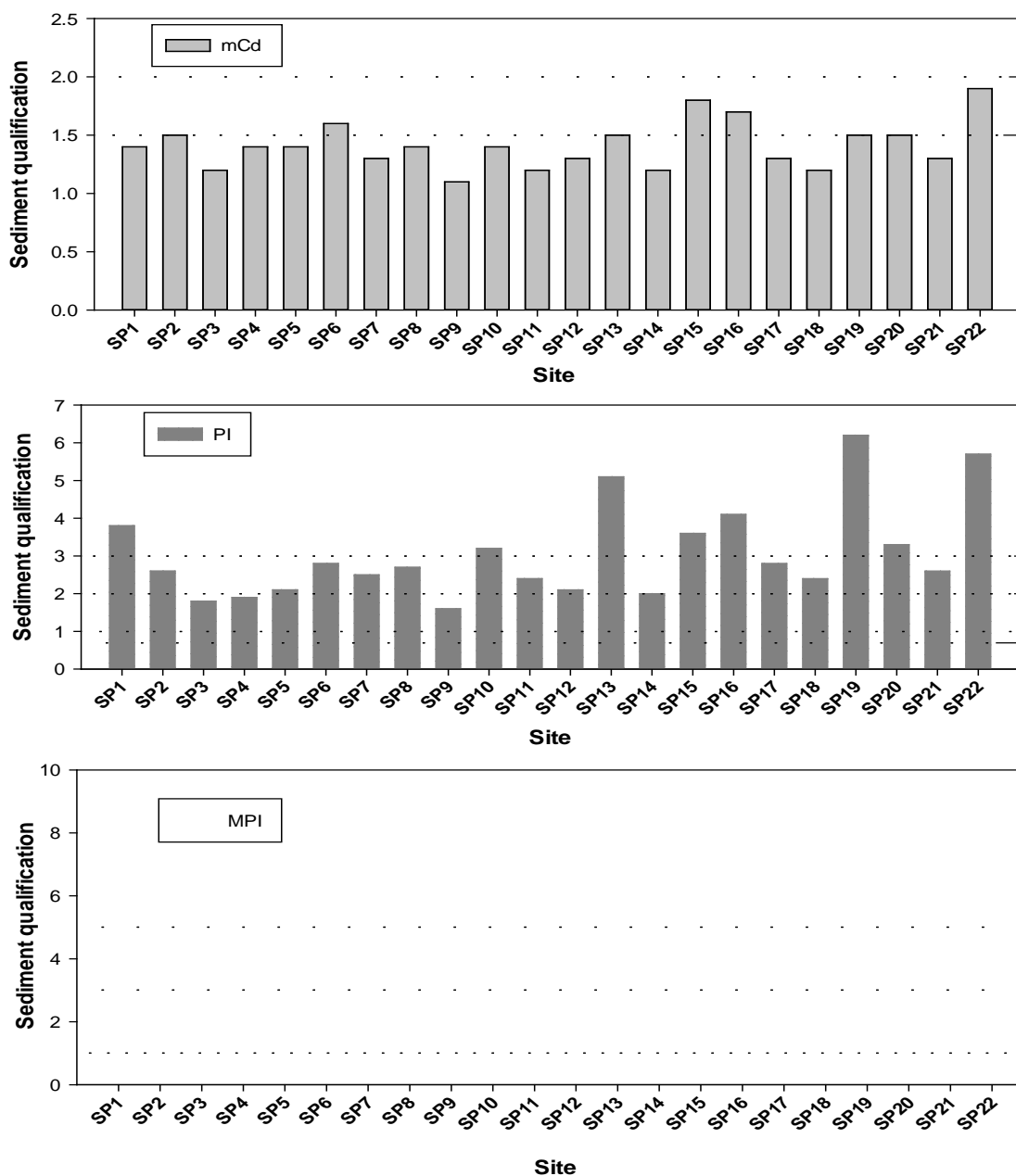


Fig. 7: Sediment quality assessment by multi-element indices (mCd: modified degree of contamination; PI: pollution index and MPI: modified pollution index). (See Table 1 for sediment classification dash lines).

3.6. Ecological risk assessment of metals in sediment

Both single and multi-element sediment quality indices cited above deal with anthropogenic input of elements and estimate contamination not pollution, which delineate toxicity (Manoj & Padhy, 2014). In addition to the anthropogenic impacts of elements in the sediment, a further assessment of the potential ecological risks of the multiple elements in the sediments is needed. In view of this, sediment quality guidelines (SQGs), potential ecological risk index (RI) and modified ecological risk index (MRI) were also applied and compared to ascertain the ecological risk posed by the trace element pollutants in the sediment.

Application of SQGs to the sediment analysed (Table S7, SM) revealed that Ag had the potential to rarely cause biological effects at SP7, SP8, SP10, SP11, SP13, SP15-SP21 as its concentration exceeded the Australian ISQG-L at those sites. Similarly, Cr (at all sites), Cu (at SP1, SP2, SP6, SP13 and SP20), Ni (at all sites except SP12, SP14, SP19, SP20 and SP22), Pb (at SP1, SP2, SP13, SP15 and SP16), Zn (at SP2, SP6, SP7, SP8, SP12, SP13, SP15, SP16, SP17, SP18 and SP20) and Hg (at SP1 and SP3) had the potential to rarely cause biological effects at the sites listed. On the other hand, with the exception of SP1 and SP3, Hg could commonly cause adverse biological effects at all sites as its concentration exceeded Australian ISQG-H values. Therefore, Hg poses considerable ecological risk at those sites. However, the SQGs are element specific and do not take into consideration the synergistic effects of multiple element mixtures which are commonly encountered in environmental samples such as sediments. Consequently, RI and MRI were also computed to account for the synergetic ecological risk posed by the sediment.

