Development of a hybrid pollution index for heavy metals in marine and estuarine sediments

James P Brady[1], Godwin A Ayoko*[1], Wayde N Martens[1] and Ashantha Goonetilleke[1]

[1]Queensland University of Technology, Science and Engineering Faculty, GPO Box 2434, Brisbane, QLD, 4001, Australia

*Correspondence to: g.ayoko@qut.edu.au; phone: 61 07 3138 2586

Abstract

Heavy metal pollution of sediments is a growing concern in most parts of the world, and numerous studies focussed on identifying contaminated sediments by using a range of digestion methods and pollution indices to estimate sediment contamination have been described in the literature. The current work provides a critical review of the more commonly used sediment digestion methods and identifies that weak acid digestion is more likely to provide guidance on elements that are likely to be bioavailable than other traditional methods of digestion. This work also reviews common pollution indices and identifies the Nemerow Pollution Index as the most appropriate method for establishing overall sediment quality. Consequently, a modified Pollution Index that can lead to a more reliable understanding of whole sediment quality is proposed. This modified pollution index is then tested against a number of existing studies and demonstrated to give a reliable and rapid estimate of sediment contamination and quality.

Keywords

Pollution index; Nemerow Pollution Index; bioavailability assessment; heavy metals; sediment contamination; modified pollution index

1.0 Introduction

Heavy metal contamination is of growing concern around the world, particularly in South East Asia where stringent regulation of pollution emission is emerging or naturally high concentrations of heavy metals can be found in groundwaters (Karim, 2000; Mandal et al., 1996; Smedley, 2003; Welch & Stollenwerk, 2003). Due to this growing concern, numerous studies that examined heavy metal contamination in marine and estuarine environments have been published in recent years (Abrahim & Parker, 2008; Birch & Taylor, 1999; Dung, Cappuyns, Swennen, & Phung, 2013; Gao et al., 1998; Kaushik, Kansal, Kumari, & Kaushik, 2009; Pengthamkeerati et al., 2013; Tang, Shan, Zhang, & Mao, 2010; Thuong, Yoneda, Ikegami, & Takakura, 2013). Many of these studies have also been driven by the fact that toxic heavy metals (such as Hg, Cd and As) are non-essential to the human body (Toffaletti, 2005) (Table 1) and their presence in the body can interfere with human biochemistry (Gaw, Cowan, O'Reilly, Stewart, & Shepherd, 1999; Pier & Bang, 1980; Toffaletti, 2005).

Table 1. Table of selected trace metals and their importance to good human health, adapted from (Toffaletti, 2005)

	Toxic Metals	**Probably Essential**	**Proven Essential**
Trace ($mg\ kg^{-1}$)			Fe, Zn, Cu
Ultratrace ($\mu g kg^{-1}$)	As, Cd, Au, Pb, Hg, Si	Ni, V, Sb	Mn, Co, Se, Mo, Cr

Although it is widely recognised that heavy metals are an ambiguous group of metals and metalloids, there is still a significant lack of consensus about the definition and the exact membership of this group of elements. Consequently, a number of reviews have set out to define heavy metals in different ways (Bhat & Khan, 2011). Because of this lack of consensus about the definition of heavy metals, they will be defined in this paper as: *any metal (or its ion), emitted from any source, that has been shown to have either a negative ecological impact or negative impact on human wellbeing and will typically have its release into the environment controlled by either agreement or legislation.* One advantage of this definition is that it covers most metals that could be considered members of the heavy metals group.

The sources of heavy metals in the environment have been broadly accepted to be either lithogenic (natural in origin) or anthropogenic (a product of human activity). Thus, in an urban environment, the major sources of anthropogenic pollution are industrial discharges (Ahdy & Youssef, 2011; De Wolf, Backeljau, & Blust, 2000; Liu, Zhao, Ouyang, Söderlund, & Liu, 2005; Mitra, Chowdhury, & Banerjee, 2012; Suh, Birch, Hughes, & Matthai, 2004; Tang, et al., 2010); storm water runoff (Birch & Taylor, 1999; Mitra, et al., 2012) and vehicle emissions (Ahdy & Youssef, 2011; Kim, Myung, Ahn, & Chon, 1998; Li, Poon, & Liu, 2001;

Suh, et al., 2004; Wright & Mason, 1999) while lithogenic sources include geological weathering due to exposure to water (Ahdy & Youssef, 2011; Kim, et al., 1998; Wilber & Hunter, 1979); volcanic activity (Ahdy & Youssef, 2011); decomposition of plant and animal remains (Ahdy & Youssef, 2011; Wilber & Hunter, 1979; Wright & Mason, 1999). The main mechanisms of deposition of heavy metals into marine environments can be distilled to point source deposition, such as stormwater drains (Birch & Taylor, 1999; Wilber & Hunter, 1979), discharge from wastewaters (Deng, Zhang, Wang, Chen, & Xu, 2010; Singh, Müller, & Singh, 2002; Sörme & Lagerkvist, 2002; Suh, et al., 2004; Tang, et al., 2010; Wright & Mason, 1999) , leachates from landfills (Ahdy & Youssef, 2011; Deng, Zheng, Fu, Lei, & Li, 2010; Wright & Mason, 1999) and direct discharge from industry sources (Ahdy & Youssef, 2011; Dinescu et al., 2004; Mitra, et al., 2012; Romic & Romic, 2003; Suh, et al., 2004; Tang, et al., 2010). Atmospheric deposition (such as dust fall and precipitation) is the other major mechanism of heavy metal enrichment (Dinescu, et al., 2004; González-Fernández, Garrido-Pérez, Nebot-Sanz, & Sales-Márquez, 2011; Gunawardena, Egodawatta, Ayoko, & Goonetilleke, 2012, 2013; Romic & Romic, 2003; Tang, et al., 2010; Wilber & Hunter, 1979; Wright & Mason, 1999). This deposition of heavy metals into marine sediments has resulted in an increase in interest on how heavy metals (and other pollutants) interact with sediments.

1.1 Heavy metals and their fate in sediments

Heavy metals undergo a number of complex interactions with sediments (Fig. 1) before being sequestered into cohesive sediments (Grecco et al., 2011; Shilla & Dativa, 2011). This sequestration may be useful in limiting long term impacts of heavy metals on marine environments (Ahdy & Youssef, 2011), but partitioning effects result in higher concentrations of heavy metals in the sediment than the accompanying water column (González-Fernández, et al., 2011), which in turn leads to increased risk of inclusion into the food chain through benthic organisms.

Another long term risk of sequestration of heavy metals into sediments is that long residence times (Imperato et al., 2003) and biogeochemical recycling processes (Liu et al., 2003) can allow for re-suspension and re-entry into the biosphere long after the source has been removed (Keskin, 2012; Williamson & Morrisey, 2000) (Fig 1).

Re-suspension of sediments in estuarine environments is of concern as estuarine systems have been demonstrated to show non-conservative sedimentary behaviour such as dilution (Chapman & Wang, 2001) and there is significant evidence that fine clay particles act as adsorption sites for heavy metal ions (Gómez-Parra, Forja, DelValls, Sáenz, & Riba, 2000). Once adsorbed to fine clay particles, heavy metal ion behaviour is then controlled by the chemical and physical properties of the water column in which they are dispersed .

The major physical properties that control the dispersion and dilution of heavy metals in estuarine environments include biotic assimilation and excretion (Chapman & Wang, 2001; Romic & Romic, 2003) and inclusion into the food chain (Romic & Romic, 2003) which subsequently results in bioaccumulation and toxicity. One important controlling factor of

biotic accumulation and excretion is the impact of microbial activity (Liu et al., 2011), which can enhance bioavailability and promote bioaccumulation. Dilution of heavy metals in marine estuarine environments is a vital link in the sequestration of heavy metals in sediments. This is because many heavy metals adsorb to clay particles (<63 µm) (Binning & Baird, 2001; Tam & Wong, 2000; Wilber & Hunter, 1979), with a strong correlation between decreasing particle size (increased surface area) and increasing adsorption (Riba, DelValls, Forja, & Gómez-Parra, 2002). Assuming that there are no changes to the conditions under which sedimentation occurred, these particles settle in areas of low flow energy (Grecco, et al., 2011). In addition to sorption to fine clay particles, organic carbon content distribution affects heavy metals distribution (Baptista Neto, Smith, & McAllister, 2000).

