Definition of baseline metal concentrations for assessing metal enrichment of sediment from the south-eastern Cape coastline of South Africa

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Abstract

Assessing metal contamination of sediment is complicated since metals are a ubiquitous, naturally occurring component of sediment, their concentrations in un-contaminated sediment can vary by orders of magnitude over relatively small spatial scales, and naturally occurring and anthropogenically introduced metals tend to accumulate in the same areas. To meaningfully interpret sediment metal data, factors affecting metal concentration variability in sediment must first be compensated for before naturally occurring and anthropogenically introduced concentrations can be differentiated. This can be accomplished through the procedure of geochemical normalisation. Baseline metal concentration models developed through this procedure can then be used to interpret metal concentrations measured in sediment from areas where anthropogenic metal inputs are suspected. In this study baseline metal concentrations in sediment from the coastal zone between the Kromme River estuary in St Francis Bay and the Nahoon River estuary in East London on the south-eastern Cape coastline of South Africa are defined, for the purpose of differentiating between natural and anthropogenically introduced metal concentrations in sediment from this region. Baseline concentration models were initially defined for three sub-regions of the coastline, and then for the region as a whole. Aluminium and iron were found to be suitable for normalising the concentrations of copper, cobalt, chromium, manganese, nickel, lead and zinc, but not concentrations of arsenic, cadmium and mercury. Baseline concentrations of arsenic, cadmium and mercury above which enrichment can be inferred were defined using cumulative probability and univariate plots. The manner in which the baseline models are used to interpret metal concentrations is demonstrated, using metal concentrations measured in sediment from the Port of East London. The baseline models are used to assess the suitability of sediment quality guidelines (SQGs) developed by the Department of Environmental Affairs and Tourism (DEAT) for assessing the quality of sediment from the coastal zone of South Africa. The Special Care Level Guideline for chromium is unsuitable for assessing the quality of sediment from the south-eastern Cape coastline since the guideline for this metal specifies a concentration that is below the baseline concentration in sediment from this region.

Keywords: Eastern Cape, sediment, metal, normalisation, baseline, contamination

Introduction

Contaminants are introduced into coastal environments from multiple anthropogenic sources. In urban areas a significant proportion of the contaminant load is introduced in solution, including through urban stormwater runoff and effluent discharge (Schiff and Gossett, 1998; Sutherland, 2000; Sutherland and Tolosa, 2000; Matthai et al., 2002; Brown and Peake, 2006). Many contaminants have low water solubility and are particle-reactive (Olsen et al., 1982), and once introduced into surface waters rapidly adsorb to suspended sediment and organic matter and are in this manner 'scavenged' from the water column through flocculation, coagulation and sedimentation (De Groot et al., 1976; Förstner and Wittman, 1979; Huh et al., 1992; Honeyman and Santschi, 1988; Mwanuzi and De Smedt, 1999; Hatje et al., 2003). As a consequence, concentrations of most contaminants in bottom sediment and at the sediment water interface usually exceed those in the overlying water column by several orders of magnitude (Horowitz, 1991; Bryan and Langston, 1992; Daskalakis and O'Connor, 1995).

Metals (for the sake of simplicity the metalloid arsenic is referred to as a metal in this study) generally do not degrade, and with continued input and limited sediment redistribution can accumulate in depositional zones to concentrations high enough to cause toxic effects to benthic and epibenthic organisms (Chapman, 1989). Bottom sediment does not only act as a sink for anthropogenically introduced metals however, but can also be significant source. Metals can be remobilised and released from sediment into the overlying water column through natural and anthropogenic disturbance, including bioturbation, storms and dredging (Förstner, 1989; Daskalakis and O'Connor, 1995; Long et al., 1995; Goossens and Zwolsman, 1996; Zoumis et al., 2001; Linge and Oldham, 2002; Eggleton and Thomas, 2004). The importance of sediment as a source for metals long after the major anthropogenic source has been removed or controlled is highlighted by the case of mercury in San Francisco Bay (USA). Although mercury loading to the bay associated with mining activities was significantly reduced during the early 20th century, mercury remobilised from sediment continues to pose a significant risk to biological and human health (Nriagu, 1994; Flegal et al., 2005).

Not surprisingly, monitoring sediment metal concentrations is the focus of attention in environmental impact/quality moni-

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toring programmes in many regions of the world. In addition to environmental concerns there are several pragmatic reasons for monitoring sediment metal concentrations. Higher concentrations of metals in sediment compared to the overlying water column make detection and measurement easier. The low and often highly variable metal concentrations in the water column, as a consequence of differences in flow (e.g. currents) and variable anthropogenic inputs, means that only a snapshot of contamination problems is obtained by investigation of this medium while analyses of metal concentrations in bottom sediment provide a more conservative, spatially and temporally integrated measure of conditions.

While assessing sediment contamination by specific organic chemicals that only have an anthropogenic origin is easy (e.g. polychlorinated biphenyls, PCBs), determining whether sediment is metal contaminated is complicated because metals are a ubiquitous, naturally occurring component of sediment. Metal concentrations in un-contaminated sediment can also vary by orders of magnitude over relatively small spatial scales depending on sediment mineralogy, granulometry and organic content amongst other factors (Loring and Rantala, 1992; Thomas and Bendell-Young, 1999; Kersten and Smedes, 2002). High metal concentrations in sediment do not automatically imply that contamination has occurred, but may simply reflect the natural mineralogical composition of the parent material and granulometry and organic matter content of the host sediment. Further, despite input and transport dissimilarities, naturally occurring and anthropogenically introduced metals tend to accumulate in the same areas (Hanson et al., 1993). To meaningfully interpret sediment metal concentrations the mineralogical and granulometric factors influencing natural variation in metal concentrations in sediment must first be compensated for before naturally occurring (baseline) concentrations can be differentiated from anthropogenically introduced concentrations (Kersten and Smedes, 2002). This is usually accomplished through the procedure of geochemical normalisation, which mathematically normalises metal concentrations to a co-occurring conservative element (the normaliser, sometimes referred to as reference element) that provides a tracer of crustal decomposition. Models generated in this manner are referred to as baseline models (The term (geochemical) baseline is used in preference to (geochemical) background, since it cannot categorically be assumed that the metal concentrations used to establish the baseline models have not been elevated through anthropogenic contributions (e.g. diffuse pollution associated with atmospheric deposition). Metal concentrations used in the present study therefore reflect baseline conditions at the time of sampling, including possible anthropogenic inputs, rather than background (natural) conditions, which are generally regarded as conditions existing prior to anthropogenic inputs of metals associated with the industrial revolution in areas with a long record of human habitation and industrialisation.). The relationship defined between a metal and the normaliser can then be used to identify anomalous metal concentrations, which may have an anthropogenic source.

The extent and magnitude of metal contamination of sediment from the coastal environment of South Africa is poorly understood, despite the fact that sediment metal concentrations are monitored on an annual basis as part of environmental quality monitoring programmes in all port environments and near some marine effluent outfalls. The most important reason for this poor understanding is that the baseline concentrations of metals in sediment for most regions of the coastline have not previously been defined, and many workers have failed to appreciate the necessity for developing such baselines before interpreting metal concentrations. Several local workers have interpreted sediment metal concentrations by simply comparing concentrations between sampling sites, under the assumption that 'high' metal concentrations reflect increased levels of contamination. This has, not surprisingly, led to the classification of sediment as being metal contaminated when in fact measured concentrations fall within the expected baseline concentration range for the area in question (see examples later). As a further complication some workers have interpreted sediment metal concentrations as reflecting contamination based on these concentrations exceeding sediment quality guidelines (SQGs). SQGs do not differentiate between baseline and anthropogenically introduced metal concentrations, but rather define metal concentrations above which adverse biological effects may be expected (with varying levels of confidence). These concentrations usually exceed the relevant metals baseline concentration for a particular area. Two different sets of SQGs have also been used by local workers over the last 15 years, namely those developed by Long and Morgan (1990) and subsequently refined by Long et al. (1995), and those proposed by the Department of Environmental Affairs and Tourism (DEAT, undated document). The metal guidelines of these SQGs often specify very different concentrations, with the consequence that sediment considered 'contaminated' using one set of SQGs is not considered so by the other.

The poor understanding of sediment metal baseline concentrations for some regions of the South African coastline is surprising since data for the definition of these concentrations are available. In the context of the present study, sediment metal concentrations from the coastal environment between the Kromme River estuary in St Francis Bay and the Nahoon River estuary in East London on the south-eastern Cape coastline (Fig. 1) were extensively investigated during the late 1970s and early 1980s. The objective of these investigations was to identify areas where there was evidence for metal contamination of sediment at that time and to collect baseline metal concentration data against which future measurements could be compared. To date over 20 000 metal concentrations have been measured in sediment from this region. A little more than half of these measurements are for sediment collected from estuaries that historically were (and many currently still are) minimally impacted by anthropogenic activities. These measurements are therefore potentially suitable for the definition of baseline concentrations. Although geochemical normalisation as a basis for defining baseline sediment metal concentrations was not new at the time that the bulk of these studies were conducted (late 1970s and early 1980s; Bruland et al., 1974; Trefry and Presley, 1976; Goldberg et al., 1979), it only came to prominence as an assessment tool during the late 1980s and early 1990s (Schropp and Windom, 1988; Windom et al., 1989; Loring, 1990; 1991; Schropp et al., 1990; Hanson et al., 1993). This, as well as the absence of powerful computers and sophisticated statistical software, account for the value inherent in these data not being fully exploited at the time. Geochemically normalised baseline models and the theory on which these are based also have application to data mining, and such application highlights several unsupported conclusions previously reached. Despite some limitations in the data available for the region in question in the present study, based on current trends in research funding in South Africa it is improbable that such an extensive database will ever be generated again and it is therefore imperative that the value inherent in these data is utilised.

