

**Richards Bay Expansion Programme:
Metal Contamination of Sediment
and Implications for Dredging –
Technical Report**

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Report Details

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1. Introduction

Transnet forecasts considerable growth in the volume of cargo imported and exported through the Port of Richards Bay over the next 30 years. This and some inefficiencies associated with the existing port layout led to Transnet identifying several expansion scenarios for the port, to accommodate the forecast growth. It is beyond the scope of this report to document the potential expansion scenarios save to state that expansion will take place predominantly in the western part of the Bay. Each expansion scenario will require the (capital) dredging and disposal of significant volumes of sediment.

A concern in any situation where sediment needs to be dredged from a port and disposed at an unconfined openwater spoil disposal ground is whether the sediment is chemically contaminated. This is because sediment is the most important fate for most contaminants anthropogenically introduced to aquatic ecosystems. There are numerous anthropogenic sources of contaminants in ports and their surroundings, which are typically highly urbanised and industrialised. Ports are also designed to provide a sheltered environment for the safe loading and offloading of cargo, but this sheltered environment facilitates the deposition and accumulation of fine-grained material onto which most anthropogenic contaminants adsorb.

Dredging contaminated sediment is of an ecological and human health concern for two main reasons. First, the dredging process physically disturbs sediment and leads to the release of contaminants dissolved in porewater (*i.e.* water between sediment grains) and changes to the sediments chemistry (Eggleton and Thomas 2004). The influx of dissolved oxygen into exposed anoxic sediment, for example, leads to an increase in its redox potential and a decrease in its pH (mainly due to the oxidation of sulphide; Förstner 1989, Reible *et al.* 2002). These changes affect particle-contaminant complexes, leading to the remobilisation of contaminants from sediment into the water column. Once released from sediment the contaminants can remain in the dissolved (or free) form, the most bioavailable form. The significance is that contaminants can only exert a

toxic effect if they are in a bioavailable form (*i.e.* can cross biological membranes). Metals such as iron and manganese are rapidly re-precipitated and deposited as insoluble oxides/hydroxides, to which newly released metals become adsorbed at varying rates and extents (Di Toro *et al.* 1990, Saulnier and Mucci 2000, Caetano *et al.* 2002). Thus, dissolved concentrations of metals usually peak in the immediate vicinity of a dredging operation and decrease sharply with distance from the operation as metals are re-precipitated or otherwise scavenged from the water column (Goosens and Zwolsman 1996, Saulnier and Mucci 2000). There is little information on the release of organic contaminants from sediment during dredging, and the data available often provides conflicting information. For example, increases in polychlorinated biphenyl concentrations in the water column have been detected a substantial distance from some dredging operations (*e.g.* USEPA 2009) whilst minor increases in the immediate vicinity of dredging or no demonstrable increase has been reported in other cases (*e.g.* Bergen *et al.* 2005, Batelle 2007).

The second reason that dredging contaminated sediment is of ecological and human health concern is that contaminants are transferred to the spoil disposal ground if unconfined openwater disposal of the sediment is permitted (*e.g.* Stronkhorst and van Hattum 2003). As the spoil descends through the water column changes to its chemistry similar to that at the dredging site may lead to the release of contaminants into the water column. Contaminants not released during disposal may be released over a protracted period as currents gradually erode sediment from the disposal ground, exposing contaminant laden deeper layers. Contaminants in the sediment can also adversely affect bottom-dwelling organisms at the disposal ground by direct or secondary toxicity.

Bioaccumulation and biomagnification are the principle routes through which higher trophic levels and humans may be impacted by contaminant release at the dredging site and spoil disposal ground. This occurs when organisms are exposed to elevated contaminant concentrations, which are either taken up directly from the water (*e.g.* across gill surfaces) or via food.

Because of the potential ecological and human health risks associated with dredging and dredged spoil disposal, a permit for the openwater disposal of dredged material in South African coastal waters is required from the Branch Oceans and Coasts of the Department of Environmental Affairs. This is in accordance with the Integrated Coastal Management Act (Act 24 of 2008) and Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter of 1972 (the London Convention) and the 1996 Protocol thereto, to which South Africa is a signatory. It is important to note that a Department of Environmental Affairs dredging permit does not cover the dredging process itself but the openwater disposal of dredged material.

2. Study Objectives

The objectives of this study were to:

1. Determine whether sediment in the proposed Port of Richards Bay expansion programme footprint is contaminated by metals,
2. Identify spatial trends in metal enrichment/contamination of sediment in the expansion footprint,
3. Estimate the likelihood that metal contamination of sediment in the expansion footprint will pose an unacceptable ecological risk when the sediment is dredged and/or disposed at an openwater spoil disposal ground offshore of Richards Bay, and
4. Identify the implications of metal contamination of sediment in the expansion footprint for a permit application authorising openwater disposal of dredged sediment.

3. Study Area

Richards Bay is a semi-enclosed estuarine embayment situated on the subtropical northeast coast of South Africa, in the province of KwaZulu-Natal (entrance at 32°02'E, 28°48'S). The Port of Richards Bay is situated within the Bay (Figure 1). For the purposes of this study the Bay is divided into the following areas: Inner Basin 1, Inner Basin 2, Inner Basin 3 (these are collectively referred to as the Inner Basin complex), Richards Bay Coal Terminal Basin and Mudflats (Figure 1). The Inner Basin complex and Richards Bay Coal Terminal Basin are of a deepwater nature, with a maintained

depth of about 22 meters. The water column over the Mudflats, in contrast, is shallow, with a depth of between about 1 - 2 meters. The Bhizolo Canal, which serves as a conduit for surface runoff, opens into the western part of the Mudflats.

Although its primary function is for the trade of bulk cargo the Port of Richards Bay is fairly unique in the context of South African ports since only about 40% of the land surface area has been developed. Large areas of relatively undisturbed natural habitat, including extensive intertidal sand and mudflats, and mangroves exist alongside port infrastructure. These habitats have retained much of their natural functioning and the Bay plays an important role in the life cycles of fish and invertebrates that show an estuarine dependence (Cyrus and Forbes 1996, Forbes *et al.* 1996, Weerts 2002, Weerts and Cyrus 2002,). The Bhizolo Canal, lined by mangroves, offers particularly important habitat for crustaceans, especially juveniles of commercially important prawn species (Weerts *et al.* 2003). These habitats also support high abundances of fish (Weerts 2002). The Bay is ranked 26th amongst South African estuaries in terms of conservation importance (Turpie *et al.* 2002), underlying its ecological importance. The presence of natural areas lends aesthetic appeal and the Bay serves as an important recreational venue for local communities, being particularly popular for water related activities such as fishing, canoeing and sailing.

4. Materials and Methods

4.1. Sampling station positions

Surface sediment was collected at 97 sampling stations positioned in a grid-like manner in the western part of Richards Bay, over an area that encompasses the proposed expansion footprint (Figure 1). The purpose of the grid-like positioning of stations was to facilitate the plotting of spatial trends for physical and chemical characteristics of sediment and probabilities for adverse effects to bottom-dwelling organisms associated with elevated metal concentrations.

4.2. Collection and processing of sediment

The upper 5 - 10 cm of sediment at each station was collected with the aid of a van Veen grab (grab

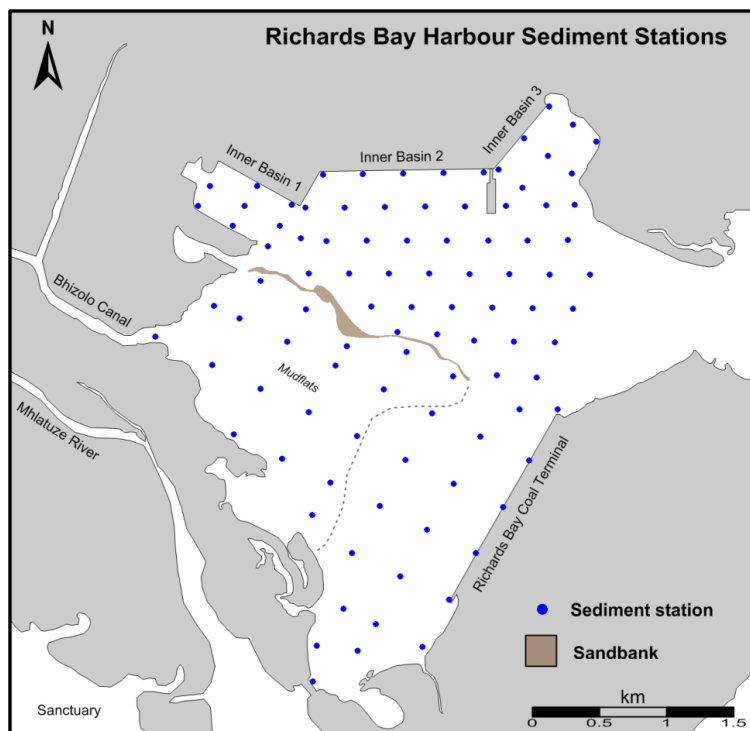


Figure 1. Map of the western part of Richards Bay showing the positions where sediment samples were collected in November 2012.

penetration dependent on sediment grain size composition). On retrieval water overlaying sediment in the grab was bled through a small hole in the side of the grab, taking care to lose as little fine-grained material as possible. The sediment was transferred to a glass bowl and homogenised using a stainless steel spoon. During homogenation, shells, stones and other material not representative of the sediment was removed when encountered. Aliquots of sediment were then distributed between two high-density polyethylene containers and stored on ice in the field. The grab was scrubbed with a hard brush and rinsed in site water between the collection of sediment samples. On return to the laboratory the sediment was frozen until analysis.

4.3. Laboratory procedures

4.3.1. Analytical laboratory

Sediment analyses were performed by the Consulting and Analytical Services Laboratory at the CSIR campus in Stellenbosch, South Africa. The laboratory is accredited by the South African National Accreditation System (SANAS) for the chemical analysis of estuarine and marine water, sediment and tissue samples.

4.3.2. Grain size composition

Sediment grain size composition was determined by wet and dry sieving the sediment into seven grain size classes, namely mud (<0.063 mm), very fine-grained sand (0.063 - 0.125 mm), fine-grained sand (0.125 - 0.250 mm), medium-grained sand (0.25 - 0.50 mm), coarse-grained sand (0.5 - 1.0 mm), very coarse-grained sand (1.0 - 2.0 mm) and gravel (>2.0 mm). The contribution of each grain size class is expressed as a fraction of bulk sediment dry weight. Sand is defined as the sum of very fine-grained, fine-grained, medium-grained, coarse-grained and very coarse-grained sand.

4.3.3. Total organic content

The sediment was oven dried, weighed and organic matter then degraded using hydrogen peroxide. The sediment was washed in distilled water, re-dried and re-weighed, and the difference in dry weight before and after organic matter degradation used to determine total organic content. Total organic content is expressed as a fraction of bulk sediment dry weight.

4.3.4. Metals

Sediment samples were freeze dried and ball milled. Approximately 1 g of dried and milled

sediment was digested in $\text{HNO}_3\text{-HCl-H}_2\text{O}_2$ according to USEPA method 3050B. This is a 'near-total' digestion method that will dissolve most elements that could become 'environmentally available' but is not designed to dissolve metals bound in silicate structures (USEPA 1996). Precision and recovery of the digestion and metal determination procedures were evaluated by analysing marine sediment reference standard PACS-2 (National Research Council of Canada) with each batch of 12 sediment samples. Since the reference material is certified for total digestion the recovery for several refractory metals (*e.g.* aluminium, chromium) was, as expected, somewhat below 100% (Table 1). Other workers have reported similar recoveries of refractory metals for certified reference materials using comparable acids (*e.g.* Hornberger *et al.* 1999, Schiff and Weisberg 1999, Pasternack and Brown 2006). The lower recovery of certain metals compared to recoveries that would be expected using aggressive acids does not invalidate the data since the relationships between metal concentrations, sediment grain size and total organic content are likely to be as strong using different acids, but the slopes and intercepts of the relationships will differ. The lower recovery does, however, have implications for the use of sediment quality guidelines to interpret the potential biological implications of metal concentrations in sediment since the guidelines are based on total concentrations. Consequently, the concentrations of metals will fall below the sediment quality guidelines in cases where a small exceedance should ordinarily be the case if total concentrations

were measured. However, this should not substantially alter the trend in exceedance discussed in a subsequent section of this report considering that most metals for which there are guidelines had extraction efficiencies exceeding 80% and often 90% (Table 1). The notable exception is chromium, which had an average extraction efficiency of about 61.7%.

4.4. Data analysis

4.4.1. Need for and use of baseline models to interpret metal concentrations

Determining whether sediment is contaminated by some chemicals is easy as these only have an anthropogenic origin (*e.g.* PCBs, DDT). The mere presence of these chemicals in sediment is indicative of contamination. Determining whether sediment is metal contaminated is far more complicated, for several reasons. First, metals are a ubiquitous, naturally occurring component of sediment. The mere presence of metals in sediment does not, therefore, imply the sediment is contaminated. Second, metal concentrations in uncontaminated sediment can vary by orders of magnitude over relatively small spatial scales depending on sediment mineralogy, granulometry and organic content amongst other factors (Wangersky 1986, Windom *et al.* 1989, Krumglaz *et al.* 1992, Loring and Rantala 1992, Thomas and Bendell-Young 1999, Kersten and Smedes 2002). Within a geologically homogenous area, grain size is the most important factor controlling natural metal concentrations in sediment (Förstner 1989). This is

Table 1. Recovery (%) of metals from standard reference material (SRM) PACS-2 (National Research Council of Canada).

SRM Replicate	Al	As	Be	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	V	Zn
1	40.4	98.1	85.0	96.8	82.6	61.0	89.4	68.7	102.3	54.6	72.3	87.8	62.4	92.4
2	42.1	91.4	91.0	90.6	82.1	63.4	98.7	74.3	104.3	61.2	78.0	94.3	66.8	92.0
3	43.6	82.6	89.0	102.1	78.0	63.8	94.7	76.2	101.0	58.5	80.5	90.7	64.3	92.3
4	42.4	91.8	110.0	96.1	78.3	61.3	93.7	69.2	99.7	57.5	79.2	83.7	66.8	92.3
5	41.8	84.7	100.0	100.8	82.3	56.6	95.9	69.0	106.3	57.3	76.3	86.5	65.9	96.6
6	44.4	85.8	110.0	101.3	84.3	64.5	91.9	70.6	93.4	55.0	71.6	84.4	61.1	96.9
7	43.3	86.2	80.0	94.9	84.5	58.5	92.9	66.9	102.3	54.5	75.7	89.6	72.7	92.1
8	44.2	87.3	84.0	93.3	80.1	64.7	95.7	66.7	108.6	62.9	84.8	97.5	71.5	92.9
Mean	42.8	88.5	93.6	97.0	81.5	61.7	94.1	70.2	102.2	57.7	77.3	89.3	66.4	93.4
Std Deviation	1.4	5.0	11.7	4.1	2.5	3.0	2.8	3.4	4.6	3.1	4.3	4.8	4.0	2.1
Minimum	40.4	82.6	80.0	90.6	78.0	56.6	89.4	66.7	93.4	54.5	71.6	83.7	61.1	92.0
Maximum	44.4	98.1	110.0	102.1	84.5	64.7	98.7	76.2	108.6	62.9	84.8	97.5	72.7	96.9
Variance	1.8	24.8	136.8	17.1	6.3	8.7	8.0	11.4	20.9	9.5	18.6	22.7	16.2	4.3
Precision	3.2	5.6	12.5	4.3	3.1	4.8	3.0	4.8	4.5	5.4	5.6	5.3	6.0	2.2

because aluminosilicates, which are the dominant natural metal-bearing phase of sediment, predominate in clay. Sand, in contrast, is comprised predominantly of metal deficient quartz. Particulate organic matter is an additional host for metals. High metal concentrations in sediment may thus simply reflect the mineralogy of parent material and/or granulometry and organic content of the host sediment, and not necessarily contamination. Third, despite input and transport dissimilarities, naturally occurring and anthropogenically introduced metals tend to accumulate in the same areas (Loring 1991, Hanson *et al.* 1993). Because of these complexities the identical metal concentration in two sediment samples collected from an aquatic ecosystem may reflect contamination in one instance and not the other, because of a difference in the granulometry and organic content of the samples.

To meaningfully interpret metal concentrations in sediment the mineralogical and granulometric factors that control the natural variation of metal concentrations must be compensated for before naturally occurring concentrations can be differentiated from anthropogenically enhanced concentrations (*i.e.* concentrations indicative of contamination). This can be accomplished by the procedure of geochemical normalisation, which mathematically normalises metal concentrations to a co-occurring conservative element that provides a tracer of crustal decomposition (Hanson *et al.* 1993, Kersten and Smedes 2002).

