

# Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand

G. M. S. Abraham · R. J. Parker

Received: 22 October 2006 / Accepted: 23 February 2007 / Published online: 17 March 2007  
© Springer Science + Business Media B.V. 2007

**Abstract** Eight sediment cores recovered from Tamaki Estuary were analysed for Cu, Pb, Zn, and Cd using downward cored sub-samples. The results indicate a significant upward enrichment in heavy metals with the highest concentrations found in the uppermost 0–10 cm layer. Assessment of heavy metal pollution in marine sediments requires knowledge of pre-anthropogenic metal concentrations to act as a reference against which measured values can be compared. Pristine values for the cored sediments were determined from flat “baseline” metal trends evident in lower core samples. Various methods for calculating metal enrichment and contamination factors are reviewed in detail and a modified and more robust version of the procedure for calculating the degree of contamination is proposed. The revised procedure allows the incorporation of a flexible range of pollutants, including various organic species, and the degree of contamination is expressed as an average ratio rather than an absolute summation number. Comparative data for normalized enrichment factors and the modified degree of contamination show that Tamaki Estuary sediments have suffered significant systematic heavy metal contamination following catch-

ment urbanization. Compared to baseline values the uppermost sediment layers show four-fold enrichment averaged across eight cores and four analysed metals.

**Keywords** Heavy metals · Enrichment factor · Degree of contamination · Sediments pollution · Tamaki Estuary · Auckland · New Zealand

## Introduction

In the study of contaminated samples, the determination of the extent or degree of pollution by a given heavy metal requires that the pollutant metal concentration be compared with an unpolluted reference material. Such reference material should be an unpolluted or pristine substance that is comparable with the studied samples. The reference material then would represent a benchmark to which the metal concentrations in the polluted samples are compared and measured. Pollution, in this case, will be measured as the amount (or ratio) of the sample metal enrichment above the concentrations present in the reference material.

In assessing the impact of heavy metal pollution on estuarine environments, a number of different reference materials and enrichment calculation methods have been used by various workers (Salomons and Förstner 1984; Müller 1969; Hakanson 1980). There is thus a considerable variation in how the impact of anthropogenic pollution on a given site is quantified. Such variation has subsequent implications for the

---

G. M. S. Abraham (✉) · R. J. Parker  
Geoenvironmental Services, 27 Erne Crescent,  
Dannemora, Auckland, New Zealand  
e-mail: g\_abraham@yahoo.com

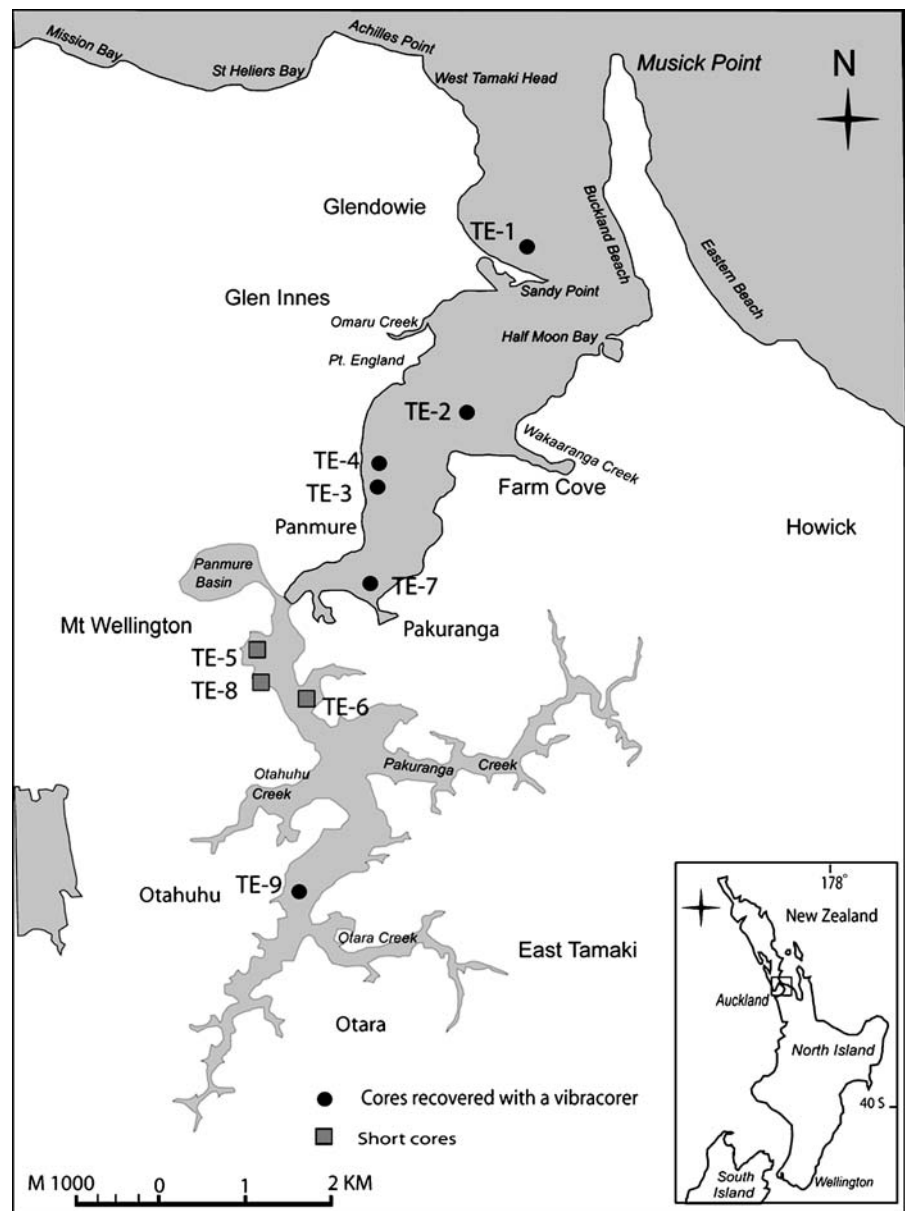
R. J. Parker  
e-mail: rob\_parker@ihug.co.nz

