Zimbabwe Journal of Science & Technology pp 82-97 Vol.11 [2016]
e-ISSN 2409-0360
Zimbabwej.sci.technol

Distribution and Seasonal Variations of Selected Heavy Metals in Seawater from Cape Town Harbour of Western Cape Province, Republic of South Africa

[*1]Hussein K. Okoro, [2]Bhekumusa J. [2]Ximba, Orla Tamba, [2]Olalekan S. Fatoki, [3]Folahan A. Adekola, [4]Reinette G. Snyman, [5]Waheed B. Yahya

[1]Analytical/Environmental Research Group; Department of Applied Chemistry, University of Johannesburg, Doornfontein Campus, P.O. Box 17011, Nind Street, Doornfontein 2028, South Africa.

[2]Environmental-Analytical Research Laboratory, Department of Chemistry, Faculty of Applied Science Cape Peninsula University of Technology, P.O. BOX 1906, Cape Town, 7535 South Africa.

[3]Environmental-Analytical Research Laboratory, Department of Industrial Chemistry Faculty of Physical Sciences, University of Ilorin, P.M.B.1515, Ilorin, Nigeria.

[4]Department of Biodiversity and Conservation Management, Faculty of Applied Sciences, Cape Peninsula University of Technology, P. O. Box 652 Cape Town 8000, South Africa.

[5]Department of Statistics, Faculty of Physical Science, University of Ilorin, P.M.B.1515, Ilorin, Nigeria.

*Corresponding author. E-mail contacts: okoroowo@yahoo.com; Okoro.hk@unilorin.edu.ng; hkoadeola@gmail.com

ABSTRACT

This study was carried out to determine the distributions and effects of seasonal variations in concentrations of some selected heavy metals namely; Cr, Mn, Co and Ni in sea water collected from twelve locations from Cape Town harbour, Western Cape Province, Republic of South Africa. The water samples were analysed for the heavy metals by inductively coupled plasma-mass spectrometry (ICP-MS) with an Agilent 7700 ICP-MS. A significant correlation was measured for Mn and Ni during winter. For Cr and Co high concentrations were recorded in summer than in winter. Metal concentrations in the harbour ranged from (8.050 ± 0.590 µg/L) to (44.580 ± 40.300 µg/L) for Cr, from (5.710 ± 1.870 µg/L) to (1054.420 ± 2556.320 µg/L) for Mn, from (0.330 ±0.090 microgram/L) to (30.700 ± 33.160 microgram/L) for Co and from (4.220 ± 4.210 µg/L) to (19.630 ± 12.180 µg/L) for Ni respectively. These results are indicative of the contribution of heavy metal pollution from the inflow of rain water, storm water drains, streams which carry runoff from industrial, urban and residential sources. High values of trace metals could be traced to anthropogenic and natural sources. Apparently, Ship repair activities are also suspected to be responsible for elevated concentrations in the upper reaches of the harbour.

***Keywords*:** Heavy metals, sea water, Inductively Couple Plasma-Mass Spectrometry, harbour.

Received: 03.10.2016 Accepted:17.10.2016.

1. INTRODUCTION

The accumulation of metals in an aquatic environment has direct negative consequences for man and the ecosystem. Metal which is required for metabolic activity in organisms, such as Mn lies in the narrow ‘‘window’’ between their essentiality and toxicity. The development of nanocomposites has been a significant area of research and has evolved significantly over the last two decades for minimising the toxic metal ions contaminants level from water system.

Though harbours are an important hub for development and commercial activities, they have reputation for being one of the most polluted marine environments (Bubb and Lester, 1996). Heavy metal discharges to the marine environment are of great concern worldwide, because they have a major ecological significance due to their toxicity and accumulative behaviour.

Heavy metals, such as manganese, copper, lead, tin, mercury and cadmium are often introduced into harbours from maintenance activities such as painting, scraping and grit blasting (Bubb and Lester, 1996; De Astudillo, L. *et al.* 2005; Fatoki *et al.,* 2012). Furthermore, TBT (tributyl tin) an anti-fouling paint used on boats to prevent the settlement of mussels, barnacles and seaweeds, is highly toxic to marine life and may put human consumers of seafood at risk. Manganese is an essential metal, since they play an important role in biological systems (Florence *et al.,* 1994).

In addition, the essential metals may also have toxic effects when they are ingested in excess. As cobalt is naturally occurring and widely dispersed element, all natural waters contain a trace level of this element; sometimes called ‘background’, i.e. the level that is present without any anthropogenic influence. Cobalt in the aquatic environment may cause long term adverse effects in the aquatic environment and may be very toxic to aquatic organisms. Co can enter the environment from a number of sources, both natural and anthropogenic. The natural sources include volcanic emissions, the weathering of rocks by the action of water and decomposition of plant waste.