The present study therefore defines baseline concentrations for several environmentally (ecotoxicologically) relevant metals in sediment from the coastal environment between the Kromme

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River estuary in St Francis Bay and the Nahoon River estuary in East London on the south-eastern Cape coastline of South Africa (Fig. 1). The manner in which baseline metal concentration models are used to infer enrichment (contamination) of sediment is demonstrated, and the models are also used to assess the suitability of SQGs developed by Long et al. (1995) and those proposed by the DEAT (undated document) for application in local coastal waters.

Background to geochemical normalisation

In addition to mineralogy, grain size is a critical factor influencing metal concentrations in sediment (Taylor and McLennan, 1981; Loring, 1990; Kersten and Smedes, 2002). Minerals that form fine-grained sediment, such as silt, contain a higher metal content in their crystalline structure compared to coarse-grained sediment, such as sand, which is comprised predominantly of metal-poor quartz. Sediments may increase their metal concentrations through surface adsorption, and since fine-grained sediments have a higher surface area to mass ratio compared to coarse-grained sediment they often sequester much higher levels of particle-reactive metals than adjacent coarser sediments (Horowitz and Elrick, 1987; Bubb et al., 1991). Furthermore, clays are generally highly (negatively) charged relative to their surface area, an important aspect considering that most metals in their free ionic form are positively charged. As a consequence, there is often a strong inverse correlation between sediment grain size and a metals concentration. This relationship is further enhanced by the common accumulation of organic matter in depositional zones, the organic matter presenting an additional surface for metal adsorption as well as contributing metals, albeit usually at low concentrations.

The objective of normalisation is to compensate for differences in metal concentrations in sediment, as influenced by differences in mineralogy, granulometry and organic matter. Two procedures can be used to normalise metal concentrations, namely primary (hereafter referred to as granulometric) and secondary (hereafter referred to as geochemical) normalisation.

Granulometric normalisation involves the isolation of a defined grain size fraction by sieving, with the aim of reducing the diluent effects of non-metal bearing minerals in coarse-grained sediment. Since grain size as a factor influencing metal concentration variability has then theoretically been compensated for, metal concentrations in samples of uncontaminated sediment derived from the same parent material should be similar. Granulometric normalisation is most applicable to the dominant metal bearing clay fraction of sediment (<2 µm; Kersten and Smedes, 2002). Metal concentrations in the clay fraction can, however, vary considerably between regions due to the contribution of other components in this fraction (e.g. colloidal matter) and often obfuscate direct comparison of metal concentrations between samples (Kersten and Smedes, 2002). Isolation of the clay fraction is also difficult and time consuming (Birch and Snowdon, 2004), often involving the collection and sieving of large volumes of sediment to obtain sufficient material for analysis. Furthermore, unless extreme care is taken there may be significant leaching of adsorbed contaminants from the sediment during wet sieving. As a result, 'coarser' fractions of the sediment are more commonly isolated (e.g. <62.5 µm, <20 µm; Sutherland, 2000; Birch and Snowdon, 2004). These fractions may, however, still contain significant concentrations of quartz (Birch and Taylor, 1999; Kersten and Smedes, 2002) and/or may have different mineralogy, with the result that observed variability in metal concentrations often needs to be further compensated for through geochemical normalisation (Matthai and Birch, 2001; Kersten and Smedes, 2002).

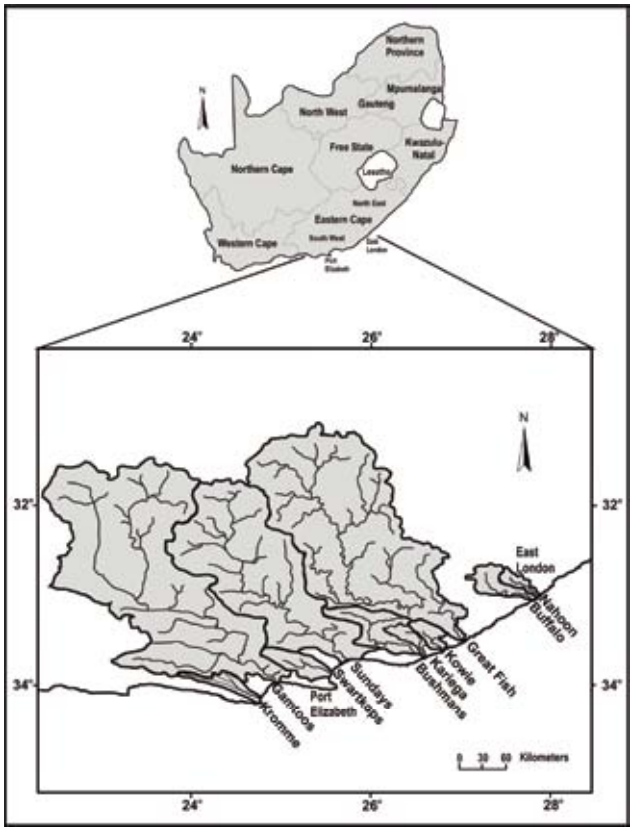

Figure 1
Maps of South Africa and the Eastern Cape showing locations of estuaries from which sediment was collected and other place names mentioned in text. The Ihlanza and Quinera River estuaries, which are not illustrated, are located between the Buffalo and Nahoon River estuaries. Bold lines indicate river catchment area.

The basis for geochemical normalisation is the fact that although absolute metal concentrations vary between crustal material from one region to another, the relative proportions of metals within material from a particular region tend to be fairly constant (Turekian and Wedepohl, 1961; Taylor and McLennan, 1981; Martin and Whitfield, 1983; Wedepohl, 1995). Metal concentrations in sediment derived from the parent material through weathering reflect the relative proportions of metals in the parent material, and determination of these ratios permits their comparison to similar ratios in sediment from areas where anthropogenic metal enrichment is suspected. Similarities or differences in the ratios of metals can then be used to infer whether or not enrichment has occurred.

The simplest geochemical normalisation approach is to express the concentration of a metal relative to the co-occurring concentration of a selected normaliser (usually a metal) in a sediment sample and to then divide this by the same ratio in anthropogenically un-impacted geological material. This permits the definition of an enrichment factor, $EF = (M/N)_{sample}/(M/N)_{baseline}$, where $(M/N)_{sample}$ is the metal:normaliser ratio in the sediment sample and $(M/N)_{baseline}$ is the metal:normaliser ratio in the anthropogenically un-impacted geological material. Although ratios for parent rock or regional sediment are most desirable as the denominator, these data are frequently not available and many workers substitute this with the Clarke value (average

concentration of the metal in the earth's crust). EFs of or below unity are taken as indicating that the metal has a natural source, and those greater than unity that the metal is enriched relative to the baseline or global average used.

Although widely used as sediment metal enrichment assessment tool, the calculated EF is highly dependent on the 'baseline' data used. Concentrations for metals in the various world-average data sets vary considerably (compare for example data for upper crust from Taylor and McLennan (1981) and Wedepohl (1995)), with the result that the calculated EF varies depending on the denominator used. Covelli and Fontolan (1997) and Rubio et al. (2000) compare data obtained using different denominators and describe the problems this leads to for determining anthropogenic enrichment. In a South African context there is, for example, a gradient in baseline concentrations of chromium along the south-east and east coasts, and evaluation of data by application of the same Clarke value for chromium fails to detect this anomaly. Clarke values (and by implication also calculated EFs) also do not incorporate natural or sampling/analytical variability in the concentration of metals. Metal concentrations may therefore be deemed as enriched (i.e. EF > 1) relative to the parent material when in fact they fall within the natural concentration range for the area. Some workers have compensated for this by assuming that enrichment occurs at an EF higher than unity (e.g. $\geq$2), but this is an arbitrary selection.

The relative constancy of the proportions of metals in sediment in particular regions and the usually strong inverse correlation between metal concentrations and sediment granulometry permits the use of an alternate geochemical normalisation approach, in which relationships between metal concentrations and the co-occurring concentration of a normaliser that provides a tracer of crustal decomposition are modelled through linear regression. By quantifying the variability in metal concentrations around the regression line (e.g. through definition of 99% prediction limits), the range in variability of baseline metal concentrations for an area can be defined and then compared to similarly normalised metal concentrations measured in sediment collected from areas where metal enrichment is suspected. Sediment samples with metal concentrations that fall within model prediction limits are considered to fall within the expected baseline range, while metal concentrations that plot above the model prediction limit are considered enriched relative to the baseline. This enrichment may be due to either natural or anthropogenic causes and site specific investigations can be sue to determine which of these is the more likely.

The use of a metal as a proxy for the natural metal-bearing phases of sediment (i.e. alumino-silicates) requires that the metal meet several conditions, namely that it:

- Is highly refractory
- Is structurally combined to one or more of the major metal-bearing phases (e.g. aluminosilicates)
- Co-varies in proportion to the naturally occurring concentrations of metals of interest
- Is insensitive to inputs from anthropogenic sources
- Is stable and not subject to environmental influences such as reduction/oxidation, adsorption/desorption and other diagenic processes that may alter sediment concentrations (Luoma, 1990).