The potential ecological risk posed by the individual metals (Er^i) as computed with both contamination and enrichment factors (C_f and E_f) is presented in Tables S8 and S9, respectively, in Supplementary Material. About 77% of the metals considered (excluding Ag, Cd and Hg) pose low ecological risk at all sites ($Er^i < 40$) irrespective of either C_f or E_f was used in the calculation. The Er^i as computed with C_f revealed that Ag and Hg present some form of ecological risk. Silver (Ag) poses moderate (SP1, SP2, SP3 and SP5), considerable (SP4, SP6, SP9, SP11, SP12, SP14, SP18 and SP22), high (SP7, SP8, SP10, SP15, SP16, SP17, SP20 and SP21) and very high (SP13 and SP19) risk at the sites listed while Hg could cause only moderate (SP1 to SP22 excluding SP15, SP16 and SP17) and considerable (SP15, SP16 and SP17) risk. On the other hand, Cd showed moderate risk at only one site (SP16). Considering the Er^i calculated using E_f , Ag presented moderate (SP2 and SP5), considerable (SP1, SP3, SP4, SP6, SP8, SP9, SP12 and SP22), high (SP7, SP10, SP11, SP14, SP15, SP17, SP18, SP20 and SP21) and very high (SP13, SP16 and SP19) risks in the sediment whereas Hg poses moderate (all sites except SP14, SP15, SP16, SP17, SP19 and SP22) and considerable (SP14, SP15, SP16, SP17, SP19 and SP22) risk in the sediments. However, Cd recorded moderate risk at three sites (SP15, SP16 and SP19).

While the Er^i calculated employing contamination factor (C_f) identify Ag as posing moderate risk at SP1 and SP3 that computed with enrichment factor (E_f) shows that Ag pose considerable risk at SP1 and SP3. Similarly, the Er^i with (C_f) indicates Ag poses considerable risk at SP11, SP14 and SP18, but Er^i with (E_f) reveals that these sites pose high risk. The Er^i with (E_f) shows SP16 pose very high risk while Er^i with (C_f) indicates that SP16 pose just high risk. Likewise, Er^i with (E_f) shows Hg poses considerable risk at SP14, SP19 and SP22, but these sites pose moderate risk when Er^i was computed with (C_f). The same applies to Cd where three sites exhibited moderate risk with Er^i computed with (E_f) instead of the one site identified with Er^i with (C_f). In general, the Er^i with (E_f) could identify polluted sites than Er^i with (C_f). In Section 3.4, it was noted that enrichment factor could detect considerable contamination (both metal and sites) than contamination factor. The use of normalisation element in the calculation of enrichment factor accounted for the conservative assessment of sediment behaviour at a site leading to the detection of any slight contamination (Brady et al., 2015). Therefore, enrichment factor could give a better estimate of ecological risk than contamination factor.

The combined ecological risks RI and MRI (computed using contamination and enrichment factors respectively) posed by metals at a site are also compared in Fig. 8. The sampling sites could be grouped into two based on their RI values. The first group comprising of sites SP1-SP5, SP9, SP12 and SP14 had $150 < RI < 300$ suggesting that these sites exhibited

moderate ecological risk. The remaining sites form the other group with $300 < RI < 600$ indicating considerable ecological risk. Conversely, MRI grouped the sites into three (SP1-SP5, SP8 and SP9), (SP2, SP6, SP7, SP10, SP11, SP12, SP14, SP15, SP17, SP18, SP20-SP22) and (SP13, SP16 and SP19) classes. The first group had MRI value between 150 and 300 indicating moderate risk, the second group suggest considerable ecological risk with $300 < MRI < 600$, while the third group had $MRI > 600$, implying very high ecological risk. Both RI and MRI recorded their highest values in the December sampling period, followed by May, June with the September sampling recording the least values at all sites (Table S10 in SM). It could be infer from section 3.2 that increase in the use of recreational boats and jetskis during the hot summers as well as a storm event three days before the sampling in December caused metal concentrations to be elevated. Wet deposition of heavy metals originating from vehicle emission and component wear is also found to be responsible for elevated metal concentrations in stormwater (Gunawardena et al., 2013).

When the RI and the MRI are compared, the MRI presents higher overall ecological risk for most of the sites (~77%) than RI (23%). This augments the observation in Section 3.4, identifying enrichment factor to be able to detect greater contamination than contamination factor. Thus, the use of MRI is more likely to give a better assessment of risk than RI. The use of MRI provides another advantage over RI as it takes into account complex sediment behaviour that are likely to occur in estuarine environments. A further comparison of both RI and MRI in different sampling period (Table S10 in SM) revealed that, the sediment pose high risk during wet season (summer) than the dry season (winter).

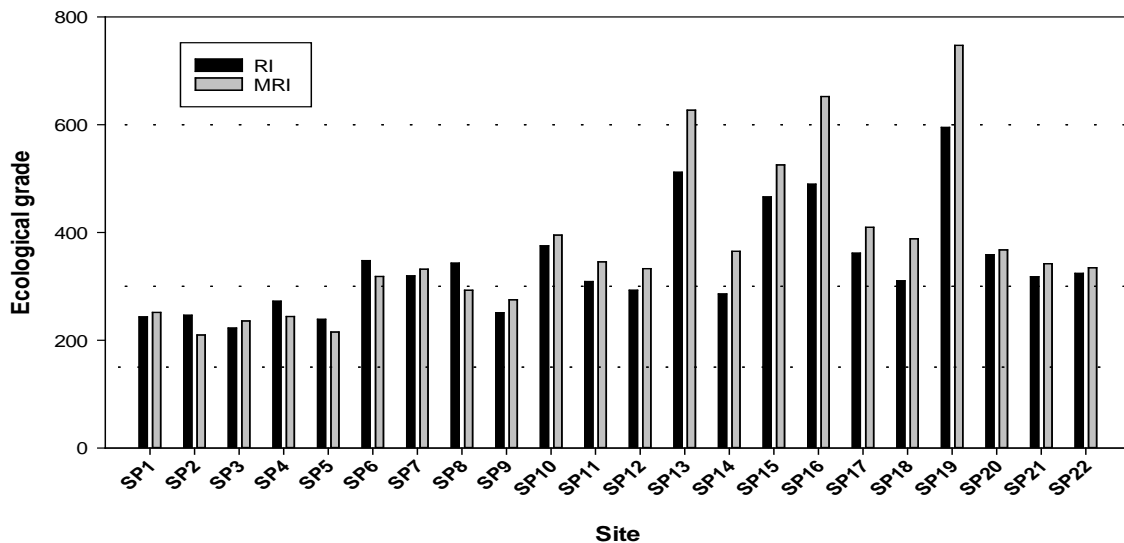


Fig. 8: Assessment of ecological risk of heavy metals in surface sediments from Brisbane River using potential ecological risk index (RI) and modified ecological risk index (MRI).