One of the main human sources of pollution into the aquatic environment is from sewage (Novotry, 2000). Manganese can be released to water by discharge from industrial facilities or as leachate from landfills and soil (Okoro *et al.,* 2011). Sea disposal of mine tailings and liquor is another source of manganese to the marine environment, particularly in tropical areas (Okoro et al., 2012). Nickel is a nutritionally essential trace metal for at least several animal species, micro-organisms and plants, therefore, either deficiency or toxicity symptoms can occur when, respectively, too little or too much Ni is taken up.

Ship repairs and industrial activities as well as other forms of water pollution cause changes to water qualities and features (Okoro *et al.,* 2013). The major sources of this metal (Ni) pollution in the aquatic ecosystems, including the ocean, are domestic waste water effluents and non-ferrous metal smelters. Therefore, the presence of high concentrations of heavy metals in sea water presents a potential danger to human health due to their extreme toxicity (Okoro *et al.,* 2014a). The heavy metal determination may be useful for measuring the pollution levels of marine environment. It may give vital information about water pollution and may help in finding ways to reduce the danger to human health. It is therefore important that Cape Town Harbour require regular monitoring in order to meet national and international guidelines on the protection of the marine environment.

One (1) year monitoring of priority metals such As, Cd, Hg, Pb and Sn in seawater from the Cape Town harbour has been carried out, their seasonal variations and pollution levels were investigated (Okoro *et al.,* 2014b). The objective of this study is to determine the concentrations of some

selected metals namely; Cr, Mn, Co and Ni in sea water collected from twelve locations from Cape Town harbour using ICP-MS and to investigate the effects of seasonal variations in concentrations of these metals across all locations in the seasons of summer and winter.

2. MATERIAL AND METHODS

2.1 Study Area

Cape Town harbour was used as the study area. The Port of Cape Town is the port of the city of Cape Town, South Africa. It is situated in Bay. Because of its position along one of the world's busiest trade routes. It is one of the busiest ports in South Africa, handling the largest amount of fresh fruits and second only to Durban as a container port. The port also has significant repair and maintenance facilities that are used by several large fishing fleets. Because of the many tourist attractions offered by Cape Town and its surrounding region, many cruise ships also berth in the port. Figure I represent the map of the sampling points on Cape Town harbour while Table 1 summarises information on sampling points, its co-ordinates and sampling depth.

The Ben Schoeman Dock is the largest outer dock of the port, where the container terminal is situated. The Duncan dock is the smallest and the older inner dock. It contains the multipurpose and fruit terminals as well as a dry dock, a repair quay and a tanker basin. The synchrolift dry dock is where the ships are lifted up for repair. The Victoria and Alfred basin used to be the main pier of the original Cape Town harbour, but now houses the Victoria and Alfred waterfront. However, this basin is still used by smaller commercial vessels such as fishing and pleasure boats (smaller passenger cruise ships). The synchrolift dry dock is where the ships are lifted up for repair. The distances between control sites 10 and 11, sites 7 and 8, sites 6 and 9, sites 3 and 4, sites 4 and 5 are 513 m, 500 m, 265 m, 1400 m, 501 m and 572 m, respectively. The overall distance covered during sampling is 16.4 km. The control sites 10 and 11 were chosen based on the previous studies and on-going monitoring programme of the CSIR (Council for Scientific and Industrial Research).

2.2 Sample collection

The water samples were collected in March 2012 and June 2012 from inside the Cape Town Harbour area in twelve locations. Twelve (12) sampling points were chosen. The samples were collected in triplicate with the help of the sampling boat and the samples were collected in glass containers which were initially washed with detergent and rinsed with distilled water. At the sampling sites, containers were rinsed with the water samples before collection. Each of the collected samples was preserved by adding concentrated HNO_3 and the pH was adjusted to 2.0. The samples were stored in the refrigerator at 4^oC before analysis.

2.3 Sample preparation

100-mL aliquot of the well-mixed sample was measured into a beaker. 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl were added respectively. The sample was covered with a ribbed watch glass or other suitable covers and heated on a steam bath, hot plate or other heating source at 90 to 95^oC until the volume has been reduced to 15-20 mL. 1 ml of conc. H_2SO_4 followed by 1 ml of 5% $KMnO_4$ solutions were added to 40 ml of water sample. The mixture was boiled for about 1minute, cooled on ice chest, transferred into a 50 ml standard flask and diluted to a volume of 50 ml. The

Figure 1: Map indicating the sampling sites on Cape Town Harbour.