A significant number of metals have been used as normalisers, including aluminium (Schropp et al., 1990; Daskalakis and O'Connor, 1995; Cooke and Drury, 1998; Weisberg et al., 1999; Roach, 2005), iron (Daskalakis and O'Connor, 1995; Schiff and Weisberg, 1999; Tanner et al., 2000), lithium (Loring, 1990, 1991; Aloupi and Angelidis, 2001; Veinott et al., 2001), rubidium (Grant and Middleton, 1990), and caesium and cobalt (Matthai and Birch, 2001). Aluminium and iron are, however, most commonly used. Of these, aluminium is generally considered to be the most suitable normaliser since it is a major constituent of fine grained alumino-silicates (clays), with which the bulk of trace metals are associated, and its concentration usually exhibits a strong inverse correlation to grain size and positive correlation to co-occurring metal concentrations. Aluminium is stable and not affected by early diagenic processes and strong redox effects commonly observed in sediments (Kersten and Smedes, 2000), and is highly refractory. Although iron is not as tightly incorporated into the crystal lattice of alumino-silicates as is aluminium, iron oxide coatings, which serve as a host for metals, are usually associated with sediments in definite quantities related to the sediment surface area. The concentration of iron consequently usually also exhibits a strong positive correlation to co-occurring concentrations of metals in sediment (Rule, 1986; Daskalakis and O'Connor, 1995; Kersten and Smedes, 2000). A potential limitation for the use of iron, however, is that it may be highly mobile in anoxic sediments, leading to its enrichment at the sediment surface through the deposition of iron oxides (Finney and Huh, 1989) or in deeper, anoxic, sediments as a result of co-precipitation with sulphides (Gobeil et al., 1997), and may lead to an underestimation of enrichment of other metals when used as the normaliser.

The natural concentrations of aluminium and iron in sediments, respectively the third and fourth most abundant elements in the earths crust (Wedepohl, 1995), are orders of magnitude higher than concentrations of metals of concern from a toxicological perspective (milligram/gram vs. microgram/gram concentrations respectively). The high natural concentrations of aluminium and iron are considered to 'swamp' the usually low inputs of toxic metals to the environment from anthropogenic sources, and their concentrations are therefore likely to remain relatively unchanged even in anthropogenically impacted areas. The low natural concentrations of trace metals are in contrast far more sensitive to anthropogenic inputs, with the result that the ratio between the metal of concern and the normaliser (aluminium or iron) is changed. Normalisation serves to detect such alterations in ratios, by comparing metal concentration ratios measured in sediment from uncontaminated locations to those in potentially metal-enriched sediment.

Materials and methods

Data sources

Data used to define baseline metal concentrations were extracted from investigations by Watling and Watling (1979; 1981; 1982a; b; c; d; e; f; 1983a), Talbot et al. (1982), Watling et al. (1982) and Watling et al. (1983). These workers measured metal concentrations in sediment from estuaries and the inter-tidal of the marine shoreline between the Kromme and Nahoon River estuaries (Fig. 1). Findings of several of these investigations are summarised by Watling and Watling (1982g; h; i; j; k; l; 1983b), Talbot et al. (1985) and Watling et al. (1985).

Sediment collection

Sediment was collected using scoops, dredges and cores (stainless steel with PVC liner; up to 600 mm length), transferred to polyethylene bags in the field and frozen (-20°C) in the laboratory until analysis (cores frozen in liners). Cores were sectioned

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longitudinally using a band saw and both halves cleaned with a stainless steel knife. One half of the core was resealed in polyethylene and reserved as a reference sample. The other half was measured and catalogued sedimentologically and then sectioned at 20 or 50 mm intervals or at obvious sedimentary boundaries.

Laboratory procedures

Sediment concentrations were determined for aluminium, iron, cadmium, copper, cobalt, chromium, manganese, mercury, nickel, lead and zinc. Analyses were undertaken in laboratories at the University of Port Elizabeth (now Nelson Mandela Metropolitan University). For all metals except mercury, sediment was dried at 90°C, disaggregated in a porcelain mortar, sieved through a 1.0 mm mesh nylon screen, and approximately 2 g weighed into a conical glass flask. Ten millilitres of concentrated HNO_3 were added and the mixture was taken to dryness on a hotplate. The residue was re-suspended in 10 mℓ of 4:1 HNO_3:$HClO_4$ and taken to dryness at 140°C. After cooling, the residue was dissolved in 10 mℓ of 1M HNO_3, filtered, and metal concentrations in solution determined using flame atomic absorption spectroscopy (Varian-Techtron AA5).

For mercury analyses, after sufficient sediment for analysis of metals described above had been removed cores were divided into 50 mm sections. The sediment was air-dried between filter paper sheets, disaggregated in a porcelain mortar, sieved through a 1.0 mm mesh nylon screen, and approximately 2 g oxidised in a tube furnace (preheated to 700°C). Oxygen was passed over the sample at a rate of 650 mℓ·min^{-1}. Exhaust gases were bubbled through a solution containing 25 mℓ of 5% potassium permanganate and 50 mℓ of 14% v/v H_2SO_4 until combustion was complete (usually about 3 min). Excess permanganate was reduced using 10% m/v hydroxylammonium chloride in 20% v/v HCl, and mercury concentrations in solution were quantified using an amalgamation trap and cold-vapour atomic absorption spectroscopy (Watling, 1978).

Sub-region delimitation and selection of unimpacted sites

Because of potential geological and geochemical differences between river catchments the most appropriate procedure for differentiating between baseline and anthropogenically introduced metal concentrations in sediment from any particular estuary is to develop models specific to individual river-estuarine systems. Although databases for most of the estuaries of concern in the present study are large, they were often not particularly suitable to the development of estuary specific baseline models due to narrow or bimodal metal concentration distributions. A potential solution was the combination of metal concentration data for estuaries in close proximity, as this would provide a wider range of normaliser, and hence other metal, concentrations. A further consideration favouring data combination was that the models could then be used to assess metal enrichment of sediment from the near-shore marine environment, where sediment has multiple provenance. Baseline models incorporating data from these different sources will integrate small, yet possibly significant, differences in sediment geochemistry. The application of the baseline models to estuaries, however, requires that the metal:normaliser relationships are comparable between estuaries. The data limitations described previously prevented a rigorous statistical comparison of relationships between estuaries, due to for example strong leverage effects in bimodally distributed metal concentrations. Differences in metal: normaliser relationships between estuaries were usually small and it was consequently decided to combine data for estuaries in close proximity from three sub-regions of the coastline as follows: Sub-Region 1: Kromme, Gamtoos, Swartkops and Sundays River estuaries; Sub-Region 2: Kariega, Bushmans, Kowie and Great Fish River estuaries; Sub-Region 3: Buffalo, Nahoon, Ihlanza and Quinera River estuaries (hereafter referred to as Sub-Regions 1, 2 and 3). Data for Sub-Regions 1 and 3 also included metal concentrations measured in sediment from the inter-tidal of the marine shoreline.

The development of baseline models requires that sediment used to develop the models be minimally impacted by anthropogenic activities. Most metal concentrations were measured in sediment collected from estuaries and from the inter-tidal of the marine shoreline where anthropogenic impacts were presumed *a priori* to be minimal based on their remoteness from large urban areas and industrial activities at the time of collection (this has changed for some systems/regions). The reader should note that although some metal concentrations incorporated into the baseline models were deemed by previous workers to reflect contamination, closer inspection of the data following normalisation often showed this not to be the situation or showed that high metal concentrations interpreted as reflecting contamination were based on anomalous data.

There were two exceptions to the inclusion of data only for systems remote from anthropogenic activities, namely the Swartkops River estuary and the East London area. Metal contamination of sediment from Algoa Bay was considered *a priori* to probably be most pronounced in the north-western sector of the bay, which receives metal inputs from the heavily industrialised city of Port Elizabeth. Although sediment from this sector of the bay is derived from several sources, the Swartkops River is one of the most important sources. The lower reaches of the Swartkops River and its estuary were already impacted by anthropogenic activities at the time of data collection (1979) and data for this system were consequently initially excluded from baseline model development for Sub-Region 1. Comparison of metal concentrations measured in the deeper regions of cores collected from the estuary to baseline models developed for Sub-Region 1 provided little evidence for metal enrichment however, but also showed that metal-normaliser relationships for this estuary may be slightly different to relationships for other estuaries from Sub-Region 1 (tending toward lower slopes). If so, then the exclusion of data from this system may lead to problems when assessing metal contamination of sediment from the north-western sector of Algoa Bay. Limitations in the data set for the Swartkops River estuary, particularly the narrow normaliser concentration range and a highly anomalous iron concentration distribution (Fig. 2 – next page) precluded a detailed statistical comparison of data between this and other estuaries from Sub-Region 1. Thus, despite possible slight differences between estuarine systems in Sub-Region 1 it was decided to nevertheless incorporate metal concentrations measured in the deepest regions (arbitrarily defined as below 480 mm from surface) of cores collected from the Swartkops River estuary.

Data used to develop baseline models for Sub-Region 3 were from estuaries situated within the boundaries of the city of East London, but were nevertheless used since there was no other data available for this region. As discussed later, baseline models developed for this sub-region are comparable to those for Sub-Regions 1 and 2, suggesting that the sediment samples were not metal contaminated at the time of collection.

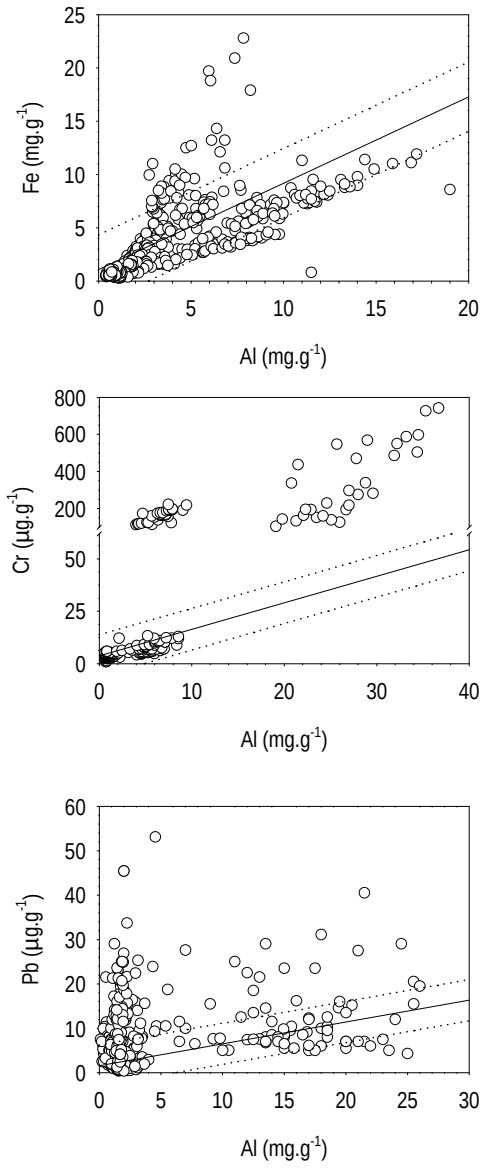

Figure 2

Examples of anomalous metal concentration distributions for (top) iron in the Swartkops River estuary, (middle) chromium in the Kromme River estuary, and (bottom) lead in the East London region. Regional baseline model regressions (solid line) and associated 99% upper and lower prediction limits (stippled lines) are superimposed on the data to illustrate the extent to which concentration distributions were anomalous.