overall assessment, monitoring and management of contaminant effects. It would clearly be advantageous if there was more consistency in the calculation methods and reference concentrations used to evaluate coastal contamination. To this end, the present paper compares a number of reference materials and enrichment calculation methods as a contribution towards building a consensus on methodologies applicable to the study of polluted estuarine sediments. The aims of the present study are therefore to (1) review the various methods for establishing

baseline metal concentrations and the calculation of the extent (or ratio) of metal enrichment; (2) propose a revised methodology for estimating the overall degree of enrichment in a series of pollutants, (3) determine suitable baseline values for cores recovered from Tamaki Estuary in Auckland; and (4) utilize these baseline values and the various calculation methods to assess and compare metal enrichment in Tamaki Estuary fine fraction sediments.

A particular aspect of the study is the contrast in enrichment ratios obtained when using continental shale

**Fig. 1** Location of Tamaki Estuary, Auckland, New Zealand. (closed circle) cores recovered with a vibracorer (closed square) short cores



reference values as compared to natural uncontaminated backgrounds obtained from cores from the area of interest. In many respects this latter method is the best approach, although in some localities core samples may not be available or it may be difficult to get below contamination effects built up over long periods of industrial and urban human activity. There is thus still a role for the judicious use of continental shale reference metal values in evaluating contaminant impacts.

**Study area**

Tamaki Estuary on the eastern side of Auckland City forms a long narrow channel about 17 km in length, and is the third largest water body in Auckland after Manukau and Waitemata harbours (Fig. 1). Tamaki Estuary is considered polluted, and grossly so in some parts (Auckland Regional Council 1990, 1992, 1999). The estuary is noted for its geographic location within the central part of Auckland, the extensive urbanisation and light to medium industrialisation along its shores, the presence of rock outcrops of both Waitemata sedimentary strata and lavas and ash from Auckland Volcanic Field, the relatively thick Holocene estuarine sedimentary sequence and the influence of both marine and fluvial processes on these sediments. Well-documented historical land use changes since c1800, from relatively pristine natural bush conditions to grain farming and then dairy farming and finally to urban housing and industrial activities, has had a considerable impact on the natural ecosystems of the Tamaki catchment and estuary (e.g. Abraham and Parker 2002; Abraham 2005). By far the greatest impact has occurred in the last 50 years With The transformation from a pastoral landscape to an urbanized and industrialized catchment (Abraham and Parker 2002).

**Field sampling and analytical methods**

Eight cores were collected from Tamaki Estuary (Fig. 1). All the cores were tightly capped and transported vertically to the laboratory where they were stored at –20°C until the time of chemical analysis. Each core was cut along its length and the core halved prior to sub-sampling with particular focus on the upper 1 m of the core. Sediment samples were wet sieved through an acid washed 63 µm nylon mesh followed by freeze-drying to minimise loss of volatile elements (Mudroch and Bourbornniere 1994). Selected heavy metals (Cu,

Pb and Zn) were determined in nitric acid digests using atomic absorption spectrometry (AAS) (Stewart 1989). Graphite Furnace Atomic Absorption Spectrometry (GFAAS) was used for Cd analysis. Precision and accuracy of the metal analyses were checked against the standard MAG-1, which is a polluted marine sediment standard prepared by the United States Geological Survey (Abraham and Parker 2002).

**Methods for estimating background and baseline concentrations**

A crucial first step in evaluating the impact of sediment pollution and the level of contamination affecting a given area is to establish a reference background or baseline sample of known metal composition. Two methods are considered, firstly the use of average crustal values as reference concentrations, while the second method seeks to establish a local baseline by analysing comparable local sediment unaffected by anthropogenic activity.

**Background values from average crustal concentrations**

In earlier environmental work (e.g. Salomons and Förstner 1984) a common method for comparing sediment metal concentrations with pre-civilisation background levels was to compare the present day metal levels with their concentrations in standard earth materials such as average shale (Turekian and Wedepohl 1961) or average crustal values (Taylor 1964). Abundances of the studied heavy metals in average continental shale and crust are presented in Table 1.

The main disadvantage of using average earth or crustal levels is that it ignores natural geochemical

**Table 1** Selected metal concentrations in average continental shale and average continental crust

Element	Average continental shale <sup>a</sup>	Average continental crust <sup>b</sup>
Cd	0.2	0.1
Cu	45	25
Pb	20	14.8
Zn	95	65

<sup>a</sup> Turekian and Wedepohl (1961).

<sup>b</sup> Wedepohl (1995).

variability, and this may lead to false anomalies being recognised or anomalous concentrations above the pristine local background may not be recognised at all (Covelli and Fontolan 1997). Another disadvantage is that the crustal values are bulk concentrations, and this undermines comparison with “fine fraction” sediment concentrations. An exception to this general observation is the average abundance values for continental shales which are naturally very rich in fine grain sizes.