The basis for geochemical normalisation is that while the absolute concentrations of metals vary between crustal material from one region to another the relative proportions of metals in crustal material from a particular region tend to be fairly constant (*e.g.* Turekian and Wedepohl 1961, Taylor and McLennan 1981, Martin and Whitfield 1983, Wedepohl 1995, Kersten and Smedes 2002). Since there is relatively little fractionation between metals and aluminosilicates during the weathering of parent material (Schropp and Windom 1988), metal concentrations in uncontaminated sediment tend to reflect the relative proportions of metals in the material from which they were derived. The relative constancy of the proportions of metals in sediment from geologically homogenous regions and the usually strong correlation between metal

concentrations and grain size permits the modelling of relationships between metal concentrations and a conservative tracer of crustal decomposition through regression analysis (usually simple linear regression but occasionally multiple linear regression). Simple linear regression models defined are generally referred to as baseline metal concentration models, or simply baseline models. The purpose of normalisation is thus to compensate for variables that control natural concentrations of metals in sediment, such that after normalisation metal concentrations in equally contaminated or uncontaminated sediment samples that have a very different granulometry do not differ significantly.

The Coastal Systems research group of the CSIR recently (2012) defined baseline models for metals in sediment from Richards Bay (report in preparation). The baseline models were refined using metal concentrations analysed in sediment collected for this study. A description of the approach used to define the baseline models is beyond the scope of this report but is available on request. Baseline models could not be defined for cadmium and mercury, with the result that baseline concentrations were defined for these metals using an alternate procedure (see section 4.4.2.).

A baseline model for comprises a linear regression and associated 99% prediction limits (Figure 2). The linear regression describes the average concentration for a metal at each co-occurring aluminium concentration, while the 99% prediction limits define the range around the average within which 99% of concentrations should fall if the sediment is uncontaminated and the data is normally distributed. The normaliser, which in this case is aluminium, is used as a proxy for the mud fraction of sediment. This is because aluminosilicates predominate in the silt and clay (mud) fraction of sediment. In Figure 2, aluminium concentrations on the extreme left of the x-axis are indicative of sediment with a very low mud fraction and on the extreme right of sediment with a very high mud fraction. The reader will note from Figure 2 that there is no single baseline concentration for chromium (and indeed most metals) in sediment but rather a range of concentrations at any particular aluminium concentration, that is, the

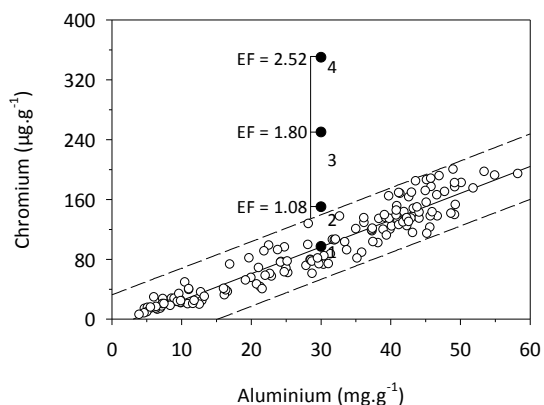


Figure 2. Aluminium normalised baseline model for chromium in sediment from Richards Bay. Open symbols represent chromium concentrations used to define the baseline model while numbered solid symbols represent four hypothetical scenarios: 1. concentration falls within baseline model upper and lower prediction limits (dashed lines flanking solid regression line) and is interpreted as not enriched; 2, 3 and 4. concentrations exceed baseline model upper prediction limit and are interpreted as reflecting various levels of enrichment that can broadly be defined as very low (2) through to high (4). Enrichment Factors (EF) for hypothetical concentrations 2, 3 and 4 are provided. Concentrations 3 and 4 would be interpreted as reflecting enrichment through an anthropogenic contribution with a high level of confidence. Scenario 2 would be interpreted as reflecting enrichment through an anthropogenic contribution with a low level of confidence.

range between the upper and lower prediction limits. Furthermore, the baseline concentration range changes in sympathy with the fraction of mud in the sediment. For example, the baseline concentration range for chromium at an aluminium concentration of 15 mg.g^{-1} , which is typical of sand dominated sediment, is between $0.38 - 85.3 \text{ } \mu\text{g.g}^{-1}$. In contrast, at an aluminium concentration of 60 mg.g^{-1} , which is indicative of very muddy sediment, the baseline concentration range is between $161.71 - 246.63 \text{ } \mu\text{g.g}^{-1}$. In both cases the difference across the range is identical ($84.92 \text{ } \mu\text{g.g}^{-1}$) but the actual range is obviously different.

The way in which the baseline models are used to interpret metal concentrations in sediment can be explained using a theoretical example, based on the baseline model for chromium in sediment from Richards Bay. The first step is to superimpose aluminium normalised chromium concentrations that require interpretation onto the baseline model. In Figure 2, four hypothetical chromium concentrations are superimposed onto the baseline

model. Chromium concentrations that fall within the baseline model upper and lower prediction limits, such as hypothetical concentration 1, are considered to fall within the baseline concentration range and are thus interpreted as not enriched. Chromium concentrations that exceed the baseline model upper prediction limit, such as hypothetical concentrations 2, 3, and 4, are interpreted as enriched.

A metal concentration that exceeds the baseline model upper prediction limit does not imply that the concentration is enhanced through an anthropogenic contribution (*i.e.* reflects contamination) but that the concentration is atypical of the data used to define the baseline model (Horowitz *et al.* 1991). Several reasons in addition to an anthropogenic contribution can lead to a metal concentration exceeding a baseline model upper prediction limit, including analytical errors, poor baseline model assumptions, the probability that metal concentrations in some samples will naturally exceed the baseline model upper prediction limit (in a normally distributed population, at the 99% prediction level 1 in every 100 concentrations could conceivably naturally exceed the limit), and natural enrichment not captured by the data set used to define the baseline model (Schropp *et al.* 1990, Rae and Allen 1993). Interpretation of metal enrichment and ultimately whether this reflects contamination thus requires consideration of ancillary factors, including possible (bio)geochemical processes leading to natural enrichment (*e.g.* diagenesis), the magnitude of the difference between a metal concentration and the baseline model upper prediction limit (*i.e.* the magnitude of enrichment), the number of different metals in sediment at a sampling station that are present at concentrations exceeding baseline model upper prediction limits, and the position of metal enriched sediment relative to known or suspected anthropogenic sources of metals. The greater the exceedance of the baseline model upper prediction limit by a metal concentration, the greater the number of metals enriched in sediment at a particular location, and the nearer the location is to known or suspected anthropogenic sources of metals the greater the likelihood that the metal concentration/s are enhanced through an anthropogenic contribution

and thus reflect contamination. In Figure 2, hypothetical chromium concentration 2 is interpreted as enriched, but whether this reflects contamination should only be concluded after considering the abovementioned ancillary factors. This is because the concentration only marginally exceeds the baseline model upper prediction limit. In the case of hypothetical chromium concentrations 3 and 4, exceedance of the baseline model upper prediction limit is pronounced and these concentrations would be interpreted as enriched due to an anthropogenic contribution with a high level of confidence, that is, the sediment at these stations is interpreted as contaminated by chromium. This interpretation would in fact be made even if no other metals in the sediment were enriched.

4.4.2. Cadmium and mercury

The concentrations of cadmium and mercury in a large proportion of sediment samples collected from Richards Bay in 2011 and 2012 were below the method detection limit (0.02 and 0.03 $\mu\text{g}\cdot\text{g}^{-1}$ respectively). Cadmium and mercury concentrations exceeding the method detection limit were very weakly correlated to aluminium concentrations, even after the trimming of outliers. Variation in the concentration of aluminium is thus not able to explain the variation in cadmium and mercury concentrations in sediment from Richards Bay, with the result that geochemical normalisation could not be used to define baseline model for these metals. Baseline cadmium and mercury concentrations above which enrichment of sediment from the Bay by these metals can be inferred were defined using cumulative frequency and probability plots, at 0.130 $\mu\text{g}\cdot\text{g}^{-1}$ and 0.03 $\mu\text{g}\cdot\text{g}^{-1}$ respectively. Because of the use of cumulative frequency and probability plots is a far more subjective approach for defining baseline concentrations compared to the baseline model approach, the baseline cadmium and mercury concentrations should be used with caution when interpreting concentrations of these metals in sediment from Richards Bay.

4.4.3. Calculation of Enrichment Factors

Baseline models are an effective tool for identifying metal enriched sediment. However, it is difficult to

visually interpret data in graphic format when a large proportion of the metal concentrations exceed the baseline model upper prediction limit, even if the data points are identified by station/sample identifiers. A more effective approach is to calculate and display Enrichment Factors, either graphically or as spatially explicit plots.

For this study Enrichment Factors (EF) were calculated as

$$EF = (M/M_{upl})$$

where

M = metal concentration in sediment sample of interest,

M_{upl} = metal concentration predicted at baseline model upper prediction limit at an aluminium concentration corresponding to that in the sediment sample of interest.

Metals in sediment at concentrations below the method detection limit were replaced with a surrogate concentration of one-half the method detection limit for calculation of Enrichment Factors.

Enrichment Factors can be visualised using the same hypothetical example discussed previously to demonstrate the way in which baseline models are used to interpret metal concentrations in sediment (Figure 2). As indicated, Enrichment Factors for hypothetical chromium concentrations 2, 3 and 4 increase the greater the exceedance of the baseline model upper prediction limit. An Enrichment Factor of 2.52, as is the case for hypothetical chromium concentration 4, means the concentration is a little over two and a half times (or 2.52 times to be precise) higher than the highest chromium concentration predicted for granulometrically equivalent but uncontaminated sediment (*i.e.* at the same corresponding aluminium concentration). It is important to note that baseline model prediction limits are not linear but biconcave, being narrowest at the average and widest at the extremes of the normaliser distribution. However, prediction limits are near enough linear if the data set used to define the baseline model is large, the data are more or less evenly distributed across the normaliser spectrum, and the variability around the regression line is narrow. The inaccurate estimation

of enrichment attributable to the assumption that the upper prediction limit is linear when it is not is small for the baseline models defined for Richards Bay and has little material effect on the interpretation of metal concentrations.

4.4.4. Assessment of sediment quality using sediment quality guidelines

An understanding of the concentrations of chemicals in sediment is essentially meaningless if these are not interpreted in the context of the potential for adverse biological effects. The ultimate objective of any sediment quality assessment, therefore, is to determine whether contaminants in the sediment are adversely affecting or have the potential to adversely affect bottom-dwelling organisms (Chapman and Anderson 2005). The baseline models and baseline concentrations for metals in sediment from Richards Bay have an important limitation in this context in that while they can be used to identify metal enriched sediment, they do not provide a measure of the potential toxicological significance of enriched concentrations, either individually or in combination. To determine whether contaminants in sediment are adversely affecting bottom-dwelling organisms some form of biological assessment is required, since this provides an understanding on whether the chemicals are present in a bioavailable form (Chapman *et al.* 1999). This may include toxicity testing and the assessment of benthic invertebrate community structure and composition. Biological assessment is, however, often lengthy, complex and expensive, and is not always definitive. This is because there are numerous factors in addition to contaminants that influence the structure and composition of bottom-dwelling organism communities; even natural factors acting alone can cause an adverse effect that would ordinarily be associated with contamination (Partridge *et al.* 2010).

No rigorously developed procedures are available for testing the toxicity of coastal sediment in South Africa, although the sea urchin fertilisation test has been used to test the toxicity of sediment porewater and elutriates. Benthic invertebrate community response indices have also not been derived for estuarine and marine ecosystems and it

is thus difficult to determine whether differences between communities is a response to the natural variability in physical and chemical characteristics of water and sediment or exposure to contaminants except in instances of gross contamination (and even here it may be difficult to identify the driver/s). Port environments provide additional challenges for determining whether benthic invertebrate community structure and composition has been altered through exposure to contaminants. Perhaps the most important are maintenance dredging and propeller wash, which are important forms of sediment disturbance and hence benthic community disturbance, and may alter the structure and composition of benthic invertebrate communities in a manner similar to contamination.

In the absence of direct measures of biological effects most workers use sediment quality guidelines to estimate the toxicological significance of contaminants in sediment to bottom-dwelling organisms. The derivation of sediment quality guidelines arose, in part, from a desire by managers and decision-makers to have a simple yet consistent tool for discriminating between chemical concentrations in sediment that are of little biological concern and those that are of greater concern, based only on the measurement of chemical concentrations. Not only would this ensure that decisions on sediment quality and future management are made in a consistent, transparent and equitable manner, but would also eliminate the need for expensive and often not definitive biological assessment required to determine whether sediment at a particular site is or is not of concern. In essence, sediment quality guidelines were conceived as a shortcut to decision-making. Sediment quality guidelines are advantageous in that they are easy to use by specialists and non-specialists, simplify decision-making, and provide a consistent benchmark for assessing sediment quality. Amongst other uses, sediment quality guidelines are used to interpret sediment chemistry data from a toxicological perspective, to identify chemicals of concern, to rank and prioritise aquatic systems or sites within systems for further attention, and to assess the suitability of dredged material for unconfined openwater disposal (Long and MacDonald 1998,

Wenning *et al.* 2002). Many workers consider sediment quality guidelines a particularly useful tool when used in combination with other sediment quality assessment tools in a weight of evidence approach (MacDonald *et al.* 1992, Ingersoll *et al.* 1997, USEPA 1997, Long and Macdonald 1998, MacDonald *et al.* 2000). However, many workers have cautioned against and indeed criticised the use of sediment quality guidelines, particularly as a standalone tool (*e.g.* O'Connor 2004, Jones-Lee and Lee 2005). They contend that sediment quality guidelines do not provide a sufficient basis for identifying the potential for adverse effects to bottom-dwelling organisms. This is because despite the soundness of the science underpinning the derivation of sediment quality guidelines, no sediment quality guidelines have been shown to consistently and reliably predict toxicity (Wenning *et al.* 2002). Elevated chemical concentrations in sediment do not always cause adverse effects to bottom-dwelling organisms, although adverse effects are usually associated with elevated chemical concentrations (Chapman *et al.* 1999). The reason is that numerous physical and chemical characteristics of sediment control the bioavailability of chemicals and hence their toxicity (*e.g.* pH, complexing ligands). Furthermore, aquatic organisms have evolved strategies to conserve and regulate essential metals in sediment in certain elevated concentration ranges without adverse effects. Sediment quality guidelines are also not applicable to mixtures of chemicals or to chemicals that bioaccumulate (Chapman *et al.* 1999).

The Department of Environmental Affairs has defined sediment quality guidelines for the purpose

Table 2. Sediment quality guidelines used to determine whether sediment identified for dredging in South African ports is of a suitable quality for unconfined openwater disposal.

Metal	Warning Level	Level I	Level II
Arsenic	42	57	93
Cadmium	1.2	5.1	9.6
Chromium	135 ^a /250 ^b	260	370
Copper	110	230	390
Mercury	0.43	0.84	1.5
Nickel	62 ^a /88 ^a	140	370
Lead	110	218	530
Zinc	270	410	960

a - for Eastern and Western Cape, b - for KwaZulu-Natal

of determining whether sediment identified for dredging in South African ports is of a suitable quality for unconfined openwater disposal. Three guidelines were defined, namely a Warning Level, Level I and Level II (Table 2). The Level I and Level II are used for decision-making. The Warning Level is only used to provide a warning of incipient metal concentration. Sediment with metals at concentrations equivalent to or lower than the Level I is regarded as posing a low risk to bottom-dwelling organisms and is of a suitable quality for unconfined openwater disposal. Sediment with metals at concentrations between the Level I and Level II is regarded as posing a potential risk to bottom-dwelling organisms, with the degree of risk increasing as the Level II is approached. A decision on whether this sediment is of a suitable quality for unconfined openwater disposal is made after consideration of the number of metal concentrations that exceed the Level I and the magnitude of exceedance at a particular station. Additional testing (*e.g.* toxicity testing of sediment elutriates) may be requested to assist decision-making. Sediment with metals at concentrations equal or higher than the Level II is regarded as posing a high risk to bottom-dwelling organisms and in the absence of other data to refute this conclusion is considered unsuitable for unconfined openwater disposal. In this situation the dredging proponent can perform additional testing and studies (*e.g.* toxicity testing of sediment elutriates, benthic invertebrate community analysis) to determine whether contaminants in the sediment are adversely affecting bottom-dwelling organisms. If the additional testing shows the contaminants are not posing an unacceptable risk then the Department of Environmental Affairs may deem the sediment suitable for unconfined openwater disposal. If the risk is unacceptable then the sediment must be disposed in a confined facility on-land.

The South African sediment quality guidelines are used in this study to assess the potential toxicological significance of metal concentrations in sediment from Richards Bay to bottom-dwelling organisms.