Development of sub-regional baseline models

Data sets for different estuaries in each sub-region were initially examined separately. Since one objective of the present study was to compare the suitability of aluminium and iron as normalisers, only samples with concentration data for both these metals were included in the initial data sets. Data sets were then examined for data below detection limits. Although the trimming below detection limit data may bias datasets, and below detection limit data are therefore sometimes replaced with surrogate values (e.g. one half of the detection limit), this was not followed in the present study since detection limits for some studies are unreported and below detection limit data comprised a small proportion (usually << 1%) of the data sets. Data were then examined by generating scatter plots of metal concentrations against co-occurring aluminium and iron concentrations. With the exception of arsenic and cadmium, and in the East London area also lead, these plots indicated generally linear relationships between most metals and the normalisers, suggesting that the relationships could be formally described through linear regression analysis. Most mercury concentrations could not be linked to aluminium or iron concentrations due to the manner in which cores were sectioned for analyses of this metal and could not be examined in the same manner (see above for sectioning of cores for mercury analyses). Where co-occurring mercury and normaliser concentration data were available, scatter plots showed a moderate linear relationship in one estuary and a very weak relationship in another.

The scatter plot for iron normalised against aluminium for sediment from the Swartkops River estuary was highly anomalous (see Fig. 2) and iron data for this system were consequently not used in further analyses. The reason for this anomalous iron distribution is uncertain but is not reflected in sediment from other estuaries in Sub-Region 1.

Like other least-square statistical procedures, least-square regression is sensitive to the presence of outliers (Grant and Middleton, 1993; 1998). Sediment samples with unusual metal chemistry can exert a major influence on regression model parameters and other statistical descriptors of data sets, leading to a bias in the direction of outliers. Although a common cause for outliers is the unknowing inclusion of metal contaminated sediment in data sets, outliers can also result from contamination and procedural errors during field collection and laboratory analysis and from errors during data capture (Loring, 1991; Grant and Middleton, 1993). In large regional data sets outliers may also reflect differences in sediment mineralogy. A variety of statistical procedures have been used to identify outliers, ranging from relatively simple to complex (see for example Matschulatt et al., 1999), while professional judgement may also occasionally be used (Grant and Middleton, 1993).

Examination of normalised metal concentration scatter and cumulative probability plots drew attention to anomalous concentrations, which were flagged as potential outliers. The outlier status of these concentrations was evaluated following a procedure similar to that outlined by Summers et al. (1996), based on Cooks distance (Cook, 1977) and leverage tests and through examination of residual plots. In a few cases professional judgement was also used to trim outliers. Particular attention was paid to the influence of outlier removal on regression model parameters when the outlier occurred at high normaliser concentrations (i.e. where outlier had potential to exert a strong leverage effect and thus affect model slope). Outlier concentrations typically were considerably higher but occasionally also lower compared to concentrations of the same metal recorded in sediment with comparable normaliser concentrations, and thus plotted well above or below regression model upper or lower prediction limits (level of statistical inference set at 99%). Where three or more outliers were detected in a sediment sample all data for the sample were trimmed from the data set, even though concentrations of other metals were not identified as outliers. Following the trimming of outliers, relationships between metal and co-occurring normaliser concentrations were formally described through linear regression analysis. Where four or more outliers were detected in a sediment sample, all data for the sample were trimmed from the data set even though concentrations of other metals were not identified as outliers. All metal concentrations for one sampling site (core) in each of the Kromme and Gamtoos River estuaries were trimmed since concentrations of most met-

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als deviated considerably from the trend for other sites (Fig. 2). The reason for this is unknown. All lead concentrations for Sub-Region 3 were trimmed since the distribution of concentrations for this metal was highly anomalous (Fig. 2).

Following the trimming of outliers, relationships between metal concentrations and co-occurring aluminium and iron concentrations for each sub-region were formally described through linear regression analysis. In most cases least-square linear regression assumptions of normality and/or constant variance of error terms were violated, and from a strict statistical point of view preclude the use of the raw data for regression analysis. Application of various commonly applied data transformations failed to provide an approximation of these assumptions. The violation of these assumptions appears in most cases to be a consequence of the preponderance of low metal concentrations in data sets. Trimming of metal concentrations associated with low aluminium and iron concentrations (low being defined relative to the range of that element in any data set, but usually <6 and <3 $mg \cdot g^{-1}$ aluminium and iron respectively) and reiteration of regressions usually resulted in regression assumptions being met (where not met violations were marginal), but regression parameters still being similar to those fitted to the untrimmed data set. Where differences in slope and/or intercept were evident, these differences could often be traced to metal concentrations at high aluminium or iron concentrations exerting a strong leverage effect on the smaller data set. Considering the similarity of the regression model parameters in trimmed and untrimmed data sets, and despite the violation of linear regression assumptions, regressions were fitted to untransformed data sets. This is consistent with the geochemical model on which normalisation is based. In general, lack of variance homogeneity does not result in biased estimates of the regression parameters, but does result in an increase in variance about these estimates (Hanson et al., 1993).

Cadmium and mercury

As previously mentioned, cadmium concentrations in all sub-regions were weakly correlated to co-occurring aluminium and iron concentrations, while most mercury concentrations could not be linked to co-occurring aluminium or iron concentrations. Variations in the concentration of aluminium or iron are consequently unable to explain variation in the concentration of cadmium, while variation in the concentration of mercury could not be modelled through linear regression. Some workers (e.g. Coakley and Poulton, 1993) have suggested that in situations where there is a poor relationship between a metal and the normaliser, no normalisation is required and the highest concentration of the metal measured in sediment from baseline locations can be used to define the concentration above which anthropogenic enrichment is inferred. This approach does not however preclude the possibility that some concentrations in the baseline data set represent outliers. Further, sediment sampling locations were not identified in an unbiased manner, and the concentration distributions for cadmium and mercury do not therefore provide an unbiased estimate of the range in concentration variability for these metals.

Univariate procedures for defining baseline concentrations above which enrichment can be inferred include the 95th percentile of concentration distributions and the mean plus twice the standard deviation amongst others (e.g. Matschullat et al., 2000). In the present study, the concentrations of cadmium and mercury above which enrichment can be inferred were estimated using univariate and cumulative probability plots, which were inspected for gaps and marked inflections at the upper range of concentrations under the assumption that these gaps and inflections represent unnaturally high concentrations (outliers). Although determination of gaps and inflections in the plots is subjective, an objective choice based on some pre-determined threshold percentile of the concentration distribution does not necessarily reflect the optimal concentration above which enrichment can be inferred. As an example, the 95th percentile of the concentration distribution could conceivably lead to the exclusion of 5% of data points that are in fact within the baseline concentration range. By the same token, concentrations that represent enrichment may not be detected since they fall within the range of 'baseline' concentrations and do not change the relationship of cumulative probability plots. The latter situation is likely to be most pronounced in areas subject to diffuse enrichment through atmospheric fallout, such as for the present study.

Arsenic

Arsenic concentrations were not determined during the historic studies from which data were extracted for the purposes of the present study and has only recently been measured in coastal sediment from the region, in the Coega area of Algoa Bay (CES, 2001; Newman, 2001; Klages and Bornmann 2003; 2005a; b) and in sediment from the upper reaches of the Nahoon River and several of its tributaries. Data from these studies were used to define the concentration above which enrichment of sediment by this metal can be inferred, using the same procedure described previously for cadmium and mercury since arsenic concentrations were also weakly correlated to co-occurring aluminium and iron concentrations. It should be noted that arsenic concentrations were extracted from sediment using a total digestion procedure ($HF\text{-}HNO_3\text{-}HClO_4$) and detected using inductively coupled plasma mass spectrophotometry (ICP-MS).

Development of regional model

Although the procedure described previously yielded statistically highly significant baseline models for each sub-region, the models for Sub-Region 3 were of limited value since the range of normaliser concentrations on which the models were based was narrow and/or concentrations were bimodally distributed, leading to strong leverage effects. The narrow concentration ranges in particular may lead to difficulties when assessing the extent of metal contamination in sediment with normaliser concentrations exceeding the maximum normaliser concentration, on which the models are based. The possibility for developing a regional model, incorporating data from all sub-regions, which would result in a wider normaliser concentration range, was therefore evaluated.