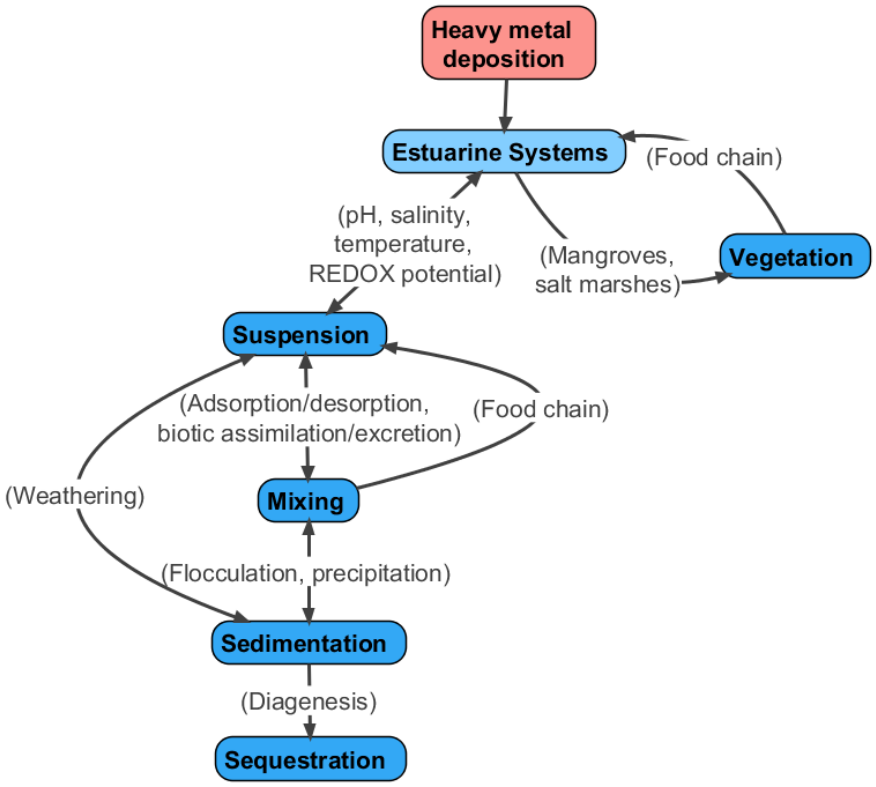

Fig. 1 Fate of metals in marine and estuarine environments

The widely accepted explanation for the correlation of heavy metal concentrations with organic carbon is chelation by organic matter to immobilise heavy metals before flocculation and precipitation (Kumar et al., 2010; Shilla & Dativa, 2011). In addition to the chelation effect of organic matter, scavenging of heavy metal ions by clay minerals is dependent on the adsorption of heavy metal ions to iron and manganese hydroxides and oxides, whose areas of negative dipoles provide active sorption sites for heavy metal ions (Singh, et al., 2002; Wilber & Hunter, 1979).

Chemical factors controlling the sequestration of heavy metals in estuarine environments include chemical properties of the water body, such as pH, temperature, salinity and redox potential of the system (Che, He, & Lin, 2003). These factors can have major effects on

processes such as adsorption and desorption (Chapman & Wang, 2001), as well as chelation, coagulation, flocculation; precipitation and sedimentation (Chapman & Wang, 2001; Che, et al., 2003; Liu, et al., 2011).

1.2 Methods of assessing the availability of heavy metals in contaminated sediments

A method for extracting the concentrations of the elements of interest is required before a sediment quality index to a sample (or set of samples) can be applied. There are a number of methods for determining the concentrations of heavy metals in sediment samples which cover a range of techniques and objectives.

The first method for determining heavy metal concentrations is to measure the total metal concentrations. This can be done in a number of ways, ranging from aqua regia digestions (the use of a hot solution of nitric acid and hydrochloric acid at 90 °C to solubilise elements not in the silicate lattice of minerals) to hydrofluoric and hydrofluoric/peroxide/hypochloric acid digestions at elevated temperatures to break down the silicate crystal lattice and accurately determine the total metal concentrations (Baptista Neto, et al., 2000; Cox & Preda, 2005; Jones & Turki, 1997; Martin, Nirel, & Thomas, 1987; Preda & Cox, 2001; Preda & Cox, 2002) and the use of microwave extraction methods (Tam & Wong, 2000).

The use of acids such as aqua regia, hydrofluoric acid and strong oxidising agents such as hydrogen peroxide to extract metals from sediment samples is limited by their abilities to break down the silicate lattice and the risk factors of using such harsh chemical methods. One method that can be used to obtain the trace metal concentrations without the use of harsh chemical extraction techniques is to use X-ray fluorescence (XRF), which is a non-destructive analytical method that relies on characteristic X-rays emitted by elements when they are excited by X-ray radiation.

X-ray fluorescence has advantages over other chemical techniques. However, the use of total metal concentrations to evaluate sediment quality is a simplistic and unrealistic method of determining bioavailable metals concentrations (Ahdy & Youssef, 2011; Lee, Kang, Jo, & Choi, 2012; Shikazono, Tatewaki, Mohiuddin, Nakano, & Zakir, 2012; Shilla & Dativa, 2011) as they do not take into consideration potential toxicity or environmental impact (Beltrán, de la Rosa, Santos, Beltrán, & Gómez-Ariza, 2010).

The major limitation in the use of total metal concentrations is that this method does not take into account the fact that heavy metals, such as chromium, may only be toxic in certain chemical forms (Zhong, Zhou, Zhu, & Zhao, 2011). Because of this limitation, it is important to identify not only what metals are present in sediments, but also the chemical species in which they are present, in order to develop an accurate understanding of the impact that they have on the sediments (Sundaray, Nayak, Lin, & Bhatta, 2011; Zhong, et al., 2011).

A number of sequential extraction methods are available to identify the sediment fraction that metals are present in (Chapman & Wang, 2001). The most commonly used method is that developed by Tessier, Cambell and Bisson (Tessier, Campbell, & Bisson, 1979) (commonly

referred to as Tessier's method) and then adapted by others (Albores, Cid, Gomez, & Lopez, 2000; Ruiz, 2001). Many of these modified Tessier methods examine fractions such as the weakly-bound acid-soluble fractions (the chlorides and carbonates), the REDOX available fractions (the reductive and oxidative fractions) and the residual fraction (the mineral lattice).

Tessier's method, (Tessier, et al., 1979) examines five fractions to assess the overall sediment concentrations of heavy metals. This method is reliable because it examines the different fractions of sediment that can contain heavy metals and extract the heavy metals from each fraction separately, allowing the development of an accurate picture of the heavy metals loadings in a sediment sample.

Although the Tessier, Campbell and Bisson method has become the most widely used method for sequential extractions for heavy metals in sediments, there are a number of criticisms that have been noted with the underlying chemical approaches. For example, the extraction of the exchangeable metals (those bound to clay particles) uses magnesium chloride and has been noted to be susceptible to changes in the ionic strength of the extractant. This can be disrupted by re-adsorption of heavy metal ions to clay particles during the extraction or the precipitation of heavy metals as oxides and hydroxides if the solution is too alkaline (Martin, et al., 1987).

The oxide fraction is the last of the common anthropogenic sources of heavy metals identified by Tessier *et al.* (Tessier, et al., 1979) and this extraction step relies on reduction at elevated temperatures to reduce the heavy metals from oxides and hydroxides to their ionic forms. A major limitation of this step is that this reduction also solubilises the manganese and iron hydroxides that are naturally occurring in clays and this can lead to the erroneous conclusion that these elements have an anthropogenic source. It has been suggested that it would be appropriate to perform the reducible extraction in two steps; the reducible and moderately reducible to resolve this issue (Martin, et al., 1987).

The major issue with using a sequential extraction method is that it does not necessarily identify the bioavailable heavy metals in a sample. A number of other options exist. Among these, the use of dilute hydrochloric acid to both desorb (via ion exchange) and break down metal carbonate has been suggested for rapidly identifying the bioavailable heavy metals present in a sample (Hu, Yu, Zhao, & Chen, 2011). The use of a such a simple method for the determination of heavy metals has merit as it examines the heavy metals that are available in the chloride (or adsorbed) phase, the carbonate phase and those elements that are weakly-bound (or reactive) to hydroxides. These elements are considered to be the most likely to react to changes in water conditions.

Another available method for the estimation of bioavailability is the determination of simultaneous extractable metals -acid volatile sulphides (SEM-AVS) (Casas & Crecelius, 1994; De Jonge, Blust, & Bervoets, 2010; Di Toro et al., 1992; Di Toro et al., 1990). These methods rely on identifying what metals can be extracted from a sediment using weak acid digestion (typically 1 M HCl) and then determining which metal sulphides are less soluble

than iron sulphide. The major advantage of using these methods is that they allow the determination of metals that are not precipitated as sulphides and are therefore bioavailable. It is noteworthy that the current Australian sediment quality guidelines (Simpson et al., 2005) use sequentially extractable metals -acid volatile sulphides as one of the methods for determining sediment quality.