4. Conclusion

The concentrations of major and trace metals (determined with LA-ICP-MS) in Brisbane River sediment are presented in this study. The distribution characteristics show that most of the metals analysed were fairly stable across sampling sites and between sampling periods. The variation patterns of elements in the sediment were found to be strongly dependent on their sources. Three sources of metals: marine sand intrusion, mixed lithogenic and sand intrusion as well as transport-related sources were identified by the two pattern recognition techniques (PCA and HCA) employed in the study.

Three single contamination indices; contamination factor, enrichment factor and index of geo-accumulation in addition to three multi-element indices; modified degree of contamination, pollution index and modified pollution index were used to assess the sediment quality. In general, the Brisbane River sediment was deemed to be contaminated especially at site SP13, SP15, SP16 and SP19, all located near bridges along the river suggesting transport related origin. Among the single indices, the use of enrichment factor was preferred for assessing contamination at a site, while the modified pollution index was also identified as the preferred multi-element index for assessing sediment quality since they take into consideration complex sediment behaviour.

Application of Australian SQGs revealed that Ag, Cr, Cu, Ni, Pb and Zn had the potential to rarely cause biological effects while Hg could commonly cause biological effects at certain sites. Also, ecological risk index (RI) values indicated that the sediment poses moderate to considerable ecological risk. From RI, a modified ecological Index (MRI) was developed using enrichment factor instead of contamination factor in order to provide an improved method for assessing ecological risk, which takes into account complex sediment behaviour when multi-elements are investigated. The MRI indicates that the sediment poses moderate to very high ecological risk. In view of this, further investigation of heavy metal speciation and bioavailability is required to ascertain the extent of pollution in the study area.

The use of enrichment factor and modified pollution index are recommended for the assessment of contamination, while modified ecological index is recommended for the assessment of risk posed by sediment when evaluating a complex environment such as an estuary. The results of the study would be valuable for researchers in environmental quality evaluation and the methods applied can also be used for pollution assessment in other environments.

Supplementary Material is provided containing tables including Pearson correlation, sedimentary features and sediment quality assessment.

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Supplementary Material for

Comparison of Pollution Indices for the Assessment of Heavy Metal in Brisbane River Sediment

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This supplementary material contains nine tables.

Table S1: Pearson correlation between metals

	Li	Al	Si	Ca	V	Cr	Mn	Fe	Co	Ni	Cu
Al	0.53										
Si	0.22	0.55									
Ca	-0.40	-0.02	0.49								
V	-0.02	0.51	0.88	0.69							
Cr	-0.07	-0.04	0.36	0.66	0.47						
Mn	0.19	0.78	0.37	-0.12	0.38	-0.29					
Fe	0.44	0.92	0.65	0.18	0.64	-0.03	0.78				
Co	0.14	0.83	0.74	0.37	0.76	0.10	0.79	0.90			
Ni	0.22	0.49	0.08	0.17	0.19	0.002	0.37	0.59	0.43		
Cu	-0.03	0.23	0.03	-0.09	0.07	-0.07	0.27	0.20	0.17	0.09	
Zn	0.11	0.09	-0.13	0.01	-0.17	0.08	0.15	0.16	0.09	0.23	0.34
As	0.08	0.20	0.40	0.40	0.45	0.53	0.07	0.26	0.35	0.13	-0.30
Se	0.28	0.42	0.59	0.21	0.47	0.08	0.31	0.45	0.39	0.29	-0.10
Ag	-0.05	-0.54	-0.42	-0.01	-0.31	0.21	-0.53	-0.47	-0.54	-0.16	-0.02
Cd	0.02	-0.11	0.33	0.45	0.22	0.59	-0.22	-0.01	0.05	-0.17	-0.01
Sn	0.02	0.08	0.81	0.64	0.75	0.5	-0.06	0.24	0.36	-0.17	-0.29
Sb	0.35	0.34	0.67	0.29	0.53	0.27	-0.01	0.44	0.34	0.01	0.004
Hg	0.02	-0.19	0.17	0.45	0.16	0.44	-0.26	0.04	-0.04	0.1	-0.07
Tl	0.43	0.69	0.79	0.15	0.67	0.14	0.48	0.67	0.68	0.06	0.13
Pb	-0.37	-0.25	-0.07	0.47	0.07	0.27	-0.09	-0.01	0.02	0.23	0.25
U	-0.07	0.22	0.79	0.73	0.85	0.58	0.08	0.41	0.51	0.08	0.07
Sr	0.44	0.15	0.35	0.97	0.56	0.66	-0.20	0.07	0.23	0.21	-0.06
	Zn	As	Se	Ag	Cd	Sn	Sb	Hg	Tl	Pb	U
As	0.22										
Se	-0.14	0.32									
Ag	0.16	-0.03	-0.33								
Cd	0.37	0.33	0.14	0.29							
Sn	-0.23	0.41	0.49	-0.06	0.51						
Sb	0.12	0.25	0.24	-0.24	0.40	0.59					
Hg	0.48	0.38	0.05	0.27	0.66	0.31	0.43				
Tl	-0.03	0.37	0.52	-0.52	0.13	0.56	0.54	-0.11			
Pb	0.66	0.15	-0.19	0.34	0.52	0.03	0.11	0.69	-0.29		
U	0.07	0.49	0.39	-0.04	0.48	0.78	0.65	0.52	0.44	0.38	
Sr	0.09	0.37	0.15	0.09	0.46	0.53	0.21	0.55	-0.002	0.59	0.68

Table S2: Sedimentary features of the Brisbane River sediment.