#### Baseline estimates from similar uncontaminated sediments

The more recent approach to establishing reference values is to compare concentrations of the target metals in contaminated and uncontaminated sediments that are mineralogically and texturally similar or identical (Salomons and Förstner 1984; Hornung et al. 1989; Williamson et al. 1992). This can best be done in cores by comparing the pollutant concentrations in the upper sediments layers with their pre-industrial concentration in the deeper layers of the same core (Siegel et al. 1994; Faganeli et al. 1991).

Using this approach for a practical assessment of contamination, it is possible to establish a local “baseline” concentration for each core by taking the mean of several low concentration samples selected from the deep, least impacted levels of sediment cores. Since pollution effects may extend to a considerable variation in depth, the selection of the low concentration samples for baseline averaging is best done by inspection of the metal trends in the lower core. Typically the trend flattens out to a relatively uniform line. The depth at which this happens may vary and the selection of the baseline samples should therefore be evaluated on a core-by-core basis rather than being based on averaging all samples below a fixed depth.

This method enables a realistic comparison to be made between the pristine sediment concentrations in the lower core with the similar but contaminated sediments in the upper layers (Williamson et al. 1992). This method is much more reasonable than comparisons with average crustal values due to the textural, mineralogical and bulk chemical similarity between the compared sediment samples. In addition both samples will have been through a similar cycle of weathering, erosion and transport with final

sedimentation under saline conditions in the case of a tidal marine dominated estuary such as Tamaki.

#### Methods for estimating pollutant impact

A number of calculation methods (e.g. Ridgway and Shimmield 2002) have been put forward for quantifying the degree of metal enrichment in sediments. Various authors (Salomons and Förstner 1984; Müller 1969; Hakanson 1980) have proposed pollution impact scales (or ranges) to convert the calculated numerical results into broad descriptive bands of pollution ranging from low to high intensity. Three methods are discussed in the following sections along with proposed modifications.

##### Enrichment factor (EF)

A common approach to estimating the anthropogenic impact on sediments is to calculate a normalized enrichment factor (EF) for metal concentrations above uncontaminated background levels (Salomons and Förstner 1984; Dickinson et al. 1996; Hornung et al. 1989). The EF calculation seeks to reduce the metal variability associated with variations in mud/sand ratios, and is a convenient tool for plotting geochemical trends across large geographic areas, which may have substantial variations in the mud (i.e. clay rich) to sand ratios.

The EF method normalises the measured heavy metal content with respect to a sample reference metal such as Fe or Al (Ravichandran et al. 1995). In this approach the Fe or Al is considered to act as a “proxy” for the clay content (Windom et al. 1989; Din 1992). Stewart (1989) applied a similar approach and used Mn for EF calculations in a study of marine sediment near Christchurch. Deely and Fergusson (1994) proposed Fe as an acceptable normalisation element to be used in the calculation of the enrichment factor since they considered the Fe distribution was not related to other heavy metals. Fe usually has a relatively high natural concentration, and is therefore not expected to be substantially enriched from anthropogenic sources in estuarine sediments (Niencheski et al. 1994). A wide range of studies have used Fe and Al normalisation as an alternative to grain size normalisation (Bresline and Sanudo-Wilhelmy 1999; Windom et al. 1989; Bruland

et al. 1974). Sharma et al. (1999) used both Al and Fe to distinguish natural and anthropogenic sources in recent sediments from Texas estuaries. Recently Matthai and Birch (2001) introduced the use of cobalt (Co) as a normalising element for determining anthropogenic pollution sources in the marine sediments off Sydney, Australia.

The EF is calculated according to the following equation:

$$EF = M_x \times Fe_b / M_b \times Fe_x$$

where  $M_x$  and  $Fe_x$  are the sediment sample concentrations of the heavy metal and Fe (or other normalising element), while  $M_b$  and  $Fe_b$  are their concentrations in a suitable background or baseline reference material (Salomons and Förstner 1984).

### Geoaccumulation index ( $I_{geo}$ )

A common approach to estimating the enrichment of metal concentrations above background or baseline concentrations is to calculate the geoaccumulation index ( $I_{geo}$ ) as proposed by Müller (1969). The method assesses the degree of metal pollution in terms of seven enrichment classes based on the increasing numerical values of the index. This index is calculated as follows:

$$I_{geo} = \log_2 C_n / 1.5 B_n$$

where  $C_n$  is the concentration of the element in the enriched samples, and the  $B_n$  is the background or pristine value of the element. The factor 1.5 is introduced to minimise the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments (Stoffers et al. 1986).

Müller (1969) proposed the following descriptive classes for increasing  $I_{geo}$  values:

$I_{geo}$ value	$I_{geo}$ class	Designation of sediment quality
>5	6	extremely contaminated
4–5	5	strongly to extremely contaminated
3–4	4	strongly contaminated
2–3	3	moderately to strongly contaminated
1–2	2	moderately contaminated
0–1	1	uncontaminated to moderately contaminated
0	0	uncontaminated