4.4.5. Sediment quality guideline quotient

Although sediment quality guidelines are widely

used they have a limitation in that they define concentrations above which adverse effects to bottom-dwelling organisms are possible for individual contaminants, but in reality sediment usually contains a mixture of contaminants. Therefore, Long *et al.* (1998) proposed the use of a mean sediment quality guideline quotient to estimate the toxicological risk posed by all chemicals in a sediment sample. In this approach concentrations of chemicals are divided by their effects-based sediment quality guideline to provide a quotient. The arithmetic mean of the quotients is then calculated to provide a unitless mean sediment quality guideline quotient (Long *et al.* 1998, 2000, 2006). This approach thus assumes that contaminant effects are additive or synergistic, with no antagonistic effects (Long *et al.* 2006, 2012). There is evidence that the incidence and magnitude of toxicity in laboratory tests and incidence of impairment to benthic invertebrate communities increases incrementally with increasing mean sediment quality guideline quotient (Long *et al.* 1998, 2006, Ingersoll *et al.* 2001, Field *et al.* 2002, McCready *et al.* 2006, Hartwell and Hameedi 2007, Birch *et al.* 2008, Long *et al.* 2012). The probability for an adverse effect is, however, dependent on the combination of chemicals and sediment quality guidelines used to calculate the quotient (Fairey *et al.* 2001, Long *et al.* 2006, McCready *et al.* 2006). Thus, although the mean sediment quality guideline quotient is calculated for each sampling station in Richards Bay, only metal concentrations were used for the calculation. The mean sediment quality guideline quotient is thus used here only to identify stations where metals in sediment from Richards Bay were present at concentrations that may be eliciting adverse effects to bottom-dwelling organisms, and should not be considered definitive. Metals in sediment at concentrations below the method detection limit were replaced with a surrogate concentration of one-half the method detection limit mean sediment quality guideline quotient calculation.

Any set of effects-based sediment quality guidelines can be used as the denominator for quotient calculation (Long *et al.* 2012). In this study the South African sediment quality guidelines were used. The Level I and Level II were both used, even though the Level II equivalent guideline is usually

used for this purpose. This is because Long *et al.* (2012) calculated mean sediment quality quotients for chemicals in sediment from Puget Sound in the northwest of the United States of America and compared the quotients to the incidence and degree of toxicity in laboratory tests and to metrics of the diversity and abundance of benthic communities for a large database. The data were evaluated to identify 'cut points' (*i.e.* thresholds) below which the frequency and magnitude of biological effects were relatively low and above which they occurred with increasing frequency or magnitude. The cut points are used in this study since Long *et al.* (2012) used the Washington State sediment quality standards as the denominator for quotient calculation. The Washington State sediment quality standards are comparable, although not always identical, to the Level I of the South African sediment quality guidelines. The cut points defined by Long *et al.* (2012) are 0.1, 0.3 and 0.5, which define four ranges of chemical exposure: Minimum (<0.1), Low (0.1 - <0.3), Moderate (0.3 - <0.5), and Maximum (≥ 0.5). Across these ranges of quotients the incidence and magnitude of toxicity in some tests increased, the abundance of most stress-sensitive benthic taxa decreased, and the abundance of most stress-tolerant taxa increased. A cut point of 0.1 appears to be the target for the protection of benthic resources, below which the probability and magnitude of adverse effects in the laboratory or field was the lowest (Long *et al.* 2012).

4.4.6. Probability for observing toxicity based on logistic regression modelling

Another approach for assessing the potential toxicological significance of metal concentrations in sediment to bottom-dwelling organisms is the logistic regression modelling approach proposed by Field *et al.* (1999, 2000). Field *et al.* (1999, 2000) derived logistic regression models that quantify the relationship between contaminant concentrations in sediment and the incidence of toxicity to two species of amphipod (*Rhepoxynius abronius* and *Ampelisca abdita*) commonly used for sediment toxicity testing purposes in North America. This approach is similar to other empirical approaches for deriving numerical sediment quality guidelines in that it was developed from matching sediment

chemistry and biological effects data. In contrast to other approaches, however, the logistic regression modelling approach does not develop ‘threshold’ concentrations (*i.e.* guidelines) but rather models that describe on a continuous scale the quantitative relationship between sediment chemistry and the probability for observing a toxic response.

Benthic invertebrates have evolved in the presence of naturally occurring metal concentrations and are adapted to these concentrations. This is important in the context of this study since baseline concentrations of metals in sediment from Richards Bay undoubtedly differ to those for coastal sediment in (at least some areas of) North America. Consequently, baseline concentrations of metals in sediment from Richards Bay may be associated with a relatively high probability for observing toxicity when using metal specific logistic regression model parameters provided by Field *et al.* (1999, 2000), but no toxic response should theoretically be evident, or *vice versa*. The calculated probabilities for toxicity are thus used here only to identify areas of the Bay where metals were present at concentrations that may be eliciting adverse effects to bottom-dwelling organisms and should not be considered definitive. It should also be noted that Wetherington *et al.* (2005) criticised the logistic regression modelling approach, contending that it classifies too many sediment samples that are non-toxic as toxic (*i.e.* false positives) and has a limited ability to predict toxicity.

Field *et al.* (1999, 2000) derived logistic regression models for individual chemicals and for multiple chemicals. Only the multiple chemical approach (so-called P_{max}) is used in this study for the sake of brevity. Metals in sediment at concentrations below the method detection limit were replaced with a surrogate concentration equivalent to the method detection limit for calculations.

4.4.7. Spatial plotting of data

As mentioned previously, sediment sampling stations were intentionally positioned in a grid-like manner to allow for the spatially explicit plotting of physical and chemical characteristics of sediment from Richards Bay. It is important to note that the statistical procedure (Kriging) used to generate the

plots uses an algorithm to interpolate trends between stations based on the nearest neighbour method. The distances between sampling stations were relatively large and the spatial plots thus define spatial trends at a coarse scale. The plots also do not include an estimate of small-scale spatial variance, which can be significant (e.g. Balls *et al.* 1997, Birch *et al.* 2001). In other words, the plots are based on the contribution or concentration of a parameter in a single sediment sample collected at each sampling station, yet a sediment sample collected just a few meters away might yield a different contribution or concentration for the relevant parameter. To overcome this problem several sediment samples in the immediate vicinity of a sampling station must be collected and analysed. However, this approach was financially prohibitive. In any case the number of separate sediment samples that should be collected is dependent on the expected variance, which itself was unknown. An alternate approach to overcoming this problem of small-scale spatial variability is to adopt a composite sampling approach. This involves the collection and combining of several sediment samples near the sampling point and integrates small-scale spatial variance, but still does not provide an understanding of variance since only a single result is obtained. Composite sampling also has the disadvantage that localised areas of high contaminant concentrations might not be detected because of the integrating effect of this approach. Of course, there is also no certainty that hotspots were not missed through the sampling approach used in this study.

The spatial plots should not, therefore, be used for predictive purposes but rather to identify broad spatial trends in the physical and chemical characteristics of sediment from Richards Bay. So-called hotspots identified by the plots provide the focus areas for more detailed high resolution sampling should this be necessary (e.g. to determine the actual spatial extent of a hotspot).

5. Results and Discussion

5.1. Sediment grain size composition

As mentioned previously, grain size is one of the most important variables that influence natural and

anthropogenic concentrations of metals in sediment. Aluminosilicates, which predominate in clay, are the major natural metal-bearing phases of sediment. The natural concentrations of most metals are consequently usually strongly positively correlated to the silt and clay (*i.e.* mud) fraction of sediment, meaning that mud dominated sediment naturally has a higher metal content than sand dominated sediment. Mud also sequesters metals that are anthropogenically introduced in solution to surface waters because of the large surface area provided for adsorption and surface electric charges that render the grains reactive (Förstner and Wittmann 1979, Horowitz and Elrick 1987, Schropp *et al.* 1990). Anthropogenically derived metals are also preferentially transported with (*i.e.* adsorbed onto) fine-grained suspended particulate material, which is ultimately deposited and accumulates in depositional areas. These are areas where the sediment is dominated by mud and form where currents are so weak that fine-grained material settles from the water column.

Sand dominated areas in contrast are characterised by strong currents, which prohibit the settlement and accumulation of fine-grained material. Sand is dominated by metal deficient quartz and this coupled with a smaller surface area to volume ratio compared to mud and the absence of surface electric charges mean that natural and anthropogenically derived metal concentrations are usually low in sand dominated sediment. There can be exceptions to this general rule, such as sand dominated sediment near vessel construction and

maintenance facilities or metal export facilities having high metal concentrations due to the introduction of metal flecks, metal-infused paint flakes and ore fragments. The propensity for metal flecks, paint flakes, ore fragments and similar material to accumulate in sand dominated sediment or to be transported further afield depends on the mass of the material and post-deposition dispersive processes (*e.g.* vessel propeller wash). In the context of Richards Bay, high metal concentrations could conceivably occur in sand dominated sediment at and near quays where metal ore is exported through the Port of Richards Bay, due to the accidental spillage or entry of ore fragments by other means.

An understanding of the grain size composition of sediment thus provides important information for identifying depositional areas in Richards Bay, where the accumulation of anthropogenically introduced metals is theoretically highest. The presence of anomalously high metal concentrations in sand dominated sediment also allows for the reaching of a conclusion on the likelihood that the metal is present in a particulate form and hence the potential toxicological significance of the concentration. Lastly, the grain size composition of sediment provides an understanding on whether the chosen normaliser for baseline model definition is a reliable proxy for the major natural metal-bearing phases of sediment.

Summary grain size composition statistics for sediment collected from Richards Bay in November

Table 3. Summary statistics for the grain size composition and total organic content of sediment collected from Richards Bay in November 2012 (n = 97). %tile = percentile, VCS = very coarse-grained sand, CS = coarse-grained sand, MS = medium-grained sand, FS = fine-grained sand, VFS = very fine-grained sand, Mean = mean grain size, TOC = total organic content.

Statistic	Gravel (%)	VCS (%)	CS (%)	MS (%)	FS (%)	VFS (%)	Mud (%)	Sand (%)	Mean (mm)	TOC (%)
Minimum	0.00	0.00	0.00	0.15	0.34	0.80	0.66	1.80	0.04	0.01
10 th %tile	0.00	0.00	0.15	0.50	2.01	2.17	1.88	5.33	0.05	0.09
20 th %tile	0.00	0.03	0.22	1.15	4.12	3.06	14.91	10.07	0.05	0.42
30 th %tile	0.00	0.06	0.34	1.84	8.29	4.00	35.07	17.65	0.06	0.80
40 th %tile	0.05	0.14	0.47	2.85	12.29	4.97	48.71	28.81	0.07	1.07
50 th %tile	0.16	0.19	0.62	4.61	14.66	5.99	61.03	37.08	0.07	1.41
60 th %tile	0.33	0.27	0.86	7.28	21.14	7.62	70.23	45.52	0.10	1.73
70 th %tile	0.76	0.48	1.22	12.27	28.84	8.92	82.35	63.95	0.12	1.96
80 th %tile	1.19	0.75	2.24	22.91	33.81	12.51	88.53	84.60	0.19	2.94
90 th %tile	2.65	1.32	3.68	50.72	42.05	17.61	94.67	97.75	0.24	3.59
Maximum	20.44	5.62	29.42	72.65	85.43	26.58	98.20	99.03	0.41	5.68
Mean	1.18	0.52	1.57	13.58	20.37	7.96	54.82	44.00	0.11	1.65

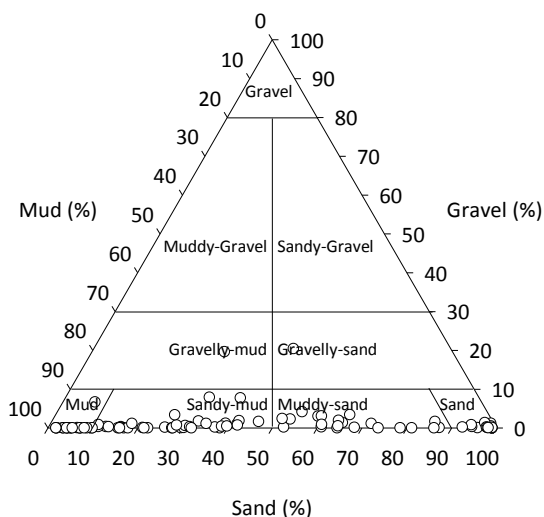


Figure 3. Ternary plot illustrating the proportional contribution of gravel, sand and mud to bulk sediment collected from Richards Bay in November 2012.

2012 are presented in Table 3. The grain size composition of sediment varied widely across the study area. The mud fraction, for example, contributed between 0.66 - 98.20% of bulk sediment weight. From a textural perspective the sediment can be divided into six facies, namely gravelly-mud, gravelly-sand, sand, muddy-sand, sandy mud, and mud (Figure 3). Mud and sandy-mud were the most prevalent facies. Spatial trends for the contribution of gravel, sand and mud to bulk sediment weight are presented in Figures 4 - 6. Mud was most prevalent in Inner Basins 1 and 2, where the sediment at only a few stations was not dominated by mud. The stations where sand was dominant were generally situated in shallow waters alongside the sand spit that separates the Inner Basin complex from the Mudflats. The sediment from Inner Basin 3 was, in contrast, almost exclusively dominated by sand. Sediment from much of the Richards Bay Coal Terminal Basin was dominated by mud, with sand more prevalent in the shallower southern part of the basin. Sediment on the Mudflats was dominated by a mix of sand and mud. Mud was generally prevalent in the middle part of the Mudflats, and sand more prevalent at and near the shallower margins. Coarse-grained material, including gravel, coarse- and very-coarse grained sand, was poorly represented, typically comprising <2% of bulk sediment weight and exceeding 10% at only one station. The highest contribution of gravel to bulk sediment weight was alongside quays in the northern part of the Richards Bay Coal Terminal

Basin.

The high mud fraction of sediment over a large proportion of the study area is indicative of the sheltered and depositional nature of Richards Bay. In other words, fine grained material entering the Bay tends to settle from the water column and accumulate on the bottom. This intimates that metals and other contaminants introduced in solution or adsorbed onto fine-grained particulate material are also likely to settle and accumulate in rather than be flushed from the Bay. Theoretically, the lowest probability for the accumulation of metals and other contaminants in sediment is for Inner Basin 3, the most southerly part of the Richards Bay Coal Terminal Basin, and the shallow margins of the Mudflats.

5.2. Sediment total organic content

Organic matter in sediment provides a binding site for metals and other contaminants (Wangersky 1986, Stumm and Morgan 1996, Schwarzenbach *et al.* 2003). Anthropogenically derived metals are also commonly transported and introduced to aquatic systems bound to fine-grained particulate matter, including particulate organic matter. An understanding of the total organic content of sediment thus provides important information for identifying the major sources and vectors for the introduction and major depositional zones for particulate organic matter in Richards Bay, and for identifying areas theoretically most susceptible to the accumulation of contaminants partial to adsorption onto particulate organic matter.

The total organic content also provides an understanding of the potential for adverse effects to bottom-dwelling organisms associated with the excessive accumulation of particulate organic matter in sediment. Although particulate organic matter is a food source for many bottom-dwelling organisms, the excessive accumulation of this matter in sediment leads to shifts in the structure and composition and in extreme cases loss of bottom-dwelling communities (Pearson and Rosenberg 1978, Gray *et al.* 2002, Hyland *et al.* 2005), with ecosystem scale implications (Solan *et al.* 2004). This occurs when the rate of particulate organic matter accumulation exceeds the rate at which it is consumed or otherwise processed by

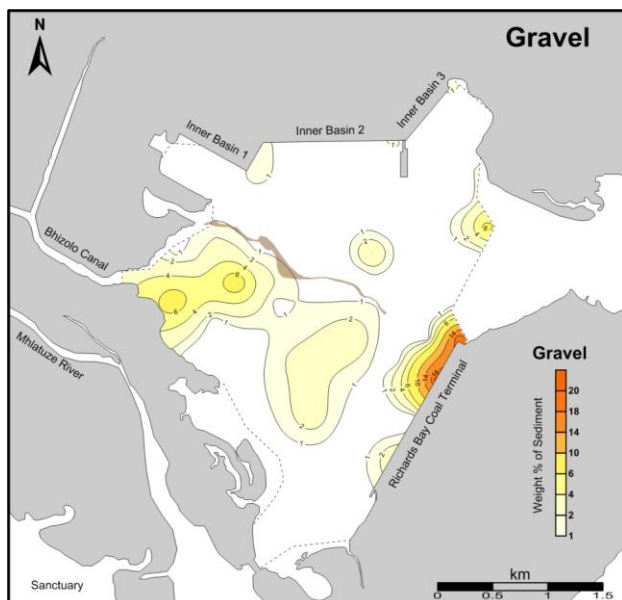


Figure 4. Spatial trend for the contribution of gravel to bulk sediment collected from Richards Bay in November 2012.

