

A note on the concentrations and bioavailability of selected metals in sediments of Richards Bay Harbour, South Africa

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Abstract

Sediments are considered to be the ultimate sink for most contaminants and therefore pose the highest risk to these aquatic environments. This paper presents the levels of metals in sediments from Richards Bay Harbour, 20 years after the construction of the harbour and studied spatial and temporal, as well as the proportion of the bioavailable metal fraction. Sediment samples were collected from nine sites in Richards Bay Harbour. Sequential extractions of metals were carried out and samples were analysed for aluminium, chromium, copper, iron, manganese and zinc. Metal concentrations in sediment samples varied only slightly between seasons but showed significant spatial variation, which was significantly correlated to sediment particle size composition. Highest metal concentrations were found in sites with substrata dominated by fine mud. Manganese and Zn had more than 50% of this concentrated in the easily reducible fractions. Zinc concentrations were not elevated when compared to historic data. More than 70% of Cr was concentrated in the inert fractions nevertheless concentrations recorded at some sites were still above action levels when considering only the bioavailable fractions.

Keywords: sediments, metals, bioavailability, sediment composition, Richards Bay Harbour

Introduction

In recent years there has been growing concern over increased contamination of estuaries and harbours from a variety of anthropogenic sources (Gümğüm et al., 1994). Reduced circulation and dispersion of sediment-bound contaminants following dredging activities in harbours make them especially susceptible to contamination (Henry et al., 1989). Heavy metals and hydrocarbons are of particular concern, due to the nature of the activities taking place in these systems. A survey of five major harbours in South Africa, showed that in four of them (Richards Bay Harbour being one), one or more of the trace metals occurred at levels greater than normal background levels (Henry et al., 1989). This is cause for concern, especially in light of the fact that Richards Bay Harbour serves as an important sheltered refuge, nursery, and feeding ground for numerous marine organisms (Forbes et al., 1996). Indeed previous studies on bioaccumulation of metals in tissue of mullet from Richards Bay Harbour and the adjacent Mhlahtuze Estuary indicated that there were elevated metal levels in the environment (Vermeulen and Wepener, 1999; Mzimela et al., 2003). However, very few data are available on metal concentrations in Richards Bay Harbour sediments and the changes in these concentrations over the years since the harbour was constructed in 1976.

Sediments are considered to be the ultimate sink for many contaminants and therefore pose the highest risk to the aquatic environment as a source of pollution (Bervoets et al., 1994; Williamson et al., 1996). However, chemical processes at the sediment-water interface are complex and consideration must be given to the physico-chemical characteristics of the sediment, such as grain size and percentage organic content, which strongly influence the availability of contaminants (Forbes and

Forbes, 1994). In addition, sediments may serve as a secondary source of pollution should variables such as pH, salinity, temperature, redox potential or ionic strength change, resulting in the release of bound contaminants back into solution (Coetzee, 1993; Dickinson et al., 1996; Baeyens et al., 2003). This is especially important in the zone of mixing where metals may be depleted from sediments due to processes of desorption as a result of increased turbidity, pH and complex recirculation patterns characteristic of estuarine and near-shore marine environments.

The mobility and bioavailability of metals in sediments strongly depend on the mineralogical and chemical forms in which they occur (Baeyens et al., 2003). It is therefore necessary to study these different forms rather than the total metal concentrations to obtain an indication of the bioavailability of metals. Since the early 1980s and 1990s sequential extraction methodologies have been developed to determine speciation of metals in sediments (Tessier et al., 1979; Coetzee, 1993). The speciation approach looks at the distribution of metals over the various sedimentary substrates, e.g. carbonates, iron and manganese oxihydroxides, organic matter, silicate, sulphides, etc. (Baeyens et al. 2003).

The aims of this study were threefold. Firstly, to determine the levels of selected metals in sediment samples 20 years after the construction of Richards Bay Harbour. Secondly to determine whether these concentrations vary seasonally and/or spatially and thirdly, what proportion of the metals measured are in the bioavailable fractions following the application of the five-phase extraction procedure described by Tessier et al. (1979).

Materials and methods

Sampling procedures

Sampling sites were selected to cover the different habitat types occurring in Richards Bay Harbour. Samples of surface

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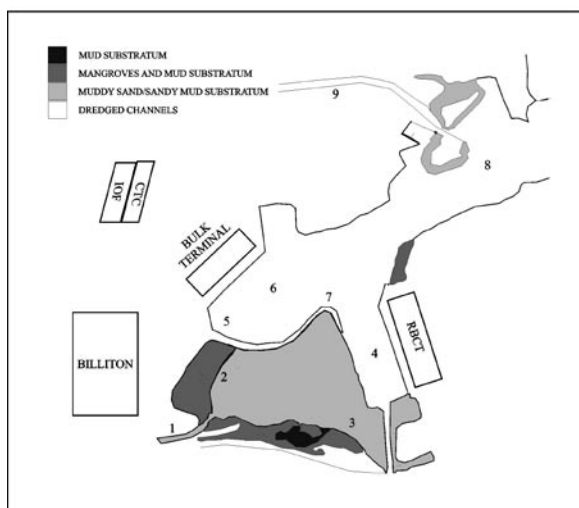
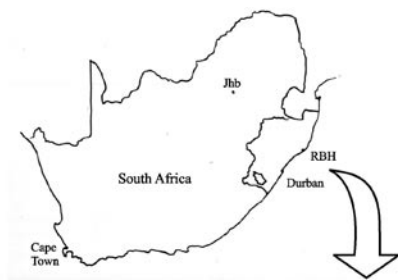