Sampling site	% Clay	% Silt	% Sand	Si/Al
SP1	34.5	30.3	35.2	3.8
SP2	38.4	31.9	29.7	3.5
SP3	34.4	32.2	33.4	3.3
SP4	38.2	15.3	46.5	4.3
SP5	37.2	32.4	30.4	3.6
SP6	33.4	16.6	50	4.6
SP7	36.1	36.1	27.8	2.9
SP8	40.2	35.6	24.2	2.6
SP9	38.6	34.5	26.9	2.9
SP10	33.6	30.1	36.3	3.0
SP11	30.5	40.1	29.4	3.1
SP12	33.7	42.6	23.7	3.2
SP13	38	39.2	22.8	3.0
SP14	33.3	45.6	21.1	3.3
SP15	32.3	45.1	22.6	3.8
SP16	30.3	34.6	35.1	3.8
SP17	26.9	54.3	18.8	3.0
SP18	28.4	56.5	15.1	3.1
SP19	31.1	53.5	15.4	3.1
SP20	26.4	51.2	22.4	3.3
SP21	34.7	33	32.3	2.9
SP22	4.3	7.2	88.5	7.1

Table S3: Background concentration values for the calculation of pollution indices

Element	Li	Al	Si	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sn	Sb	Hg	Tl	Pb	U	Sr
Background values	37	99681	996467	15759	144	341	443	51905	18.3	21.7	251	158	11.3	0.9	0.3	0.8	9.8	1.6	0.9	0.5	37.1	2.7	293

Table S4: Contamination factors (C_f) of surface sediments in Brisbane River (yellow highlighted – moderately contaminated)

	Li	Al	Si	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sn	Sb	Hg	Tl	Pb	U	Sr
SP1	1.1	1.0	1.2	1.2	1.2	1.5	2.4	1.3	1.3	1.2	5.2	1.1	1.1	1.0	1.5	1.1	0.8	1.2	1.4	1.1	1.4	1.1	1.1
SP2	1.2	1.2	1.3	1.8	1.3	2.3	2.4	1.5	1.6	1.4	3.3	1.4	1.3	1.0	1.5	1.0	1.3	1.2	1.5	1.1	1.5	1.5	1.4
SP3	1.1	1.0	1.0	1.0	0.9	1.6	2.1	1.1	1.2	1.0	2.3	1.0	1.1	1.1	1.5	1.1	1.2	1.1	1.4	1.0	0.9	1.0	1.0
SP4	1.5	1.2	1.5	0.8	1.2	1.7	2.3	1.5	1.5	1.3	2.1	1.2	1.2	1.0	2.0	1.1	2.1	1.7	1.7	1.2	1.1	1.4	0.9
SP5	1.4	1.2	1.3	1.3	1.2	1.7	2.6	1.4	1.5	1.3	1.8	1.1	1.5	1.1	1.5	1.1	1.5	1.2	1.6	1.2	0.9	1.2	1.1
SP6	1.7	1.1	1.6	0.8	1.1	1.8	2.4	1.4	1.3	1.2	3.7	1.5	1.3	1.2	2.0	1.2	2.4	1.4	1.9	1.2	1.3	1.5	0.9
SP7	1.2	1.0	0.9	0.8	0.9	2.8	2.0	1.2	1.2	1.3	1.6	1.3	1.5	1.1	2.3	1.1	0.8	1.1	1.6	1.1	0.8	1.0	0.9
SP8	1.6	1.2	0.9	0.8	1.0	1.5	2.5	1.5	1.3	1.4	2.5	1.4	1.3	1.1	2.5	1.1	1.1	1.3	1.7	1.2	1.3	0.9	0.9
SP9	1.4	1.0	0.8	0.6	0.8	1.1	2.0	1.2	1.1	1.1	1.3	1.1	1.1	1.0	2.0	1.0	0.9	1.1	1.7	1.1	0.8	0.7	0.7
SP10	1.3	1.0	0.9	1.3	1.0	2.8	2.0	1.2	1.2	1.1	1.6	1.2	1.5	1.0	4.3	1.1	1.0	1.0	1.7	1.0	1.1	1.0	1.2
SP11	1.3	0.9	0.9	0.8	0.8	1.4	1.6	1.1	1.1	1.0	1.8	1.2	1.3	1.0	3.2	1.1	0.8	1.2	1.5	1.1	1.0	0.9	0.8
SP12	1.3	0.9	0.9	1.1	0.8	1.5	1.2	1.1	1.0	1.0	1.7	1.3	1.2	1.0	2.7	1.1	1.7	1.6	1.6	1.0	1.0	1.0	1.0
SP13	1.2	0.9	0.8	1.0	1.0	2.0	1.7	1.1	1.0	1.0	3.5	1.3	1.2	1.0	7.0	1.0	1.1	1.0	1.5	1.0	1.7	1.3	1.1
SP14	1.1	0.8	0.8	1.1	0.8	1.8	1.3	1.0	1.0	0.9	1.6	1.2	1.2	1.0	2.6	1.0	0.8	1.1	1.8	1.0	0.9	0.9	1.2
SP15	1.2	0.9	1.1	1.8	1.2	3.1	1.3	1.2	1.2	1.3	2.5	1.4	1.5	1.1	4.8	1.2	1.8	1.6	2.5	1.0	3.2	2.0	1.6
SP16	1.1	0.8	0.9	2.0	0.9	3.4	1.3	1.1	1.1	1.3	2.1	1.6	1.3	1.0	5.5	1.4	2.4	1.1	2.2	1.0	3.4	1.3	1.8
SP17	1.4	0.9	0.8	1.0	0.8	1.6	1.2	1.2	1.0	1.1	2.9	1.3	1.3	1.0	2.7	1.1	1.0	1.3	2.0	1.1	1.2	1.0	1.0
SP18	1.2	0.8	0.8	0.8	0.7	1.3	0.8	1.0	1.0	1.0	2.1	1.3	1.4	1.0	2.2	1.0	1.1	1.2	1.5	1.1	1.3	0.9	0.9
SP19	1.3	0.8	0.8	0.9	0.8	2.0	0.7	1.0	0.9	1.0	1.7	1.0	1.2	1.0	8.7	1.2	1.9	1.1	1.7	1.0	0.9	1.0	0.9
SP20	1.5	1.0	1.0	1.1	0.9	4.4	0.9	1.1	1.0	1.0	3.5	1.3	1.3	1.0	2.6	1.2	0.9	1.4	1.8	1.1	0.9	1.1	1.0
SP21	1.5	1.0	0.8	1.4	0.9	2.2	1.0	1.2	1.0	1.6	1.6	0.9	1.1	1.1	2.4	0.9	0.8	1.1	1.6	1.0	0.7	0.9	1.3
SP22	1.3	1.0	2.2	2.4	1.8	4.2	1.4	1.3	1.4	1.0	0.9	0.9	1.6	1.2	2.2	1.3	7.8	1.7	1.9	1.3	0.8	2.4	1.7