Ideally, the development of a regional model requires similarity of slopes and intercepts for sub-regional models. This was not the situation however, with regression slopes and/or intercepts for several metals differing significantly between sub-regions. However, there was no consistent trend in this regard, either between the different metals using aluminium or iron as the normaliser or between the different normalisers, although regression slopes and intercepts for Sub-Regions 2 and 3 were usually statistically similar. Although these differences suggest possible differences in sediment mineralogy between the sub-regions, data limitations for Sub-Regions 1 and 3 are to some extent also responsible. As an example, inclusion of data for the Gamtoos River estuary into the models for Sub-Region 1 tended to increase regression slopes and result in differences

to other sub-regions for some metals. Removal of data for the Gamtoos River estuary and reiteration of regressions usually produced models with slopes that were statistically similar to Sub-Regions 2 and 3. In some cases statistical differences in slope and/or intercept also appear to be a consequence of large data sets and low variability in measured metal concentrations in sub-regions. Predicted concentrations of metals at an extrapolated aluminium concentration of 70 $mg \cdot g^{-1}$ differed by between 3.678 and 26.62 $\mu g \cdot g^{-1}$ between sub-regions, amounting to differences of between 0.525 and 3.80 $\mu g \cdot g^{-1}$ per 10 $mg \cdot g^{-1}$ aluminium. The extent to which these small differences are biologically important is uncertain, but was considered to be minimal and in spite of differences in model slopes and intercepts between sub-regions' data were combined and a regional model developed.

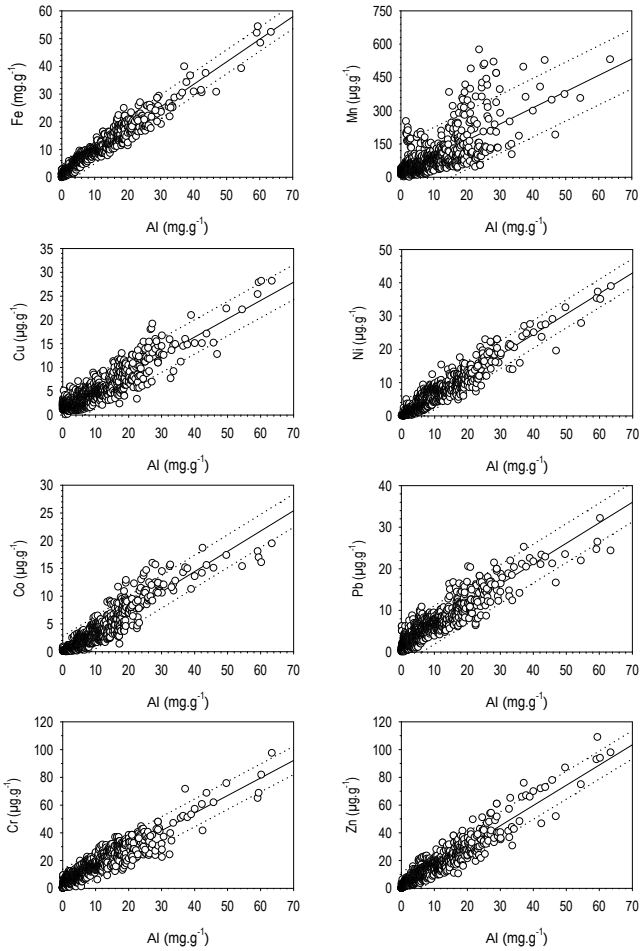

Figure 3
Metal-aluminium baseline relationships for coastal sediment between the Kromme River estuary in St Francis Bay and the Nahoon River estuary in East London on the Eastern Cape coast. Linear regression (solid line) and associated 99% prediction limits (stippled lines) are superimposed on the data.

For the purposes of the present study, the strengths of relationships as determined through correlation coefficient (r) or coefficient of determination (r^2) were classified as strong (0.80 to 1.00), moderate (0.60 to 0.79), weak (0.40 to 0.59), and very weak (0.00 to 0.39).

Results and discussion

Baseline models

Parameters for aluminium and iron normalised sub-regional and regional baseline models are presented in Tables 1 to 8, while aluminium normalised regional baseline models are presented in Fig. 3. Linear relationships between all metals and co-occurring concentrations of aluminium and iron in each sub-region were statistically highly significant ($p < 0.001$) with the exception of cadmium in Sub-Regions 2 and 3, which were not significant ($p > 0.05$). Linear relationships for the regional models were also highly significant ($p < 0.001$), including for cadmium (Tables 7 and 8). With the exception of cadmium, coefficients of determination for most metals were high (r^2 usually >0.80) and regression slopes were both positive and significantly different to zero. Model intercepts were, with few exceptions, significantly different to zero. Coefficients of determination for cadmium in the sub-regional and regional models were low (maximum $r^2 = 0.088$), with slopes occasionally negative and frequently not significantly different to zero.

Comparison of aluminium and iron as normalisers

Three regression parameters were used to compare the suitability of aluminium and iron as normalisers, namely model intercept, significance and coefficient of determination. The first two parameters differed between models depending on the normal-

TABLE 1
Regression parameters for metal:aluminium relationships in sediment from Sub-Region 1. All relationships were significant at $p < 0.001$. Metal concentrations in $\mu g \cdot g^{-1}$ with exception of aluminium and iron, which are in $mg \cdot g^{-1}$. r^2 = coefficient of determination, n = sample size on which regression is based, Outliers = number of data points identified as outliers, BDL = concentrations below analytical detection limit, Missing = sampling sites with no data for relevant metal, Normality = assessment of data normality, Constant variance = assessment of data variance.

Metal	Formula	r^2	n	Outliers	BDL	Missing	Normality	Constant variance
Iron	Fe = 0.932 + (0.886 * Al)	0.971	673	1	0	143	Fail	Fail
Cadmium	Cd = 0.0397 + (0.00391 * Al)	0.067	814	0	0	2	Fail	Fail
Copper	Cu = 0.945 + (0.412 * Al)	0.877	813	3	0	0	Fail	Fail
Cobalt	Co = -0.0102 + (0.341 * Al)	0.725	725	4	87	0	Fail	Fail
Chromium	Cr = 2.782 + (1.307 * Al)	0.928	773	43	0	0	Fail	Fail
Manganese	Mn = 16.109 + (8.198 * Al)	0.663	789	27	0	0	Fail	Fail
Nickel	Ni = -0.0620 + (0.655 * Al)	0.934	714	12	90	0	Fail	Fail
Lead	Pb = 1.519 + (0.505 * Al)	0.859	783	14	19	0	Fail	Fail
Zinc	Zn = 1.132 + (1.679 * Al)	0.953	814	0	2	0	Fail	Fail

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TABLE 2

Regression parameters for metal: iron relationships in sediment from Sub-Region 1. All relationships were significant at p < 0.001. Metal concentrations in µg·g^{-1} with exception of aluminium and iron, which are in mg·g^{-1}. r^2 = coefficient of determination, n = sample size on which regression is based, Outliers = number of data points identified as outliers, BDL = concentrations below analytical detection limit, Missing = sampling sites with no data for relevant metal, Normality = assessment of data normality, Constant variance = assessment of data variance.

Metal	Formula	r^2	N	Outliers	BDL	Missing	Normality	Constant variance
Aluminium	Al = -0.933 + (1.110 * Fe)	0.968	670	4	0	0	Fail	Fail
Cadmium	Cd = 0.0396 + (0.00458 * Fe)	0.064	668	0	3	3	Fail	Fail
Copper	Cu = 0.554 + (0.464 * Fe)	0.844	667	7	0	0	Fail	Fail
Cobalt	Co = -0.440 + (0.421 * Fe)	0.852	596	7	71	0	Fail	Fail
Chromium	Cr = 1.421 + (1.461 * Fe)	0.929	635	39	0	0	Fail	Fail
Manganese	Mn = 7.064 + (9.525 * Fe)	0.780	644	30	0	0	Fail	Fail
Nickel	Ni = -0.643 + (0.747 * Fe)	0.942	570	14	90	0	Fail	Fail
Lead	Pb = 0.631 + (0.583 * Fe)	0.895	630	29	15	0	Fail	Fail
Zinc	Zn = -0.994 + (1.871 * Fe)	0.942	669	4	1	0	Fail	Fail

TABLE 3

Regression parameters for metal: aluminium relationships in sediment from Sub-Region 2. All relationships were significant at p < 0.001 with exception of cadmium, where p = 0.261. Metal concentrations in µg·g^{-1} with exception of aluminium and iron, which are in mg·g^{-1}. r^2 = coefficient of determination, n = sample size on which regression is based, Outliers = number of data points identified as outliers, BDL = concentrations below analytical detection limit, Missing = sampling sites with no data for relevant metal, Normality = assessment of data normality, Constant variance = assessment of data variance.

Metal	Formula	r^2	N	Outliers	BDL	Missing	Normality	Constant variance
Iron	Fe = 1.204 + (0.781 * Al)	0.944	443	1	0	0	Fail	Fail
Cadmium	Cd = 0.0900 - (0.000540 * Al)	0.003	435	0	0	9	Fail	Fail
Copper	Cu = 2.065 + (0.288 * Al)	0.801	434	10	0	0	Fail	Fail
Cobalt	Co = 0.125 + (0.321 * Al)	0.823	439	5	0	0	Fail	Fail
Chromium	Cr = 6.174 + (1.156 * Al)	0.881	431	13	0	0	Fail	Fail
Manganese	Mn = 3.158 + (9.585 * Al)	0.466	437	7	0	0	Fail	Fail
Nickel	Ni = 0.464 + (0.540 * Al)	0.91	440	4	0	0	Fail	Fail
Lead	Pb = 0.927 + (0.566 * Al)	0.864	434	10	0	0	Fail	Fail
Zinc	Zn = 1.657 + (1.301 * Al)	0.932	427	17	0	0	Fail	Fail

TABLE 4

Regression parameters for metal: iron relationships in sediment from Sub-Region 2. All relationships were significant at p < 0.001 with exception of cadmium, where p = 0.131. Metal concentrations in µg·g^{-1} with exception of aluminium and iron, which are in mg·g^{-1}. r^2 = coefficient of determination, n = sample size on which regression is based, Outliers = number of data points identified as outliers, BDL = concentrations below analytical detection limit, Missing = sampling sites with no data for relevant metal, Normality = assessment of data normality, Constant variance = assessment of data variance.