Figure 1

Location of main industries, sediment composition and sampling sites for Richards Bay Harbour (Billiton – Aluminium Smelter; IOF – fertilizer plant; CTC – Woodchip Factory; RBCT – coal terminal)

Sediments were collected at nine sites on a seasonal basis between April 1996 and December 1997 (Fig. 1). Sediment samples were collected using a Van Veen grab. Care was taken to ensure complete closure of the jaws. In order to eliminate possible contamination from the metal construction of the grab sampler, sub-samples were taken from the centre of the grab sample with a fluorocarbon plastic tube (USEPA, 1992). Surface samples (top 10 cm 100 mm of core as well as the compacted fine ooze just above the surface) were transferred into polyethylene vessels and stored at -60°C pending analyses. All samples were analysed within six months of collection (ASTM, 2000).

Sub-samples for analysis of grain size and organic content were preserved in 4% formalin. The Marine Geosciences Unit at the University of Natal, Durban did grain size analysis, using a settling tube to measure settling velocities (sand fraction only). For organic content, triplicate sub-samples were oven dried at 60°C for 24 h to remove any moisture and then weighed. Samples were then incinerated at 600°C for a minimum of 6 h. Percentage organic content was determined by reweighing after incineration.

Preparation for metal analysis

Sediment samples for total metal content were weighed, and dried for 24 h at 60°C . Samples were then wet digested using nitric acid to perchloric acid ratio of 2:1, and made up to 50 ml using doubly-distilled water. For sediment extractions the wet equivalent of 1 g sediment was used after moisture content had been determined. Sequential extraction was done on sedi-

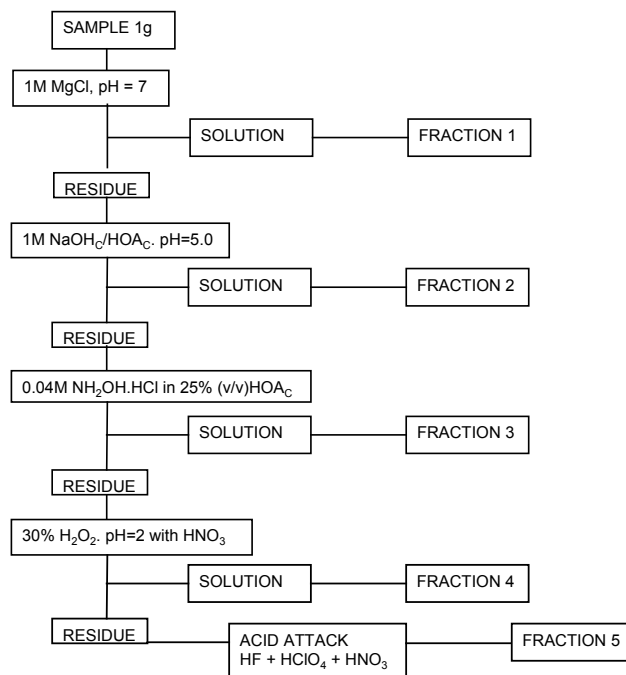


Figure 2

Flow diagram depicting the five-phase sequential extraction procedure used (adapted from Tessier et al., 1979 and Coetzee, 1993)

ment samples according to the methods of Tessier et al. (1979). All samples were analysed in triplicate. We do not present the detailed methodology in this paper since it is given by (Coetzee, 1993) but summary of this five-phase extraction method is presented in Fig. 2.

Aluminium (Al), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) in total sediments and sediment fractions were measured by flame furnace atomic absorption spectrophotometry using a Varian SpectrAA 50B spectrophotometer fitted with a deuterium arc background corrector. Calibration was carried out using matrix matched calibration standards. Analytical accuracy was determined using Standard Reference Material (SRM) of the National Bureau of Standards: Buffalo River sediment (SRM 2704). Recoveries were within 6% of the certified values. Arsenic, cadmium, lead and mercury concentrations were found to be below detection limits (0.1 mg/kg) and have therefore been omitted.

Statistical analysis

Data were analysed for spatial and temporal variations using two-way ANOVA and the relationship between metal concentrations, water physico-chemical characteristics and grain size were analysed by Spearman's Rank Correlation analysis and Principle Component Analysis (Zar, 1996). Significance levels of tests were taken as $p \leq 0.05$.