### Degree of contamination ( $C_d$ )

Hakanson (1980) proposed an overall indicator of contamination based on integrating data for a series of seven specific heavy metals and the organic pollutant PCB. This method is based on the calculation for each pollutant of a contamination factor ( $C_f$ ). However the  $C_f$  requires that at least five surficial sediment samples are averaged to produce a mean pollutant concentration which is then compared to a baseline pristine reference level, according to the following equation:

$$C_f = M_x / M_b$$

where  $M_x$  and  $M_b$  respectively refer to the mean concentration of a pollutant in the contaminated sediments and the pre-industrial “baseline” sediments. The study by Hakanson (1980) analysed seven specific heavy metals (As, Cd, Cu, Cr, Hg, Pb, Zn) and the organic pollutant PCB and thus considers eight possible measures of contamination. Hakanson's study also proposed that the *numeric sum* of the eight specific contamination factors expressed the *overall degree* (Hakanson 1980) of sediment contamination ( $C_d$ ) using the following formula:

$$C_d = \sum_{i=1}^8 C_f^i$$

The calculated  $C_d$  is therefore defined as the sum of the  $C_f$  for the eight pollutant species specified by Hakanson (1980). The  $C_d$  is aimed at providing a measure of the degree of overall contamination in surface layers in a particular core or sampling site. However the Hakanson (1980) classification terminologies and calculation formula is based on and is restricted to the seven metals plus PCB specified in Hakanson's study. Furthermore all eight species must be analysed in order to calculate the correct  $C_d$  for the range of classes defined by Hakanson (1980).

### Modified degree of contamination ( $mC_d$ )

As a result of the above limitations, Abraham (2005) presented a modified and generalised form of the Hakanson (1980) equation for the calculation of the overall degree of contamination at a given sampling or coring site as follows.

- (1) The modified formula is generalised by defining the degree of contamination ( $mC_d$ ) as the sum of

all the contamination factors ( $C_f$ ) for a given set of estuarine pollutants divided by the number of analysed pollutants.

- (2) The mean concentration of a pollutant element is based on the analysis of at least three samples of the impacted sediments (taken from either the uppermost layers of a core or from the associated surficial sediments)
- (3) The baseline concentrations are determined from lower core concentrations or from similar nearby uncontaminated sediments.

The modified equation for a generalised approach to calculating the degree of contamination is given below:

$$mC_d = \frac{\sum_{i=1}^{i=n} C_f^i}{n}$$

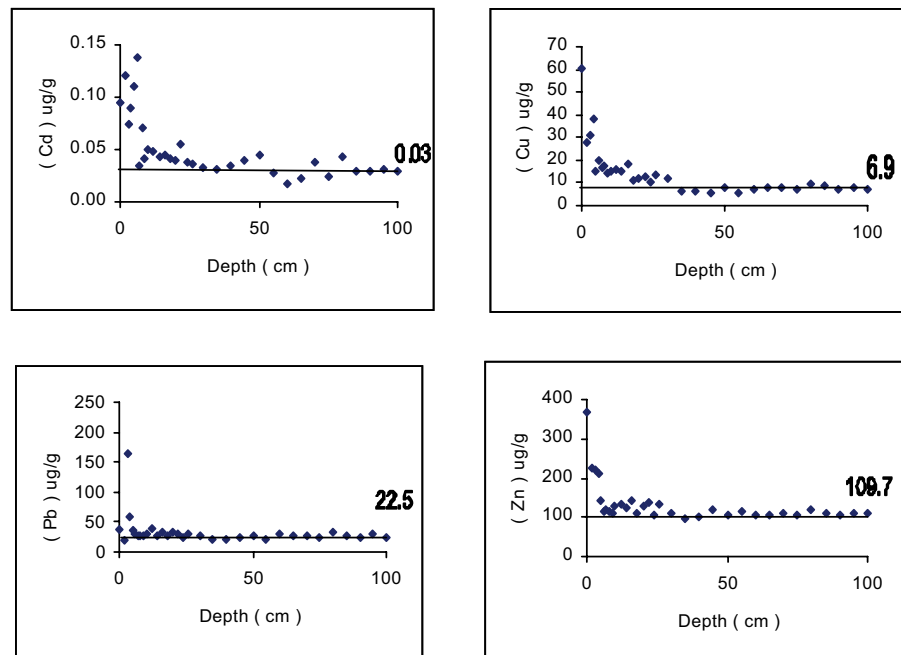
where  $n$  = number of analysed elements and  $i$  =  $i$ th element (or pollutant) and  $C_f$  = Contamination factor. Using this generalised formula to calculate the  $mC_d$  allows the incorporation of as many metals as the study may analyse with no upper limit. The expanded

range of possible pollutants can thus include both heavy metals and organic pollutants should the latter be available for the studied samples. For the classification and description of the modified degree of contamination ( $mC_d$ ) in estuarine sediments the following gradations are proposed:

$mC_d < 1.5$	Nil to very low degree of contamination
$1.5 \leq mC_d < 2$	Low degree of contamination
$2 \leq mC_d < 4$	Moderate degree of contamination
$4 \leq mC_d < 8$	High degree of contamination
$8 \leq mC_d < 16$	Very high degree of contamination
$16 \leq mC_d < 32$	Extremely high degree of contamination
$mC_d \geq 32$	Ultra high degree of contamination

An intrinsic feature of the  $mC_d$  calculation is that it produces an overall average value for a range of pollutants. As with any averaging procedure, care must however be used in evaluating the final results since the effect of significant metal enrichment spikes for individual samples may be hidden within the overall average result. An example of this is copper in core TE-1 in the lower Tamaki Estuary as discussed below.