Generally, small benthic organisms are used to examine the bioavailability and toxicity of heavy metals to organisms (Bryan, 1971; Ofiara & Seneca, 2006). Several studies have used biotic indicators as water body and sediment quality indicators (Abal & Dennison, 1996; Jones, O'Donohue, Udy, & Dennison, 2001; Ofiara & Seneca, 2006; Pantus & Dennison, 2005; Park et al., 2010; Riosmena-Rodríguez, Talavera-Sáenz, Acosta-Vargas, & Gardner, 2010). The use of biological monitoring has also been identified in the Australian sediment quality guidelines as a useful tool for the determination of heavy metals contamination (Simpson, et al., 2005) through the use of benthic organisms. The major advantage of bioavailability testing is that it assesses the metals that are available to benthic organisms and are therefore available to the rest of the food chain (Abdolahpur Monikh, Maryamabadi, Savari, & Ghanemi, 2013; Ali, Elazein, & Alian, 2011; Blasco, Arias, & Sáenz, 1999; Park, et al., 2010; Soto, Kortabitarte, & Marigomez, 1995). However, the major disadvantages of the use of benthic organisms for sediment quality monitoring include the facts that the testing takes time as the organisms need to be cultivated, and some benthic organisms adapt to high concentrations of some metals better than other species, which can lead to an inaccurate assessment of sediment toxicity.

1.3 Methods for assessing heavy metal contamination

A large number of single and multi-element methods are available for assessing heavy metal contamination in sediments. These indices generally strive to provide a qualification of contamination rather than a quantification of contamination due to a number of factors. The most important factor is that it is generally very difficult to determine what the original composition of the sediment was in terms of the elements of interest, unless historical data is available and this tends not to be the case. Also of concern is that if there is no historical data, then there is a requirement for an analogue of non-contaminated sediment. This implies sampling from a site outside of the contaminated area. This raises issues of accounting for sedimentary and lithogenic inputs of heavy metals.

Several studies have identified the average crustal elemental composition for continents (de Caritat & Cooper, 2011; Gao, et al., 1998; Hans Wedepohl, 1995) as well as the average composition of specific sedimentary rocks, such as shales (Dung, et al., 2013). Such studies effectively provide an analogue of unpolluted and historical sediments, although these analogues are not specific to the catchment of interest, which is a limitation.

Single and multiple element contamination indices can be used to qualify the quality of marine sediments. The simplest and most direct method of qualifying sediment quality is to

use a contamination factor (Equation 1), which provides a ratio between an element at the sampling site and the same element at a background site (some examples are listed later).

$$CF = \frac{C_{site}}{C_{Background}} \quad (1)$$

Although the contamination factor is easily determined and provides information about how an element has been concentrated between the site of interest and a background site, it does not take into consideration lithogenic and sedimentary inputs of the element of interest. This could be a source of error when estuarine environments are considered, as they are areas of intense sedimentation with significant input from terrestrial waterways.

Geoaccumulation indices (Equation 2) were proposed by Muller (1969) in describing metal accumulation in the sediments of the Danube River. To minimise the impact of lithogenic enrichment and enrichment caused by sediment inputs from multiple sources, the background concentration of the element of interest is multiplied by 1.5. The primary advantage of geoaccumulation indices in the qualification of sediments is that Muller (1969) identified six classes of contamination in sediments (Table 2) which can be used to qualify the contamination of an index by any particular element.

$$I_{geo} = log\left(\frac{C_x}{1.5 \times B_x}\right) \quad (2)$$

Table 2. Sediment quality thresholds for the geoaccumulation index, enrichment factors and Hakanson's modified degree of contamination indices

Class	**Qualification of sediment**	**I_{geo}**[a] (Muller, 1969)	**EF Value**[b] (Qingjie, Jun, Yunchuan, Qingfei, & Liqiang, 2008)	**mC_d Value**[c] (Hakanson, 1980)
0	Unpolluted	≤ 0	EF < 1	$mC_d < 1.5$
1	Slightly polluted	0-1	1 < EF < 3	$1.5 < mC_d < 2$
2	Moderately polluted	1-2	3 < EF < 5	$2 < mC_d < 4$
3	From moderately polluted to strongly polluted	2-3	5 < EF < 10	$4 < mC_d < 8$
4	Strongly polluted	3-4	10 < EF < 25	$8 < mC_d < 16$
5	From strongly polluted to extremely polluted	4-5	25 < EF < 50	$16 < mC_d < 32$
6	Extremely polluted	≥ 5	EF > 50	$mC_d > 32$

[a]Equation 2
[b]Equation 3
[c]Equation 4

Geoaccumulation indices are logarithmic, and this implies that they would be best used to qualify sediments that have significant enrichment due to major urbanisation or industrialisation; this in turn reduces their sensitivity to minor contamination. In addition, the

multiplication of the background concentration of the element of interest by a factor of 1.5 appears to be arbitrary and does not take into account situations where a large number of sediments interact in a complex manner (such as in estuarine environments) and the processes that may be occurring (some examples will be given later).

In order to negate the effect of terrestrial sedimentary input, it is possible to use Enrichment Factors (Equation 3) to standardise the impact of terrestrial inputs by normalising the element of interest against an element that has no anthropogenic source, such as aluminium (Qingjie, et al., 2008).

$$EF = \frac{\left(\frac{C_x}{C_{ref}}\right)_{Sample}}{\left(\frac{C_x}{C_{ref}}\right)_{Background}} \quad (3)$$

The advantage provided by normalisation against an element is that non-conservative sediment behaviour (such as concentration rather than dilution) is accounted for by the ratio of the element of interest against the normalising element. Normalisation using an element that has no anthropogenic source or is present in high enough concentrations that anthropogenic sources have little effect is that natural variations in the sediment are minimised, resulting in the enrichment factors ideally identifying anthropogenic pollution sources.

Enrichment Factors can be used to qualify sediment quality (Table 2) and it is generally accepted that an Enrichment Factor greater than one indicates an anthropogenic source of the element of interest (Çevik, Göksu, Derici, & Fındık, 2009).

Although Enrichment Factors, have found significant use in the past for assessing sediment contamination (Çevik, et al., 2009; Kaushik, et al., 2009; Pengthamkeerati, et al., 2013; Qingjie, et al., 2008; Thuong, et al., 2013), they can be limited by the choice of the normalising element. For example, aluminium is often used as a normalising element as it is recognised as an element without an anthropogenic source (Qingjie, et al., 2008). The use of aluminium in urban and industrial areas has the potential to be misleading as acidification of soils from anthropogenic sources has been linked to mobilised aluminium (Driscoll et al., 2001). However, the chemistry of aluminium in the environment is poorly understood, with little work available on the environmental behaviour and toxicity of anthropogenic aluminium (Klöppel, Fliedner, & Kördel, 1997; Krewski et al., 2007).

Sediments that are naturally aluminium poor, such as sands (which are essentially silicates) can result in elevated Enrichment Factors when compared against terrestrial sediment sources. The same issues can be encountered with iron (Fe), which is a major clay element that may be significantly enriched or depleted due to sediment sources and industrial contamination. A similar argument can be made for other major sediment elements (Qingjie,

et al., 2008) such as manganese (Mn), titanium (Ti) and Vanadium (V). Silicon is not a viable normalising element due to the stable nature of the silicate lattice of many minerals and the difficulty in dissolving the silicate lattice using extreme acid digestions (such as HF). In addition, the large variability in the silicon concentration of sediments can also be a limiting factor.

The high variability of sediments can also be a limiting factor in using trace elements to normalise heavy metal concentrations and calculating Enrichment Factors. For example, tantalum (Ta) and other ultra-trace metals have been considered as normalising elements in calculating Enrichment Factors (Pengthamkeerati, et al., 2013; Thuong, et al., 2013). However, they are not widely used because the use of normalising elements is dependent on estuarine sediments exhibiting conservative behaviour (such as simple dilution), which may not always be the case as re-suspension of sediment can occur (Chapman & Wang, 2001).

Although a number of single element pollution indices are available, there are a number of limitations to their use. The most obvious limitation is that they are only applicable to a single element, which means that they do not take into consideration the complex nature of heavy metal contamination in urban and industrial environments, where a number of contaminants are present together. There are also issues in accounting for the background concentrations and the complex, non-conservative behaviour of sediments.