Results and discussion

Seasonal variations in concentrations of all six metals in surface sediments were only slight ($p > 0.05$). All except Cr, were highest in autumn and spring (Fig. 3). Chromium concentrations were the highest in winter. Aluminium ($F=3.49$, $p < 0.05$) and Mn ($F=3.57$, $p < 0.05$) concentrations were significantly less in summer (Fig. 3 and Fig. 4).

Sediment characteristics allow for accumulation and integration of metal discharges over time (Thompson et al., 1984; Tsai et al., 2003). Sediment analysis may therefore provide important geographical information on contaminant inputs into an aquatic ecosystem such as Richards Bay Harbour (Long and Chapman, 1985). There were significant spatial variations in concentrations of all six metals in the sediment (Figs. 3 and 4). Aluminium ($F=17.92$; $p<0.01$), Cu ($F=13.36$; $p<0.01$), Fe ($F=10.06$; $p<0.01$) and Mn ($F=15.91$; $p<0.01$) concentrations were significantly lower at Sites 3, 5, 7 and 9. Chromium ($F=7.07$; $p<0.01$) and Zn ($F=5.45$; $p<0.01$) concentrations at Sites 3, 5, 7 and 9 were significantly less than Sites 4 and 6. In general, all six metals were the highest at Site 6. The main sources of metal contamination are therefore at Sites 1, 2, 4, 6 and 8. Sites 4, 6 and 8 are all related to handling of metal products at the loading terminals and in the main shipping channel. Sites 1 and 2 are related to runoff from industry upstream in the Bhizolo Channel.

Many factors influence the accumulation and bioavailability of metals in sediments. Concentrations and variability observed may be due to other abiotic factors such as the physico-chemical properties of the overlying water and/ or variability in sediment composition (Magnusson et al., 1996). Metal concentrations in sediments showed positive correlations to conductivity ($r=0.41$; $p<0.01$) and salinity ($r=0.43$; $p<0.01$). This may explain the consistently low metal concentrations at Site 9, which has significantly lower salinity and conductivity than the remaining sites. However, it does not account for variability observed in sediment metal concentrations at the different sites. Tables 1 and 2 give the sediment analysis for each site and Fig. 5 is the graphic representation of PCA for this analysis, showing the location of samples as defined by grain size and sediment metal concentrations. The two axis of the PCA plot explains 72% of the variation in metal concentrations in sediments from Richards Bay Harbour. Percentage organic content ($r=0.59$; $p<0.01$) and percentage mud ($r=0.75$; $p<0.01$) showed strong positive correlations to metal concentrations. The sites with the highest mud and organic content (i.e. Sites 4, 6 and 8) also had the highest metal concentrations. These results were expected since it is well documented that metal concentrations increase in regions that are dominated by fine particular matter (Zhou et al., 2003; Håkanson et al., 2004).

Total metal concentrations do not necessarily reflect bioavailability (Coetzee, 1993; Thompson et al., 1984). Sequential extraction gives some indication of the availability of the metals. Results should however be viewed as a reflection of the metals behaviour rather than for the existence of any defined phases (Coetzee, 1993). Tables 3 and 4 give the results of seasonal and spatial variation in metal concentrations found in the different fractions (F1 to F5). As the metal concentrations increase from fractions 1 to 5 the metals become less bioavailable and therefore fractions 1 to 3 are regarded as the mobile fractions. If a high percentage of the metal occurs in these fractions it may be a sign of potential pollution

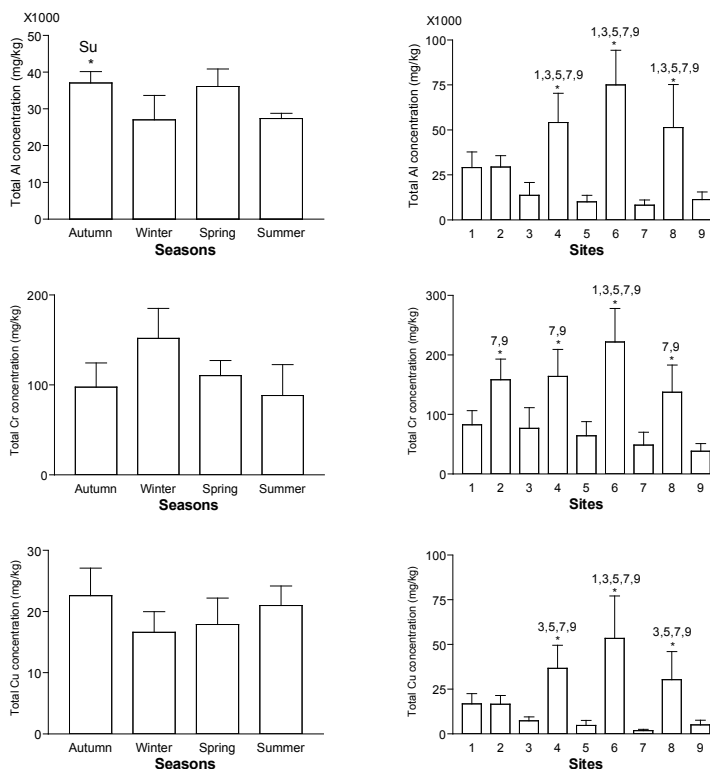


Figure 3
Temporal and spatial variations in the mean concentrations (\pm SD) of aluminum (Al), chromium (Cr), and copper (Cu) in total sediment samples collected in Richards Bay Harbour from April 1996 to December 1997. Asterisks with depicted season and site number above bar indicates significant difference ($p \leq 0.05$).