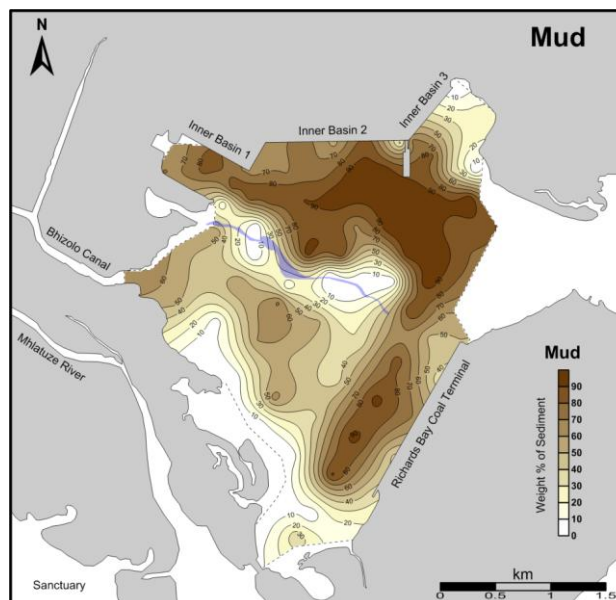


Figure 6. Spatial trend for the contribution of mud to bulk sediment collected from Richards Bay in November 2012.

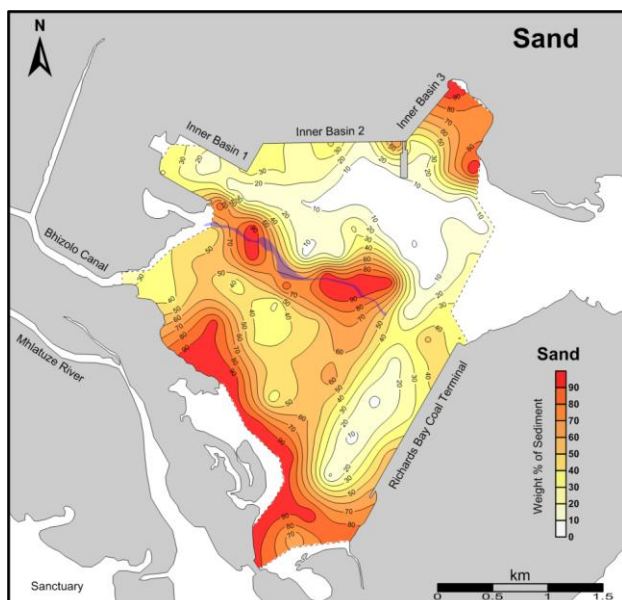


Figure 5. Spatial trend for the contribution of sand to bulk sediment collected from Richards Bay in November 2012.

bottom-dwelling organisms. This leads to a shift in dominance by smaller, more abundant opportunistic species and the proliferation of bacteria. These changes are driven by dissolved oxygen depletion and increases in the concentration of ammonia and sulphide by-products (Diaz and Rosenberg 1995, Gray *et al.* 2002, Hyland *et al.* 2005, Wildish and Pohle 2005, Hargrave *et al.* 2008, Pelletier *et al.* 2011). The sulphide by-products are from sulphate-reducing bacteria, which produce (hydrogen) sulphide when they metabolise under anoxic conditions (Hyland *et*

al. 2005). Hydrogen sulphide is toxic to most aquatic organisms at low concentrations. Some bottom-dwelling organisms (*e.g.* certain species of polychaete) are able to tolerate elevated hydrogen sulphide concentrations and this has made them useful indicators of sediment organic enrichment. However, as the rate of particulate organic matter accumulation increases even these sulphide-tolerant taxa cannot survive and the sediment becomes progressively azoic with respect to benthic macrofauna, to the extent that eventually only single cell organisms such as protozoa, ciliates and flagellates capable of living in sulphide-rich sediment remain (Fenchel and Riedl 1970, Pelletier *et al.* 2011).

Summary statistics for the total organic content of sediment are presented in Table 3. As was the case for grain size composition the total organic content of sediment varied widely across the study area, contributing between 0.01 - 5.68% of bulk sediment weight. Although a spatial plot of the contribution of total organic content to bulk sediment weight (Figure 7) is informative it does not provide an understanding on whether the total organic content is possibly enhanced through anthropogenic inputs. In the absence of significant anthropogenic contributions of particulate organic matter there is usually a strong positive relationship between the mud fraction and total organic content of sediment.

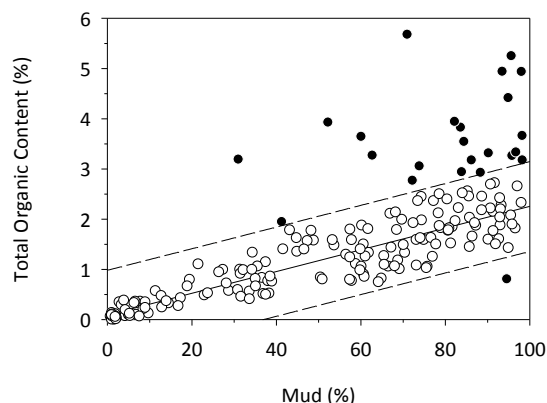


Figure 7. Baseline model for total organic content in sediment from Richards Bay, with data used to define the baseline model (open symbols) and outliers (solid symbols) for sediment collected in November 2012 superimposed.

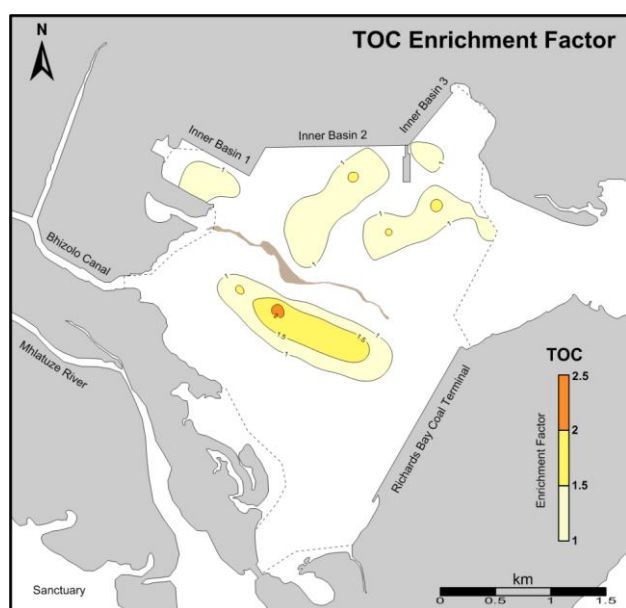


Figure 8. Spatial trend for particulate organic matter (total organic content, TOC) enrichment of sediment collected from Richards Bay in November 2012.

This is because these fine-grained materials are similarly deposited on or winnowed from sediment depending on prevailing hydrodynamic conditions. The organic matter is also progressively consumed by bottom-dwelling organisms, preventing its excessive accumulation. The Coastal Systems research group of the CSIR recently (2012) defined a baseline model for the total organic content of sediment from Richards Bay (report in preparation). The baseline model was updated using total organic content data for sediment collected for this study. The baseline model is used to interpret the total organic content of sediment in the same manner as baseline models for metals. Superimposing the total organic content for sediment collected for this

study onto the baseline model identifies the total organic content of sediment at 23 (24% of all) stations as anomalous (Figure 8). In all but one case the anomaly reflected enrichment. As was the case for metals, an Enrichment Factor for the total organic content of sediment at each station was calculated. The spatial plot of Enrichment Factors shows that enrichment was patchy in the Inner Basin complex (Figure 8). The highest magnitude enrichment was for a sausage-like section of sediment on the Mudflats, but the excess particulate organic matter here is probably of a natural rather than anthropogenic origin considering its proximity to fringing vegetation. Visual inspection of sediment showed that enrichment at some stations in Inner Basins 2 and 3 was attributable to the inclusion of fragments of wood chips, which are exported from the Port of Richards Bay (predominantly from the finger jetty between Inner Basins 2 and 3).

Although sediment in the study area is enriched with particulate organic matter the magnitude of enrichment is not so high that there is a likelihood of anoxia developing in surface sediment and at the sediment-water interface due to the decomposition of this material, with the possible exception of some parts of Inner Basin 2 where wood chips have deposited in sediment. There is this also a low probability that the oxygen demand created by the decomposition of particulate organic matter exposed through dredging will lead to a significant reduction in water column dissolved oxygen concentration.

5.3. Metals

5.3.1. General

Summary statistics for metal concentrations in sediment collected from Richards Bay in November 2012 are presented in Table 4. Figure 9 presents the baseline models and baseline cadmium and mercury concentrations with aluminium normalised metal concentrations in sediment collected for this study superimposed. Summary statistics for metal Enrichment Factors are provided in Table 5.

5.3.2. Iron

Iron was enriched in sediment at five stations (Figure 9). The magnitude of enrichment at four

stations on the Mudflats was too low to conclude that the excess iron had an anthropogenic source (Figure 10). Iron is subject to diagenetic enhancement under certain conditions, leading to its natural enrichment in surface sediment, and this rather than contamination probably accounts for the enrichment of sediment on the Mudflats.

Although the magnitude of enrichment at the remaining station in Inner Basin 2 was low, it was nevertheless sufficient to suspect the excess iron had an anthropogenic source. The station was immediately adjacent to the sand spit that separates the Inner Basin complex from the Mudflats (Figure 10). As discussed below the sediment at this station was enriched by other metals (*e.g.* vanadium) and supports the conclusion that the excess iron had an anthropogenic source.

5.3.3. Arsenic

Arsenic was enriched in sediment at seven stations in Inner Basins 1, 2 and 3, at one station in the Richards Bay Coal Terminal Basin, and at eight stations on the Mudflats (Figures 9 and 11). Although the magnitude of enrichment was typically low, it was high enough at one station in Inner Basin 1 and at three stations on the Mudflats to suspect the excess arsenic had an anthropogenic source. Anthropogenic sources of arsenic to the Bay are uncertain.

5.3.4. Barium

Barium was enriched in sediment at one station alongside a quay in the Richards Bay Coal Terminal Basin (Figures 9 and 12). The magnitude of

enrichment was too low to conclude the excess barium had an anthropogenic source. This said, sediment at this station was enriched by other metals and it cannot thus be discounted that the excess barium had an anthropogenic source.

5.3.5. Beryllium

Beryllium was enriched in sediment at 16 stations, the majority alongside or near quays in Inner Basins 1 and 2 and the Richards Bay Coal Terminal Basin (Figures 9 and 13). The magnitude of enrichment at the majority of stations was too low to conclude the excess beryllium had an anthropogenic source. This said, numerous of the stations were situated alongside or near quays in Inner Basins 1 and 2 and this and the fact that sediment at these stations was enriched by other metals suggests the excess beryllium may have had an anthropogenic source. Anthropogenic sources of beryllium to the Bay are uncertain.

5.3.6. Cadmium

Cadmium was enriched in sediment at 22 stations in Inner Basins 1, 2 and 3 (Figures 9 and 14). The magnitude of enrichment at stations in Inner Basin 1 and the western part of Inner Basin 2 was sufficient to conclude the excess cadmium had an anthropogenic source. Although anthropogenic sources of cadmium to Richards Bay are uncertain these are potentially numerous, including metal ores, scrap metal and phosphate rock, in which cadmium is an important impurity. There is also a possibility that some of the cadmium enrichment was attributable to natural processes. Diatoms (microalgae) sequester cadmium in their frustules.

Table 4. Summary statistics for metal concentrations in sediment collected from Richards Bay in November 2012 (Al and Fe in mg.g^{-1} , all other metals in $\mu\text{g.g}^{-1}$, $n = 97$). %tile = percentile, < = below method detection limit, as indicated.

Statistic	Metal														
	Al	Fe	As	Ba	Be	Cd	Co	Cu	Cr	Mn	Hg	Ni	Pb	V	Zn
Minimum	3.91	2.15	0.58	8.48	0.06	<0.02	1.32	1.04	6.26	72.77	<0.03	0.88	2.00	5.76	3.93
10 th %tile	6.71	6.44	2.15	15.42	0.14	<0.02	3.12	2.66	19.57	121.84	<0.03	5.23	3.64	16.84	10.77
20 th %tile	14.02	14.74	4.35	37.39	0.42	<0.02	5.96	12.91	63.53	225.44	<0.03	18.40	6.82	31.87	37.24
30 th %tile	24.63	22.81	5.28	65.02	0.78	<0.02	9.81	25.81	81.58	434.40	<0.03	25.29	10.79	43.90	51.01
40 th %tile	31.54	33.08	7.48	84.26	0.99	<0.02	13.47	35.94	132.06	539.22	<0.03	35.54	13.44	60.78	67.62
50 th %tile	38.98	39.43	8.64	105.55	1.23	0.03	16.11	43.01	145.52	628.32	<0.03	39.58	16.92	71.42	82.06
60 th %tile	42.59	43.98	9.55	114.76	1.55	0.06	17.16	55.16	179.15	673.48	<0.03	45.51	19.09	75.71	95.67
70 th %tile	45.30	45.72	10.48	122.42	1.69	0.10	17.89	80.87	200.00	733.82	<0.03	55.81	20.02	80.93	105.86
80 th %tile	48.92	48.40	11.66	129.83	1.80	0.16	18.99	126.27	242.34	789.84	<0.03	61.32	23.20	83.98	123.92
90 th %tile	51.53	52.02	13.90	140.88	2.08	0.24	19.91	197.49	311.79	924.46	0.04	72.65	25.79	91.41	145.37
Maximum	59.91	61.90	25.00	168.01	2.71	1.18	23.98	476.89	454.44	1 884.45	0.16	129.03	119.52	316.03	297.41
Mean	33.61	33.57	8.46	89.37	1.19	0.10	13.57	78.78	159.04	588.93	0.04	41.65	16.62	62.89	84.89

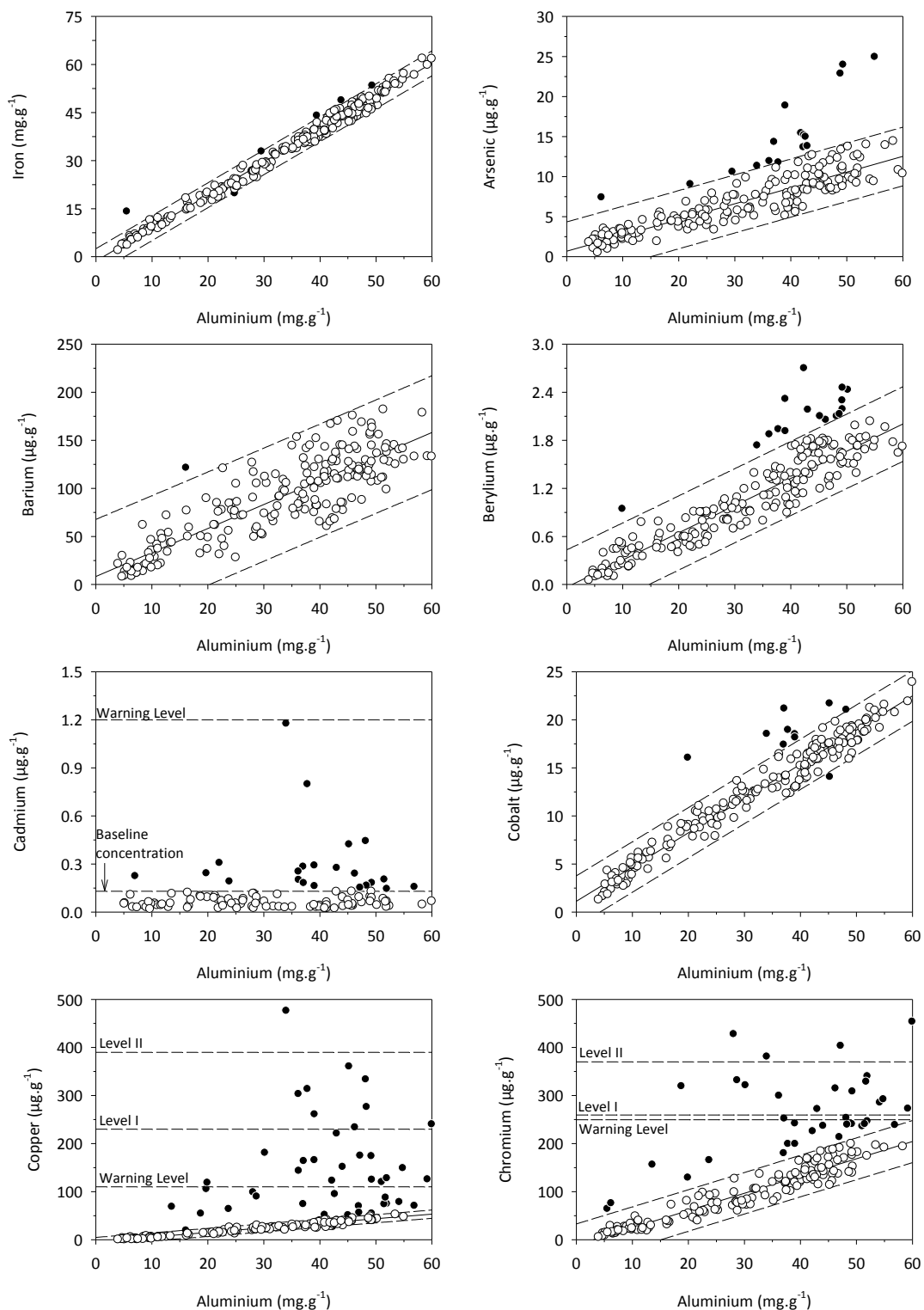


Figure 9. Aluminium normalised baseline models for metals in sediment from Richards Bay, with baseline (open symbols) and outlier concentrations (solid symbols) for sediment collected in November 2012 superimposed. Sediment quality guidelines used to determine whether sediment identified for dredging in South African ports is of a suitable quality for unconfined openwater disposal are indicated when these fall within the y-axis range. Metal concentrations denoted by solid symbols above the upper prediction limit or baseline cadmium or mercury concentration are enriched.