**Fig. 2** Variation of heavy metals with depth in core TE-2. The *solid line* represents the calculated base line concentration



**Table 2** Enriched metal concentrations in Tamaki Estuary fine fraction sediments based on the average of the three highest concentration samples in the top 10 cm of each core

Core	Fe Percent	Cd µg/g	Cu µg/g	Pb µg/g	Zn µg/g
TE-1	3.0	0.11	20.7	50.7	166.0
TE-2	2.2	0.11	43.1	121.6	271.6
TE-4	2.3	1.02	46.8	69.0	235.5
TE-5	1.8	0.14	39.8	85.0	264.0
TE-6	1.7	0.10	29.8	66.8	195.5
TE-7	2.8	0.09	27.2	64.0	137.6
TE-8	3.7	0.48	29.3	56.7	161.5
TE-9	2.6	0.19	39.2	72.2	226.1
Average	2.51	0.28	34.5	73.3	207.2

**Calculation of heavy metal enrichment in Tamaki Estuary sediments**

In order to illustrate the advantages and disadvantages of the different approaches, the above enrichment calculation methods are applied in the following sections to analytical data from Tamaki Estuary cores. The aim of the comparison is to derive realistic estimates for the amount of contamination that has impacted Tamaki Estuary sediments.

**Enriched concentrations**

Appraisal of the eight Tamaki Estuary cores shows a distinctive enrichment of heavy metals towards the surface as shown in Fig. 2 for core TE-2. In order to derive average representative metal concentrations for the uppermost layers, the three most enriched fine

fraction samples in the upper 10 cm of each core were averaged for the analysed elements (Table 2).

**Baseline concentrations**

Tamaki Estuary fine fraction metal concentration trends decrease significantly with depth and generally form a flat “baseline” (Fig. 2). Metal estimates for pristine pre-industrial sediments in each Tamaki Estuary core were therefore calculated by averaging five low concentration samples in the flat baseline area of the cores (Table 3).

**Enrichment factor (EF)**

In calculating the normalized enrichment factors (EF), the original Salomons and Förstner (1984) equation was substituted in the present study by Fe because Al data was not available. Iron correlation coefficient

**Table 3** Baseline metal concentrations in fine fraction sediment samples from Tamaki Estuary based on the average of the five lowest concentrations at depth in each core

Core	Fe Percent	Cd µg/g	Cu µg/g	Pb µg/g	Zn µg/g
TE-1	3.8	0.08	1.4	22.1	50.6
TE-2	2.8	0.03	6.9	22.5	109.7
TE-4	2.9	0.13	11.1	12.0	75.4
TE-5	3.2	0.09	15.3	19.1	77.7
TE-6	3.6	0.07	26.7	25.8	129.3
TE-7	3.7	0.06	11.2	27.4	47.5
TE-8	1.3	0.07	18.1	26.3	24.7
TE-9	1.4	0.07	14.8	24.0	64.9
Average	2.8	0.08	13.2	22.4	72.5

**Table 4** Enrichment factors (EF) for Tamaki Estuary fine fraction sediments normalised with respect to the iron content in continental shales

$EF = M_{\text{sample}} \times Fe_{Cs} / Fe_{\text{sample}} \times M_{Cs}$  where  $Cs$  is the average metal concentration for continental shale (Turekian and Wedepohl 1961).

Core	Cd	Cu	Pb	Zn	Average
Te-1	1.2	1.0	5.6	3.8	2.9
Te-2	1.6	2.9	18.3	8.6	7.9
Te-4	15.2	3.1	10.3	7.4	9.0
Te-5	2.7	3.3	15.9	10.4	8.1
Te-6	1.9	2.6	13.0	8.1	6.4
Te-7	1.0	1.5	7.7	3.5	3.4
Te-8	4.3	1.2	5.1	3.1	3.4
Te-9	2.4	2.2	9.3	6.1	5.0
Average	3.8	2.2	10.6	6.4	5.8

data in the studied sediments indicates that Fe concentrations are generally not correlated to the other metals (Abraham 2005).

For comparison, normalized EF values were calculated using the continental shale abundance of Fe (6.75%, Turekian and Wedepohl 1961) as well as using the average concentration of iron in the lower part of the studied cores (Table 3). According to Sinex and Helz (1981) the EF is generally not very sensitive to the choice of baseline. However in the present study the EF data normalised to continental shale Fe, when compared to EF data calculated using the pristine lower core concentrations, demonstrates that the EF values for most of the elements will change considerably (Tables 4 and 5). Using the continental shale Fe concentration as a normaliser results in significantly higher average EF values (grand average = 5.8) as compared to average values determined using the actual Fe content in each core (grand average = 4.3).

In view of these conflicting features it is clear that normalized EF values calculated using continental shale concentrations need to be interpreted with caution. Clearly for Tamaki Estuary the most appropriate and relevant procedure is to use the core iron

values for normalisation. The resulting normalised grand average EF indicates a four-fold metal enrichment in fine fraction sediments in the upper layers of Tamaki Estuary cores (Table 5).

#### Geoaccumulation index ( $I_{\text{geo}}$ )

The  $I_{\text{geo}}$  method was used to calculate the metal contamination levels for the recovered cores from Tamaki Estuary. The average  $I_{\text{geo}}$  class is 1–2 indicating uncontaminated to moderately contaminated levels. Details of the  $I_{\text{geo}}$  values for individual elements in the eight cores are presented in Table 6. The negative  $I_{\text{geo}}$  values found in the table are the results of relatively low levels of contamination for some metals in some cores and the background variability factor (1.5) in the  $I_{\text{geo}}$  equation.

#### Modified degree of contamination ( $mC_d$ )

In Tamaki Estuary the revised Hakanson equation was used to calculate the modified degree of contamination ( $mC_d$ ) for the four analysed elements (Cd, Cu, Pb and Zn). The results for each core are presented in

**Table 5** Enrichment factors (EF) for Tamaki Estuary fine fraction sediments normalised with respect to the iron content in the bottom of each core

$EF = M_{\text{sample}} \times Fe_{\text{baseline}} / Fe_{\text{sample}} \times M_{\text{baseline}}$  where baseline refers to the average metal concentrations determined in the lower part of the core.