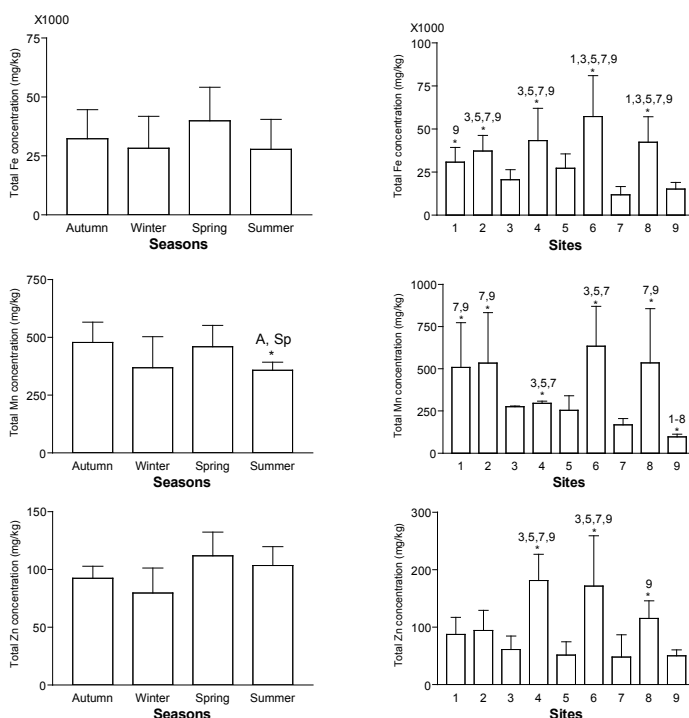


Figure 4
Temporal and spatial variations in the mean concentrations (\pm SD) of iron (Fe), manganese (Mn), and zinc (Zn) in total sediment samples collected in Richards Bay Harbour from April 1996 to December 1997. Asterisks with depicted season and site number above bar indicates significant difference ($p \leq 0.05$).

TABLE 1
Geometric gradation of sediment particle size (μm) and description of each size class based on the Wentworth Scale

Particle Size (μm)	Description
4000-2000	> Very coarse sand (>VCS)
2000-1000	Very coarse sand (VCS)
1000-500	Coarse sand (CS)
500-250	Medium sand (MS)
250-125	Fine sand (FS)
125-63	Very fine sand (VFS)
63-4	Mud (MUD)

TABLE 2
Results of grain size and organic content analysis (%ORG). Values are presented as the average percentage of the four quarterly sampling surveys. Although not presented the RSD based on the replicates analysed for each survey was <10%.

Site	%>VCS	%VCS	%CS	%MS	%FS	%VFS	%MUD	%ORG
1	0.13	0.14	0.56	8.95	34.05	7.83	48.38	5.93
2	0.13	0.05	0.20	2.53	10.45	24.88	61.88	4.93
3	0.13	0.38	4.83	37.08	41.14	3.35	13.13	3.83
4	0.00	0.01	0.03	0.31	0.65	0.88	98.13	19.61
5	0.38	0.81	7.43	25.55	38.00	19.29	11.38	3.96
6	0.00	0.01	0.05	0.18	0.44	0.33	98.88	19.82
7	0.63	0.20	3.45	26.53	47.01	17.84	3.50	2.62
8	0.00	0.04	0.08	0.53	1.91	4.59	92.88	14.72
9	0.00	0.31	5.18	39.63	37.78	6.75	10.38	2.02

due to the greater mobility and thus indirectly greater bioavailability (Usero et al., 1998). Pempkowiak et al. (1999) did indeed find that metal bioaccumulation in two bivalve species from the Norwegian and Baltic seas were related to metal concentrations predominating in the mobile phase of sediments. Fraction 5 is the inert fraction and is an indication of the naturally occurring inert metals (Coetzee, 1993). The greatest percentage of the metals was associated with the last, inert fraction, when the crystalline silicate structures are destroyed. More than 60% of Mn and 40% of Zn is associated with fractions 1-3 (the more mobile ones) in the muddy sediments while the predominantly sandy sediments (Sites 3, 5, 7 and 9) contained more than half of the metals in the refractory, last fraction. For both these metals, over 50% was found in one of the three available fractions. Studies are currently underway in Richards Bay Harbour to assess the relationship between metal bioavailability, benthic infaunal community structure, metal bioaccumulation in benthic invertebrates and sediment toxicity.