Marine influence Harbour points Control points

Table 1: Summary of sampling sites with their coordinates and sampling depths

Sampling sites	Coordinates	Sampling depth	Description
1	S33 55.053 E18 26.236	14 m	Duncan Dock
2	S33 54.982 E18 26.707	12 m	Duncan Dock
3	S33 54.571 E18 26.842	14 m	Ben Schoeman Dock
4	S33 54.518 E18 27.184		Inside Sea 500m away from Point 3
5	S33 54.502 E18 27.566	15 m	Inside Sea 500m away from Point 4
6	S33 54.574 E18 25.550	10 m	Duncan Dock
7	S33 54.411 E18 25.190	12 m	Robinson Dry Dock
8	S33 54.535 E18 25.279	14 m	Synchrolift
9	S33 53.827 E18 26.140	8 m	Entrance to harbour
10	S33 53.862 E18 25.809	3 m	Control A
11	S33 53.926 E18 25.496	6 m	Control B
12	S33 54.367 E1825.370	12 m	Robinson Dry Dock 2.

set of blank sample were prepared in the same manner.

2.4 Instrumentation

The water samples were analyzed for the elements (Cr, Mn, Co and Ni) by inductively coupled plasma- mass spectrometry (ICP-MS) with an Agilent 7700 ICP-MS. The Agilent 7700 instrument was used with a Meinhart nebuliser and silica cyclonic with continuous nebulisation. The operating parameters were: plasma RF power: 1.550 W; sample depth: 8.0mm; Carrier gas: 1.08 L/min; nebulizer pump: 0.10 rps; helium gas: 5.3 mL/min.

2.5 Statistical analyses

The Statistical Analysis Software (SAS) and R statistical package (www.cran.org) were used to analyse the data. Few data preparations were carried out using SPSS 17.0. Two-way analysis of variance was performed to determine the metals that have high level of concentration in the seawater in different locations over the two seasons. Significant differences in the average metal concentrations, for the four trace metals, were determined using the Duncan Multiple range tests of equality of means. Principal Component Analysis (PCA) was equally carried out on the data to determine the level of contribution of each metal to water pollution. The scree plot, plotted from the Eigen values of the correlation matrix was used to determine the order of the increase in concentration values for the metals.

3. RESULTS AND DISCUSSION

The percent distribution and concentrations of all the metals investigated is presented in Figure 2a-2d and Table 2, respectively. The concentration of Cr in the sea water samples ranged from 8.050 ± 0.590 µg/L to 44.580 ± 40.300 µg/L for all the locations. The mean concentration of the two seasons summer and winter for Cr were 19.670 ± 20.130 µg/L and 18.580 ± 13.980 µg/L. For Cr there was no significant variation between summer and winter.The PCA in Figure 3a shows the correlation between metals according to location. Figure IIIa showed that Cr and Co correlated more in the Robinson Dry dock while Mn and Ni correlated more inside the sea and Entrance to harbour. Figure 3b showed that Cr and Co correlated more in summer while while Mn and Ni correlated more in winter. This may be due to activities involved in the location (Robinson Dry Dock), repair quay and tanker basin.

The concentration of Mn in the sea water samples ranged from 5.710 ± 1.870 µg/L to 1054.420 ± 2556.320 µg/L for all the locations.The mean concentration of the two seasons, summer and winter, for Mn were recorded as 7.070 ± 3.530 µg/L and 200.950 ± 1041.750 µg/L. For Mn, there was no significant variation between summer and winter. Mn and Ni have a similar correlation in location 4 and 9. There was a significant correlation between Mn and Ni during winter. This among others, may be due to the contributions of heavy metals contained in the inflow of rainwater and runoffs from domestic and urban drains. The concentration of Co in the seawater samples ranged from 0.330 ± 0.090 µg/L to 30.700 ± 33.160 µg/L. Co correlated more with Cr in the Robinson Dry Dock (Figure 3a) and correlated more with Cr during the winter season (Figure 3b). The mean concentration of the two seasons summer and winter for Co were recorded as 5.48 ± 16.970 µg/L and 1.190 ±1.740 µg/L For Co there is a significant variation between summer and winter. The decrease in the concentration in winter may be due to the climatic factors such as dilution effect.