Table S5: Enrichment factor (E_f) of surface sediments in Brisbane River

Site	Li	Si	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sn	Sb	Hg	Tl	Pb	U	Sr
SP1	1.1	1.2	1.3	1.2	1.5	2.4	1.3	1.4	1.2	5.3	1.1	1.1	1.0	1.6	1.1	0.8	1.3	1.5	1.1	1.5	1.2	1.1
SP2	1.0	1.1	1.6	1.1	2.0	2.0	1.3	1.3	1.2	2.8	1.2	1.1	0.9	1.3	0.9	1.1	1.1	1.3	1.0	1.3	1.3	1.2
SP3	1.2	1.1	1.0	0.9	1.6	2.2	1.2	1.2	1.1	2.4	1.0	1.1	1.2	1.6	1.2	1.3	1.1	1.5	1.1	0.9	1.1	1.0
SP4	1.4	1.3	0.7	1.0	1.5	2.1	1.3	1.3	1.1	1.8	1.1	1.1	0.9	1.8	0.9	1.9	1.5	1.6	1.0	1.0	1.3	0.8
SP5	1.2	1.1	1.2	1.0	1.6	2.3	1.3	1.4	1.1	1.6	1.0	1.4	0.9	1.3	1.0	1.4	1.1	1.5	1.0	0.8	1.1	1.0
SP6	1.5	1.4	0.7	1.0	1.7	2.2	1.3	1.2	1.1	3.3	1.4	1.2	1.1	2.8	1.1	2.2	1.3	1.8	1.1	1.2	1.4	0.8
SP7	1.3	0.9	0.9	1.0	2.9	2.1	1.2	1.2	1.4	1.7	1.4	1.6	1.1	3.4	1.1	0.9	1.2	1.6	1.1	0.9	1.0	0.9
SP8	1.4	0.8	0.7	0.9	1.3	2.2	1.3	1.1	1.2	2.1	1.2	1.1	1.0	3.0	1.0	0.9	1.1	1.4	1.0	1.1	0.8	0.8
SP9	1.5	0.9	0.7	0.9	1.2	2.2	1.3	1.2	1.2	1.5	1.2	1.3	1.1	2.2	1.1	1.0	1.2	1.9	1.2	0.9	0.8	0.8
SP10	1.4	0.9	1.4	1.1	3.0	2.1	1.3	1.3	1.1	1.7	1.3	1.5	1.1	4.5	1.1	1.1	1.1	1.8	1.1	1.2	1.0	1.2
SP11	1.5	1.0	0.8	0.9	1.6	1.8	1.2	1.2	1.1	2.0	1.4	1.4	1.2	3.6	1.2	0.9	1.3	1.7	1.2	1.2	1.0	1.0
SP12	1.5	1.0	1.3	0.9	1.7	1.4	1.3	1.2	1.1	1.9	1.5	1.3	1.1	3.0	1.3	1.9	1.8	1.9	1.2	1.2	1.1	1.1
SP13	1.5	0.9	1.3	1.2	2.5	2.1	1.3	1.3	1.2	4.4	1.6	1.4	1.2	8.6	1.2	1.4	1.3	1.9	1.3	2.1	1.6	1.4
SP14	1.4	1.1	1.4	1.1	2.3	1.7	1.3	1.3	1.2	2.1	1.5	1.6	1.3	3.3	1.3	1.1	1.4	2.3	1.3	1.2	1.2	1.5
SP15	1.3	1.2	2.1	1.4	3.5	1.4	1.4	1.3	1.5	2.8	1.6	1.7	1.2	5.4	1.4	2.0	1.8	2.9	1.1	3.6	2.3	1.9
SP16	1.5	1.2	2.7	1.2	4.6	1.7	1.5	1.5	1.7	2.8	2.2	1.7	1.3	7.3	1.9	3.2	1.5	3.0	1.3	4.5	1.7	2.3
SP17	1.6	0.9	1.1	0.9	1.8	1.4	1.3	1.1	1.2	3.3	1.5	1.4	1.2	4.2	1.2	1.2	1.5	2.3	1.2	1.3	1.1	1.1
SP18	1.6	1.0	1.0	0.9	1.7	1.0	1.2	1.2	1.2	2.6	1.6	1.7	1.3	4.0	1.3	1.3	1.5	1.9	1.4	1.6	1.1	1.1
SP19	1.6	1.0	1.2	1.0	2.5	0.9	1.3	1.2	1.2	2.2	1.3	1.5	1.3	10.9	1.5	2.3	1.4	2.1	1.2	1.1	1.2	1.1
SP20	1.5	1.0	1.1	1.0	4.5	1.0	1.1	1.0	1.0	3.5	1.3	1.3	1.0	3.7	1.3	0.9	1.4	1.8	1.1	0.9	1.2	1.0
SP21	1.6	0.9	1.5	1.0	2.3	1.1	1.3	1.1	1.7	1.7	1.0	1.2	1.2	3.7	1.0	0.9	1.2	1.7	1.1	0.7	1.0	1.4
SP22	1.3	2.2	2.5	1.8	4.3	1.5	1.4	1.5	1.0	1.0	0.9	1.6	1.2	2.2	1.3	8.1	1.8	2.0	1.3	0.8	2.4	1.8