Concentrations of Cr, Fe and Mn in sediments were high when compared to concentrations reported in other South African harbours (Henry et al., 1989). The concentrations of Cu and Zn were very similar to total concentrations in Pearl River Estuary (Liu et al., 2003), whilst they were lower when compared to Cu and Zn from the polluted Naples (Adomo et al., 2005) and Barcelona harbours (Guerva-Riva et al., 2004). However Cr and Mn levels were very similar to those recorded in the latter studies. The concentrations of Al and Fe in Barcelona Harbour (Guerva-Riva et al., 2004) were nearly an order of magnitude greater than those measured in Richards Bay Harbour. Table 5 presents historical and current data for concentrations of metals in Richards Bay Harbour. Unfortunately Al has not been monitored before. Metals that have been monitored show a considerable increase since the construction of the harbour in the mid 1970s. The concentrations measured in this study were comparable to those found by Archibald and Parsons (1998) who did a once-off survey of a few sites in Richards Bay Harbour. Comparison of these values with South African guideline or action levels, indicate that the majority of the sites are above these levels for Cr and that Sites 4, 6 and 8 are above these action limits for Cu and Zn as well. The action levels presented in Table 5 are the more stringent action or concern levels. However, it must be borne in mind that the Cr concentrations are predominantly in the inert fractions 4 and 5 and would thus have a low risk of being taken up by organisms. It is

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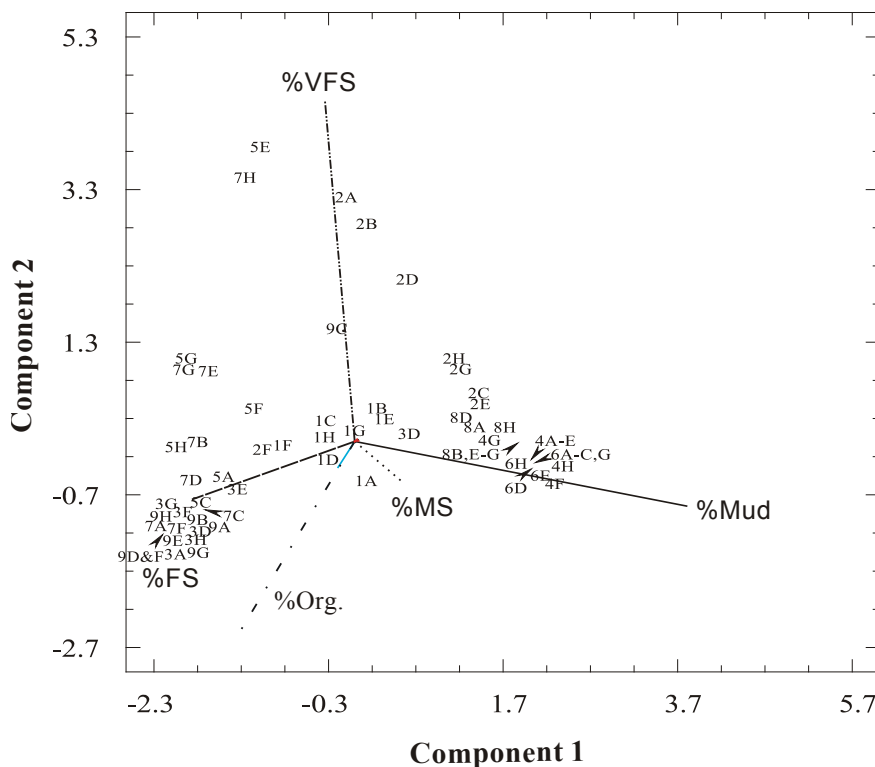


Figure 5

Standard centred PCA of total metal concentrations and sites 1-9 for four seasons for the first two axes of the data set from April (autumn) 1996 to December (summer) 1997. Sites (represented by numerals) during corresponding seasons (autumn 1996 = a to summer 1997 = g) are plotted on the axes.

TABLE 3
Sequential extraction of sediment samples showing seasonal variation. The different fractions are expressed as a percentage of the average total concentration. The precision of the analytical replicates was calculated as the relative standard deviation (RSD) and for all total metal concentrations and percentage contribution of extraction fractions during all seasons the RSD was <20%.