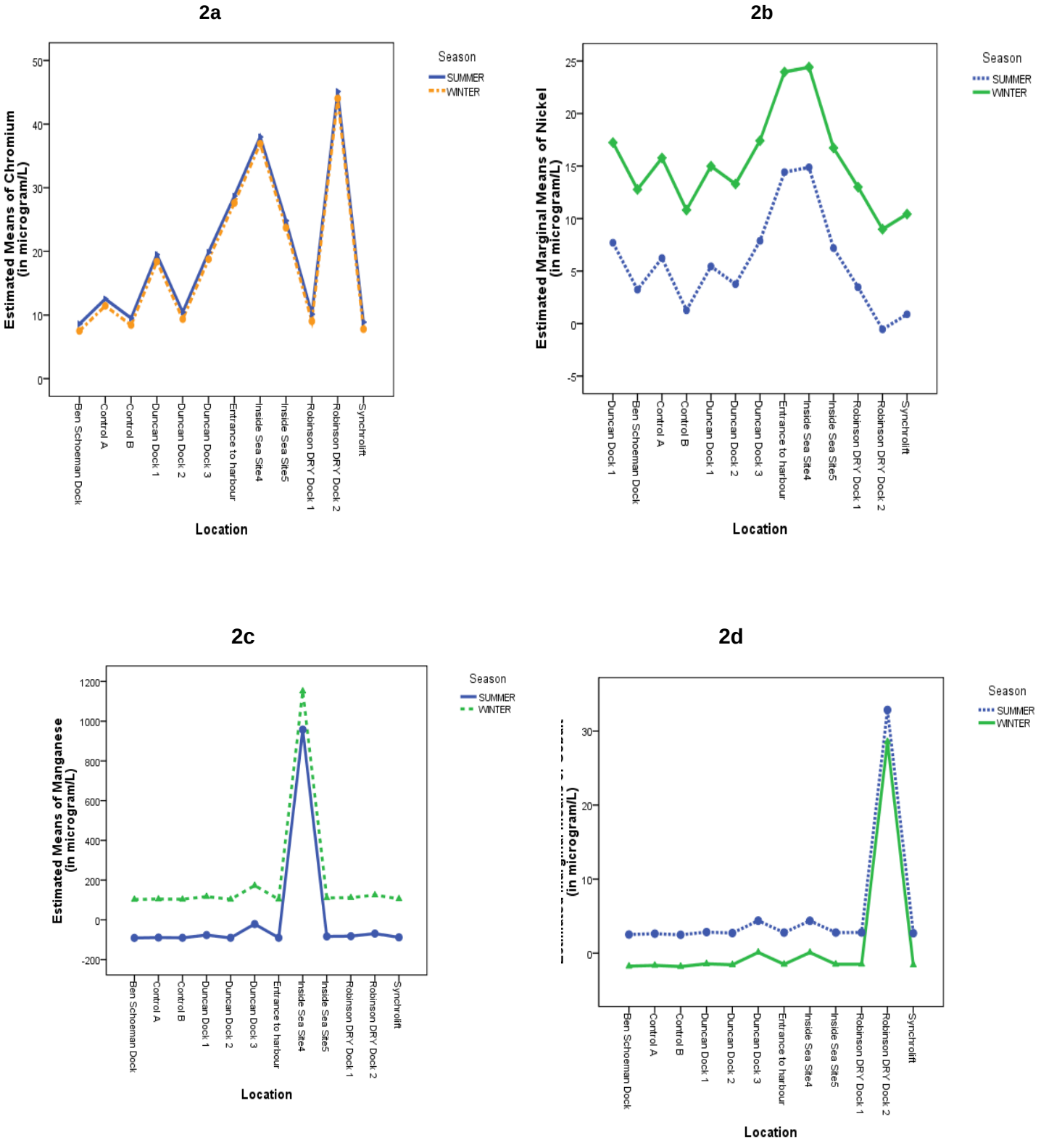

Figure 2a- 2d: Distribution of metals across locations during summer and winter Seasons in µg/L

Table 2: Mean concentrations ± standard deviation of metals µg/L in each location at two different seasons

Metals		Seasons		
	Locations	**Summer**	**Winter**	**Mean location**
Cr	Duncan Dock 1	15.140±0.320	22.740±0.810	18.930±4.200
	Duncan Dock 2	9.920±1.220	9.880±1.310	9.900 ± 1.130
	Benschoeman Dock	8.530±0.380	7.560±0.090	8.050 ± 0.590
	Inside Sea 1	34.520±1.310	40.390±14.940	37.450±10.010
	Inside Sea 2	15.320±3.230	33.210±1.410	24.260±10.050
	Duncan Dock3	12.410±1.240	26.220±2.960	19.310±7.830
	Robinson Dry Dock 2	80.890±10.190	8.270±1.240	44.580±40.300
	Synchrolift	8.330±1.190	8.320±0.470	8.330 ± 0.810
	Entrance to Harbour	13.420±4.320	42.890±3.050	28.160±16.480
	Control A	16.040±4.700	7.940±1.190	11.980±5.390
	Control B	10.970±1.420	6.940±1.600	8.960±2.590
	Robinson Dry Dock	10.540±1.460	8.590±0.310	9.570±1.430
	Mean seasons	19.670±20.1300	18.580±13.980	
	CV5			
	P≤0.05	***		***
	Interaction P≤0.05			
Mn	Duncan Dock 1	10.980±1.660	29.590±9.950	20.290±12.020
	Duncan Dock 2	3.640±0.570	8.910±1.740	6.280±3.110
	Benshoeman Dock	4.160±0.430	7.260±1.160	5.710±1.870
	Inside Sea 1	7.720±2.270	2101.110±3612.50	1054.42±2556.32
	Inside Sea 2	5.820±3.520	21.130±3.190	13.470±8.900
	Duncan Dock 3	5.870±1.090	145.730±92.620	75.800±96.440
	Robinson Dry Dock 1	6.600±0.280	22.800±3.330	14.700±9.120
	Synchrolift	7.130±1.710	10.320±0.610	8.730±2.090
	Entrance to Harbour	5.370±1.370	7.960±1.230	6.660±1.830
	Control A	6.950±2.650	8.480±1.610	7.720±2.140
	Control B	4.920.900	8.250±1.240	6.590±2.070
	Robinson Dry Dock 2	15.730±0.830	39.860±3.010	27.790±13.360
	Mean seasons	7.070±3.530	200.950±1041.750	
	CV5			
	P≤0.05		****	