Limitations with single element pollution indices have led to the development of multiple element indices which have been presented in the research literature to assess sediment quality. The two most common multiple element indices are the modified contamination index developed by Hakanson (Hakanson, 1980) and more recently, the Nemerow Pollution Index (Nemerow, 1991), which is becoming more widely accepted.

Hakanson's modified degree of contamination index (mC_d) (Hakanson, 1980) uses a suite of elements to take a more integrated look at the contamination of a site by heavy metals (Equation 4). By using the contamination factors (CF, Equation 1) for individual sites and taking their average (dividing by the number of elements, n), it is possible to easily qualify the quality of sediment based on a number of elements (as evident in Table 3) (Abrahim & Parker, 2008).

$$mC_d = \frac{\sum_{i=1}^{n} Cf^i}{n} \quad (4)$$

Using a suite of elements is a good starting point for assessing the contamination of sediments. However, the modified degree of contamination index is slightly skewed when one element is heavily contaminated. This is because the contribution of one element is averaged over the suite of elements and the impact of this element is then reduced to the average impact of all of the elements across the sediment. An example would be the comprehensive contamination by an element such as mercury in sediment that is otherwise pristine. The sediment could be toxic to all organisms, but the mC_d index could indicate that the sediment has a low degree of contamination.

One approach to overcome the problems identified with the modified degree of contamination index is to use the Nemerow Pollution Index (PI) (Nemerow, 1991) to indicate the quality of sediment. The index is similar to the modified degree of contamination index in that it uses the average of the contamination factors (see Equation 1) ($CF_{average}$) of a suite of elements. However, it also takes into consideration the impact of contamination of one element by using the maximum contamination factor (CF_{max}) to develop a weighted average according to Equation 5. By using a weighted average, the Nemerow Pollution Index allows the qualification of sediment quality that is much more considerate of the effect of a single element.

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

The Nemerow Pollution Index also uses much lower trigger points (Table 3) than the modified degree of contamination index, with a value greater than 3 indicating that the sediment of interest is heavily contaminated.

The Nemerow Pollution Index has some disadvantages in that it uses contamination factors, which are limited by not accounting for the behaviour of sediments within estuaries and the possibilities of multiple sediment sources. However, the use of the Nemerow Pollution Index has been considered to be the most comprehensive method of assessing sediment quality. For this reason, the Nemerow Pollution Index has been increasingly used in recent years (Cheng, Shi, & Zhu, 2007; Guang, Jian, Yue, Caiyun, & Qing, 2010; He, Wang, & Tang, 1998; Jing, 2006; Mohammed, Loganathan, Kinsela, Vigneswaran, & Kandasamy, 2012; Nemerow, 1991; Qingjie, et al., 2008; Wen-qiang, 2008).

2.0 Developing a modified Pollution Index for use in estuarine and marine environments

Although the Nemerow Pollution Index has been increasingly used in recent years, there are some limitations relating to its use. The first limitation is that, compared to other pollution indices, the thresholds for the Nemerow Pollution Index trigger are very low, giving potential false positives for heavily contaminated sediments similar to the modified degree of contamination index (Equation 4), which can potentially result in over-reporting of contamination. The second limitation is the use of contamination factors (Equation 1) to determine the index. This does not consider the possibility that sediment behaviour is non-conservative in many estuarine environments.

Due to these limitations, an improved method for determining the Pollution Index is proposed by using Enrichment Factors (Equation 3) to calculate a modified pollution index according to Equation 6 which would allow for the non-conservative behaviour of sediments due to normalisation against an element such as Al or Fe.

$$MPI = \sqrt{\frac{(\overline{EF})^2 + (EF_{max})^2}{2}} \quad (6)$$

Another advantage of using a modified Pollution Index (MPI) is that the sediment qualification thresholds can be adjusted to give a more accurate qualification of sediment that is unlikely to overstate sediment contamination. A proposed set of thresholds for sediment quality is presented in Table 3, along with a comparison with the current Nemerow Pollution Index thresholds.

Table 3. Trigger values for the Nemerow and Modified Nemerow pollution indices

Class	**Sediment Qualification**	**Nemerow Pollution Index[a] (PI) (Nemerow, 1991)**	**Modified Pollution Index[b] (MPI)**
0	Unpolluted	PI < 0.7	MPI < 1
1	Slightly Polluted	0.7 < PI < 1	1 < MPI < 2
2	Moderately polluted	1 < PI < 2	2 < MPI < 3
3	Moderately-heavily polluted	--	3 < MPI < 5
4	Heavily polluted	2 < PI < 3	5 < MPI < 10
5	Severely polluted	PI > 3	10 < MPI

[a]Equation 5
[b]Equation 6

Because the derivation of the Modified Pollution Index (MPI) is calculated from enrichment factors (EF), it is possible to use the EF thresholds as a basis for sediment quality assessment. The advantage of using EFs to calculate thresholds is twofold. First, the Enrichment Factor thresholds are well established in the literature and second, the use of EF thresholds gives a realistic assessment of sediment quality and account for complex sediment behaviour.

2.1 Comparison of pollution indices for selected studies

In the example discussed in this paper, five recent studies on heavy metals contamination in soils and sediments were examined and the reported concentrations were used to calculate Geoaccumulation indices (Table 4), Nemerow Pollution Indices and modified Pollution Indices (Table 5).

These studies included work by Cevic et al. (2009) assessing heavy metals in Seyhan Dam in Turkey, Pengthamkeerati et al (2013) examining heavy metals contamination in the Mae Klong estuary in Thailand, Thuong et al (2013) looking at contamination in Hanoi, Vietnam. Kaushik, et al. (2009) examining contamination in the Yumana River in India and Abrahim and Parker (2008) near Auckland, New Zealand. As shown by Table 4, there is an overlap of some of the elements examined in each of these studies and the levels of contamination

indicated by the geoaccumulation indices (Table 4) are low for most elements, with the exception of Cd.

The geoaccumulation indices (Table 4) tend to under-report the more seriously polluted sites, which is evident for the values for Ni and Cd in the study by Kaushik *et al.* (2009). In this case, the enrichment factors sediment qualification is high, however, the geoaccumulation index sediment quality guidelines suggest that the sediments are not as polluted for Ni. This is reflected by all elements in the study by Abrahim and Parker (2008). This suggests that the use of geoaccumulation indices can under-report the contamination of a site by an element, which is of concern given the risk assessment approach now favoured when assessing sediment quality.

Table 4. Geoaccumulation indices (Equation 4) for a range of elements

	Element								
Study	**Fe**	**Mn**	**Ni**	**Pb**	**Cu**	**Zn**	**Cd**	**Cr**	**As**
Çevik, et al. (2009)	-0.8	-0.7	--	--	-1.8	-1.9	2.3	-0.2	--
Kaushik, et al. (2009)	-2.1	--	2.7	--	--	--	3.4	0.7	--
Pengthamkeerati, et al. (2013)	-1.3	-0.2	-3.1	-1.1	-2.4	-0.9	--	--	--
Thuong, et al. (2013)	-1.0	-1.3	-0.7	1.2	0.4	1.7	3.3	-0.3	2.1
Abrahim and Parker (2008)				1.3	-1.0	0.5	-0.1		

In each of the studies examined, the multi-element pollution indices (Table 5) suggest that there is cause for concern, as the Nemerow Pollution Indices show severe enrichment, with the exception of Pengthamkeerati et al. (2013).

Table 5. Comparison of the Modified Pollution Indices and Nemerow Pollution Indices of elements

Study	**PI[a]**	**MPI[b]**	**Sediment Quality[c]**	
			PI	**MPI**
Cevic *et al.* (2009)	5.2	6.3	5	4
Kaushik *et al.* (2009)	12	36.0	5	5
Pengthamkeerati *et al.* (2013)	1.1	1.7	2	1
Thuong *et al.* (2013)	10.7	14.5	5	5
Abrahim and Parker (2008)	3.0	8.5	5	4

[a]Equation 5
[b]Equation 6
[c]From Table 3

The Nemerow Pollution Indices all indicate severe contamination (a value of 3), with the exception of Pengthamkeerati et al. (2013), who reported moderate contamination. The study by Kaushik et al. (2009) in particular show a high degree of contamination. There are two major reasons for these high values. The first is that the Nemerow Pollution Index is a weighted average rather than just the average contamination factor, making a higher value for the index more likely, and the second is that the trigger thresholds are lower than those for the other indices. This makes the Nemerow Pollution Index more likely to identify high levels of contamination for a suite of elements. In the context of sediment quality assessment, this is an advantage over the other indices, as a high value for the Nemerow Pollution Index is more likely to result in further examination to identify the sources of contamination.