Metal	Season	Fraction					Total (mg/kg)
		F1	F2	F3	F4	F5	
Al	Autumn	0.00	0.00	6.72	9.66	83.61	37 057
	Winter	0.00	0.00	4.98	9.43	85.59	26 965
	Spring	0.00	0.00	5.46	9.93	84.61	36 062
	Summer	0.00	0.00	3.20	6.52	90.28	27 395
Cr	Autumn	0.00	0.00	15.94	13.01	71.05	97.63
	Winter	0.00	0.00	14.30	12.57	73.14	151.70
	Spring	0.00	0.00	9.41	7.85	82.74	110.28
	Summer	0.00	0.00	11.08	6.44	82.48	88.30
Cu	Autumn	0.00	0.00	36.50	12.22	51.29	22.64
	Winter	0.00	0.00	15.73	20.11	64.17	16.63
	Spring	0.00	0.00	19.43	29.00	51.57	17.90
	Summer	0.00	0.00	21.44	11.94	66.63	20.96
Fe	Autumn	0.00	0.13	26.94	12.80	60.13	32 325
	Winter	0.00	0.02	23.64	12.74	63.60	28 192
	Spring	0.00	0.00	28.42	14.96	56.62	39 886
	Summer	0.00	0.08	24.29	10.69	64.94	27 778
Mn	Autumn	0.29	8.21	46.29	6.95	38.26	478.00
	Winter	1.18	7.81	32.41	9.39	49.22	367.66
	Spring	1.14	7.08	44.48	8.27	39.04	458.57
	Summer	0.32	10.09	48.20	7.54	33.85	357.22
Zn	Autumn	2.98	0.00	37.55	14.21	45.26	92.21
	Winter	3.40	1.46	32.20	15.64	47.29	79.56
	Spring	5.82	0.00	38.67	20.02	35.49	111.49
	Summer	4.62	3.70	34.59	9.29	47.81	103.27

only the Zn concentrations that may be a cause for concern since the greatest percentage of metals are bound to the bioavailable fraction. However, when one considers the pre-harbour construction period (Cloete and Oliff, 1976) then Zn concentrations are very similar to those reported in this study.

Richards Bay Harbour is the largest harbour in South Africa and handles double the annual tonnage of all of the other harbours combined. It has the capacity to develop into the one of the largest harbours in the world since only 40% of the available land has been developed (NPA, 2005). With envisaged increased development, dredging activities and disposal of dredged material will produce changes in oxic and anoxic conditions, which may in turn affect metal mobility. The information provided in terms of potential for metal mobilisation would be useful for waste management decision making. The application of sequential extraction as an evaluation tool in sediment assessment has been proposed for Flemish waterways (Van Ryssen et al., 1999). Although the results from this study are based on historical data, they can already provide an indication of the potential for metal mobilisation, bioavailability and ultimately toxicity in Richards Bay Harbour.

Conclusions

Metal concentrations in the sediment varied only slightly between seasons. Sediment concentrations showed significant spatial variation, which was strongly correlated to sediment

composition. Highest metal concentrations were found at Sites 4, 6, and 8. However, only Mn and Zn had more than 50% of this concentrated in the available fractions. Zinc is however not high when compared to historic data. On the other hand, despite the fact that more than 70% of Cr is concentrated in the inert fraction of sediments, concentrations recorded at Site 6 are still above action levels. The main concerns are therefore Mn, Zn and Cr and in particular, site 6. Sediments in the vicinity of Site 6 are the most contaminated. Due to the potential for ongoing development in the harbour measures need to be taken to address the potential for secondary pollution of this area through the disturbance of these contaminated sediments.

Acknowledgements

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References

ADAMO P, ARIENZO M, IMPERATO M, NAIMO D, NARDI G and STANZIONE D (2005) Distribution and partition of heavy metals