	Interaction P≤0.05			***	***
Co	Duncan Dock 1		0.530±0.090	0.870±0.240	0.690±0.250
	Duncan Dock 2		0.670±0.350	0.450±0.140	0.560±0.270
	Benshoeman Dock		0.390±0.100	0.350±0.130	0.370±0.110
	Inside Sea 1		0.960±0.160	3.480±5.140	2.220±3.530
	Inside Sea 2		0.450±0.130	0.810±0.180	0.630±0.240
	Duncan Dock 3		0.330±0.020	4.140±0.490	2.230±2.110
	Robinson Dry Dock 1		0.290±0.090	0.990±0.160	0.640±0.410
	Synchrolift		0.380±0.240	0.710±0.060	0.550±0.240
	Entrance to Harbour		0.300±0.130	0.950±0.090	0.630±0.370
	Control A		0.450±0.130	0.500±0.190	0.470±0.150
	Control B		0.340±0.090	0.310±0.110	0.330±0.090
	Robinson Dry Dock 2		60.660±7.460	0.740±0.130	30.700±33.160
	Mean seasons		5.480±16.970	1.190±1.740	
	CV				
	P≤0.05	***			***
	Interaction P≤0.05	***			
Ni	Duncan Dock 1		7.900±0.490	13.280±2.160	10.590±3.260
	Duncan Dock 2		4.850±2.560	12.200±3.010	8.530±4.740
	Benshoeman Dock		5.860±1.540	10.150±1.830	8.000±2.790
	Inside Sea 1		10.190±0.900	29.090±10.090	19.640±12.180
	Inside Sea 2		6.490±2.240	17.420±2.690	11.969±6.380
	Duncan Dock 3		4.370±0.490	20.920±3.970	12.650±9.410
	Robinson Dry Dock 1		5.150±0.140	11.320±0.290	8.230±3.380
	Synchrolift		3.850±0.680	7.460±0.710	5.660±2.070
	Entrance to Harbour		5.550±1.260	32.840±1.540	19.190±15.000
	Control A		8.960±0.690	13.040±1.190	11.000±2.390
	Control B		5.220±1.940	6.870±0.620	6.050±1.590
	Robinson Dry Dock 2		0.470±0.090	7.970±1.490	4.220±4.210
	Mean seasons		5.740±2.690	15.210±8.690	
	CV5				
	P≤0.05		***		***
	Interaction P≤0.05		***		

Table 3: Eigen values of the Correlation Matrix

Metals	**Eigen values**
Cr	1.780
Mn	1.210
Co	0.930
Ni	0.070

Table 4: Table of results of Duncan Multiple Range Test of Comparisons of Mean Metals' Concentrations across the locations.

Locations	***Mean Metal Concentrations**			
	Cr	**Ni**	**Mn**	**Co**
Control A	11.990 **a**	11.010 **b**	7.720 **a**	0.480 **a**
Control B	8.960 **a**	6.050 **a**	6.590 **a**	0.330 **a**
Duncan Dock 1	18.940 **b**	10.590 **b**	20.290 **c**	0.700 **a**
Duncan Dock 2	9.900 **a**	8.530 **a**	6.270 **a**	0.570 **a**
Duncan Dock 3	19.310 **b**	12.650 **b**	75.800 **d**	2.240 **a**
Inside Sea Site 4	37.460 **d**	19.650 **c**	1054.420 **e**	2.230 **a**
Inside Sea Site 5	24.270 **c**	11.960 **a**	13.470 **b**	0.630 **a**
Ben Schoeman Dock	8.050 **a**	8.000 **a**	5.710 **a**	0.370 **a**
Robinson DRY Dock 1	9.570 **a**	8.240 **a**	14.700 **b**	0.640 **a**
Robinson DRY Dock 2	44.590 **d**	4.220 **a**	27.800 **c**	30.710 **b**
Entrance to Harbour	28.160 **c**	19.190 **c**	6.660 **a**	0.630 **a**
Synchrolift	8.330 **a**	5.660 a	8.730 **a**	0.550 **a**
p-value	**< 0.0001**	**< 0.0001**	**0.017**	**< 0.0001**

*Mean metal concentrations that bear the same letters are not significantly different from one another while those with different letters are significantly different at 5% significance level

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The concentration of Ni in the sea water samples ranged from 4.220 ± 4.210 µg/L to 19.640 ± 12.180 µg/L. The mean concentration of the two seasons summer and winter for Ni was 5.740 ± 2.690 µg/L and 15.210 ± 8.690 µg/L. For Ni there was a significant variation between summer and winter. High concentration values were recorded for Ni during winter. The increase in concentration during winter season may be due to the contribution of the inflow of rainwater in the harbour. From the Eigen values the scree plot was plotted and it shows that the order of increase in concentration values for the metals is Cr > Mn > Co > Ni (Figure 4). The Eigen and p- values reported in Table 3 and 4 are from the analysis of variance tests of equality of treatment effects.