Metal	Formula	r^2	N	Outliers	BDL	Missing	Normality	Constant variance
Aluminium	Al = -0.522 + (1.209 * Fe)	0.944	443	0	0	0	Fail	Fail
Cadmium	Cd = 0.0861 - (0.000738 * Fe)	0.005	434	0	0	9	Fail	Fail
Copper	Cu = 1.714 + (0.361 * Fe)	0.823	432	11	0	0	Fail	Fail
Cobalt	Co = -0.199 + (0.398 * Fe)	0.828	438	5	0	0	Fail	Fail
Chromium	Cr = 5.042 + (1.429 * Fe)	0.880	430	13	0	0	Fail	Fail
Manganese	Mn = -2.609 + (11.532 * Fe)	0.451	436	7	0	0	Fail	Fail
Nickel	Ni = -0.0577 + (0.662 * Fe)	0.912	436	7	0	0	Fail	Fail
Lead	Pb = 0.491 + (0.693 * Fe)	0.846	434	9	0	0	Fail	Fail
Zinc	Zn = 0.229 + (1.631 * Fe)	0.942	424	19	0	0	Fail	Fail

iser and sub-region, with no consistent trend. The theoretical basis for bivariate geochemical normalisation is based on metal deficient quartz and metal bearing clay as end members. The baseline models should therefore theoretically have a zero intercept when the normaliser concentration is zero. Sediment is not, however, comprised exclusively of quartz or clay minerals, but has other substrates that contribute or act as hosts for metals (e.g. organic matter) that may affect the intercept sign, as can analytical variability at low metal concentrations (Kersten and Smedes, 2002). Model intercepts were usually lower when iron was used as the normaliser, suggesting that this is the better normaliser. Differences in intercept values were however small and there is no compelling reason to select one normaliser above the other.

Arsenic, cadmium and mercury

Arsenic and cadmium concentrations were weakly correlated to co-occurring aluminium and iron concentrations, while most mercury concentrations could not be linked to normaliser concentrations. Variations in the concentration of aluminium or iron consequently cannot be used to explain variations in the concentration of arsenic or cadmium, while mercury could not be modelled at all in this manner. A univariate approach, by inspecting cumulative probability and univariate plots for marked inflections and gaps respectively, was therefore used to determine the concentration above which enrichment of sediment by these metals can be inferred. This procedure is demonstrated for cadmium and mercury in Fig. 4. Cadmium and mercury concentrations identified as outliers were recorded throughout the study area, and thus were considered not to represent natural extremes for a particular area.

The concentrations of cadmium and mercury, above which enrichment of sediment from each sub-region can be inferred, were defined as 0.322 and 0.097 $\mu g \cdot g^{-1}$ respectively for Sub-Region 1, 0.360 and 0.092 $\mu g \cdot g^{-1}$ for Sub-Region 2, and 0.300 and 0.100 $\mu g \cdot g^{-1}$ for Sub-Region 3. The largest difference between sub-regions was thus evident for cadmium. It should be noted that there were too few mercury concentrations for Sub-Region 3 to define the concentration above which enrichment can be inferred with a high degree of confidence, even though the concentration defined was similar to that for the other sub-regions. Concentrations above which enrichment for the entire region

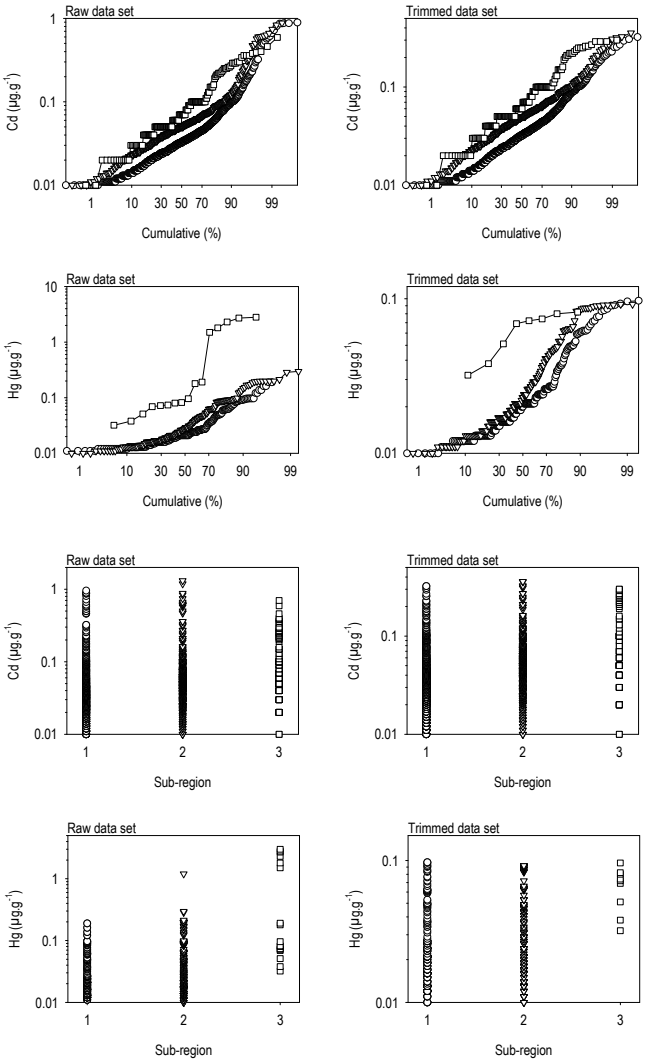

Figure 4
Illustration of the procedure used to define baseline concentrations above which enrichment of sediment by cadmium and mercury can be inferred. Symbols: ○ = Sub-Region 1, ∇ = Sub-Region 2, □ = Sub-Region 3.

TABLE 5
Regression parameters for metal: aluminium relationships in sediment from Sub-Region 2. All relationships were significant at $p < 0.001$ with exception of cadmium, where $p = 0.055$. Metal concentrations in $\mu g \cdot g^{-1}$ with exception of aluminium and iron, which are in $mg \cdot g^{-1}$. Lead concentrations for this sub-region were highly anomalous, and were not therefore used to develop baseline models (see text for additional information). r^2 = coefficient of determination, n = sample size on which regression is based, Outliers = number of data points identified as outliers, BDL = concentrations below analytical detection limit, Missing = sampling sites with no data for relevant metal, Normality = assessment of data normality, Constant variance = assessment of data variance.

Metal	Formula	r^2	N	Outliers	BDL	Missing	Normality	Constant variance
Iron	Fe = 0.788 + (0.795 * Al)	0.944	149	0	0	0	Fail	Fail
Cadmium	Cd = 0.131 - (0.00252 * Al)	0.025	147	0	0	2	Fail	Fail
Copper	Cu = 1.093 + (0.342 * Al)	0.858	141	8	0	0	Fail	Fail
Cobalt	Co = -0.175 + (0.343 * Al)	0.935	142	7	0	0	Fail	Fail
Chromium	Cr = 5.236 + (1.333 * Al)	0.898	138	11	0	0	Fail	Fail
Manganese	Mn = 42.068 + (2.733 * Al)	0.482	144	5	0	0	Fail	Fail
Nickel	Ni = 0.315 + (0.568 * Al)	0.902	146	3	0	0	Fail	Fail
Lead	No data							
Zinc	Zn = 2.165 + (1.284 * Al)	0.873	148	1	0	0	Fail	Fail

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TABLE 6

Regression parameters for metal:iron relationships in sediment from Sub-Region 3. All relationships were significant at $p < 0.001$ with exception of cadmium, where $p = 0.055$. Metal concentrations in $\mu g \cdot g^{-1}$ with exception of aluminium and iron, which are in $mg \cdot g^{-1}$. Lead concentrations for this sub-region were highly anomalous, and were not therefore used to develop baseline models (see text for additional information). r^2 = coefficient of determination, n = sample size on which regression is based, Outliers = number of data points identified as outliers, BDL = concentrations below analytical detection limit, Missing = sampling sites with no data for relevant metal, Normality = assessment of data normality, Constant variance = assessment of data variance.

Metal	Formula	r^2	N	Outliers	BDL	Missing	Normality	Constant variance
Aluminium	Al = -0.563 + (1.187 * Fe)	0.944	149	0	0	0	Fail	Fail
Cadmium	Cd = 0.133 - (0.00305 * Fe)	0.025	147	0	0	2	Fail	Fail
Copper	Cu = 0.806 + (0.426 * Fe)	0.856	141	8	0	0	Fail	Pass
Cobalt	Co = -0.466 + (0.436 * Fe)	0.908	145	4	0	0	Fail	Fail
Chromium	Cr = 4.078 + (1.760 * Fe)	0.769	147	2	0	0	Fail	Fail
Manganese	Mn = 30.544 + (6.418 * Fe)	0.295	149	0	0	0	Fail	Fail
Nickel	Ni = -0.170 + (0.708 * Fe)	0.895	149	0	0	0	Fail	Fail
Lead	No data; see text for reasons							
Zinc	Zn = 1.001 + (1.614 * Fe)	0.881	149	0	0	0	Fail	Fail

TABLE 7

Regression parameters for metal:aluminium relationships in sediment between the Kromme River estuary in St Francis Bay and the Nahoon River estuary in East London on the Eastern Cape coast. All relationships were significant at $p < 0.001$. Metal concentrations in $\mu g \cdot g^{-1}$ with exception of aluminium and iron, which are in $mg \cdot g^{-1}$. r^2 = coefficient of determination, n = sample size on which regression is based, Outliers = number of data points identified as outliers, BDL = concentrations below analytical detection limit, Missing = sampling sites with no data for relevant metal, Normality = assessment of data normality, Constant variance = assessment of data variance.