	Site	Fraction					Total (mg/kg)
		F1	F2	F3	F4	F5	
Al	1	0.00	0.00	6.00	12.49	81.51	28 971
	2	0.00	0.00	5.10	9.45	85.45	29 414
	3	0.00	0.00	4.77	7.58	87.64	13 634
	4	0.00	0.00	4.61	6.00	89.39	54 049
	5	0.00	0.00	3.95	6.43	89.62	9 986
	6	0.00	0.00	4.58	11.45	83.97	75 026
	7	0.00	0.00	6.23	7.83	85.93	8 125
	8	0.00	0.00	4.73	9.55	85.72	51 364
	9	0.00	0.00	4.74	4.11	91.15	11 333
Cr	1	0.00	0.00	23.76	16.63	59.61	82.8
	2	0.00	0.00	10.12	10.02	79.86	158.4
	3	0.00	0.00	5.11	3.28	91.61	76.8
	4	0.00	0.00	21.36	13.76	64.88	164.2
	5	0.00	0.00	8.40	6.40	85.20	64.3
	6	0.00	0.00	13.12	14.69	72.19	221.9
	7	0.00	0.00	11.32	5.42	83.26	48.5
	8	0.00	0.00	16.92	14.62	68.46	137.4
	9	0.00	0.00	16.09	8.54	75.37	38.4
Cu	1	0.00	0.00	30.08	18.60	51.32	16.8
	2	0.00	0.00	20.83	18.12	61.04	16.6
	3	0.00	0.00	4.71	1.92	93.37	7.4
	4	0.00	0.00	24.96	17.70	57.34	36.7
	5	0.00	0.00	0.00	0.00	100.00	4.7
	6	0.00	0.00	27.18	25.57	47.25	53.5
	7	0.00	0.00	0.00	0.00	100.00	1.8
	8	0.00	0.00	19.42	22.51	58.06	30.4
	9	0.00	0.00	9.24	11.85	78.91	5.02
Fe	1	0.00	0.05	34.86	15.86	49.23	30 806
	2	0.00	0.18	30.91	16.01	52.89	37 179
	3	0.00	0.00	13.54	5.89	80.56	20 539
	4	0.00	0.09	27.67	8.86	63.39	43 08
	5	0.00	0.02	24.31	15.29	60.39	27 221
	6	0.00	0.00	22.14	17.08	60.78	57 310
	7	0.00	0.08	19.70	10.46	69.76	11 934
	8	0.00	0.02	22.85	14.74	62.39	42 441
	9	0.00	0.05	46.78	8.40	44.77	15 127
Mn	1	0.63	12.08	57.40	9.46	20.43	508.4
	2	0.41	8.33	55.33	8.28	27.66	534.1
	3	0.30	4.39	15.07	2.22	78.03	275.5
	4	1.11	12.11	59.13	10.25	17.41	695.8
	5	1.12	6.10	42.36	7.33	43.09	254.9
	6	0.73	7.32	54.23	14.78	22.95	633.5
	7	0.41	4.27	20.26	3.75	71.32	167.7
	8	0.68	13.37	49.21	10.62	26.13	534.3
	9	2.56	3.91	34.49	5.27	53.76	97.3
Zn	1	5.13	5.28	46.26	15.40	27.92	87.4
	2	4.13	0.00	28.62	17.96	49.28	94.4
	3	5.02	2.51	16.27	10.04	66.16	61.0
	4	1.49	1.86	49.55	13.83	33.28	181.1
	5	3.73	0.00	38.87	13.96	43.44	51.3
	6	2.39	0.73	39.92	19.75	37.21	171.4
	7	7.51	0.00	27.81	11.28	53.40	48.1
	8	3.32	1.01	28.43	19.10	48.13	115.2
	9	10.54	0.00	36.37	5.16	47.93	73.2

- in surface and sub-surface sediments of Naples city port. *Chemosphere* In Press, Corrected Proof. Available online 12 May 2005. <http://www.sciencedirect.com/science/journal/00456535>. doi:10.1016/j.physletb.2003.10.071.
- ARCHIBALD C and PARSONS G (1998) Sediment assessment programme for the Port of Richards Bay. Heavy Metal Survey (1998): Final Report. CSIR, Durban.
- ASTM (2000) E 1391-94 Standard guide for collection, storage, characterization, and manipulation of sediments for toxicological testing. In: *ASTM Standards on Environmental Sampling* Vol. 11.05. Conshohocken, PA. 768-788.
- BAEYENS W, MONTENY F, LEERMAAKERS M and BOULLION S (2003) Evaluation of sequential extractions on dry and wet sediments. *Anal. Bioanal. Chem.* **376** 890-901.
- BERVOETS L, PANIS L and VERHEYEN R (1994) Trace metal levels in water, sediments and *Chironomus gr. thummi*, from different water courses in Flanders (Belgium). *Chemosphere* **29** (8) 1591-1601.
- CLOETE CE and OLIFF WD (1976) South African Marine pollution survey report 1974-1975. South African National Scientific Programmes Report 8. CSIR, Pretoria.
- COETZEE PP (1993) Determination and speciation of heavy metals in sediments of the Hartbeespoort Dam by sequential extraction. *Water SA* **19** (4) 291-300.
- DEPARTMENT OF ENVIRONMENTAL AFFAIRS AND TOURISM (DEA&T) (1998) Environmental Impact management Guideline Document: EIA Regulations-Implementation of Sections 21, 22 and 26 of the Environmental Conservation Act, Department of Environmental Affairs and Tourism, Pretoria.
- DICKINSON WW, DUNBAR GB and McCLEOD H (1996) Heavy metal history from cores in Wellington Harbour, New Zealand. *Environ. Geol.* **27** 59-69.
- FORBES VE and FORBES TL (1994) *Ecotoxicology in Theory and Practice*. Chapman & Hall, London.
- GUEVARA-RIBA A, SAHUQUILLO A, RUBIO R and RAURET G (2004) Assessment of metal mobility in dredged harbour sediments from Barcelona, Spain. *Sci. Total Environ.* **321** 241-255.
- GÜMGÜM B, ÜNLÜ E, TEZ Z and GÜLSÜN Z (1994) Heavy metal pollution in water, sediment and fish from the Tigris River, Turkey. *Chemosphere* **29** (1) 111-116.
- HÅKANSON H, GYLLENHAMMAR A and BROLIN A (2004) A dynamic compartment model to predict sedimentation and suspended particulate matter in coastal areas. *Ecol. Model.* **175** (4) 353-384.
- HENNIG HF-KO (1985) Review of metal concentrations in southern African coastal waters, sediments and organisms. South African National Scientific Programmes Report No. 108. CSIR, Pretoria.
- HENRY JL, MCGIBBON S, DAVIS G, MACKAY RM and MOLDAN AGS (1989) Heavy metals, carbon and hydrocarbons in the sediments of Table Bay Harbour. Department of Environmental Affairs, Sea Fisheries Research Institute Report No. 4. Gavin and Sales, Cape Town.
- LIU WX, LI XD, SHEN ZG, WANG DC, WAI OWH and LI YS (2003) Multivariate statistical study of the metal enrichment in sediments of the Pearl River Estuary. *Environ. Pollut.* **121** 377-388.
- LONG ER and CHAPMAN PM (1985) A sediment quality triad: measures of sediment contamination, toxicity and informal community composition of Puget Sound. *Mar. Pollut. Bull.* **16** (10) 405-415.
- MAGNUSSON K, EKELUND R, DAVE G, GRANMO Å, FÖRLIN L, WENNERBERG L, SAMUELSSON M-O, BERGGEN M and BRORSTRÖM-LUNDEN E (1996) Contamination and correlation with toxicity of sediment samples from the Skagerrak and Kattegat. *J. Sea Res.* **35** (1-3) 223-234.