In areas where productivity is high the continual sinking of senescent diatoms can lead to an increase in cadmium concentrations in sediment (Cassis *et al.* 2011). The significance in this context is that monitoring and research performed by the

Coastal Systems research group of the CSIR has shown that microalgal biomass is usually highest in Inner Basin 1 and the western part of Inner Basin 2.

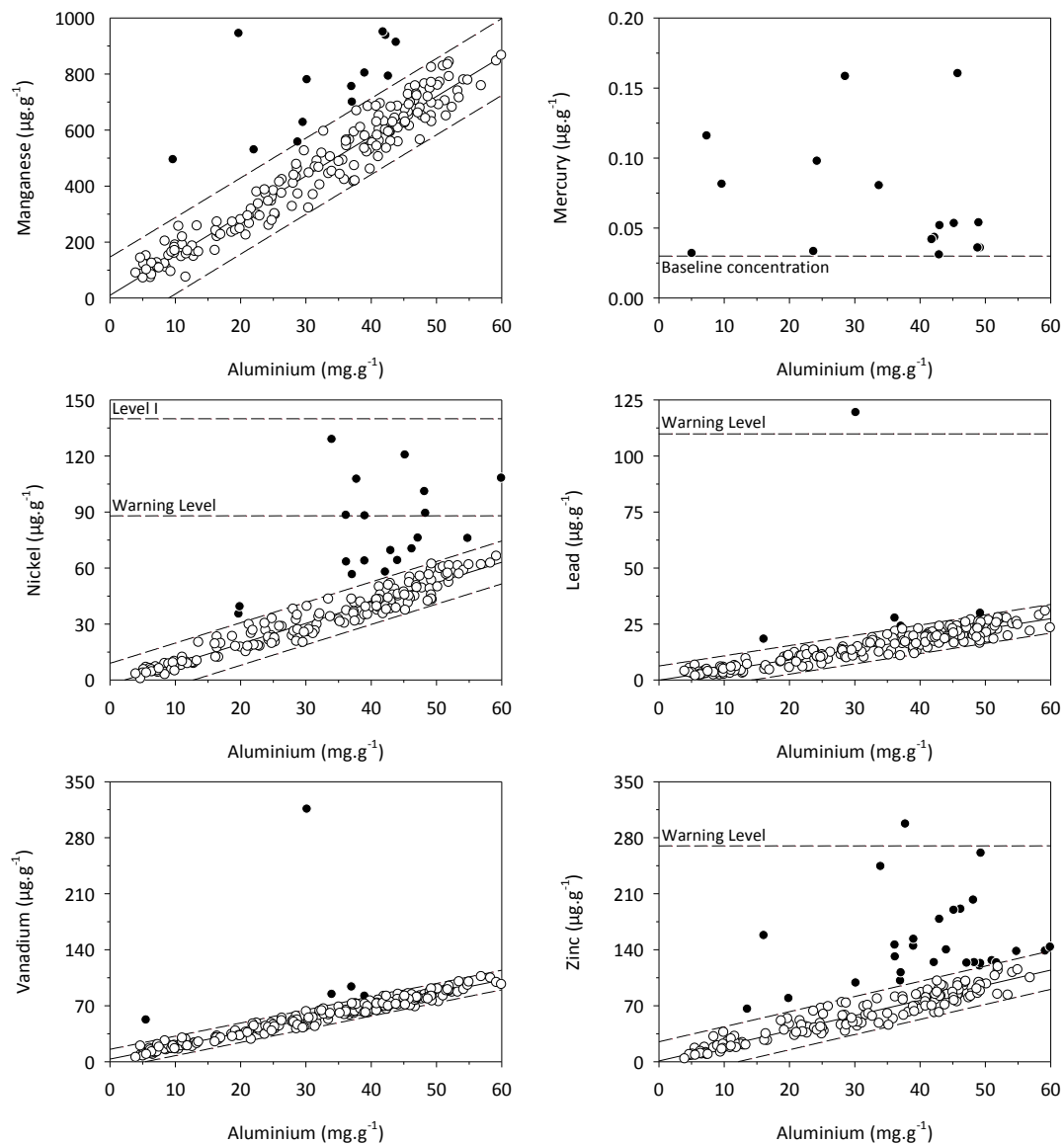


Figure 9 continued. Aluminium normalised baseline models for metals in sediment from Richards Bay, with baseline (open symbols) and outlier concentrations (solid symbols) for sediment collected in November 2012 superimposed. Sediment quality guidelines used to determine whether sediment identified for dredging in South African ports is of a suitable quality for unconfined openwater disposal are indicated when these fall within the y-axis range. Metal concentrations denoted by solid symbols above the upper prediction limit or baseline cadmium or mercury concentration are enriched.

Table 5. Summary statistics for Enrichment Factors calculated from aluminium normalised baseline models for metals in sediment collected from Richards Bay in November 2012 (n = 97).

Statistic	Metal													
	Fe	As	Ba	Be	Cd	Co	Cu	Cr	Mn	Hg	Ni	Pb	V	Zn
Minimum	0.33	0.11	0.11	0.11	0.15	0.26	0.12	0.14	0.32	0.50	0.06	0.23	0.27	0.13
10 th %tile	0.66	0.40	0.18	0.22	0.15	0.52	0.22	0.34	0.48	0.50	0.32	0.41	0.60	0.30
20 th %tile	0.79	0.50	0.33	0.40	0.15	0.71	0.58	0.54	0.67	0.50	0.50	0.51	0.69	0.56
30 th %tile	0.86	0.57	0.45	0.56	0.15	0.78	0.70	0.64	0.75	0.50	0.66	0.58	0.79	0.64
40 th %tile	0.88	0.64	0.55	0.64	0.15	0.84	0.83	0.74	0.80	0.50	0.71	0.67	0.83	0.75
50 th %tile	0.90	0.67	0.62	0.70	0.20	0.86	0.91	0.84	0.83	0.50	0.79	0.70	0.85	0.82
60 th %tile	0.92	0.72	0.66	0.76	0.48	0.89	1.20	0.96	0.87	0.50	0.85	0.73	0.87	0.88
70 th %tile	0.93	0.80	0.68	0.83	0.73	0.90	2.16	1.14	0.90	0.50	0.89	0.77	0.89	0.97
80 th %tile	0.94	0.90	0.72	0.92	1.22	0.92	3.28	1.27	1.01	0.50	0.99	0.81	0.91	1.08
90 th %tile	0.97	1.09	0.78	1.10	1.87	0.99	4.87	1.58	1.27	1.42	1.28	0.90	0.95	1.52
Maximum	1.76	1.72	1.14	1.45	9.06	1.49	13.01	3.25	2.68	5.35	2.82	5.97	4.89	3.12

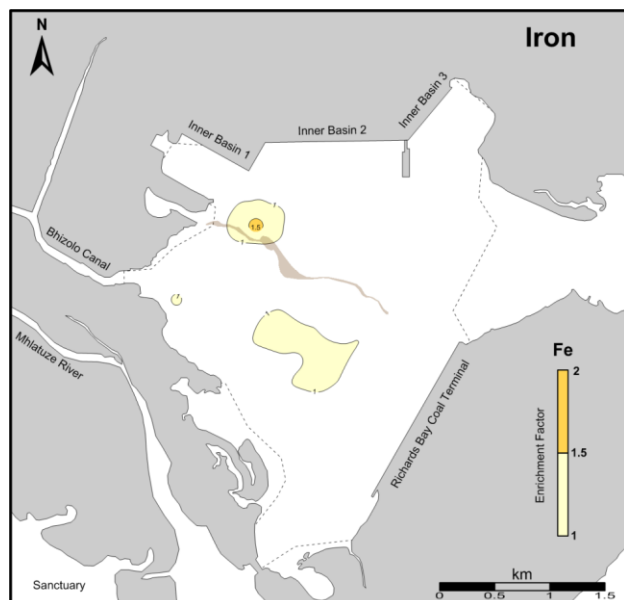


Figure 10. Spatial trend for iron enrichment of sediment collected from Richards Bay in November 2012.

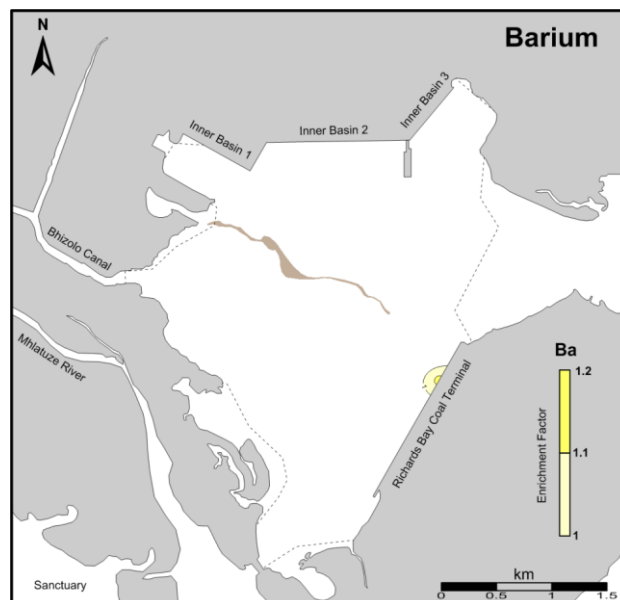


Figure 12. Spatial trend for barium enrichment of sediment collected from Richards Bay in November 2012.

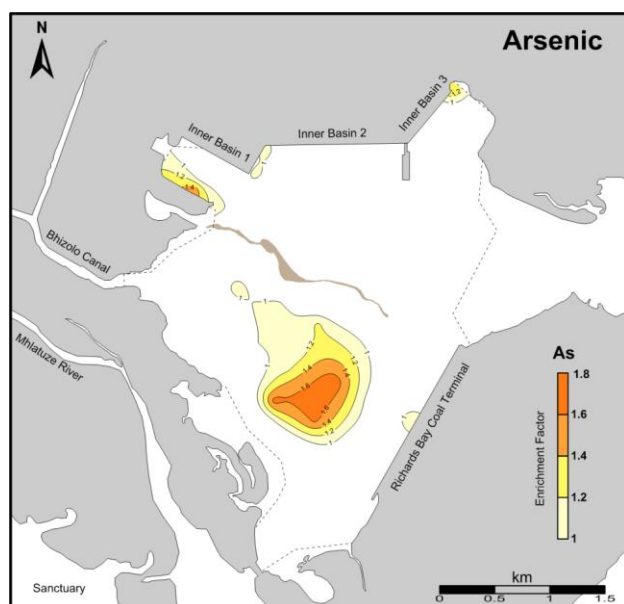


Figure 11. Spatial trend for arsenic enrichment of sediment collected from Richards Bay in November 2012.

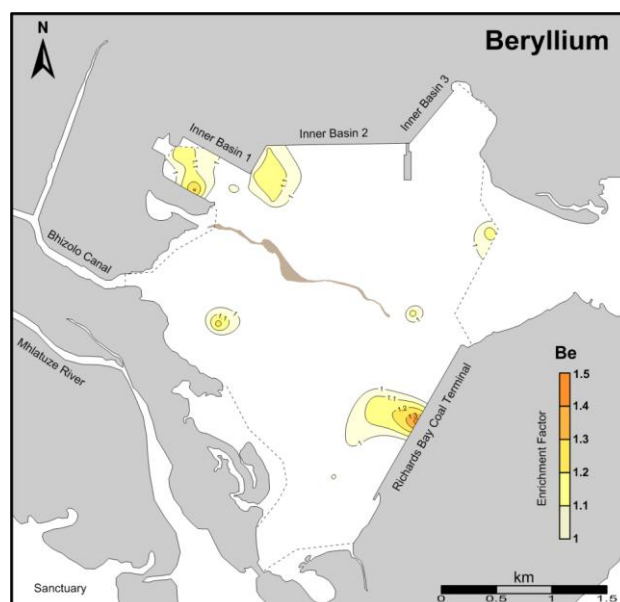


Figure 13. Spatial trend for beryllium enrichment of sediment collected from Richards Bay in November 2012.

5.3.6. Cobalt

Cobalt was enriched in sediment at eight stations in Inner Basins 1 and 2 and one station in Inner Basin 3, all alongside and near quays (Figures 9 and 15). The magnitude of enrichment at some stations combined with the fact that sediment at these stations was enriched by other metals suggests the excess cobalt had an anthropogenic source.

Anthropogenic sources of cobalt to Richards Bay are uncertain. A significant source of cobalt is the recycling of scrap metal, while phosphate fertilisers

also contain cobalt as an impurity (Kim *et al.* 2006). The significance is that scrap metal is exported from the port whilst phosphate-based fertiliser is produced at an industry near the Bay. The production of fertiliser does not, however, appear to be a significant source of cobalt to the Bay. This conclusion is based on the fact that gypsum, a byproduct of fertiliser and phosphoric acid production, is discharged to the marine environment off Richards Bay through two outfalls but sediment near the outfalls is rarely enriched with cobalt (*e.g.* CSIR 2012).

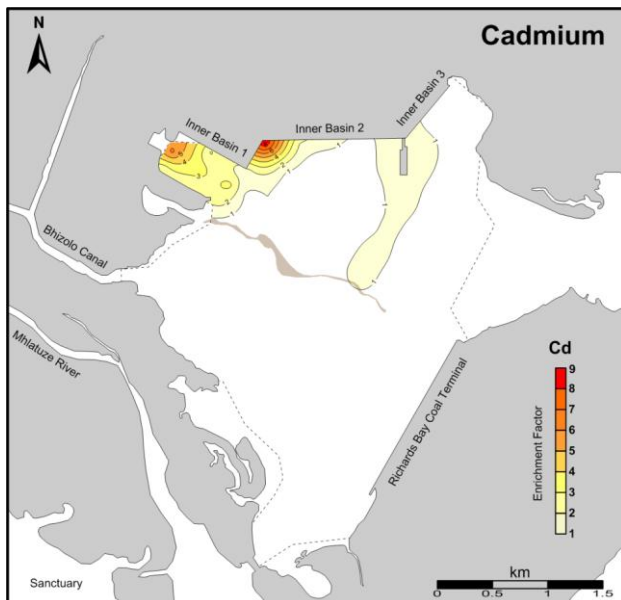


Figure 14. Spatial trend for cadmium enrichment of sediment collected from Richards Bay in November 2012.

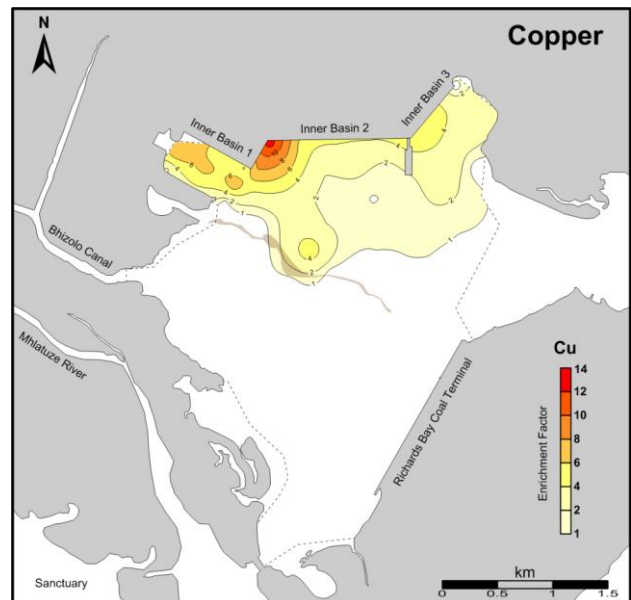


Figure 16. Spatial trend for copper enrichment of sediment collected from Richards Bay in November 2012.

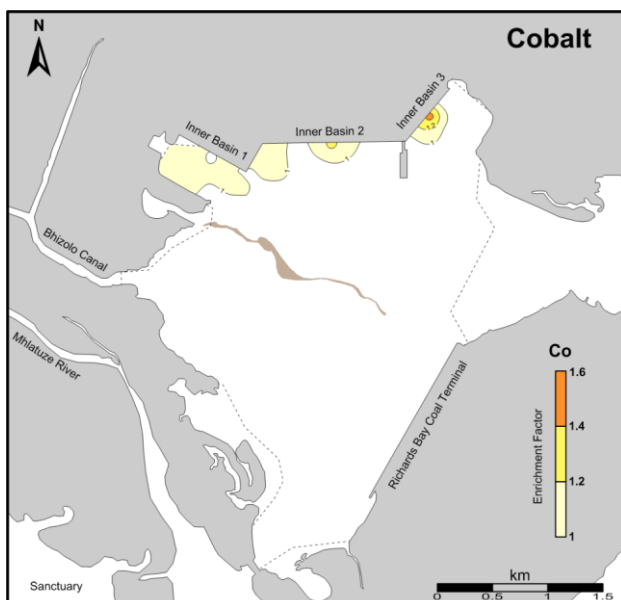


Figure 15. Spatial trend for cobalt enrichment of sediment collected from Richards Bay in November 2012.