Table 5 above indicates that there is a difference between the two pollution indices, with the Modified Pollution Indices reporting equal or lower trigger values for sediment quality when compared to the standard Nemerow Pollution Indices for each of the studies. Although the modified Pollution Indices are still high, this is most likely due to the high enrichment factors of some elements.

To further expand on this, a larger sample of studies were analysed and their Enrichment Factors were calculated and can be seen in Table 6 below. The Modified Pollution Index and the average Enrichment were also calculated and the results demonstrate that generally, the Enrichment Factors for the studies reported earlier (Cevic et al., (2009) Kaushik et al., 2009; Pengthamkeerati et al., 2013; Thuong et al., 2013; Abrahim and Parker, 2008) show that when compared to Geoaccumulation indices, the Enrichment Factors tend to point towards more heavily polluted sediments. This is particularly true of the work of Kaushik et al. (2009), who found elevated Ni and Cd, but the I_{geo} under-reported the extent of contamination. This is also true for all elements in the study by Abrahim and Parker (2008), providing further evidence that the Geoaccumulation index may be limited in application to complex environments.

When the average Enrichment Factor and the Modified Pollution Indices are compared against each other in Table 6, it is clear that the MPIs indicate greater overall contamination for the suites of elements studied in each paper. This gives a clear indication that the use of Modified Pollution Indices is more likely to give a better assessment of risk than a single element index or an average of Enrichment Factors. The use of an MPI provides an advantage of the Nemerow Pollution Index as it takes into consideration complex sediment behaviour that are likely to occur in marine and estuarine environments.

Table 6. Enrichment Factors, average EF and Modified Pollution Indices from a number of recently published works

Study	Enrichment Factors[a]											Average EF	MPI[b]
	Fe	Mn	Ni	Pb	Cu	Zn	Cd	Cr	As	Co	Hg		
Cevic et al (2009)	--	1.1	--	--	0.5	0.5	8.5	1.3	--	--	--	2.4	6.2
Kaushik et al (2009)	--	--	9.4	--	--	--	8.5	1.4	--	--	--	6.4	8.1
Penthamkeerati et al (2013)	--	2.2	0.5	1.4	0.9	5.5	--	--	--	--	--	2.1	4.2
Thuong et al (2013)	--	0.8	1.3	4.5	2.6	6.8	19.9	1.6	8.7	--	--	5.8	14.7
Abrahim (2008)	--	--	--	10.6	2.2	6.4	3.8	--	--	--	--	5.8	8.5
Ghrefeat & Yusuf (2006)	--	0.36	--	--	1.3	3.6	30	--	--	--	--	8.8	22.1
Chen et al (2007)	--	--	--	8	3.9	8.3	16.5	2.5	--	--	41.8	13.5	31.1
Ghrefat, Abu-Rukah & Rosen (2010)	--	1.4	3.4	17	1.6	2	85	2.7	--	13.6	--	15.8	61.1
Pempkowiak (1991)	--	--	1	2.1	2.1	1.8	1.6	1.1	--	1	4.8	1.9	3.7
Zhang et al (2009)	--	1.6	2	1.7	1.5	1.6	3.3	2.8	--	--	--	2.1	2.8
Lee, Fang & Hsieh (1998)	--	--	1.5	4.4	0.8	2.8	1.3	0.6	--	--	--	1.9	3.4
Singh et al (2002)	1	0.9	1	2	2	2.1	4.4	2.4	--	1	--	1.9	3.4

[a]See Equation 3

[b]See Table 3 and Equation 6

3.0 Conclusions

Estuarine environments are complex areas where a number of simultaneous processes occur. These processes impact the behaviour and bioavailability of heavy metals suspended in water and sediments. A number of pollution indices have been proposed to identify contamination by heavy metals in these environments. Many of these cover single and multiple elements. Some of the indices also attempt to account 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.

Among these sediment quality indices, the use of enrichment factors was determined to be the preferred single element index for assessing contamination at a site by a particular metal, while the Nemerow Pollution Index was identified as the preferred multi-element index for assessing sediment quality when a suite of elements are the focus. From this, a Modified Pollution Index was developed using enrichment factors rather than contamination factors in order to develop an improved method for assessing sediment quality, that takes into consideration complex sediment behaviour when a suite of elements are investigated, as compared to the pollution indices currently used.

4.0 References

Abal, E. G., & Dennison, W. C. (1996). Seagrass depth range and water quality in southern Moreton Bay, Queensland, Australia. *Marine and Freshwater Research*, *47*(6), 763-771. Retrieved from http://www.publish.csiro.au/paper/MF9960763. doi:doi:10.1071/MF9960763

Abdolahpur Monikh, F., Maryamabadi, A., Savari, A., & Ghanemi, K. (2013). Heavy metals' concentration in sediment, shrimp and two fish species from the northwest Persian Gulf. *Toxicology and Industrial Health*. Retrieved from http://tih.sagepub.com/content/early/2013/02/04/0748233713475498.abstract. doi:10.1177/0748233713475498

Abrahim, G., & Parker, R. (2008). Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environmental Monitoring and Assessment*, *136*(1), 227-238. Retrieved from http://dx.doi.org/10.1007/s10661-007-9678-2. doi:10.1007/s10661-007-9678-2

Ahdy, H. H. H., & Youssef, D. H. (2011). Fractionation analysis of some heavy metals in sediments of the north-western part of the Red Sea, Egypt. *Chemistry and Ecology*, 1-17. Retrieved from http://dx.doi.org/10.1080/02757540.2010.547488. doi:10.1080/02757540.2010.547488

Albores, A. F., Cid, B. P., Gomez, E. F., & Lopez, E. F. (2000). Comparison between sequential extraction procedures and single extractions for metal partitioning in sewage sludge samples. [10.1039/B001983F]. *Analyst*, *125*(7), 1353-1357. Retrieved from http://dx.doi.org/10.1039/B001983F. doi:10.1039/b001983f

Ali, A. A., Elazein, E. M., & Alian, M. A. (2011). Determination of Heavy Metals in Four Common Fish, Water and Sediment Collected from Red Sea at Jeddah Isalmic Port Coas. *Journal of Applied Environmental and Biological Sciences*, *1*(10), 453-459.

Baptista Neto, J. A., Smith, B. J., & McAllister, J. J. (2000). Heavy metal concentrations in surface sediments in a nearshore environment, Jurujuba Sound, Southeast Brazil. *Environmental Pollution*, *109*(1), 1-9. Retrieved from http://www.sciencedirect.com/science/article/B6VB5-3YXB1S5-M/2/1d9a1838a1e2637847abff948d6bdcf5.

Beltrán, R., de la Rosa, J., Santos, J., Beltrán, M., & Gómez-Ariza, J. (2010). Heavy metal mobility assessment in sediments from the Odiel River (Iberian Pyritic Belt) using sequential extraction. *Environmental Earth Sciences, 61*(7), 1493-1503. Retrieved from http://dx.doi.org/10.1007/s12665-010-0465-y. doi:10.1007/s12665-010-0465-y

Bhat, U. N., & Khan, A. B. (2011). Heavy metals: An ambiguous category of inorganic contaminants, nutrients and toxins. *Research Journal of Environmental Sciences, 5*(8), 682-690.

Binning, K., & Baird, D. (2001). Survey of heavy metals in the sediments of the Swartkops River Estuary, Port Elizabeth South Africa. *Water S. A., 27*(4), 461-466.

Birch, G., & Taylor, S. (1999). Source of heavy metals in sediments of the Port Jackson estuary, Australia. *The Science of The Total Environment, 227*(2-3), 123-138. Retrieved from http://www.sciencedirect.com/science/article/B6V78-3W7PV6M-4/2/ab2b2a88bc830c0caff411a30ac412c9.

Blasco, J., Arias, A. M., & Sáenz, V. (1999). Heavy metals in organisms of the River Guadalquivir estuary: possible incidence of the Aznalcóllar disaster. *The Science of The Total Environment, 242*(1-3), 249-259. Retrieved from http://www.sciencedirect.com/science/article/B6V78-3Y80G6V-M/2/7d3211ae87ac3a84f1022edf5bfe6f25.

Bryan, G. W. (1971). The effects of heavy metals (other than mercury) on marine and estuarine organisms. *Proceedings of the Royal Society. B, Biological sciences, 177*, 389-410.

Casas, A. M., & Crecelius, E. A. (1994). Relationship between acid volatile sulfide and the toxicity of zinc, lead and copper in marine sediments. *Environmental Toxicology and Chemistry, 13*(3), 529-536.