Core	Cd	Cu	Pb	Zn	Average
Te-1	1.4	14.7	2.3	3.3	5.4
Te-2	4.6	7.9	6.8	3.1	5.6
Te-4	10.0	5.4	7.4	4.0	6.7
Te-5	2.8	4.6	7.8	5.9	5.3
Te-6	3.0	2.4	5.5	3.2	3.5
Te-7	1.8	3.2	3.1	3.8	3.0
Te-8	2.4	0.5	0.7	2.2	1.5
Te-9	2.9	2.8	3.2	3.7	3.2
Average	3.6	5.2	4.6	3.7	4.3



**Table 6** Index of geoaccumulation ( $I_{geo}$ ) in surface fine fraction sediments compared to lower core baseline values in Tamaki Estuary cores

Core	Index of geoaccumulation ( $I_{geo}$ )				$I_{geo}$ class	Sediment quality
	Cd	Cu	Pb	Zn		
TE-1	-0.17	3.28	0.60	1.13	0–4	uncontaminated to strongly contaminated
TE-2	1.27	2.06	1.85	0.72	1–3	uncontaminated to moderately and strongly contaminated
TE-4	2.37	1.49	1.94	1.06	2–3	moderately to strongly contaminated
Te-5	0.09	0.80	1.57	1.18	1–2	uncontaminated to moderately contaminated
Te-6	-0.08	-0.42	0.79	0.01	0–1	uncontaminated to moderately contaminated
Te-7	-0.11	0.69	0.64	0.95	0–1	uncontaminated to moderately contaminated
Te-8	2.21	0.11	0.52	2.12	1–3	uncontaminated to moderately and strongly contaminated
TE-9	0.86	0.82	1.00	1.22	1–2	uncontaminated to moderately contaminated
Average	0.81	1.10	1.11	1.05	1–2	uncontaminated to moderately contaminated

Table 7 along with the near four-fold mCd grand average for all cores. The mCd for the individual cores generally lie in the range 2–5 as shown in Fig. 3. Four of the eight cores have mCd values above four and three cores have values above 2. The mCd data indicate significant anthropogenic impact in all cores except possibly TE-6. Using the classification system proposed for the modified equation, the overall range of mCd values indicate a moderate to high degree of contamination in Tamaki Estuary sediments.

**Discussion**

The results of the various methods for calculating heavy metal enrichment in Tamaki Estuary sediments are summarised in Table 8. The average results demonstrate that, using the continental shale as a reference concentration, the  $EF_{(c-shale)}$  factor is relatively high. By contrast the results for  $EF_{(b-core)}$  and  $mC_{d (b-core)}$  are similar (Table 8) with their mean

indicating an average fourfold enrichment compared to pristine “base line” sediment at depth in the cores.

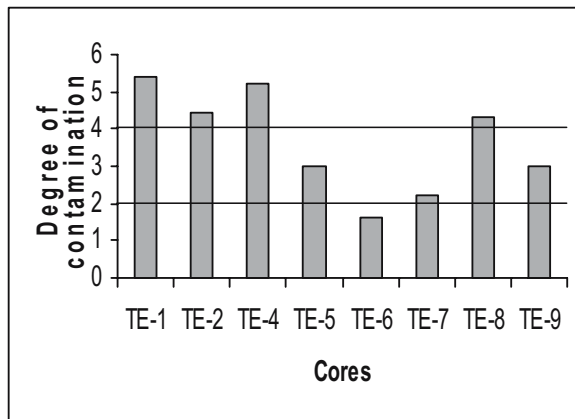
The  $I_{geo}$  factor is not readily comparable to the other indices of metal enrichment due to the nature of the  $I_{geo}$  calculation, which involves a log function, and a background multiplication of 1.5. Based on the classification system proposed for  $I_{geo}$  factors, Tamaki Estuary cores are classed on average as uncontaminated to moderately contaminated. The  $I_{geo}$  “uncontaminated” designation is clearly inappropriate as part of an overall description of the heavy metal results for cored sediments from this estuary.

The modified degree of contamination,  $mC_{d (b-core)}$  as proposed in the present study, is based on integrating and averaging all the available analytical data for a set of sediment samples. This modified method can therefore provide an integrated assessment of the overall enrichment and contamination impact of groups of pollutants in sediments.

In considering the average  $mC_d$  results, it should be noted that compared to baseline data, copper is

**Table 7** Modified degree of contamination ( $mC_d$ ) and contamination factors ( $C_f$ ) using lower core baseline values for heavy metals in fine fraction sediments from Tamaki Estuary cores

Core	Contamination factors				sum $C_f$	$mC_d$
	Cd	Cu	Pb	Zn		
TE-1	1.3	14.6	2.3	3.3	21.5	5.4
TE-2	3.6	6.3	5.4	2.5	17.8	4.5
TE-4	7.8	4.2	5.7	3.1	20.8	5.2
TE-5	1.6	2.5	4.5	3.4	12.0	3.0
TE-6	1.4	1.1	2.6	1.5	6.6	1.7
TE-7	1.4	2.4	2.3	2.9	9.0	2.3
TE-8	7.0	1.6	2.2	6.5	17.3	4.3
TE-9	2.7	2.7	3.0	3.5	11.9	3.0
Average	3.4	4.4	3.5	3.3	14.6	3.7



**Fig. 3** Histogram of the modified degree of contamination ( $mC_d$ ) using Zn, Cu, Pb and Cd in cored sediments from Tamaki Estuary. The *horizontal lines* represent boundaries between low, moderate and high degrees of contamination

significantly enriched in some lower estuary cores (particularly in core TE-1, Table 7). This localised enrichment is considered to be linked to the use of copper-based antifouling paint on yachts moored in the lower estuary.