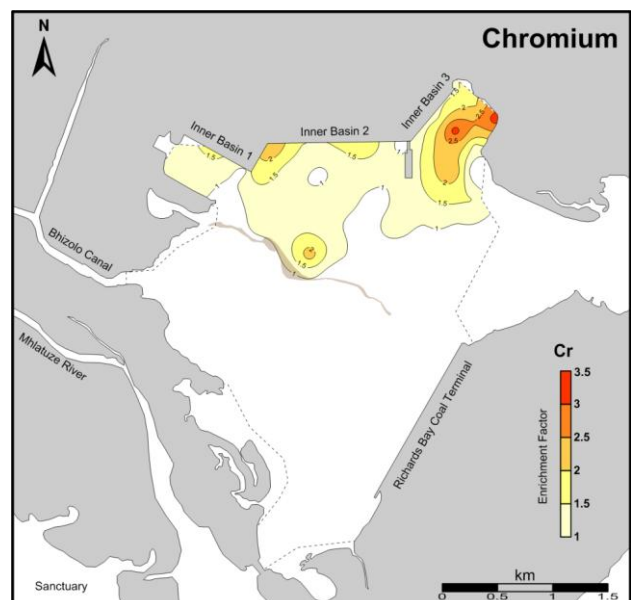


Figure 17. Spatial trend for chromium enrichment of sediment collected from Richards Bay in November 2012.

5.3.7. Copper

Copper was the most frequently (widespread) enriched metal (44% of stations; Figures 9 and 16). The highest Enrichment Factor (13.01) for any metal was for copper. All stations where sediment was enriched with copper were situated in the Inner Basin complex, with the most pronounced enrichment for sediment alongside and near quays (Figure 16). The magnitude of enrichment combined with the fact that sediment at most stations was enriched by other metals suggests the excess copper had an anthropogenic source.

Anthropogenic sources of copper to the Bay are uncertain but potentially numerous, including the export of metal ore and scrap metal. Copper is also an important impurity of phosphate rock that is imported through the port. An additional but difficult to quantify anthropogenic source of copper is its leaching from antifouling coatings applied to the hulls of vessels. Copper is widely used as a biocide in the coatings and is the source of significant water and sediment quality impairment in marinas and ports throughout the world (e.g. Schiff *et al.* 2007, Carson *et al.* 2009). However,

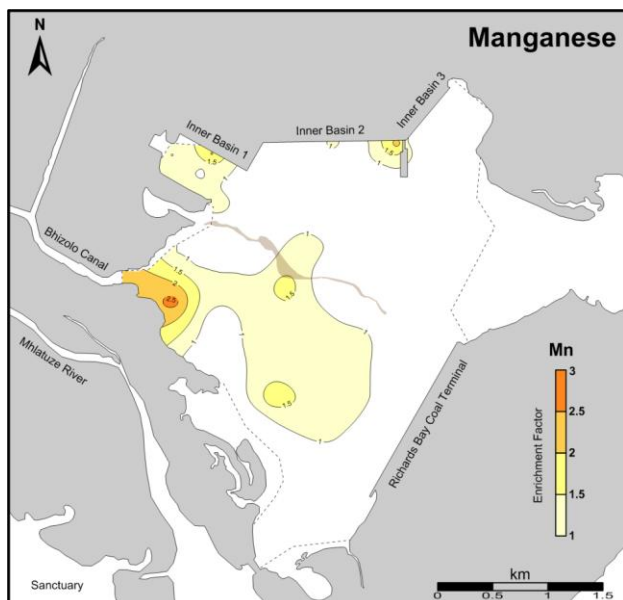


Figure 18. Spatial trend for manganese enrichment of sediment collected from Richards Bay in November 2012.

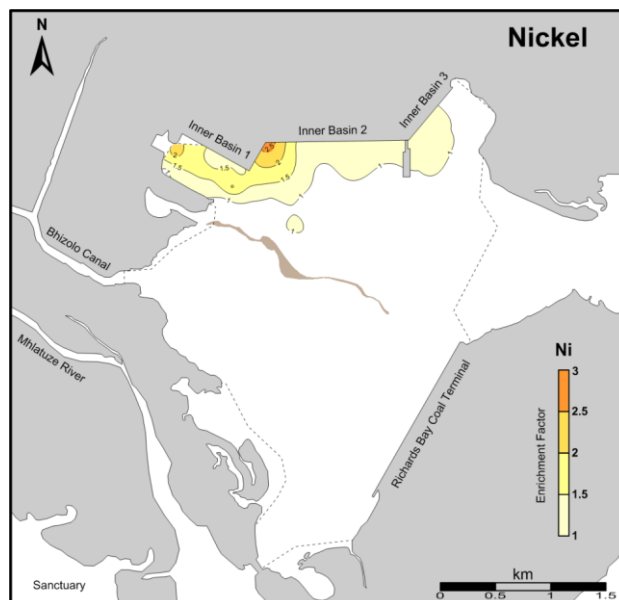


Figure 20. Spatial trend for nickel enrichment of sediment collected from Richards Bay in November 2012.

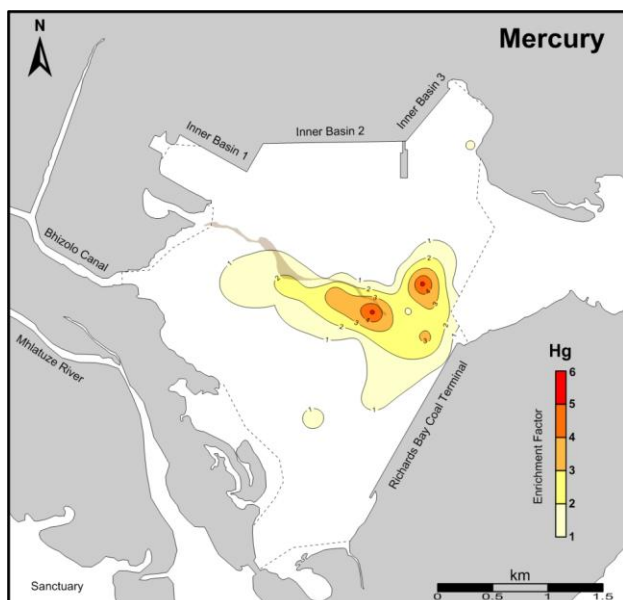


Figure 19. Spatial trend for mercury enrichment of sediment collected from Richards Bay in November 2012.

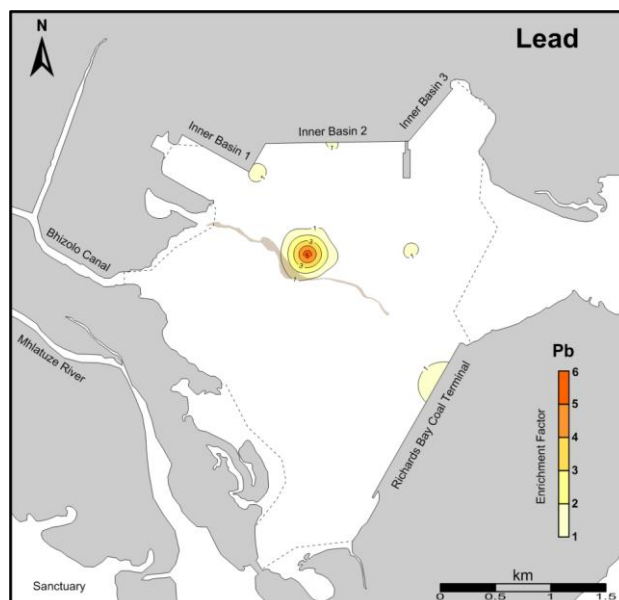


Figure 21. Spatial trend for lead enrichment of sediment collected from Richards Bay in November 2012.

since copper was not a contaminant of sediment in the Richards Bay Coal Terminal Basin the contribution of copper from vessel antifouling coatings seems minimal.

5.3.8. Chromium

Chromium was the second most frequently enriched metal (34% of stations; Figure 9). All stations where sediment was enriched with chromium were situated in the Inner Basin complex (Figure 17). There is little doubt the excess chromium had an anthropogenic source

considering that chromium ore is exported through the Port of Richards Bay. The most pronounced enrichment was for sediment in Inner Basin 3, where most of the ore is exported (Figure 17). The accidental spillage and/or entrainment of ore particles by surface runoff and possibly even wind is the most likely route of entry for chromium into the Bay.

5.3.9. Manganese

Manganese was enriched in sediment at 20 stations, most on the Mudflats (Figures 9 and 18).

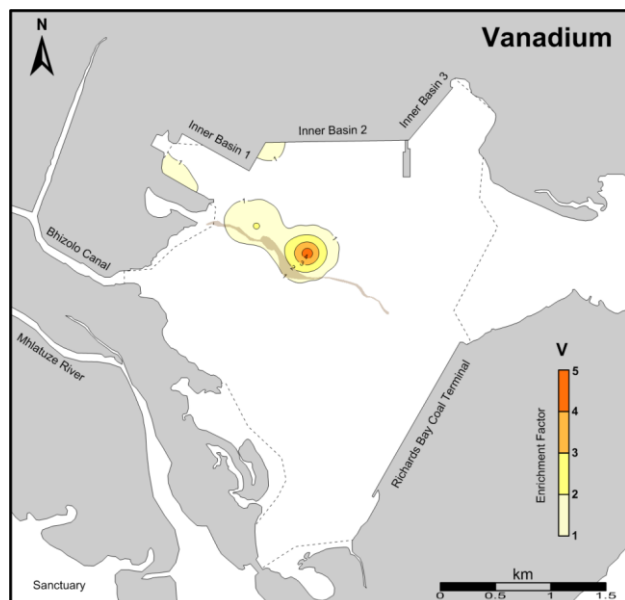


Figure 22. Spatial trend for vanadium enrichment of sediment collected from Richards Bay in November 2012.

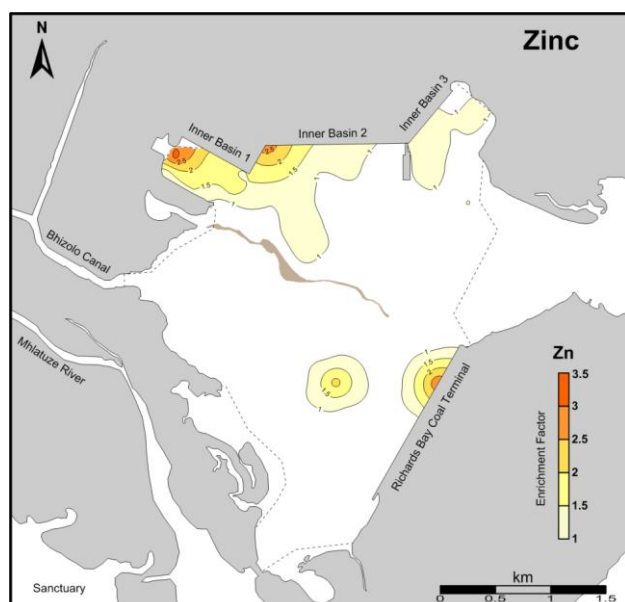


Figure 23. Spatial trend for zinc enrichment of sediment collected from Richards Bay in November 2012.

Most of the remaining stations were alongside and near quays in Inner Basins 1 and 2. The magnitude of enrichment at some stations in Inner Basins 1 and 2 and the fact that sediment at these stations was enriched by other metals suggests the excess manganese had an anthropogenic source. The situation was probably different for the Mudflats. Manganese is subject to diagenetic enhancement under certain conditions, leading to its natural enrichment in surface sediment, and this rather than contamination probably accounts for the enrichment of sediment on the Mudflats.

5.3.10. Mercury

Mercury was enriched in sediment at 16 stations, the majority in the Richards Bay Coal Terminal Basin and on the Mudflats (Figures 9 and Figure 19). The clustering of stations and magnitude of enrichment suggests the excess mercury had an anthropogenic source. However, previous research performed by the Coastal Systems research group of the CSIR (report in preparation and unpublished data) has not revealed significant mercury contamination of sediment from the Mudflats or Richards Bay Coal Terminal Basin, making the enrichment an interesting feature.

5.3.11. Nickel

Nickel was enriched in sediment at 19 stations alongside and near quays in the Inner Basin complex (Figures 9 and 20). The magnitude of enrichment at many stations was sufficient to conclude the excess nickel had an anthropogenic source. This is supported by the fact that sediment at most stations was enriched by other metals. Anthropogenic sources of nickel to the Bay are uncertain, but probably include the accidental spillage of metal ore fragments and scrap metal flakes during vessel loading.

5.3.12. Lead

Lead was enriched in sediment at five isolated stations (Figures 9 and 21). The magnitude of enrichment at four stations was too low to conclude the excess lead had an anthropogenic source. The magnitude of enrichment at the remaining station, near the sand spit that separates the Inner Basin complex from the Mudflats (Figure 21), was high enough to conclude the excess lead had an anthropogenic source. This is supported by the fact that the sediment at this station was enriched by other metals.

5.3.13. Vanadium

Vanadium was enriched in sediment at five stations, all in Inner Basins 1 and 2 (Figures 9 and 22). The magnitude of enrichment at most stations was low, but since sediment at many stations was enriched by other metals this suggests the excess vanadium may have had an anthropogenic source. The highest magnitude enrichment was for a station situated near the sand spit that separates

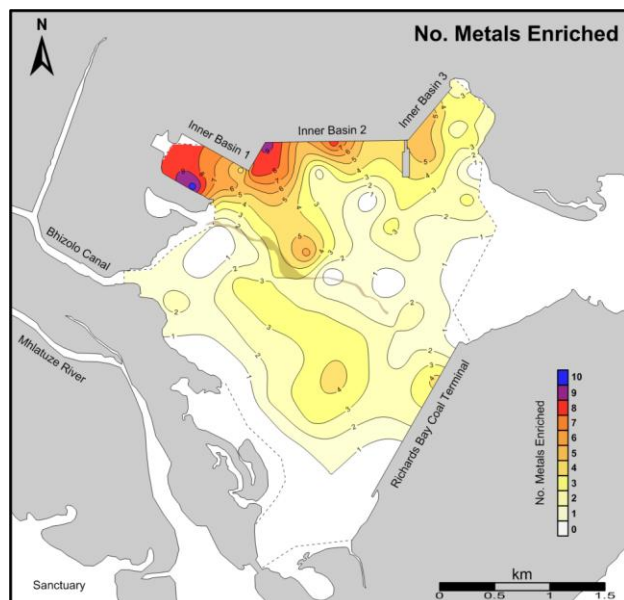


Figure 24. Spatial trend for the number of metals enriched in sediment collected from Richards Bay in November 2012.

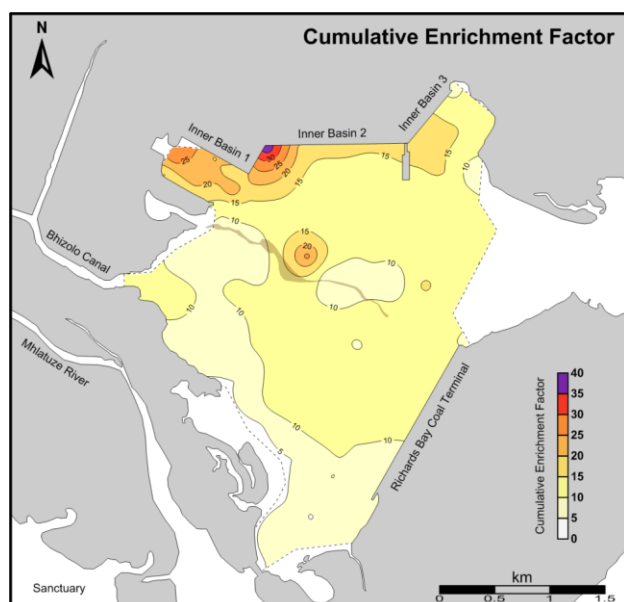


Figure 25. Cumulative Enrichment Factor spatial trend for sediment collected from Richards Bay in November 2012.

the Inner Basin complex from the Mudflats (Figure 22). Anthropogenic sources of vanadium to the Bay are uncertain.