Çevik, F., Göksu, M., Derici, O., & Fındık, Ö. (2009). An assessment of metal pollution in surface sediments of Seyhan dam by using enrichment factor, geoaccumulation index and statistical analyses. *Environmental Monitoring and Assessment, 152*(1-4), 309-317. Retrieved from http://dx.doi.org/10.1007/s10661-008-0317-3. doi:10.1007/s10661-008-0317-3

Chapman, P. M., & Wang, F. (2001). Assessing sediment contamination in estuaries. *Environmental Toxicology and Chemistry, 20*(1), 3-22. Retrieved from http://dx.doi.org/10.1002/etc.5620200102. doi:10.1002/etc.5620200102

Che, Y., He, Q., & Lin, W.-Q. (2003). The distributions of particulate heavy metals and its indication to the transfer of sediments in the Changjiang Estuary and Hangzhou Bay, China. *Marine Pollution Bulletin, 46*(1), 123-131. Retrieved from http://www.sciencedirect.com/science/article/B6V6N-47MHXHP-4/2/1104d7bcf1643af15e7dc1b62ee477b6.

Cheng, J.-l., Shi, Z., & Zhu, Y.-w. (2007). Assessment and mapping of environmental quality in agricultural soils of Zhejiang Province, China. *Journal of Environmental Sciences, 19*(1), 50-54.

Cox, M., & Preda, M. (2005). Trace Metal Distribution Within Marine and Estuarine Sediments of Western Moreton Bay, Queensland, Australia: Relation to Land Use and Setting. *Geographical Research, 43*(2), 173-193. Retrieved from http://eprints.qut.edu.au/22284/.

de Caritat, P., & Cooper, M. (2011). *National Geochemical Survey of Australia: The Geochemical Atlas of Australia*: Geoscience Australia.

De Jonge, M., Blust, R., & Bervoets, L. (2010). The relation between acid volatile sulfides (AVS) and metal accumulation in aquatic invertebrates: implications of feeding behavior and ecology. *Environmental Pollution, 158*(5), 1381-1391.

De Wolf, H., Backeljau, T., & Blust, R. (2000). Heavy metal accumulation in the periwinkle Littorina littorea, along a pollution gradient in the Scheldt estuary. *Science of The Total Environment, 262*(1-2), 111-121. Retrieved from http://www.sciencedirect.com/science/article/B6V78-4183J08-C/2/f106e8f443ed121daed371b681163cfb.

Deng, H.-G., Zhang, J., Wang, D.-Q., Chen, Z.-L., & Xu, S.-Y. (2010). Heavy metal pollution and assessment of the tidal flat sediments near the coastal sewage outfalls of shanghai, China. *Environmental Earth Sciences, 60*(1), 57-63. Retrieved from http://dx.doi.org/10.1007/s12665-009-0169-3. doi:10.1007/s12665-009-0169-3

Deng, Y., Zheng, B., Fu, G., Lei, K., & Li, Z. (2010). Study on the total water pollutant load allocation in the Changjiang (Yangtze River) Estuary and adjacent seawater area. *Estuarine, Coastal and Shelf Science, 86*(3), 331-336. Retrieved from http://www.sciencedirect.com/science/article/B6WDV-4XR5N8K-1/2/f653892ac5d1c413758855ea78ba79a5.

Di Toro, D. M., Mahony, J. D., Hansen, D. J., Scott, K. J., Carlson, A. R., & Ankley, G. T. (1992). Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environmental Science & Technology, 26*(1), 96-101.

Di Toro, D. M., Mahony, J. D., Hansen, D. J., Scott, K. J., Hicks, M. B., Mayr, S. M., & Redmond, M. S. (1990). Toxicity of cadmium in sediments: The role of acid volatile sulfide. *Environmental Toxicology and Chemistry, 9*(12), 1487-1502.

Dinescu, L. C., Steinnes, E., Duliu, O. G., Ciortea, C., Sjobakk, T. E., Dumitriu, D. E., . . . Haralambie, M. (2004). Distribution of some major and trace elements in Danube Delta lacustrine sediments and soil. *Journal of Radioanalytical and Nuclear Chemistry, 262*(2), 245-354.

Driscoll, C. T., Lawrence, G. B., Bulger, A. J., Butler, T. J., Cronan, C. S., Eagar, C., . . . Weathers, K. C. (2001). Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies: The effects of acidic deposition in the northeastern United States include the acidification of soil and water, which stresses terrestrial and aquatic biota. *BioScience, 51*(3), 180-198.

Dung, T., Cappuyns, V., Swennen, R., & Phung, N. (2013). From geochemical background determination to pollution assessment of heavy metals in sediments and soils. *Reviews in Environmental Science and Bio/Technology*, 1-19. Retrieved from http://dx.doi.org/10.1007/s11157-013-9315-1. doi:10.1007/s11157-013-9315-1

Gao, S., Luo, T.-C., Zhang, B.-R., Zhang, H.-F., Han, Y.-W., Zhao, Z.-D., & Hu, Y.-K. (1998). Chemical composition of the continental crust as revealed by studies in East China. *Geochimica et Cosmochimica Acta, 62*(11), 1959-1975. Retrieved from http://www.sciencedirect.com/science/article/pii/S0016703798001215. doi:10.1016/s0016-7037(98)00121-5

Gaw, A., Cowan, R. A., O'Reilly, D. S. J., Stewart, M. J., & Shepherd, J. (1999). Metal Poisoning. In *Clinical Biochemistry* (second edition ed., pp. 114-118). Sydney: Churchill Livingstone.

Gómez-Parra, A., Forja, J. M., DelValls, T. A., Sáenz, I., & Riba, I. (2000). Early Contamination by Heavy Metals of the Guadalquivir Estuary After the Aznalcóllar Mining Spill (SW Spain). *Marine Pollution Bulletin, 40*(12), 1115-1123. Retrieved from http://www.sciencedirect.com/science/article/B6V6N-41WJY0N-7/2/b37cb6608ff0c37f4df771ef2bc36b98.

González-Fernández, D., Garrido-Pérez, M., Nebot-Sanz, E., & Sales-Márquez, D. (2011). Source and Fate of Heavy Metals in Marine Sediments from a Semi-Enclosed Deep Embayment Subjected to Severe Anthropogenic Activities. *Water, Air & Soil Pollution*, 1-12. Retrieved from http://dx.doi.org/10.1007/s11270-011-0782-0. doi:10.1007/s11270-011-0782-0

Grecco, L., Gómez, E., Botté, S., Marcos, Á., Marcovecchio, J., & Cuadrado, D. (2011). Natural and anthropogenic heavy metals in estuarine cohesive sediments: geochemistry and bioavailability. *Ocean Dynamics, 61*(2), 285-293. Retrieved from http://dx.doi.org/10.1007/s10236-010-0354-7. doi:10.1007/s10236-010-0354-7

Guang, X., Jian, X., Yue, Z., Caiyun, Z., & Qing, W. (2010, 18-20 June 2010). Application of Nemerow Pollution Index in Landscape River Water Quality Assessment of Tianjin. In *4th International Conference on Bioinformatics and Biomedical Engineering (iCBBE), 2010* (pp. 1-4).

Gunawardena, J., Egodawatta, P., Ayoko, G. A., & Goonetilleke, A. (2012). Role of traffic in atmospheric accumulation of heavy metals and polycyclic aromatic hydrocarbons. *Atmospheric Environment, 54*(0), 502-510. Retrieved from http://www.sciencedirect.com/science/article/pii/S1352231012001732. doi:http://dx.doi.org/10.1016/j.atmosenv.2012.02.058

Gunawardena, J., Egodawatta, P., Ayoko, G. A., & Goonetilleke, A. (2013). Atmospheric deposition as a source of heavy metals in urban stormwater. *Atmospheric Environment, 68*(0), 235-242. Retrieved from http://www.sciencedirect.com/science/article/pii/S1352231012011302. doi:http://dx.doi.org/10.1016/j.atmosenv.2012.11.062

Hakanson, L. (1980). An ecological risk index for aquatic pollution control.a sedimentological approach. *Water Research, 14*(8), 975-1001. Retrieved from http://www.sciencedirect.com/science/article/pii/0043135480901438. doi:10.1016/0043-1354(80)90143-8

Hans Wedepohl, K. (1995). The composition of the continental crust. *Geochimica et Cosmochimica Acta, 59*(7), 1217-1232. Retrieved from http://www.sciencedirect.com/science/article/pii/0016703795000382. doi:10.1016/0016-7037(95)00038-2

He, M., Wang, Z., & Tang, H. (1998). The chemical, toxicological and ecological studies in assessing the heavy metal pollution in Le An River, China. *Water Research, 32*(2), 510-518.