*Yellow highlighted – considerable enrichment

*Red highlighted – significant enrichment

Table S6: Index of geo-accumulation (I_{geo}) of surface sediments in Brisbane River

Site	Li	Al	Si	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sn	Sb	Hg	Tl	Pb	U	Sr
SP1	-0.3	-0.4	-0.2	-0.2	-0.2	0.0	0.5	-0.1	-0.1	-0.2	1.2	-0.3	-0.3	-0.4	0.0	-0.3	-0.6	-0.2	0.0	-0.3	0.0	-0.3	-0.3
SP2	-0.2	-0.2	-0.1	0.2	-0.1	0.4	0.5	0.0	0.1	-0.1	0.8	0.0	-0.1	-0.4	0.0	-0.4	-0.1	-0.2	0.0	-0.3	0.0	0.0	-0.1
SP3	-0.3	-0.4	-0.4	-0.4	-0.5	0.0	0.3	-0.3	-0.3	-0.4	0.4	-0.4	-0.3	-0.3	0.0	-0.3	-0.2	-0.4	-0.1	-0.4	-0.5	-0.4	-0.4
SP4	0.0	-0.2	0.0	-0.6	-0.3	0.1	0.4	0.0	0.0	-0.2	0.3	-0.2	-0.2	-0.4	0.3	-0.3	0.4	0.1	0.1	-0.3	-0.3	-0.1	-0.5
SP5	-0.1	-0.3	-0.2	-0.1	-0.3	0.2	0.5	0.0	0.0	-0.2	0.2	-0.3	0.0	-0.4	0.0	-0.3	0.0	-0.2	0.1	-0.3	-0.5	-0.2	-0.3
SP6	0.1	-0.3	0.1	-0.6	-0.4	0.2	0.5	-0.1	-0.1	-0.2	0.9	0.0	-0.1	-0.2	0.7	-0.2	0.5	0.0	0.3	-0.2	-0.1	0.0	-0.6
SP7	-0.2	-0.4	-0.5	-0.6	-0.5	0.6	0.3	-0.2	-0.2	-0.1	0.1	-0.1	0.0	-0.3	0.8	-0.4	-0.6	-0.3	0.0	-0.3	-0.6	-0.4	-0.6
SP8	0.1	-0.2	-0.5	-0.6	-0.4	0.0	0.5	0.0	-0.2	-0.1	0.5	0.0	-0.2	-0.3	0.8	-0.3	-0.3	-0.1	0.1	-0.2	-0.2	-0.5	-0.5
SP9	-0.1	-0.4	-0.6	-0.9	-0.6	-0.3	0.3	-0.2	-0.3	-0.3	-0.1	-0.3	-0.3	-0.4	0.3	-0.4	-0.5	-0.3	0.1	-0.3	-0.6	-0.7	-0.8
SP10	-0.1	-0.4	-0.5	-0.1	-0.4	0.6	0.3	-0.2	-0.2	-0.3	0.1	-0.2	0.0	-0.4	1.0	-0.3	-0.4	-0.4	0.1	-0.4	-0.3	-0.4	-0.2
SP11	-0.1	-0.5	-0.6	-0.7	-0.6	-0.1	0.0	-0.3	-0.3	-0.4	0.2	-0.2	-0.2	-0.4	0.8	-0.3	-0.7	-0.2	0.0	-0.3	-0.4	-0.5	-0.6
SP12	-0.1	-0.5	-0.5	-0.3	-0.6	0.0	-0.2	-0.3	-0.4	-0.4	0.1	-0.1	-0.3	-0.4	0.6	-0.3	0.1	0.1	0.1	-0.4	-0.4	-0.5	-0.4
SP13	-0.2	-0.6	-0.7	-0.4	-0.4	0.3	0.1	-0.3	-0.4	-0.4	0.9	-0.1	-0.2	-0.4	1.5	-0.4	-0.3	-0.4	0.0	-0.4	0.2	-0.2	-0.3
SP14	-0.3	-0.6	-0.6	-0.3	-0.6	0.2	-0.1	-0.4	-0.4	-0.5	0.1	-0.2	-0.2	-0.4	0.5	-0.4	-0.6	-0.3	0.2	-0.4	-0.5	-0.5	-0.2
SP15	-0.2	-0.5	-0.3	0.2	-0.2	0.7	-0.2	-0.2	-0.3	-0.1	0.5	0.0	0.0	-0.4	1.2	-0.2	0.2	0.1	0.5	-0.4	0.8	0.3	0.1
SP16	-0.3	-0.6	-0.5	0.3	-0.5	0.8	-0.2	-0.3	-0.3	-0.2	0.3	0.1	-0.1	-0.4	1.3	-0.1	0.5	-0.3	0.4	-0.4	0.8	-0.2	0.2
SP17	-0.1	-0.5	-0.6	-0.4	-0.6	0.1	-0.2	-0.2	-0.4	-0.3	0.7	-0.1	-0.2	-0.4	0.9	-0.3	-0.4	-0.1	0.3	-0.3	-0.2	-0.4	-0.4
SP18	-0.2	-0.6	-0.7	-0.6	-0.7	-0.1	-0.6	-0.4	-0.5	-0.4	0.3	-0.2	-0.1	-0.4	0.8	-0.4	-0.3	-0.2	0.0	-0.3	-0.2	-0.6	-0.5
SP19	-0.1	-0.6	-0.7	-0.5	-0.6	0.3	-0.7	-0.4	-0.5	-0.4	0.1	-0.4	-0.2	-0.4	1.8	-0.2	0.2	-0.3	0.1	-0.4	-0.5	-0.4	-0.5
SP20	0.0	-0.4	-0.4	-0.3	-0.5	1.1	-0.5	-0.3	-0.4	-0.4	0.8	-0.2	-0.1	-0.4	0.9	-0.2	-0.5	-0.1	0.2	-0.3	-0.6	-0.3	-0.4
SP21	0.0	-0.4	-0.6	-0.1	-0.5	0.4	-0.4	-0.2	-0.4	0.1	0.1	-0.5	-0.3	-0.3	0.8	-0.5	-0.6	-0.3	0.0	-0.4	-0.8	-0.5	-0.2
SP22	-0.2	-0.4	0.4	0.5	0.2	1.0	0.0	-0.1	-0.1	-0.4	-0.5	-0.5	0.0	-0.2	0.4	-0.2	1.7	0.1	0.2	-0.1	-0.6	0.5	0.1