Clearly in any survey of marine, estuarine or freshwater sediments, the best approach is to penetrate below the present day surface contamination and sample the pristine or least contaminated sediments available at depth in cores from the target survey area. This will allow the determination of realistic baseline values for the target area. This approach will work best in areas that have only suffered relatively recent contamination such as in countries that have relatively young industrial histories (e.g. Australia and New

Zealand), where it is possible in most cases to get below the level of first anthropogenic impact.

Ridgway and Shimmield (2002) draw attention to the considerable depth to which metal contamination may exist in old heavily industrialised countries such as in Europe. In these countries it may not be possible to get below the anthropogenic impact unless deep vibra-cores are used to penetrate several meters into the sediments. However for samples from these extended depths, the direct sedimentological and mineralogical similarities with surface sediments become less reliable and hence their comparability and suitability more tenuous as good reference samples.

This difficulty in establishing good baseline reference samples in old heavily industrialised countries is a reminder of the role of average continental shale and crustal data for reference purposes. Alternatively, due to shortcomings in using average shale and crustal data, reference environmental concentrations may need to be more focussed with the reference data based on regional and/or worldwide compilations of pristine or near-pristine estuarine sediment metal compositions derived from cored sediment samples in which clear baseline trends are indeed visible. To this end the baseline data for cored fine fraction sediments in Tamaki Estuary makes a useful contribution.

## Conclusions

The impact of anthropogenic heavy metal pollution on Tamaki Estuary was evaluated using Enrichment Factors (EF), geoaccumulation indices ( $I_{geo}$ ) and

**Table 8** Summary of average enrichment indices for Cd, Cu, Pb and Zn in Tamaki Estuary fine fraction cored sediments calculated using various methods

Core	Average $I_{geo}$ (b-core)	Average EF <sub>(c-shale)</sub>	Average EF <sub>(b-core)</sub>	$mC_d$ (b-core)
TE-1	1.2	2.9	5.4	5.4
TE-2	1.5	7.9	5.6	4.5
TE-4	1.7	9.0	6.7	5.2
TE-5	0.9	8.1	5.3	3.0
TE-6	0.08	6.4	3.5	1.7
TE-7	0.5	3.4	3.0	2.3
TE-8	1.2	3.4	1.5	4.3
TE-9	0.9	5.0	3.2	3.0
Average all cores	1.0	5.8	4.3	3.7

( $I_{geo}$  = index of geoaccumulation, EF = enrichment factor using Fe as normaliser and baseline values from continental shale and base of core,  $mC_d$  = modified degree of contamination, c-shale=continental shale, b-core=base of core)

modified degrees of contamination ( $mC_d$ ) for Cu, Pb, Zn and Cd in fine fraction sediments in eight cores.

The geoaccumulation indices ( $I_{geo}$ ) are distinctly variable and suggest that fine fraction sediments in the various Tamaki Estuary cores range from uncontaminated to moderately contaminated with respect to the analysed metals. The uncontaminated  $I_{geo}$  designation is clearly not supported by the other methods for calculating metal pollution impact in Tamaki Estuary.

Normalised enrichment factor (EF) values for four heavy metals were calculated for Tamaki Estuary using (1) the continental shale abundance of Fe and (2) the average concentration of Fe in the lower part of the studied cores. The results show that using the Fe concentration in the continental shale as a normaliser produces higher average EF values for Cu, Pb, Zn and Cd as compared to average values determined using the actual Fe content in each core. The latter method is however the most relevant to Tamaki Estuary and the normalized EF results demonstrate a fourfold metal enrichment in the fine fraction sediments in the upper layers of Tamaki Estuary cores.

In Tamaki Estuary pollution impact at an individual location is best evaluated using enrichment factors incorporating reference metal concentrations from associated pristine lower core ‘baseline’ sediments.

With regard to an overall measure of heavy metal contamination applicable to estuarine or coastal sediments, the present study proposes a modified and generalised form of the Hakanson (1980) pollution impact equation. A modified degree of contamination ( $mC_d$ ) is proposed in which the sum of the individual contamination factors is divided by the number of analysed pollutants. Using this approach the average  $mC_d$  (b-core) is 3.7, with  $mC_d$  (b-core) values generally ranging from 2 to 5. Overall, the range of  $mC_d$  values indicates a moderate to high degree of fine fraction sediment contamination in Tamaki Estuary cores.

**Acknowledgments** The authors wish to thank Murray Gregory, Scott Nichol and Fadhil Sadooni for their assistance in the field and for helpful comments at various stages in the work. In addition, we wish to acknowledge and thank Carol Stewart, John Wilmhurst, Vincent Lane and Noel Renner for help and assistance with geochemical analyses.

**References**

Abraham, G., & Parker, R. (2002). Heavy metal contaminants in Tamaki Estuary: Impact of city development and

growth, Auckland, New Zealand. *Environmental Geology*, 42, 883–890.

Abraham, G. M. S. (2005). Holocene sediments of Tamaki Estuary: Characterisation and impact of recent human activity on an urban estuary in Auckland, New Zealand. Ph.D. thesis, University of Auckland, Auckland, New Zealand, 361p.

Auckland Regional Council (1990). Bathing beaches water quality surveys, 1990–1991, Technical publication, Auckland Regional Water Board No. 88.