Results from Table 5 generally showed that more metal concentrations are generated by Manganese with high level of variability over time. Whereas, the least (minimal) metal concentrations are produced by Cobalt in all the locations combined.

Table 5: Summary statistics of the four metal concentrations in seawater Table Bay harbour in South Africa for all the locations combined

Metals	Mean Concentration for all the locations	Std. Deviation
Chromium (Cr)	19.130	17.220
Manganese (Mn)	104.010	737.910
Cobalt (Co)	3.340	12.170
Nickel (Ni)	10.480	7.970

Table 6: Correlation matrix from Pearson correlation coefficients showing the degree of relationships among the four types of metal concentrations experienced in the seawater harbour in South Africa. The p-values of the Pearson correlation test are given in parentheses.

Metals	Chromium (Cr)	Manganese (Mn)	Cobalt (Co)	Nickel (Ni)
Chromium (Cr)	1			
Manganese (Mn)	0.058 (0.630)	1		
Cobalt (Co)	0.764** (< 0.0001)	0.062 (0.608)	1	
Nickel (Ni)	0.312**(0.008)	0.142 (0.234)	-0.226 (0.056)	1

**Indicates that the correlation coefficient is significant at 1% and 5% significance level

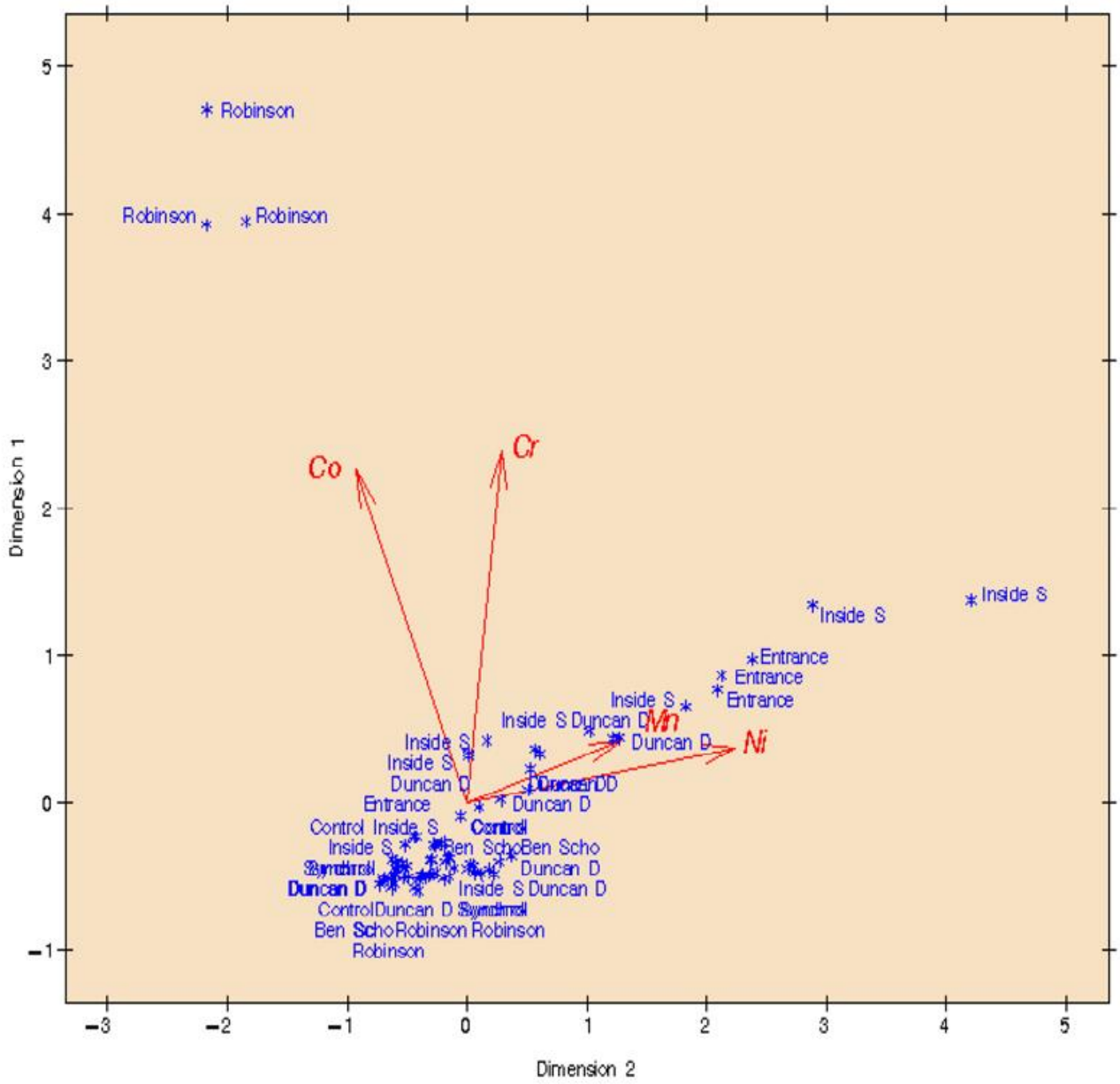

Figure 3a: The correlation between the metals according to location.

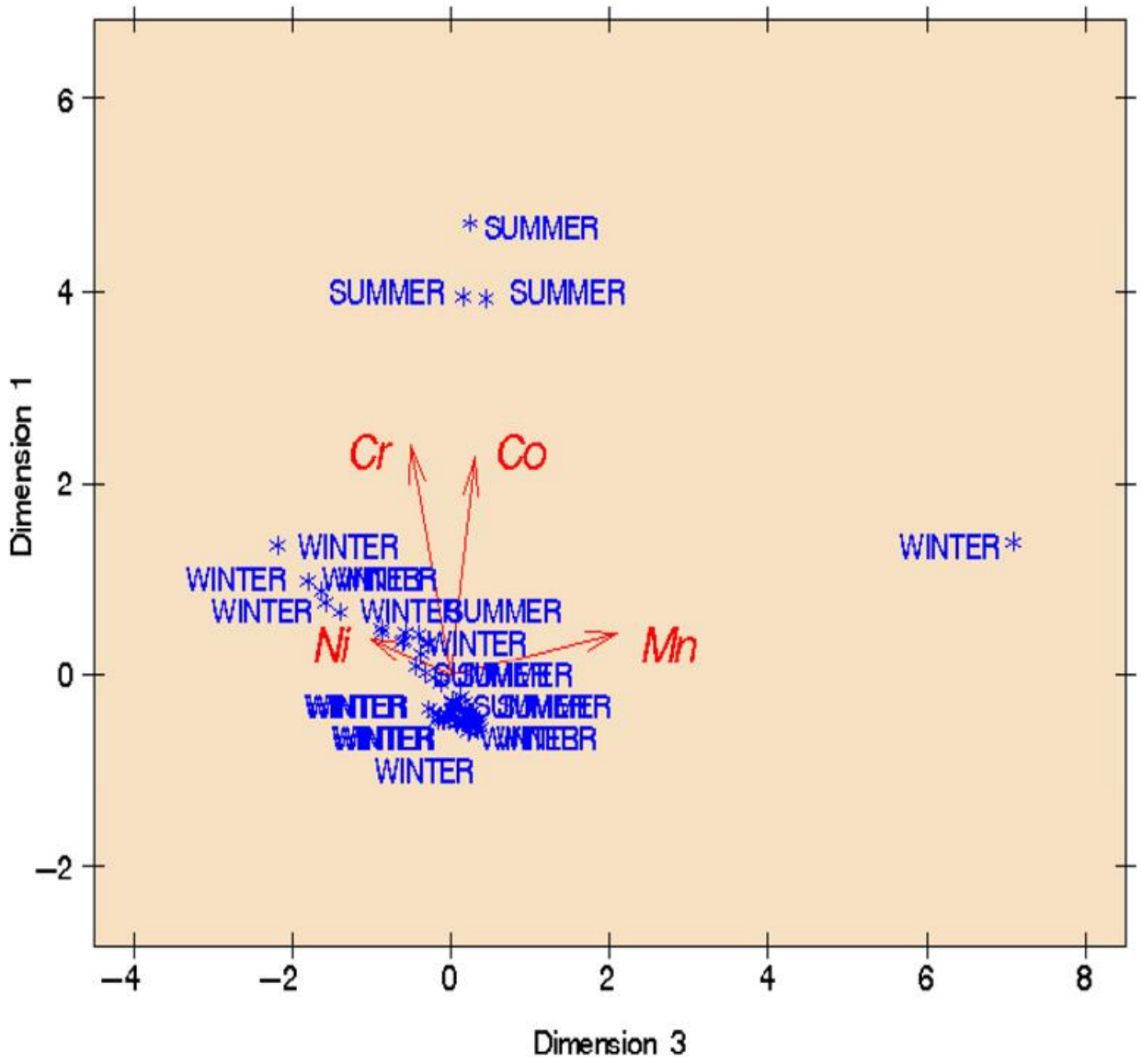

Figure 3b: The correlation between the metals according to seasons.