*Yellow highlighted – moderately polluted

1 Table S7: Comparison of metal concentration with Australia and New Zealand Interim Sediment
 2 Quality Guidelines

	As	Ag	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn
Australian ISQG-L	20	1	1.5	80	65	0.15	21	50	2	200
Australian ISQG-H	70	3.7	10	370	270	1	52	220	25	410
SP1	9.1	0.5	0.7	112.9*	110.2*	1.0*	25.4*	53.5*	0.9	174.7
SP2	10.8	0.5	0.6	175.3*	69.8*	1.1**	30.3*	56.4*	0.9	226.2*
SP3	8.9	0.5	0.7	117.5*	48.7	1.0*	21.9*	32.6	0.8	156.0
SP4	10.2	0.7	0.7	129.5*	44.0	1.2**	27.3*	40.7	1.2	191.5
SP5	12.7	0.5	0.7	131.8*	37.7	1.1**	27.4*	32.7	0.8	181.6
SP6	11.1	1.0	0.8	137.3*	77.9*	1.4**	26.1*	48.6	1.0	244.2*
SP7	12.7	1.1*	0.7	208.3*	34.4	1.1**	28.9*	31.3	0.8	207.8*
SP8	10.6	1.2*	0.7	116.7*	53.2	1.2**	29.5*	46.5	1.0	227.2*
SP9	9.5	0.7	0.6	81.5*	28.4	1.2**	23.8*	31.4	0.8	176.9
SP10	12.0	1.4*	0.7	214.7*	34.2	1.2**	23.3*	40.9	0.7	193.6
SP11	10.4	1.1*	0.7	105.1*	38.1	1.1**	21.9*	38.8	0.9	195.0
SP12	9.5	0.9	0.7	113.3*	35.4	1.2**	21.0	38.0	1.1	206.3*
SP13	9.7	2.3*	0.6	153.8*	75.4*	1.1**	21.8*	64.6*	0.8	205.1*
SP14	10.3	0.9	0.6	134.3*	34.6	1.3**	20.1	33.7	0.8	186.3
SP15	12.2	1.6*	0.8	234.5*	53.2	1.8**	28.4*	119.2*	1.1	228.9*
SP16	10.9	1.8*	0.9	260.5*	45.2	1.6**	27.2*	125.8*	0.8	257.1*
SP17	10.4	1.2*	0.7	119.4*	62.7	1.4**	23.3*	43.4	0.9	210.9*
SP18	11.5	1.1*	0.6	100.7*	44.5	1.1**	21.4*	47.4	0.9	200.6*
SP19	9.9	2.9*	0.8	153.6*	36.7	1.2**	20.8	32.4	0.8	158.4
SP20	10.9	1.2*	0.8	332.4*	73.7*	1.2**	20.9	31.6	1.0	202.6*
SP21	9.5	1.1*	0.6	162.5*	34.2	1.1**	34.4*	25.2	0.8	145.4
SP22	12.8	0.7	0.8	314.7*	19.8	1.3**	20.9	29.8	1.2	141.8

3 *Exceeded Australian ISQG-L

4 **Exceeded Australian ISQG-H

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14 Table S8: Potential Ecological Risk Indices for heavy metals computed using contamination
 15 factor.

Tr^i	Er^i													RI
	Ag 50 ^a	As 10 ^b	Cd 30 ^b	Co 5 ^a	Cr 2 ^b	Cu 5 ^b	Hg 40 ^b	Ni 5 ^c	Sb 5 ^a	Sn 5 ^a	V 5 ^a	Zn 1 ^b	Pb 5 ^b	
SP1	77*	11	32	7	3	26	57*	6	6	4	6	1	7	243
SP2	76*	13	30	8	5	16	62*	7	6	7	6	1	8	247
SP3	75*	11	33	6	3	11	57*	5	5	6	4	1	4	223
SP4	99**	12	32	7	3	10	70*	7	9	11	6	1	5	273
SP5	75*	15	33	8	3	9	65*	7	6	8	6	1	4	239
SP6	152**	13	37	7	4	18	78*	6	7	12	5	2	7	348
SP7	164***	15	32	6	6	8	62*	7	6	4	5	1	4	320
SP8	175***	13	34	6	3	12	67*	7	7	5	5	1	6	343
SP9	101**	11	30	6	2	7	69*	6	6	4	4	1	4	251
SP10	214***	15	32	6	6	8	67*	5	5	5	5	1	6	376
SP11	159**	13	33	5	3	9	62*	5	6	4	4	1	5	309
SP12	133**	12	34	5	3	8	66*	5	8	9	4	1	5	293
SP13	351 [#]	12	30	5	4	18	61*	5	5	6	5	1	9	512
SP14	129**	12	31	5	4	8	72*	5	5	4	4	1	5	286
SP15	241***	15	37	6	6	12	102**	7	8	9	6	1	16	467
SP16	275***	13	42*	6	7	11	89**	7	6	12	4	2	17	490
SP17	184***	13	32	5	3	15	82**	5	7	5	4	1	6	362
SP18	159**	14	31	5	3	10	61*	5	6	5	4	1	6	310
SP19	433 [#]	12	36	5	4	9	67*	5	6	9	4	1	4	595
SP20	180***	13	37	5	9	17	71*	5	7	5	5	1	4	359
SP21	172***	11	28	5	4	8	62*	9	6	4	5	1	3	318
SP22	108**	16	38	7	8	5	76*	5	9	39	9	1	4	324