Auckland Regional Council (1992). Tamaki catchment and estuary: Review of water quality, Auckland. Auckland Regional Council, New Zealand, Technical publication No. 20.

Auckland Regional Council (1999). Tamaki Estuary water quality survey 1985–1997: Review report, Auckland Regional Council, New Zealand, Technical publication No. 105.

Bresline, V. T., & Sanudo-Wilhelmy, S. A. (1999). High spatial resolution sampling of metals in the sediment and water column in port Jefferson Harbour, New York. *Estuaries*, 22, 669–680.

Bruland, K. W., Bertine, K., Koide, M., & Goldberg, E. D. (1974). History of metal pollution in southern California coastal zone. *Environmental Science and Technology*, 8, 425–432.

Covelli, S., & Fontonlan, G. (1997). Application of a normalisation procedure in determining regional geochemical baselines. *Environmental Geology*, 30, 34–45.

Deely, J. M., & Fergusson, J. E. (1994). Heavy metal and organic matter concentration and distributions in dated sediments of a small estuary adjacent to a small urban area. *The Science of the Total Environment*, 153, 97–111.

Dickinson, W. W., Dunbar, G. B., & McLeod, H. (1996). Heavy metal history from cores in Wellington Harbour, New Zealand. *Environmental Geology*, 27, 59–69.

Din, T. B. (1992). Use of aluminum to normalize heavy metal data from estuarine and coastal sediments of straits of Melaka. *Marine Pollution Bulletin*, 24, 484–491.

Faganeli, J., Planinc, R., Pezdic, J., Smodis, B., Stegnar, P., & Ogorelec, B. (1991). Marine geology of the Gulf of Trieste (northern Adriatic): Geochemical aspects. *Marine Geology*, 99, 93–108.

Hakanson, L. (1980). Ecological risk index for aquatic pollution control, a sedimentological approach. *Water Research*, 14, 975–1001.

Hornung, H., Karm, M. D., & Cohen, Y. (1989). Trace metal distribution on sediments and benthic fauna of Haifa Bay, Israel. *Estuarine, Coastal and Shelf Science*, 29, 43–56.

Matthai, C., & Birch, G. (2001). Detection of anthropogenic Cu, Pb, and Zn in continental shelf sediments off Sydney, Australia – A new approach using normalisation with cobalt. *Marine Pollution Bulletin*, 42, 1055–1063.

Mudroch, A., & Bourbonniere, R. A. (1994). Sediment preservation processing and storage. In A. Mudroch, S. D. Mackinght (Eds), *Hand book of techniques for aquatic sampling*, 2nd edn. Boca Raton.

Müller, G. (1969). Index of geoaccumulation in the sediments of the Rhine River. *Geojournal*, 2, 108–118.

Niencheski, L. F., Windom, H. L., & Smith, R. (1994). Distribution of particulate trace metal in Patos Lagoon Estuary (Brazil). *Marine Pollution Bulletin*, 28, 96–102.

- Ravichandran, M., Baskaran, M., Santschi, P. H., & Bianchi, T. (1995). History of trace metal pollution in Sabine-Neches Estuary, Beaumont, Texas. *Environmental Science and Technology*, 29, 1495–1503.
- Ridgway, J., & Shimmield, G. (2002). Estuaries as repositories of historical contamination and their impact on shelf seas. *Estuarine, Coastal and Shelf Science*, 55, 903–928.
- Salomons, W., & Förstner, U. (1984). Metals in the hydrocycle. Springer, Berlin Heidelberg Tokyo.
- Sharma, V. K., Rhudy, K. B., Koenig, R., Baggett, A. T., Hollyfield, S., & Vazquez, F. G. (1999). Metals in sediments of Texas estuaries, USA. *Journal of Environmental Science and Health*, 34, 2061–2073.
- Siegel, F. R., Slaboda, M. L., & Stanley, D. J. (1994). Metal pollution loading, Manzalah Lagoon. Nile Delta, Egypt: Implications for aquaculture. *Environmental Geology*, 23, 89–98.
- Sinex, S. A., & Helz, G. R. (1981). Regional geochemistry of trace elements in Chesapeake Bay. *Environmental Geology*, 3, 315–323.
- Stewart, C. (1989). Spatial and temporal trends in trace metal deposition in Canterbury, New Zealand. Ph.D. thesis, University of Canterbury, Christchurch, New Zealand.
- Stoffers, P., Glasby, G. P., Wilson, C. J., Davis, K. R., & Watter, P. (1986). Heavy metal pollution in Wellington Harbour. *New Zealand Journal of Marine and Freshwater Research*, 20, 495–512.
- Taylor, S. R. (1964). The abundance of chemical elements in the continental crust – A new table. *Geochimica Cosmochimica Acta*, 28, 1273–1285.
- Turekian, K. K., & Wedepohl, D. H. (1961). Distribution of the elements in some major units of the earth's crust. *Bulletin Geological Society of America*, 72, 175–192.
- Wedepohl, K. H. (1995). The composition of the continental crust. *Geochimica Cosmocheimica Acta*, 59, 1217–1232.
- Williamson, R. B., Blom, A., Hume, T. M., Glasby, G. P., & Larcomb, M. (1992). Heavy metals in Manukau Harbour sediments. Water Quality Centre Technical Publication No. 23.
- Windom, H. L., Smith, R. G. Jr., & Rawlinson, C. (1989). Particulate trace metal composition and flux across the south eastern US continental shelf. *Marine Chemistry*, 27, 283–297.