5.3.14. Zinc

Zinc was the third most frequently enriched metal (31% of stations; Figure 9). The most widespread and pronounced enrichment was for sediment in the Inner Basin complex, particularly Inner Basins 1 and 2 (Figure 23). In fact, sediment at only two stations beyond the Inner Basin complex was enriched with zinc, both in the Richards Bay Coal

Terminal Basin. The magnitude of enrichment at the latter stations was sufficient to conclude the excess zinc had an anthropogenic source. The magnitude of enrichment at numerous stations in the Inner Basins 1 and 2 combined with the fact that sediment at most stations was enriched by other metals also suggests the excess zinc had an anthropogenic source. Anthropogenic sources of zinc to the Bay are uncertain, but probably include the export of metal ores and scrap metal. An additional but difficult to quantify anthropogenic source of zinc is its leaching from antifouling coatings applied to the hulls of vessels. Zinc is used as a biocide and more commonly as a booster to enhance the toxicity of other biocides, or to facilitate the erosion process of antifouling coatings (Watermann *et al.* 2005). Zinc cathodic protection devices on vessels have also been identified as important sources of this metal in ports (*e.g.* Trefry *et al.* 1983). However, since zinc was not an important contaminant of sediment in the Richards Bay Coal Terminal Basin, the contribution of zinc from vessel antifouling coatings and cathodic protection devices seems minimal.

5.3.15. Number of metals enriched and cumulative Enrichment Factor

Sediment in ports and aquatic ecosystems with densely urbanised and industrialised surroundings is rarely contaminated by a single metal, due to the typically numerous point and non-point anthropogenic sources of metals (and other contaminants) to these environments. The number of metals enriched in sediment at a particular location thus provides a line of evidence on the probability that the excess concentrations have an anthropogenic rather than a natural source.

The number of metals enriched in sediment at any particular station in Richards Bay was highest in the Inner Basin complex, and more specifically in sediment alongside and near quays (Figure 24). The highest number of metals enriched was ten, at a station in Inner Basin 1 (Figure 24). The sediment at a further eight stations in Inner Basins 1 and 2 was enriched by seven, eight or nine metals. The fact that sediment with the highest number of metals enriched was alongside and near quays provides little doubt that the excess metal concentrations had an anthropogenic source. The sediment at 21

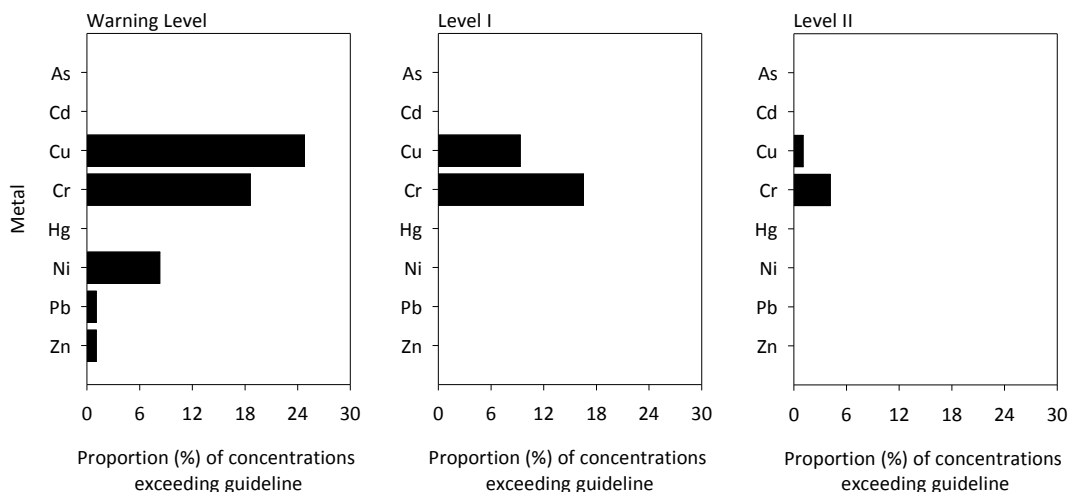


Figure 26. Proportion of stations at which various metals were present in sediment collected from Richards Bay in November 2012 at concentrations exceeding the Warning Level, Level I and Level II of the sediment quality guidelines used to determine whether sediment identified for dredging in South African ports is of a suitable quality for unconfined openwater disposal.

(or 22% of) stations was not metal enriched, while sediment at a further 20% of stations was enriched by a single metal. Most of the latter stations were in the southern parts of the Mudflats and Richards Bay Coal Terminal Basin (Figure 24).

The major disadvantage of using the number of metals enriched in sediment as a line of evidence on the probability that excess metal concentrations have an anthropogenic rather than a natural source is that a metal enriched to a very low magnitude is scored equivalently to a metal enriched to a very high magnitude. There are thus only two possibilities, namely the sediment is either metal enriched or not enriched. However, the potential ecological implications of differences in the magnitude of enrichment may be very different. A line of evidence that compensates for this disadvantage is the cumulative Enrichment Factor, which is the sum of Enrichment Factors for all metals in sediment at a particular station.

The cumulative Enrichment Factor spatial trend identifies sediment alongside and near quays in the Inner Basin complex as the most problematic from a metal contamination perspective (Figure 25). Sediment at a station situated near the sand spit that separates the Inner Basin complex from the Mudflats also had a high cumulative Enrichment Factor.

5.3.16. Assessment of sediment quality using sediment quality guidelines

As mentioned previously, sediment quality guidelines were recently defined for determining whether sediment identified for dredging in South African ports is of a suitable quality for unconfined openwater disposal. Three guidelines were defined, namely the Warning Level, Level I and Level II. Only the Level I and Level II are used for decision-making - the Warning Level is used to provide a warning of incipient metal contamination of sediment.

Metal concentrations identified as enriched are compared to the sediment quality guidelines in Figure 9, when the guidelines fall within the y-axis range of the plots. The proportion of stations at which metal concentrations in sediment exceeded guidelines is presented in Figure 26, whilst spatial trends in exceedance are presented in Figures 27 - 29. The reader should note that sediment quality guidelines were not defined for all metals but rather those metals considered toxicologically important.

Concentrations of copper, chromium, nickel, lead and zinc exceeded the Warning Level, at a relatively high proportion of stations in the case of copper and chromium (Figures 9 and 26). All stations where the Warning Level was exceeded were situated in the Inner Basin complex (Figure 27). Based on previous discussions it should come as no surprise that most of the stations were alongside

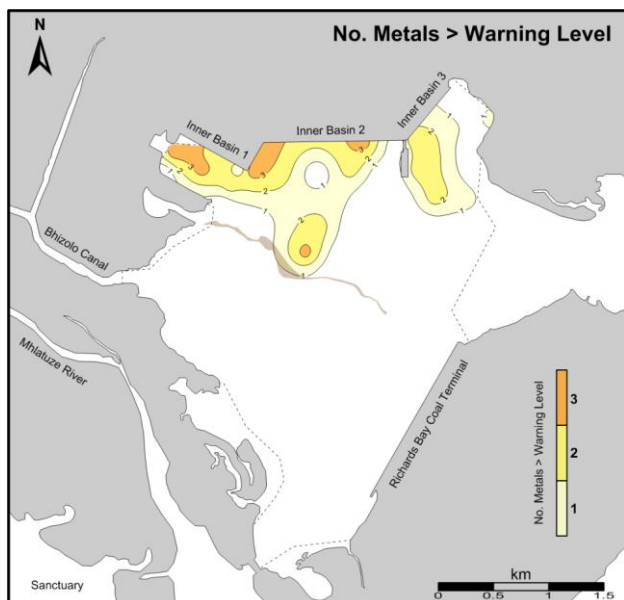


Figure 27. Spatial trend for the number of metal concentrations in sediment collected from Richards Bay in November 2012 that exceed the Warning Level of the sediment quality guidelines used to determine whether sediment identified for dredging in South African ports is of a suitable quality for unconfined openwater disposal.

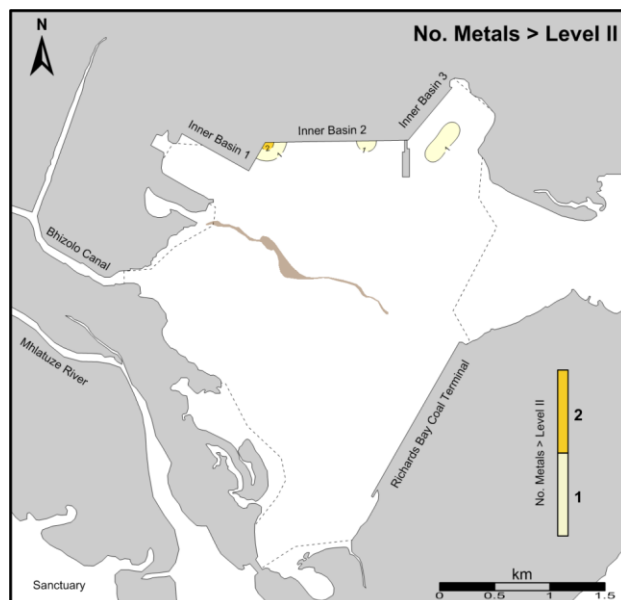


Figure 29. Spatial trend for the number of metal concentrations in sediment collected from Richards Bay in November 2012 that exceed the Level II of the sediment quality guidelines used to determine whether sediment identified for dredging in South African ports is of a suitable quality for unconfined openwater disposal.

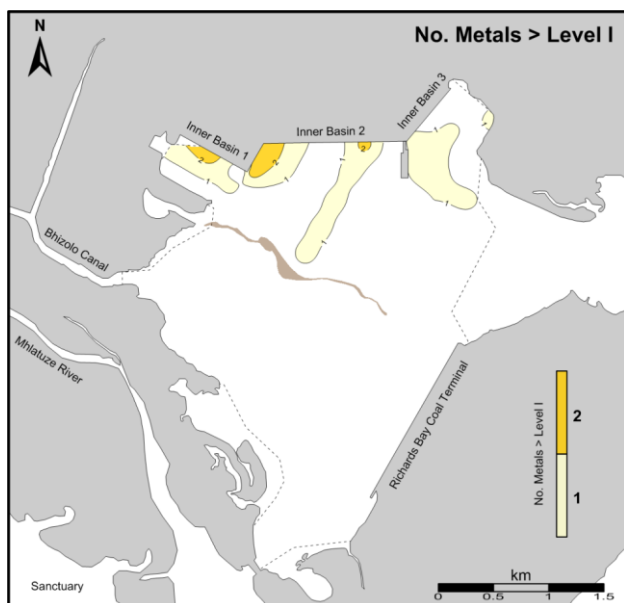


Figure 28. Spatial trend for the number of metal concentrations in sediment collected from Richards Bay in November 2012 that exceed the Level I of the sediment quality guidelines used to determine whether sediment identified for dredging in South African ports is of a suitable quality for unconfined openwater disposal.

where the Level II was exceeded were alongside quays in Inner Basin 2 and near quays in Inner Basin 3 (Figure 29). No metal concentrations in sediment from the Richards Bay Coal Terminal Basin and Mudflats, and indeed also a large part of the Inner Basin complex exceeded sediment quality guidelines (Figures 27 - 29).

Based on the exceedance of sediment quality guidelines the highest potential for adverse effects to bottom-dwelling organisms due to metal contamination of sediment was alongside and near quays in the Inner Basin complex, and more specifically in areas identified in Figures 28 and 29.

5.3.17. Assessment of sediment quality using mean sediment quality guideline quotients

A disadvantage of using the number of metals in sediment that exceed sediment quality guidelines as a line of evidence of the potential risk to bottom-dwelling organisms is that a metal concentration that marginally exceeds a guideline is scored equivalently to a metal concentration that substantially exceeds a guideline. There are thus only two possibilities, namely the concentration exceeds a guideline or it does not. The probability for a toxic effect, however, increases with

and near quays. As stated previously, the Warning Level is only intended to provide a warning of incipient metal contamination, while the Level I and Level II are used for decision-making. Copper and chromium concentrations exceeded the Level I and Level II, albeit only at 1 and 4 stations for the Level II respectively (Figures 26, 28 and 29). Stations

increasing metal concentration. A line of evidence that compensates for this disadvantage is the mean sediment quality guideline quotient, which is normalised to sediment quality guidelines. The higher the mean sediment quality guideline quotient the greater the likelihood of adverse effects to bottom-dwelling organisms. Three cut points defined by Long *et al.* (2012) were used to evaluate mean sediment quality guideline quotients, namely 0.1, 0.3 and 0.5, which define four ranges of chemical exposure: Minimum (<0.1), Low (0.1 - <0.3), Moderate (0.3 - <0.5), and Maximum (≥ 0.5). Across the quotient ranges the incidence and magnitude of toxicity in some toxicity tests increased, the abundance of most stress-sensitive benthic taxa decreased, and the abundance of most stress-tolerant taxa increased. A cut point of 0.1 (i.e. delimiter for Low exposure category) appears to be the target for protection of benthic resources, below which the probability and magnitude of adverse effects in the laboratory or field was the lowest (Long *et al.* 2012).

The spatial trend for Level I and Level II sediment quality guideline quotients is presented in Figures 30 and 31. The mean sediment quality guideline quotient is obviously higher when the Level I is used as the denominator because this guideline is lower than the Level II. The majority of quotients using either the Level I or Level II as the denominator fall within the Minimum and Low exposure categories (75% and 98% of all stations respectively), with only 3% falling into the Maximum exposure category for Level I quotients and none for Level II quotients (Figure 32). The exposure categories are, however, technically only appropriate to the mean sediment quality guideline quotient calculated using the Level I as the denominator.

The highest quotients were for sediment in the Inner Basin complex, and then usually at stations alongside and near quays (Figures 30 and 31). The areas where the exposure category was Maximum (i.e. quotients ≥ 0.5 in Figures 30 and 31) correspond to only two of the four stations where the Level II was exceeded. Two stations in Inner Basin 3 where exceedance of the Level II was evident did not fall into the Maximum exposure category, but a station in Inner Basin 1 did yet there

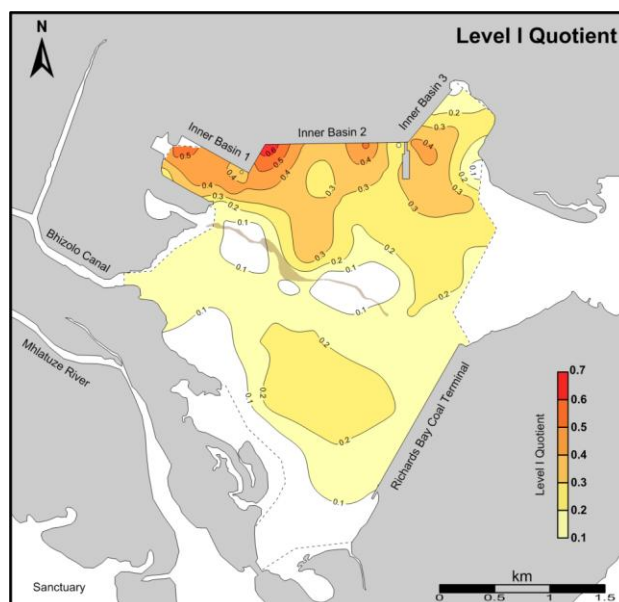


Figure 30. Spatial trend for the mean sediment quality guideline quotient calculated using the Level I as the denominator for sediment collected from Richards Bay in November 2012. Exposure cut points (or exposure categories) defined by Long *et al.* (2012) are Minimal exposure = <0.1, Low exposure = 0.1 - <0.3, Moderate exposure = 0.3 - <0.5, High Exposure = ≥ 0.5 .

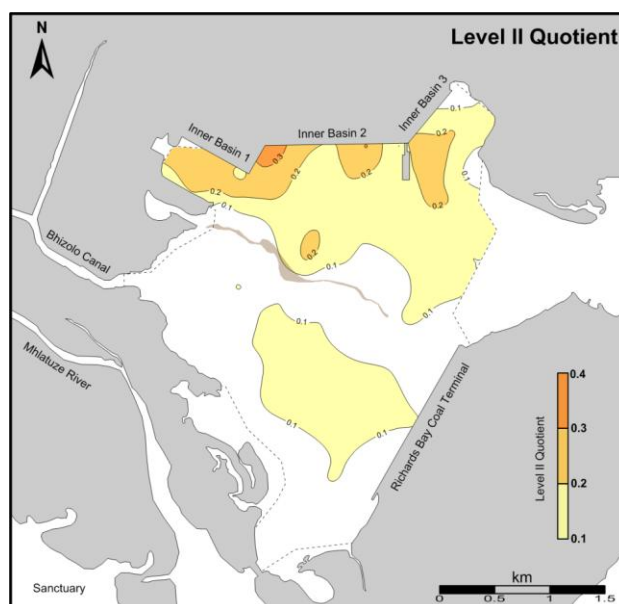


Figure 31. Spatial trend for the mean sediment quality guideline quotient calculated using the Level II as the denominator for sediment collected from Richards Bay in November 2012. Exposure cut points (or exposure categories) defined by Long *et al.* (2012) are Minimal exposure = <0.1, Low exposure = 0.1 - <0.3, Moderate exposure = 0.3 - <0.5, High Exposure = ≥ 0.5 .

was no Level II exceedance. Despite these differences the mean sediment quality guideline quotients also identify the highest potential for adverse effects to bottom-dwelling organisms due to metal contamination as alongside and near

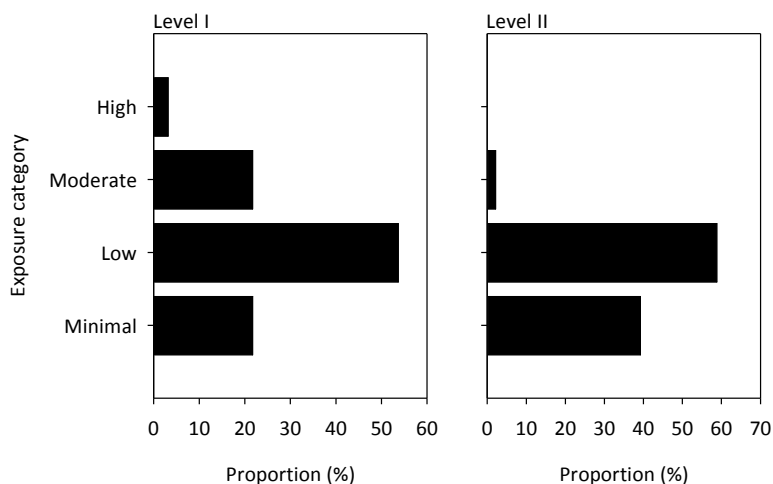


Figure 32. Proportion of stations in Richards Bay at which sediment quality guideline quotients fall into different exposure categories defined by Long *et al.* (2012) for sediment collected in November 2012.