TABLE 5
Range of concentrations of metals (mg/kg) recorded in sediments
of Richards Bay Harbour during this and other studies

Sampling date	Al	Cu	Cr	Fe	Mn	Zn	Reference
1996-1997	8125-75 026	1.82-53.5	38.4-221.9	11 934-57 310	97.3-695.8	48.1-181.1	Current study
1985	ND	25.0	114	22 800	376	53	Henry et al. (1989)
	ND	ND	9.29 - 139.61	805-11 261	ND	ND	Oliff (1976)
	ND	8.3-12.0	ND	19-28.9	ND	66-175	Cloete and Oliff (1976)
1972-1981	ND	1.1-40.0	74.80	800-29 000	ND	14-179	Hennig (1985)
1998	ND	10.0-258	21-339.8	ND	ND	14-193.0	Archibald and Parson (1998)
Guidelines	ND	50	50	ND	ND	150	LC-SA

ND – No data
 LC-SA: London Dumping Convention Thresholds as used in South Africa (DEA&T, 1998)

- MZIMELA HM, WEPENER V and CYRUS DP (2003) Seasonal variation of selected metals in sediments, water and tissues of the groovy mullet, *Liza dumerelii* (Mugilidae) from the Mhlathuze Estuary, South Africa. *Mar. Pollut. Bull.* **46** 659-676.
- NPA (NATIONAL PORTS AUTHORITY) (2005) Richards Bay. <http://www.npa.co.za/Ports/Richards%20Bay>. Accessed on 28 July 2005.
- OLIFF WD and TURNER WD (1976) National Marine Pollution Surveys, East Coast Section, 2nd Annual Report. NIWR, Durban.
- PEMPKOWIAK J, SIKORA A and BIERNACKA E (1999) Speciation of heavy metals in marine sediments vs their bioaccumulation by mussels. *Chemosphere* **39** (2) 313-321.
- THOMPSON SA, LUOMA SN, JOHANSSON CE and CAIN DJ (1984) Comparison of sediments and organisms in identifying sources of biologically available trace metals concentrations. *Water Res.* **18** (6) 755-765.
- TSAI LJ, YU KC, HO ST, CHANG JS and WU TS (2003) Correlation of particle sizes and metal speciation in river sediment. In: Bruen M (ed.) *Diffuse Pollution and Basin Management. Proc. 7th Int. Specialised IWA Conf.* Dublin, Ireland. 14-26 – 14-29.
- USERO J, GAMERO M, MORILLO J and GARCIA I (1998) Comparative study of three sequential extraction procedures for metals in marine sediments. *Environ. Int.* **24** (4) 487-496.
- VAN RYSSSEN R, LEERMAKERS M and BAEYENS W (1999) The mobilisation potential of trace metals in aquatic sediments as a tool for sediment quality classification. *Environ. Sci. Pollut.* **2** 75-86.
- VERMEULEN L and WEPENER V (1999) Spatial and temporal variations of metals in Richards Bay Harbour (Richards Bay Harbour), South Africa. *Mar. Pollut. Bull.* **39** (1) 304-307.
- WILLIAMSON RB, VAN DAM LF, BELL RG, GRENN MO and KIM JP (1996) Heavy metal and suspended sediment fluxes from a contaminated intertidal inlet (Manukau Harbour, New Zealand). *Mar. Pollut. Bull.* **32** (11) 812-822.
- ZHOU JL, LIU YP and ABRAHAMS PW (2003) Trace metal behaviour in the Conwy estuary, North Wales. *Chemosphere* **51** 5 429-440.