Hu, G., Yu, R., Zhao, J., & Chen, L. (2011). Distribution and enrichment of acid-leachable heavy metals in the intertidal sediments from Quanzhou Bay, southeast coast of China. *Environmental Monitoring and Assessment, 173*(1-4), 107-116. Retrieved from http://dx.doi.org/10.1007/s10661-010-1374-y. doi:10.1007/s10661-010-1374-y

Imperato, M., Adamo, P., Naimo, D., Arienzo, M., Stanzione, D., & Violante, P. (2003). Spatial distribution of heavy metals in urban soils of Naples city (Italy). *Environmental Pollution, 124*(2), 247-256. Retrieved from http://www.sciencedirect.com/science/article/B6VB5-483025G-2/2/33ecb6b953c0ead8eff5d1b85f2039e2.

Jing, D. (2006). An Application of the Nemerow Pollution Index in the Quality Assessment of the Seawater Environment in the Vicinity of Terrestrial Drains [J]. *Journal of Fujian Fisheries, 1*, 000.

Jones, A. B., O'Donohue, M. J., Udy, J., & Dennison, W. C. (2001). Assessing Ecological Impacts of Shrimp and Sewage Effluent: Biological Indicators with Standard Water Quality Analyses. *Estuarine, Coastal and Shelf Science, 52*(1), 91-109. Retrieved from http://www.sciencedirect.com/science/article/B6WDV-458W57V-2Y/2/cfec3de82c92c9c63767c9f7e7133733.

Jones, B., & Turki, A. (1997). Distribution and speciation of heavy metals in surficial sediments from the Tees Estuary, north-east England. *Marine Pollution Bulletin, 34*(10), 768-779. Retrieved from

http://www.sciencedirect.com/science/article/B6V6N-3WTP1T0-1G/2/ed7acb067105cb3786d19588039bcdcf.

Karim, M. (2000). Arsenic in groundwater and health problems in Bangladesh. *Water Research, 34*(1), 304-310.

Kaushik, A., Kansal, A., Kumari, S., & Kaushik, C. (2009). Heavy metal contamination of river Yamuna, Haryana, India: Assessment by metal enrichment factor of the sediments. *Journal of Hazardous Materials, 164*(1), 265-270.

Keskin, Ş. (2012). Distribution and accumulation of heavy metals in the sediments of Akkaya Dam, Nigde, Turkey. *Environmental Monitoring and Assessment, 184*(1), 449-460. Retrieved from http://dx.doi.org/10.1007/s10661-011-1979-9

Kim, K. W., Myung, J. H., Ahn, J. S., & Chon, H. T. (1998). Heavy metal contamination in dusts and stream sediments in the Taejon area, Korea. *Journal of Geochemical Exploration, 64*(1-3), 409-419. Retrieved from http://www.sciencedirect.com/science/article/B6VCP-3VWF85X-1M/2/3322819fb2c9a5098776cca8d3798c35.

Klöppel, H., Fliedner, A., & Kördel, W. (1997). Behaviour and ecotoxicology of aluminium in soil and water-Review of the scientific literature. *Chemosphere, 35*(1), 353-363.

Krewski, D., Yokel, R. A., Nieboer, E., Borchelt, D., Cohen, J., Harry, J., . . . Rondeau, V. (2007). Human health risk assessment for aluminium, aluminium oxide, and aluminium hydroxide. *Journal of Toxicology and Environmental Health, Part B, 10*(S1), 1-269.

Kumar, R., Joseph, C. S., Gireesh Kumar, M. M., Renjith, T. R., Manju, M. N., & Chandramohanakumar, N. (2010). Spatial Variability and Contamination of Heavy Metals in the Inter-tidal Systems of a Tropical Environment. *International Journal of Environmental Research, 4*(4), 691-700.

Lee, P.-K., Kang, M.-J., Jo, H., & Choi, S.-H. (2012). Sequential extraction and leaching characteristics of heavy metals in abandoned tungsten mine tailings sediments. *Environmental Earth Sciences, 66*(7), 1909-1923. Retrieved from http://dx.doi.org/10.1007/s12665-011-1415-z. doi:10.1007/s12665-011-1415-z

Li, X., Poon, C.-S., & Liu, P. S. (2001). Heavy metal contamination of urban soils and street dusts in Hong Kong. *Applied Geochemistry, 16*(11-12), 1361-1368. Retrieved from http://www.sciencedirect.com/science/article/B6VDG-433NPP0-8/2/59ecbecc0732b9c52977638e6a2e5a8c.

Liu, B., Hu, K., Jiang, Z., Yang, J., Luo, X., & Liu, A. (2011). Distribution and enrichment of heavy metals in a sediment core from the Pearl River Estuary. *Environmental Earth Sciences, 62*(2), 265-275. Retrieved from http://dx.doi.org/10.1007/s12665-010-0520-8. doi:10.1007/s12665-010-0520-8

Liu, W. H., Zhao, J. Z., Ouyang, Z. Y., Söderlund, L., & Liu, G. H. (2005). Impacts of sewage irrigation on heavy metal distribution and contamination in Beijing, China. *Environment International, 31*(6), 805-812. Retrieved from http://www.sciencedirect.com/science/article/B6V7X-4GG2J5F-5/2/897595a96bf25f977e5c47dd64bc3555.

Liu, W. X., Li, X. D., Shen, Z. G., Wang, D. C., Wai, O. W. H., & Li, Y. S. (2003). Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary. *Environmental Pollution, 121*(3), 377-388. Retrieved from http://www.sciencedirect.com/science/article/B6VB5-461XGGT-2/2/0bbe760fcb0b235e1bc08ef9b7fea1c9.

Mandal, B. K., Chowdhury, T. R., Samanta, G., Basu, G. K., Chowdhury, P., Chanda, C. R., . . . Tamili, D. K. (1996). Arsenic in groundwater in seven districts of West Bengal, India- the biggest arsenic calamity in the world. *Current science. Bangalore, 70*(11), 976-985.

Martin, J. M., Nirel, P., & Thomas, A. J. (1987). Sequential extraction techniques, promises and Problems. *Marine Chemistry, 22*(2-4), 313-341.

Mitra, A., Chowdhury, R., & Banerjee, K. (2012). Concentrations of some heavy metals in commercially important finfish and shellfish of the River Ganga. *Environmental Monitoring and Assessment, 184*(4), 2219-2230. doi: 10.1007/s10661-011-2111-x.

Mohammed, T., Loganathan, P., Kinsela, A., Vigneswaran, S., & Kandasamy, J. (2012). Enrichment, inter-relationship, and fractionation of heavy metals in road-deposited

sediments of Sydney, Australia. *Soil Research, 50*(3), 229-238. Retrieved from http://www.publish.csiro.au/paper/SR12010. doi:http://dx.doi.org/10.1071/SR12010

Muller, G. (1969). Index of geoaccumulation in sediments of the Rhine. *Geojournal, 2*, 108-118.

Nemerow, N. L. (1991). *Stream, lake, estuary, and ocean pollution*. New York, United States.

Ofiara, D. D., & Seneca, J. J. (2006). Biological effects and subsequent economic effects and losses from marine pollution and degradations in marine environments: Implications from the literature. *Marine Pollution Bulletin, 52*(8), 844-864. Retrieved from http://www.sciencedirect.com/science/article/B6V6N-4K428X2-1/2/7e6412be81ba979a7f8597b2f38c5e42.

Pantus, F., & Dennison, W. (2005). Quantifying and Evaluating Ecosystem Health: A Case Study from Moreton Bay, Australia. *Environmental Management, 36*(5), 757-771. Retrieved from http://dx.doi.org/10.1007/s00267-003-0110-6.

Park, J.-S., Lee, J.-S., Kim, G.-B., Cha, J.-S., Shin, S., Kang, H.-G., . . . Kim, Y.-H. (2010). Mercury and Methylmercury in Freshwater Fish and Sediments in South Korea Using Newly Adopted Purge and Trap GC-MS Detection Method. *Water, Air, & Soil Pollution, 207*(1), 391-401. Retrieved from http://dx.doi.org/10.1007/s11270-009-0144-3. doi:10.1007/s11270-009-0144-3

Pengthamkeerati, P., Kornkanitnan, N., Sawangarreruks, S., Wanichacheva, N., Wainiphithapong, C., & Sananwai, N. (2013). Assessment of heavy metals in sediments of the Don Hoi Lot area in the Mae Klong estuary, Thailand. *Journal of Environmental Science and Health, Part A, 48*(11), 1356-1364. Retrieved from http://www.tandfonline.com/doi/abs/10.1080/10934529.2013.781881. doi:10.1080/10934529.2013.781881

Pier, S. M., & Bang, K. M. (1980). The role of heavy metals in human health. In N. M. Trieff (Ed.), *Environment and Health* (pp. 367-409). Ann Arbor: Ann Arbor Science.