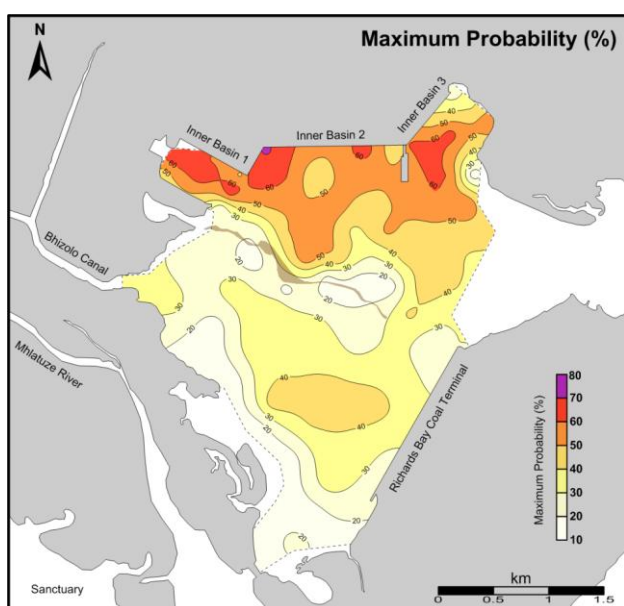


Figure 33. Spatial trend for the maximum probability (P_{max}) for observing toxicity in sediment collected from Richards Bay in November 2012, as modelled through the logistic regression modelling approach of Field *et al.* (1999, 2002).

quays in the Inner Basin complex. The quotients provide little evidence for potential adverse effects to bottom-dwelling organisms due to metal contamination in the Richards Bay Coal Terminal Basin and on the Mudflats.

5.3.18. Assessment of sediment quality using logistic regression models for the probability of observing toxicity

The highest probability for metal concentrations in sediment eliciting direct toxic effects to bottom-dwelling organisms was for the Inner Basin complex, with the highest probability (P_{max}) of 72%

for a station alongside a quay in Inner Basin 2 (Figure 33). The probability was greater if individual metals are considered, with the highest probability of 89% for a copper concentration in sediment from the same station mentioned above. All P_{max} probabilities for observing toxicity >50% were for stations in the Inner Basin complex.

The highest potential for adverse effects to bottom-dwelling organisms due to metal contamination of sediment identified using logistic regression modelling agrees broadly with the mean sediment quality guideline approach.

5.3.19. Consideration of the various lines of evidence

Each line of evidence used in this study provides a slightly different understanding of sediment quality in Richards Bay. However, when used together in a weight of evidence approach they attest to the spatial extent and magnitude and potential toxicological risk of sediment metal contamination to bottom-dwelling organisms as most pronounced in the Inner Basin complex. It is important to note that the various lines of evidence used to identify the toxicological significance of metal concentrations only identify potential risk. Although benthic community data has limitations, when properly analysed it remains the most ecologically relevant line of evidence regarding possible impacts to bottom-dwelling organisms (McPherson *et al.* 2008). Thus, until such time as the status of benthic invertebrate communities in Richards Bay is evaluated it will not be possible to

determine whether the potential risk is a realised risk. There is, for example, a relatively strong probability that much of the chromium (and possibly other metals) at contaminant concentrations in sediment is not in a bioavailable form but rather incorporated into metal ore fragments. This conclusion is based on the grain-size composition of sediment in Inner Basin 3. As stated previously, anthropogenically derived metals introduced into coastal waters in solution are partial to adsorption onto fine-grained material. These metals are 'loosely' bound to sediment and most likely to be remobilised when conditions in sediment change (*e.g.* pH, oxidation), as during dredging. When remobilised they may be in a bioavailable form, that is, have the potential to exert toxic effects. Also, if bottom-dwelling organisms ingest the sediment then these 'loosely' bound metals can be easily released from sediment by acids in the digestive tract of the organisms and absorbed. However, the sediment in Inner Basin 3 was almost exclusively dominated by sand, especially in areas where the sediment was most contaminated by chromium. This implies that the chromium was probably present in a particulate form and less likely to cause adverse effects unless the particles are ingested by bottom-dwelling organisms. Further evidence for the chromium probably being in a particulate form comes from water quality measurements recently made for Richards Bay (February 2013) by the Coastal Systems research group of the CSIR on behalf of Transnet National Ports Authority. These measurements showed that concentrations of metals (including chromium) at 12 stations across the Bay were below South African water quality guidelines. In fact, concentrations of most metals at most stations were below the method detection limit (*i.e.* were too low to accurately quantify in the laboratory).

The reader will have noted from previous discussions that sediment situated a considerable distance from quays in the Inner Basin complex is metal contaminated. The most likely explanation is that ore fragments and metal flecks were dispersed away from quays by the propeller wash of tug boats assisting the berthing of vessels.

6. Implications for Dredging

To appreciate the implications of the findings of this study in terms of dredging for the proposed expansion programme it is necessary to again consider decision-making associated with the South African sediment quality guidelines. Sediment with metals at concentrations equivalent to or lower than the Level I is regarded as posing a low toxicological risk to bottom-dwelling organisms and is of a suitable quality for unconfined openwater disposal. Sediment with metals at concentrations between the Level I and Level II is regarded as posing a potential toxicological risk to bottom-dwelling organisms, the risk increasing as the Level II is approached. A decision on whether this sediment is of a suitable quality for unconfined openwater disposal is made after considering the number of metal concentrations that exceed the Level I and the magnitude of exceedance. Additional testing (*e.g.* chemical analysis and toxicity testing of sediment elutriates) may be requested to assist decision-making. Sediment with metals at concentrations equivalent to or higher than the Level II is regarded as posing a high toxicological risk to bottom-dwelling organisms and in the absence of other data to refute this conclusion is considered unsuitable for unconfined openwater disposal. In this situation the dredging proponent can perform additional studies (*e.g.* toxicity testing, benthic invertebrate community analysis) to determine whether contaminants in the sediment are indeed posing an unacceptable risk to bottom-dwelling organisms. If the findings show that the contaminants do not pose an unacceptable risk then the Department of Environmental Affairs may deem the sediment suitable for unconfined openwater disposal.

No metal concentrations in sediment samples collected from the Richards Bay Coal Terminal Basin and Mudflats exceeded sediment quality guidelines, meaning there will be no limitation to openwater disposal of sediment dredged from these parts of the expansion footprint. Sediment at four stations, two in Inner Basin 2 and two in Inner Basin 3 theoretically cannot be disposed offshore because copper and/or chromium concentrations in the sediment exceeded the Level II. Should the Department of Environmental Affairs prohibit

openwater disposal of this sediment then Transnet will need to commission a further study to determine whether metals in the sediment are eliciting adverse effects to bottom-dwelling organisms (e.g. either through elutriate chemical or toxicity testing), or alternately will have to dispose of the sediment on-land. The potential implications of metal concentrations for sediment disposal on-land in terms of environmental and human health are beyond the scope of this study. It is extremely important to note that follow-up sampling might not detect similarly high metal concentrations in sediment from the same areas if the contamination is highly localised, due to metal ore fragments and flecks in the sediment, and the sediment is dispersed and turned over by propeller wash and so on.

The concentrations of copper at 9 stations and chromium at 6 stations in the Inner Basin complex exceeded the Level I but fell below the Level II. The Department of Environmental Affairs will make a decision on the suitability of this sediment for openwater disposal after considering how many metal concentrations exceeded the Level I at each station and how close the concentrations were to the Level II. Based on the latter there is a possibility that additional testing may be required, although the scientists that prepared this report are unaware of situations where additional testing has been requested for metal concentrations falling between the Level I and Level II.

Several additional factors mitigate against the expense and delay that will be incurred through additional testing of sediment and it may be strategic to communicate these to the Department of Environmental Affairs when applying for an openwater disposal permit. First, sediment at one station in Inner Basin 3 where a chromium concentration exceeded the Level II was dominated by sand. In fact, as stated previously the sediment across much of Inner Basin 3 was dominated by sand. Sand has a low binding capacity for metals and implies the chromium concentrations are probably present in a particulate rather than sediment-sorbed form. This is important since only sediment-sorbed forms can be remobilised from sediment into the water column during dredging. Particulate forms are unlikely to cause adverse

effects unless they are ingested by bottom-dwelling organisms.

Second, the only test that has been used to test the toxicity of sediment from South African coastal waters is the sea urchin fertilisation test. The test is used to test the toxicity of porewater and sediment elutriates (latter essentially a rinse of sediment), but is not suitable for whole sediment testing. Sea urchin gametes are also sensitive to hydrogen sulphide and ammonia, which occur naturally in sediment, but can be enhanced through anthropogenic contaminant inputs (principally organic material). Where porewater and/or elutriates of sediment have been found to be toxic it has often been difficult to identify the cause of toxicity, because there is often too little porewater to analyse chemically or elutriates were not tested chemically. In fact, porewater and/or elutriates of sediment have sometimes been shown to be toxic even in the absence of metal (and other chemical) contamination of the sediment. Thus, even if toxicity testing of sediment is requested it will be difficult to attribute toxicity evident to metal contamination unless the elutriate is also analysed for metals and other contaminants.

This study focussed on metal concentrations in surface sediment, which provides a record of 'recent' contamination. In depositional environments contaminants are gradually covered by sediment. Depending on the history of anthropogenic contaminant introduction and rate of sediment deposition, deeper layers of sediment can be more contaminated than surface sediment. It is for this reason that many jurisdictions require the analysis of sediment extracted from cores, to determine whether deeper sediment poses an ecological risk when it is dredged. The obvious question then is whether sediment from cores should also be analysed. This decision should only be made after considering several mitigating factors. The most important is that there is no point analysing deeper layers of sediment deposited thousands of years ago and which consequently never been exposed to anthropogenic contaminants. If the depth of sediment that is routinely disturbed by maintenance dredging, propeller wash and so on is about a meter or less in depth then the findings for surface sediment can be

assumed to reflect conditions through this depth. Thus, a geotechnical study should be used to inform whether core samples need to be analysed. If so then the study should only focus areas in Inner Basins 1, 2 and 3 where metal contamination of sediment was most pronounced.

There has been little research on the degree to which sediment from Richards Bay is contaminated by other chemicals that are usually the focus of attention in dredging programmes in other areas of the world. These include polycyclic aromatic hydrocarbons, pesticides and so on. This is due to the fact that the Department of Environmental Affairs reaches a decision on the suitability of sediment identified for dredging in South African ports for openwater disposal based only on the degree of metal contamination. From an environmental due diligence perspective, however, other chemicals that are potential contaminants of sediment should be the focus of attention since these pose a far more significant ecological and human health risk compared to metals. Recent monitoring performed by the Coastal Systems research group of the CSIR on behalf of Transnet National Ports Authority (CSIR 2011) identified hydrocarbon contamination of sediment alongside quays in the Inner Basin complex and Richards Bay Coal Terminal Basin, and in the Bhizolo Canal. The magnitude of contamination was generally low, but too few stations were sampled to develop an understanding of the spatial extent of contamination. Hydrocarbons, polychlorinated biphenyls, organochlorine pesticides and flame retardants have been detected in sediment from the Bhizolo Canal and pans and streams near the Bay (e.g. Pieters 2007, Roos 2010) and it is possible these chemicals are also contaminants of sediment in the proposed expansion footprint. The extent and significance of the contamination is obviously unknown, since the chemicals have not been the focus of recent studies in the Bay.

7. Recommendations

Unless the anthropogenic sources of metals to Richards Bay are identified, reduced and controlled there can be no expectation of an improvement in sediment quality in the Bay, and challenges posed by the possible prohibition of openwater disposal

of dredged material will continue to arise. With few exceptions (e.g. chromium) the findings of this study do not allow for identification of the actual anthropogenic sources of metals to the Bay. However, spatial trends for the frequency and magnitude of metal contamination of sediment allow for the identification of areas where water and landside anthropogenic inputs are most pronounced. This provides the focus for identifying the actual metal sources. From a metal contamination perspective the most significant anthropogenic sources of metals to the Bay appear to be port associated activities. The most significant of these appears to be the accidental spillage of metal ore fragments and scrap metals during vessel loading, with the most important areas in this context being the 600 and 700 series of berths (i.e. Inner Basin complex). In contrast to most other ports in South Africa, metal inputs to the Bay from surrounding urbanised and industrialised areas appears to be minimal, simply because the Bay's immediate surroundings are not highly urbanised and industrialised areas. Where industrial areas are situated near the Bay surface runoff from these areas generally first drains into canals and streams that discharge into the Bay, with the result that there is likely to be significant scavenging (filtering) of metals by the time the runoff reaches the Bay proper.

It is thus recommended that Transnet National Ports Authority implement procedures to identify the anthropogenic sources of metals to Richards Bay, and then reduce and control inputs from these sources. The particular focus should be on the loading and offloading of vessels. The priority metals for source identification, reduction and control are copper, chromium and zinc. There seems little doubt the most important source of chromium contamination is the accidental spillage of chromium ore during vessel loading. The source/s of copper and zinc are less certain. The introduction of metals to the Bay by surface runoff (stormwater) should also be investigated and where appropriate source control procedures should be formulated and implemented. The importance of stormwater runoff is highlighted by the fact that the most significant metal contamination of sediment was at a station situated at the western most portion of berth 701,

that is, in the area where the 600 and 700 series berths meet. Surface runoff is discharged through a stormwater outfall below the water surface at this point and sediment at this point was the most metal contaminated of all areas examined in this study.

The importance of scrap metals exported through the port as a source of metals to Richards Bay is evident from the findings of a soil contamination study at a former scrap metal storage area at the Dry Bulk Terminal (WSP 2011). Superimposing the concentrations of metals analysed in soil samples from this site identifies the upper 0.5 m of the soil horizon as significantly contaminated by cadmium, copper, mercury, lead and zinc. The mercury contamination was, in fact, particularly pronounced.

The scientists that prepared this report are aware that procedures to identify the sources and control the entry of metals into Richards Bay have already been formulated. The widespread and significant metal contamination of sediment in the Bay implies the procedures are not effective and/or not rigorously enforced. A review of the procedures and stricter enforcement may be warranted. There will of course still be sources of metals to the Bay that are beyond the control of Transnet National Ports Authority, including the leaching of metals from vessel hull antifouling coatings.

8. Conclusions

To reiterate, the objectives of this study were to:

1. Determine whether sediment in the proposed Port of Richards Bay expansion programme footprint is contaminated by metals,
2. Identify spatial trends in metal enrichment/contamination of sediment in the expansion footprint,
3. Estimate the likelihood that metal contamination of sediment in the expansion footprint will pose an unacceptable ecological risk when the sediment is dredged and/or disposed at an openwater spoil disposal ground offshore of Richards Bay, and
4. Identify the implications of metal contamination of sediment in the expansion footprint for a permit application authorising openwater

disposal of dredged sediment.

This study provided a high resolution spatial understanding of metal contamination of sediment in the expansion footprint. At the time of collection in November 2011, sediment in some parts of the expansion footprint was metal contaminated, most notably by copper, chromium and zinc.

Different approaches used to identify the potential toxicological significance of metal concentrations in sediment to bottom-dwelling organisms identified the highest risk for sediment at and near quays in the Inner Basin complex. However, whether the potential risk is a realised risk is uncertain since it is unknown whether the metals are present in a bioavailable form.

There is a possibility that the Department of Environmental Affairs may prohibit unconfined openwater disposal of sediment dredged from small areas of Inner Basins 2 and 3, where copper and/or chromium concentrations in the sediment exceeded the Level II of the South African sediment quality guidelines.

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