16 *40 < Er^i < 80 Moderate risk

17 ** 80 < Er^i < 160 Considerable risk

18 *** 160 < Er^i < 320 High risk

19 [#] Er^i > 320 Very high risk

20 ^a Aksu, 1998

21 ^b Hakanson, 1980

22 ^c Jiao et al., 2015

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27 Table S9: Potential Ecological Risk Indices for heavy metals computed using enrichment
 28 factor.

Tr^i	Er^i													MRI
	Ag 50 ^a	As 10 ^b	Cd 30 ^b	Co 5 ^a	Cr 2 ^b	Cu 5 ^b	Hg 40 ^b	Ni 6 ^c	Sb 5 ^a	Sn 5 ^a	V 5 ^a	Zn 1 ^b	Pb 5 ^b	
SP1	80**	11	33	7	3	27	60*	6	7	4	6	1	8	252
SP2	65*	11	27	7	4	14	52*	6	6	6	6	1	7	210
SP3	80**	11	36	6	3	12	60*	6	6	7	5	1	5	236
SP4	90**	11	27	7	3	9	64*	6	8	10	5	1	5	244
SP5	65*	14	30	7	3	8	60*	6	6	7	5	1	4	215
SP6	140**	12	33	6	3	17	72*	6	7	11	5	1	6	318
SP7	170***	16	33	6	6	9	64*	7	6	5	5	1	5	332
SP8	150**	11	30	6	3	11	56*	6	6	5	5	1	6	293
SP9	110**	13	33	6	2	8	76*	6	6	5	5	1	5	275
SP10	225***	15	33	7	6	9	72*	6	6	6	6	1	6	395
SP11	180***	14	36	6	3	10	68*	6	7	5	5	1	6	346
SP12	150**	13	39	6	3	10	76*	6	9	10	5	2	6	333
SP13	430#	14	36	7	5	22	76*	6	7	7	6	2	11	627
SP14	165***	16	39	7	5	11	92**	6	7	6	6	2	6	365
SP15	270***	17	42*	7	7	14	116**	8	9	10	7	2	18	526
SP16	365#	17	57*	8	9	14	120**	9	8	16	6	2	23	653
SP17	210***	14	36	6	4	17	92**	6	8	6	5	2	7	410
SP18	200***	17	39	6	3	13	76*	6	8	7	5	2	8	389
SP19	545#	15	45*	6	5	11	84**	6	7	12	5	1	6	748
SP20	185***	13	39	5	9	18	72*	5	7	5	5	1	5	368
SP21	185***	12	30	6	5	9	68*	9	6	5	5	1	4	345
SP22	110**	16	39	8	9	5	80**	5	9	41	9	1	4	335

29 *40 < Er^i < 80 Moderate risk

30 ** 80 < Er^i < 160 Considerable risk

31 *** 160 < Er^i < 320 High risk

32 # Er^i > 320 Very high risk

33 ^a Aksu, 1998

34 ^b Hakanson, 1980

35 ^c Jiao et al., 2015

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40 Table S10: Potential Ecological Risk Indices of heavy metals computed at a site for different
 41 sampling periods.

Site	<i>RI</i>				<i>MRI</i>			
	June, 2014	September, 2014	December, 2014	May, 2015	June, 2014	September, 2014	December, 2014	May, 2015
SP1	213.8	201.3	225.3	224.0	221.7	208.8	233.6	232.3
SP2	195.2	189.5	205.3	205.0	166.0	161.1	174.6	174.3
SP3	236.3	236.2	314.6	297.8	250.1	250.0	332.9	315.2
SP4	195.5	204.1	219.8	213.9	174.7	182.4	196.4	191.2
SP5	193.4	200.0	201.5	195.9	174.0	180.0	181.3	176.3
SP6	319.0	294.3	329.6	321.3	291.5	269.0	301.2	293.6
SP7	331.6	314.4	402.5	350.0	344.1	326.2	417.6	363.1
SP8	315.6	304.0	384.1	368.3	269.6	259.7	328.1	314.6
SP9	288.9	281.6	383.0	379.8	316.5	308.5	419.6	416.2
SP10	382.4	375.1	531.3	455.8	401.8	394.1	558.1	478.8
SP11	322.9	266.1	354.6	346.0	361.5	297.9	397.1	387.4
SP12	286.3	245.7	299.2	340.8	325.4	279.2	340.0	387.3
SP13	497.1	477.0	543.2	530.7	608.7	584.1	665.2	650.0
SP14	278.7	272.8	308.7	283.8	355.7	348.2	394.0	362.2
SP15	455.0	446.3	491.7	474.9	512.5	502.7	553.8	534.9
SP16	413.9	354.7	679.5	511.9	551.6	472.6	905.5	682.2
SP17	314.0	299.0	420.4	414.6	355.6	338.6	476.2	469.6
SP18	317.3	297.7	315.6	309.4	398.2	373.5	396.1	388.2
SP19	562.2	444.9	751.3	621.6	706.7	559.3	944.5	781.4
SP20	358.9	315.2	399.9	362.1	367.9	323.1	409.9	371.2
SP21	300.8	290.7	371.8	308.7	326.4	315.4	403.4	334.9
SP22	206.9	153.9	535.9	399.3	213.9	159.2	554.1	412.8

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