Preda, M., & Cox, M. E. (2001). Trace metals in acid sediments and waters, Pimpama catchment, southeast Queensland, Australia. *Environmental Geology, 40*(6), 755-768.

Retrieved from http://dx.doi.org/10.1007/s002540100318. doi:10.1007/s002540100318

Preda, M., & Cox, M. E. (2002). Trace metal occurrence and distribution in sediments and mangroves, Pumicestone region, southeast Queensland, Australia. *Environment International, 28*(5), 433-449. Retrieved from http://www.sciencedirect.com/science/article/pii/S0160412002000740. doi:10.1016/s0160-4120(02)00074-0

Qingjie, G., Jun, D., Yunchuan, X., Qingfei, W., & Liqiang, Y. (2008). Calculating pollution indices by heavy metals in ecological geochemistry assessment and a case study in parks of Beijing. *Journal of China University of Geosciences, 19*(3), 230-241.

Riba, I., DelValls, T. A., Forja, J. M., & Gómez-Parra, A. (2002). Influence of the Aznalcóllar mining spill on the vertical distribution of heavy metals in sediments from the Guadalquivir estuary (SW Spain). *Marine Pollution Bulletin, 44*(1), 39-47. Retrieved from http://www.sciencedirect.com/science/article/B6V6N-44YDH85-J/2/ead5d5f090c3c23d6181847252db33c2.

Riosmena-Rodríguez, R., Talavera-Sáenz, A., Acosta-Vargas, B., & Gardner, S. (2010). Heavy metals dynamics in seaweeds and seagrasses in Bahía Magdalena, B.C.S., México. *Journal of Applied Phycology, 22*(3), 283-291. Retrieved from http://dx.doi.org/10.1007/s10811-009-9457-2. doi:10.1007/s10811-009-9457-2

Romic, M., & Romic, D. (2003). Heavy metals distribution in agricultural topsoils in urban area. *Environmental Geology, 43*(7), 795-805. Retrieved from http://dx.doi.org/10.1007/s00254-002-0694-9. doi:10.1007/s00254-002-0694-9

Ruiz, F. (2001). Trace Metals in Estuarine Sediments from the Southwestern Spanish Coast. *Marine Pollution Bulletin, 42*(6), 481-489. Retrieved from http://www.sciencedirect.com/science/article/B6V6N-438TTRR-8/2/c22b18227b616bce60af46be99ba6c95.

Shikazono, N., Tatewaki, K., Mohiuddin, K., Nakano, T., & Zakir, H. (2012). Sources, spatial variation, and speciation of heavy metals in sediments of the Tamagawa River in Central Japan. *Environmental Geochemistry and Health, 34*(1), 13-26. Retrieved from http://dx.doi.org/10.1007/s10653-011-9409-z. doi:10.1007/s10653-011-9409-z

Shilla, D., & Dativa, J. (2011). Speciation of heavy metals in sediments from the Scheldt estuary, Belgium. *Chemistry and Ecology, 27*(1), 69-79. Retrieved from http://www.informaworld.com/10.1080/02757540.2010.529075.

Simpson, S. L., Batley, G. E., Chariton, A. A., Stauber, J. L., King, C. K., Chapman, J. C., . . . Maher, W. A. (2005). *Handbook for Sediment Quality Assessment.* Sydney, Australia.

Singh, M., Müller, G., & Singh, I. (2002). Heavy Metals in Freshly Deposited Stream Sediments of Rivers Associated with Urbanisation of the Ganga Plain, India. *Water, Air and Soil Pollution, 141*(1-4), 35-54. Retrieved from http://gateway.library.qut.edu.au/login?url=http://proquest.umi.com/pqdweb?did=2136852021&Fmt=7&clientId=14394&RQT=309&VName=PQD.

Smedley, P. L. (2003). Arsenic in groundwater—south and east Asia. In *Arsenic in ground water* (pp. 179-209): Springer.

Sörme, L., & Lagerkvist, R. (2002). Sources of heavy metals in urban wastewater in Stockholm. *The Science of The Total Environment, 298*(1-3), 131-145. Retrieved from http://www.sciencedirect.com/science/article/B6V78-460M69M-1/2/a82988a42552500b7ab22cde8e5b10da.

Soto, M., Kortabitarte, M., & Marigomez, I. (1995). Bioavailable heavy metals in estuarine waters as assessed by metal/shell-weight indices in sentinel mussels *Mytilus galloprovincialis*. *Marine Ecology Progress Series, 125*, 127-136.

Suh, J.-Y., Birch, G. F., Hughes, K., & Matthai, C. (2004). Spatial distribution and source of heavy metals in reclaimed lands of Homebush Bay: the venue of the 2000 Olympic Games, Sydney, New South Wales. *Australian Journal of Earth Sciences, 51*, 53-66.

Sundaray, S. K., Nayak, B. B., Lin, S., & Bhatta, D. (2011). Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments--A case study: Mahanadi basin, India. *Journal of Hazardous Materials, 186*(2-3), 1837-1846. Retrieved from http://www.sciencedirect.com/science/article/B6TGF-51SFK50-4/2/776172e99ba423ec6ba663c1095df7ce.

Tam, N. F. Y., & Wong, Y. S. (2000). Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environmental Pollution, 110*(2), 195-205. Retrieved from http://www.sciencedirect.com/science/article/B6VB5-40NFSK0-2/2/763ae34a64129eab55e3706e3995bef8.

Tang, W., Shan, B., Zhang, H., & Mao, Z. (2010). Heavy metal sources and associated risk in response to agricultural intensification in the estuarine sediments of Chaohu Lake Valley, East China. *Journal of Hazardous Materials, 176*(1-3), 945-951. Retrieved from http://www.sciencedirect.com/science/article/B6TGF-4XVC4V9-1/2/eac92c2885871369bf47d694abc5da10.

Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry, 51*(7), 844-851. Retrieved from http://dx.doi.org/10.1021/ac50043a017. doi:10.1021/ac50043a017

Thuong, N. T., Yoneda, M., Ikegami, M., & Takakura, M. (2013). Source discrimination of heavy metals in sediment and water of To Lich River in Hanoi City using multivariate statistical approaches. *Environ Monit Assess, 185*(10), 8065-8075. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/23512487. doi:10.1007/s10661-013-3155-x

Toffaletti, J. G. (2005). Trace Elements. In M. L. Bishop, E. P. Fody & L. E. Schoeff (Eds.), *Clinical Chemistry: Principles, Procedures, Correlations* (pp. 364-377). Sydney: Lippincott Williams & Wilkins.

Welch, A. H., & Stollenwerk, K. G. (2003). *Arsenic in ground water*: Kluwer Academic Publishers Dordrecht.

Wen-qiang, W. (2008). Application of Aggregative Index Number Method in Groundwater Quality Evaluation [J]. *Water Conservancy Science and Technology and Economy, 1*, 022.

Wilber, W. G., & Hunter, J. V. (1979). The impact of urbanization on the distribution of heavy metals in bottom sediments of the Saddle River. *JAWRA Journal of the American Water Resources Association, 15*(3), 790-800. Retrieved from http://dx.doi.org/10.1111/j.1752-1688.1979.tb00397.x. doi:10.1111/j.1752-1688.1979.tb00397.x

Williamson, R. B., & Morrisey, D. J. (2000). Stormwater Contamination of Urban Estuaries. 1. Predicting the Build-Up of Heavy Metals in Sediments. *Estuaries*, *23*(1), 56-66. Retrieved from http://www.jstor.org/stable/1353225.

Wright, P., & Mason, C. F. (1999). Spatial and seasonal variation in heavy metals in the sediments and biota of two adjacent estuaries, the Orwell and the Stour, in eastern England. *The Science of The Total Environment*, *226*(2-3), 139-156. Retrieved from http://www.sciencedirect.com/science/article/B6V78-3WJ7RD9-5/2/8fd5ed8247f42153f463bd141525d510.

Zhong, X.-L., Zhou, S.-L., Zhu, Q., & Zhao, Q.-G. (2011). Fraction distribution and bioavailability of soil heavy metals in the Yangtze River Delta—A case study of Kunshan City in Jiangsu Province, China. *Journal of Hazardous Materials*, *198*(0), 13-21. Retrieved from http://www.sciencedirect.com/science/article/pii/S0304389411012313. doi:10.1016/j.jhazmat.2011.10.003