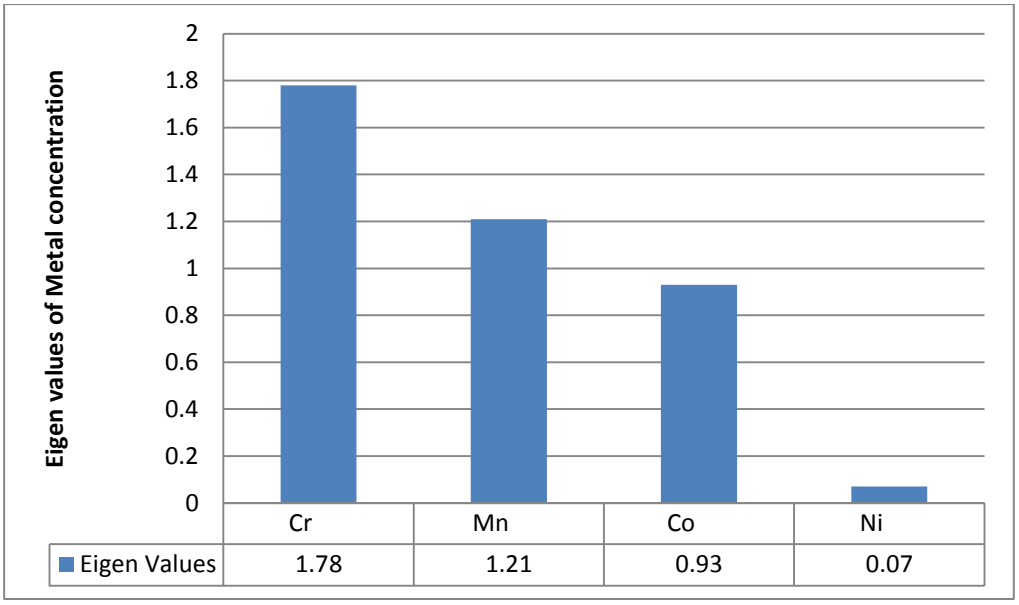

Figure 4: The screen plot of Eigen values showing the order of increase in concentration values of the metals

The correlation results in table 6 show that there is significant positive association in the amount of chromium & cobalt and chromium & nickel concentrations in the seawater. no significant association is found in the amount of concentrations from cobalt & manganese and cobalt & nickel ($p > 0.050$).

The average metal concentration levels in the sea water samples were compared with the national and international standards for metals as shown in Table 7. The mean concentrations obtained for the metals studied were higher than those recorded in the literature (Ren et al., 2006; Suren and Kul, 2007. Mn and Ni

concentrations found in the sea water samples are far higher than the permissible limits allowed by national and international regulations.

Heavy metal pollution of Cape Town harbour could be anthropogenic sources such as: industrial activities taking place in the harbour, inflows from the storm water /stream discharging from urban/industrial areas in and around the harbour (Rainbow, 1995). In addition, vast and rapid increase in industrialization and urbanization in developing countries like SouthAfrica, have led to high metal pollution of the environment. Increase in metal loads can as well be attributed to discharge of sewage and industrial spoil dumping of ballast water (Ren et al., 2006; Suren and Krull, 2007) Nevetherless, it is necessary to step up the regular monitoring and adequate control measures in order to ensure compliance with national and international regulations on the protection of the marine water.

Table 7: Comparison of metal concentration (µg/L) in sea water with other guidelines

References	Cr	Mn	Co	Ni
Cape Town Harbour	44.580±40.300	1054.420±2556.320	30.700±33.160	19.640±12.180
AO &PO (2004)	-		30.000	-
HELCOM (2004)				0.100-0.500
USEPA (1984)		0.400 - 1000		
UK(IS)		0.200 - 25.500	-	-
Botany bay, AUSTR	-		0.190	2.600

4. CONCLUSION

The concentration levels of heavy metals, namely Cr, Mn, Co and Ni were determined in the twelve locations inside Cape Town harbour. The levels of Co and Ni appeared generally to be normal in all the locations. The effects of seasonal variations on metals concentrations have been attributed to anthropogenic and natural factors. Probable sources of the metal pollution in the catchment appear to be diffused and include urban runoff in the catchment. This is due to contributions from natural and point sources in the area. This study further revealed that the average metal concentrations level in the sea water (Cape Town Harbour) were higher than the national and international standards. It is therefore important that Cape Town Harbour be regularly monitored in order to meet national and international standards on the protection of the marine environment.

ACKNOWLEDGEMENTS

The authors wish to thank the management of Cape Peninsular University of Technology, Cape Town, South Africa for URF 2011/2012 grant awarded HK Okoro for this research study. Acknowledgement also goes to Mr Sebastian Brown, Alistair Aldonis and Ashley Davids of CSIR, South Africa for being part of the sampling team. Thanks also go to Dr Afolayan, Department of English Language, University of Ilorin for the editorial assistance.

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