Metal	Formula	r^2	N	Outliers	BDL	Missing	Normality	Constant variance
Iron	Fe = 1.121 + (0.801 * Al)	0.944	1192	3	0	0	Fail	Fail
Cadmium	Cd = 0.0564 + (0.00201 * Al)	0.020	1325	0	0	13	Fail	Fail
Copper	Cu = 1.028 + (0.384 * Al)	0.841	1320	18	0	0	Fail	Fail
Cobalt	Co = -0.192 + (0.366 * Al)	0.878	1226	10	102	0	Fail	Fail
Chromium	Cr = 3.770 + (1.263 * Al)	0.880	1274	64	0	0	Fail	Fail
Manganese	Mn = 19.876 + (7.326 * Al)	0.554	1296	42	0	0	Fail	Fail
Nickel	Ni = -0.0298 + (0.614 * Al)	0.913	1231	17	90	0	Fail	Fail
Lead	Pb = 1.574 + (0.492 * Al)	0.848	1155	15	19	149	Fail	Fail
Zinc	Zn = 1.365 + (1.458 * Al)	0.909	1323	14	1	0	Fail	Fail

TABLE 8

Regression parameters for metal:iron relationships in sediment between the Kromme River estuary in St Francis Bay and the Nahoon River estuary in East London on the Eastern Cape coast. All relationships were significant at $p < 0.001$. Metal concentrations in $\mu g \cdot g^{-1}$ with exception of aluminium and iron, which are in $mg \cdot g^{-1}$. r^2 = coefficient of determination, n = sample size on which regression is based, Outliers = number of data points identified as outliers, BDL = concentrations below analytical detection limit, Missing = sampling sites with no data for relevant metal, Normality = assessment of data normality, Constant variance = assessment of data variance.

Metal	Equation	r^2	N	Outliers	BDL	Missing	Normality	Constant variance
Aluminium	Al = -0.780 + (1.158 * Fe)	0.946	1190	5	0	0	Fail	Fail
Cadmium	Cd = 0.0607 + (0.00205 * Fe)	0.014	1183	0	0	13	Fail	Fail
Copper	Cu = 0.641 + (0.459 * Fe)	0.840	1174	21	0	0	Fail	Pass
Cobalt	Co = -0.585 + (0.445 * Fe)	0.884	1097	8	90	0	Fail	Fail
Chromium	Cr = 2.668 + (1.483 * Fe)	0.877	1136	59	0	0	Fail	Fail
Manganese	Mn = 13.438 + (8.657 * Fe)	0.563	1151	44	0	0	Fail	Fail
Nickel	Ni = -0.572 + (0.729 * Fe)	0.911	1087	18	90	0	Fail	Fail
Lead	Pb = 0.748 + (0.600 * Fe)	0.873	1011	16	19	149	Fail	Fail
Zinc	Zn = -0.612 + (1.758 * Fe)	0.930	1178	16	1	0	Fail	Fail

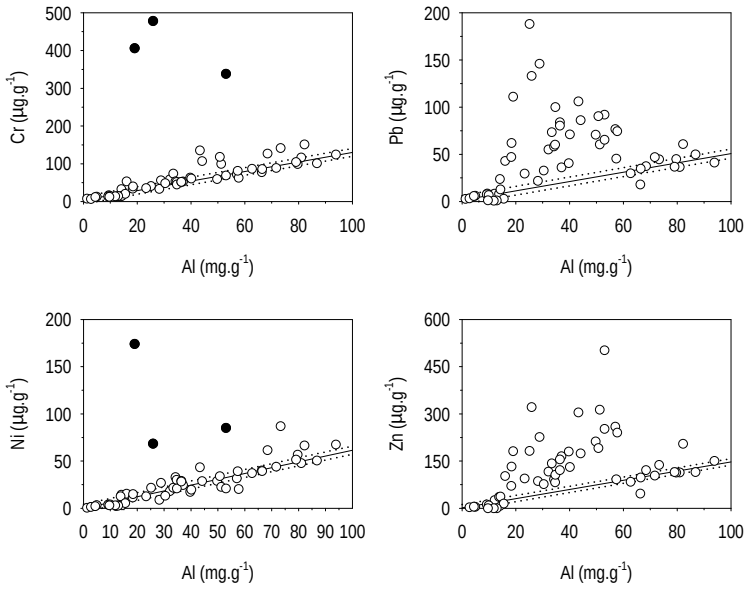

Figure 5

Regional aluminium normalised baseline models for chromium, nickel, lead and zinc, with baseline data removed and the models now overlaid with aluminium normalised chromium, nickel, lead and zinc concentrations measured in surficial sediment from the Port of East London between 2004 and 2007 (data provided by Hensburg, 2007). Metal concentrations that fall within the model upper and lower 99% prediction limits are considered to fall within the expected range for the region, while concentrations that plot above the upper prediction limit are considered to be enriched and may reflect contamination. Chromium and nickel concentrations denoted by solid symbols were measured in sediment collected off the dry dock facility in the port (see text for further discussion).

can be inferred were determined as 0.360 $\mu g \cdot g^{-1}$ for cadmium and 0.097 $\mu g \cdot g^{-1}$ for mercury.

The concentration of arsenic above which enrichment for the entire region can be inferred was defined as 15.65 $\mu g \cdot g^{-1}$. It is important to note that arsenic concentrations used to define this concentration were measured in sediment from only two locations in the region, with very different granulometry (coarse marine sand vs. finer grained riverine sand and mud). Definition of the baseline concentration has thus assumed that there is no sub-regional difference in the baseline concentration of this metal, as was concluded for other metals. Unlike cadmium and mercury, most of the arsenic concentrations identified as outliers were recorded in sediment from two small tributaries of the Nahoon River. It is uncertain whether or not these reflect natural extremes or outliers through anthropogenic enrichment, but it has been taken as the latter since the concentrations were high.

Application of baseline models for assessing metal enrichment of sediment

Although the baseline models will be used during future studies to assess metal enrichment of sediment from the region in question, it is useful to provide an example of how the models are applied for this purpose. The regional aluminium normalised baseline models for chromium and lead are presented in Fig. 5, with the baseline data points removed and now overlaid with aluminium normalised concentrations of these metals measured in surficial sediment from the Port of East London during dredge spoil monitoring programmes between 2004 and 2007 (data used with permission of the National Ports Authority of South Africa; metal concentrations extracted from sediment using a mixture of HF, HNO_3 and HCl acids at the CSIR laboratory in Durban).

Metal concentrations that plot within the baseline model upper and lower prediction limits fall within the expected baseline concentration range for sediment from the region, while concentrations that plot above the upper prediction limit represent enrichment. It is important to note that metal concentrations that plot above the model upper prediction limit do not necessarily imply that the enrichment has an anthropogenic source, but rather that these concentrations are atypical of the data set used to generate the model. Several possible reasons, in addition to anthropogenic inputs, may lead to a metal concentration exceeding the model upper prediction limit, including analytical errors, poor model assumptions, the probability that metal concentrations in some samples will naturally exceed the prediction limit (in a normal population, at 99% prediction limit 1 in every 100 concentrations could conceivably exceed the limit), and natural enrichment not captured by the baseline data set (Schropp et al., 1990; Rae and Allen, 1993). Interpretation of enrichment therefore requires consideration of ancillary factors, including possible (bio) geochemical processes leading to natural enrichment, the absolute difference between measured metal concentrations and model upper prediction limits, evaluation of the number of metals at a sampling site exceeding model upper prediction limits, and the location of enriched sediment relative to known or potential anthropogenic metal sources. The larger the difference between a measured metal concentration and model upper prediction limit and the greater the number of metals enriched in sediment from a particular sampling site the higher the likelihood that the metal concentration is enhanced through an anthropogenic source.

A high proportion of lead and zinc concentrations measured in sediment from the Port of East London between 2004 and 2007 have exceeded baseline model upper prediction limits (Fig. 5). This and the often large differences between these concentrations and model upper prediction limits provides evidence that lead and zinc contamination of sediment from the port is widespread (samples were collected throughout the port) and in some areas considerable. Although not evident in Fig. 5, the trend in enrichment has not been temporally consistent, with considerably less enrichment during 2007 than between 2004 and 2006. Although there are potentially numerous anthropogenic sources of lead and zinc to the port, stormwater runoff from the heavily urbanised and industrialised surroundings was probably an important and possibly the predominant source. Lead and zinc are common contaminants of stormwater runoff from heavily urbanised and industrialised surroundings, derived from such sources as petroleum (lead), galvanised roofing material and vehicle tyres (zinc). In the case of East London, several streams and canals drain stormwater from the surroundings to the port. Lead emitted from vehicle exhausts and zinc from roof-

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ing material corrosion and tyre wear are deposited on impervious surfaces and subsequently mobilised to stormwater conveyance systems during rainfall events. Although the use of lead as a petroleum additive is banned in South Africa, the ban only came into effect during 2006 and it will be interesting to see whether lead enrichment of sediment from the port decreases in future. The baseline model developed for lead will provide a tool for tracking any change.

In contrast, most chromium and nickel concentrations recorded in sediment from the port since 2004 fall within or near baseline model upper and lower prediction limits (Fig. 5). Three concentrations of chromium and three concentrations of nickel that substantially exceed model upper prediction limits (Fig. 5) were coincidentally measured in sediment collected off the dry dock facility in the port, and suggest that this facility is the source of these metals. Chromium and nickel are important constituents of stainless steel and the coincident high concentrations may reflect the unknowing inclusion of stainless steel fragments in sediment samples.

These practical examples illustrate how the baseline models can simplify assessment and communication of metal enrichment of sediment. The baseline models can also be used to determine enrichment factors (i.e. number of times by which a metal concentration exceeds the model upper prediction limit), providing a further tool for assessing and communicating spatial and temporal trends in metal enrichment. Additional applications include examination of data for procedural or laboratory errors and as a screening tool to promote the cost-effective use of other tests (e.g. pore-water or toxicity testing conducted only on sediment where enrichment is observed (Schropp et al., 1990).

Assessment of DEAT sediment quality guidelines

Although the baseline models developed in the present study can be used to assess metal enrichment of sediment, the models have an important limitation in that they do not provide a measure of the potential biological (ecotoxicological) significance of metal concentrations that exceed model upper prediction limits, either individually or in combination. High metal concentrations do not automatically imply adverse biological effects since such effects depend on metal bioavailability, which in turn depends on the strength of metal binding with sedimentary phases (Di Toro et al., 1990; Bryan and Langston, 1992; Fan et al., 2002; Voie et al., 2002). It is for this reason that many workers concurrently use empirically derived numerical SQGs for the protection of aquatic life to assess sediment quality when direct measures of adverse biological effects are not possible (e.g. toxicity testing). Numerical SQGs for the protection of aquatic life define concentrations of contaminants in sediment that may be associated with adverse biological effects, with varying levels of confidence. Although the ability of SQGs to predict adverse biological effects has been the subject of considerable debate (e.g. O'Connor and Paul, 2000), they are widely regarded as a valuable tool for assessing hazards associated with contaminated sediment when used as part of a weight of evidence approach. SQGs are especially useful for identifying areas where sediment quality warrants further assessment, such as through dedicated toxicity testing.

Matching estuarine and marine sediment chemistry and adverse biological effects data from the South African coastline are insufficient to permit the derivation of numerical SQGs. Furthermore, estuarine and marine sediment toxicity testing procedures using indigenous species have not been developed and the responses of indigenous species to most toxicants and environmental conditions that have implications for assessing toxicity are unknown. During the early to mid-1990s most local workers consequently assessed sediment quality using SQGs developed initially by Long and Morgan (1990) for the National Oceanic and Atmospheric Association (NOAA) Status and Trends Programme (USA) and subsequently revised by Long et al. (1995) for specific application to estuarine and marine environments. Since the late 1990s, SQGs proposed by DEAT for South African coastal waters (undated document; hereafter referred to as DEAT SQGs) have increasingly but not exclusively been used for this purpose.

The DEAT SQGs were developed to bring compliance with the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (London Convention), to which South Africa is a signatory, but they have no regulatory status. Documentation relating to the DEAT SQGs is limited, and it is difficult to determine the basis for the development or the narrative intent of the guidelines. The DEAT SQGs were apparently developed using a 'middle of the road' approach (Jackson, 2005) based on guidelines from several countries/regions. SQGs for Canada, Hong Kong, Ireland, Iceland, Germany and Norway are listed in the documentation, and it is presumed that SQGs from these countries/regions were used as a basis for DEAT SQG development.

Although the DEAT SQGs are being used to assess the quality of sediment destined for dredging from South African ports, their suitability for this purpose has not previously been evaluated. Although a detailed assessment of the DEAT SQGs will be the focus of a future study, the baseline models developed in the present study provide an opportunity to illustrate the inappropriateness of some of the guidelines. The DEAT SQGS define two action levels, and thus three concentration ranges, for so-called Annex 1 (cadmium and mercury) and Annex 2 metals (arsenic, chromium, copper, lead, nickel and zinc). The first guideline is referred to as the Action Level (AL) in the case of Annex 1 metals and the Special Care Level (SCL) in the case of Annex 2 metals. The second guideline is referred to as the Prohibition Level (PL) for both Annex categories. The DEAT SQGs appear not to adopt a biological effects based approach but rather a geochemical approach, since the guidelines state that sediment with metal concentrations above the SCL but below the PL is considered to be 'moderately contaminated', and that containing metal concentrations exceeding the PL as 'highly contaminated'. The guidelines also specify cumulative concentrations for Annex 1 and Annex 2 metals.

Figure 6 compares the regional aluminium normalised baseline models for some metals to the relevant SCL guidelines. The SCL guidelines for copper, lead and zinc are considerably higher than baseline concentrations of these metals in sediment from the south-eastern Cape, but that for chromium intersects the baseline model. Consequently, concentrations of chromium that fall within the baseline concentration range but exceed the SCL guideline are classified as moderately contaminated. The nickel SCL is close to intersecting the baseline model at high co-occurring aluminium concentrations, that is, in fine-grained sediment, and misclassification is less frequent.

As an example of misclassification, Fig. 7 presents the regional baseline model for chromium with the baseline data points removed and the model now overlaid with the SCL guideline for chromium and aluminium normalised chromium concentrations measured in surficial sediment from the Port of East London during dredge spoil monitoring programmes between 2004 and 2007. Despite the fact that most chromium concentra-

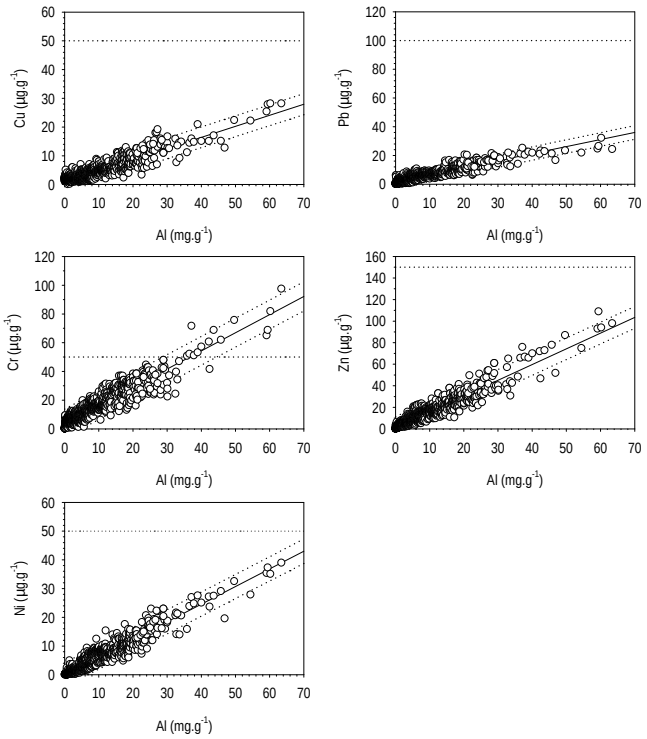

Figure 6
Comparison of DEAT Special Care Level (SCL; horizontal stippled line) guideline to aluminium normalised baseline models for certain metals in coastal sediment between the Kromme River estuary in St Francis Bay and the Nahoon River estuary in East London on the Eastern Cape coast.

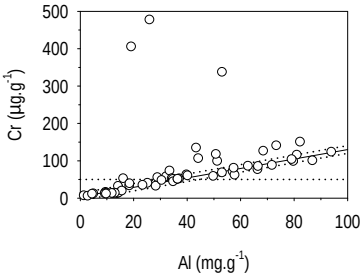

Figure 7
Aluminium normalised regional baseline model for chromium, with the baseline data points removed and the model now overlaid with aluminium normalised chromium concentrations measured in sediment from the Port of East London between 2004 and 2007. The horizontal stippled line represents the DEAT SCL guideline for chromium.

tions fall within, or close to, the baseline model prediction limits, numerous concentrations exceed the SCL guideline and are consequently incorrectly classified as moderately contaminated. The SCL guideline for chromium is clearly inappropriate for application to the south-eastern Cape coastline. This reflects a failure to consider regional differences in baseline metal concentrations when international SQGs were adopted for the development of the DEAT SQGs. The DEAT SQGs suffer additional limitations not discussed here, to the extent that if our ability to detect adverse impacts associated with metal contamination of sediment from the South African coastline is to be improved then it is imperative that new, locally relevant SQGs be defined. Although new SQGs should be developed using synoptic measurements of biological community structure, sediment toxicity and sediment contaminant concentrations rather than through the adoption of SQGs developed for other regions of the world, even if research/monitoring to generate data for this purpose is initiated in the near future it will still take some time for sufficient data to be generated. It is suggested therefore that interim SQGs be defined through the adoption of international SQGs, but which are evaluated to ensure they have local relevance. Baseline models developed in the present study can be used to guide the definition of these interim SQGs. The reader should note that baseline metal concentrations differ between regions of the South African coastline to the extent that a single set of interim SQGs will not be appropriate for application throughout this coastline. The baseline models can also be used to identify regional anomalies and to guide the definition of regionally specific interim SQGs.

Future research

Baseline models could obviously only be developed for those metals for which data are available. There are consequently no baseline models for several ecotoxicologically important metals (e.g. silver). The baseline models were developed using metal concentrations extracted from sediment using partial digestion, and may consequently not be suitable for interpreting metal concentrations extracted from sediment using total digestion procedures, as is now a common practice in studies of coastal sediment. This said, the models are likely only to be limited in this context for coarse sediments since metal concentrations are efficiently extracted from fine grained sediments by acids used in partial digestion. Future studies need to develop models for a wider suite of metals, based on metal concentrations extracted from sediment using hydrofluoric acid, and designed to encompass as wide a range of granulometric variability in Eastern Cape estuaries as is possible. Sediment collection locations should ideally be identified using a probability based sampling design (e.g. random-stratified sampling design).

Although the baseline models can be used to assess metal enrichment of sediment and thereby reach conclusions regarding metal contamination, an important limitation of the models is that they do not provide a measure of the potential biological significance of measured metal concentrations that exceed model prediction limits. It is imperative that future studies establish the incidence of adverse effects to benthic/epibenthic biota associated with different concentrations of chemicals in sediment, for the eventual purpose of defining locally relevant SQGs to support the interpretation of sediment chemistry data. Sediment quality monitoring programmes in local port environments provide an ideal opportunity to collect data for this purpose.

The development of sediment toxicity testing procedures for coastal waters, using indigenous species, also requires urgent attention. To date, appropriate authorities have displayed little inclination for making available funding for the development of toxicity tests for coastal waters. This situation needs to change if our ability to assess the impacts of anthropogenic chemical contamination of coastal environments is to be improved.

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