Article-1

Poll Res. 37 (4) : 1-22 (2018)

ISSN 0257–8050

METAL CONCENTRATIONS IN *MYTILUS GALLOPROVINCIALIS* ALONG THE WEST COAST OF THE CAPE PENINSULA, CAPE TOWN, SOUTH AFRICA

C. SPARKS[1]*, J. ODENDAAL[2], R. TOEFY[1] AND R. SNYMAN[1]

[1]*Department of Conservation and Marine Sciences, Cape Peninsula University of Technology, PO Box 652, Cape Town, 8000, South Africa*

[2]*Department of Environmental and Occupational Studies, Cape Peninsula University of Technology, PO Box 652,*

(Recieved 3 December, 2017; accepted 5 February, 2018)

ABSTRACT

Concentrations of metals (Fe, Mn, Cu, Cd, Zn and Pb) in the mediterranean mussel *Mytilus galloprovincialis* were investigated at five sites along the west coast of the Cape Peninsula, Cape Town. The mussels were collected seasonally for one year starting from autumn 2010 and analysed using an ICP-MS. On the spatial and temporal scales, metal concentrations differed, with no clear trends. Of the five sites sampled, metal concentrations were lowest at Scarborough, the southern-most site, and seasonally, lowest during summer.The results indicated that most metals in the soft tissue of mussels were below the recommended concentrations (internationally), permissible legal limit (for South Africa) as well as historical data (for the same area) suggesting that biota in the coastal area sampled was not contaminated by metals. There is however a need for continuous biomonitoring the coastal area of South Africa as the results found here might not apply to the rest of the South African coastline.

KEY WORDS : Metals, Mussels, Cape Town, Seasonal variation, Temporal variation, biomonitoring

INTRODUCTION

There is a growing concern about the increasing concentrations of metals in the coastal environment (water and sediments) due to their ability to bioaccumulate in organisms and the subsequent adverse effects that high concentrations of metals can have on the biota (Morse *et al.,* 1993; Besada *et al.,* 2011). The sources of the metals are varied and include freshwater (Forget, 2003), atmospheric sources (Williams *et al.,* 1998), natural components of the marine environment (Ansari *et al.,* 2004; Besada *et al.,* 2011) as well as anthropogenic discharges (Goldberg and Bertine, 2000). The continual release of metals from anthropogenic sources has resulted in concern about the integrity of coastal environments, in particular those with high tourism revenues (Goldberg and Bertine 2000; Beaumont *et al.,* 2007; Besada *et al.,* 2011), as polluted environments could result in decreased revenue (Beaumont *et al.,* 2007).

The effects of metals in the environment are often not evident until large scale effects such as changes in ecosystem structure and function can be detected (Cevika *et al.,* 2008). By then the metals could have accumulated in organisms (as well as the food chain) (Besada *et al.,* 2011) and this results in people consuming seafood that has been exposed to metals, with potential dire consequences to their health (Cevika *et al.,* 2008; Joksimovic *et al.,* 2011). Knowledge about the levels of metals within systems are therefore important as these could provide information that could prevent people being exposed to detrimental levels of metals and provide information about the toxicity of organisms prevalent in the ecosystem. Determination of metal concentrations in organisms should therefore be part of any assessment and monitoring programme of

***Corresponding author's email:** sparksc@cput.ac.

coastal systems (Shulkin *et al.,* 2003).

The Mediterranean mussel, *Mytilus galloprovincialis,* is a predominantly sublittoral mussel prevalent along the coasts of southern Africa. These mussels can densely cover rocky shores up to nearly 1 m above the low water spring tide (Du Plessis, 1977; Griffiths, 1981). These mussels form extensive beds in the lower intertidal and subtidal zones, in particular along the west and southwest coast of South Africa (Griffiths, 1981). The distribution of *M. galloprovincialis* is from Walvis Bay in Namibia to the north, to Port Alfred along the south coast of South Africa (Branch *et al.,* 2010). Over the past 30 years, *M. galloprovincialis* has become increasingly dominant as an alien mussel, often displacing the local species, *Choromytilusmeridionalis,* due to its ability to tolerate a wider range of environmental conditions (Griffiths, 1981). This dominance could also be because *M. galloprovincialis* are superior bioaccumulators of many chemical substances and they are therefore able to tolerate exposure to pollutants such as metals (Cevik *et al.,* 2008). Although extensive studies have been done on metal accumulation in mussels in other parts of the world, in particular the northern hemisphere (Sarki *et al.,* 1995; Cajaraville *et al.,* 2000; Cevik *et al.,* 2008; Ünlü *et al.*, 2008; Besada *et al.*, 2011), such investigations are sparse in the southern hemisphere and can be considered to be non-existent in South Africa since the 1980's (O' Donoghue and Marshall, 2003).

Marine bivalves are known to accumulate metals to relatively high concentrations in their tissue and shells without apparent negative physiological effects (Regoli 1998; Goldberg and Bertine, 2000). This therefore makes them ideal organisms to monitor the levels of metals in the marine environment (Goldberg, 1975; Goldberg, 1986; Shulkin *et al.*, 2003) as they have been recorded to accumulate metals by factors of 10^2 to 10^5 (Besada *et al.,* 2011). To promote a uniform and general approach to marine pollution monitoring, Goldberg (1975) proposed a global monitoring programme using mussels as indicator organisms. This monitoring programme, the Mussel Watch Programme (MWP) has been functional internationally since 1976 (Goldberg *et al.,* 1983) and in South Africa, mussel sampling has been conducted since 1985 by the South African national government agency: the Department of Environmental Affairs (DEA). Sparks *et al.,* (2014) published the results of the mussel monitoring done by DEA for the period 1985 to 2008, but no publication about the concentration in mussels in the region has been published since then. Given that Cape Town is a major tourist destination (Anon, 2008) and has one of the busiest ports in the country, it is important to know the concentrations of metalsin the region. Sampling biota such as mussels for metal analysis will provide information about whether metals in marine organisms (such as in *Mytilus. galloprovincialis*) are toxic for human consumption and possibly pose health risks.

The objective of this study was to determine the concentrations of metals in *Mytilus galloprovincialis* along the west coast of the Cape Peninsula, Cape Town and compare these to previously published data in order to ascertain the health of the coastal biota of the Cape Peninsula in Cape Town, South Africa.

MATERIALS AND METHODS

Mussel sampling

Specimens (n = 6) of *Mytilus galloprovincialis* were collected seasonally for one year starting from autumn 2010. Sampling took place at five sites on the west coast of the Cape Peninsula, South Africa: Scarborough (34°11'S, 18°17'E), Hout Bay (34°02'S, 18°21'E), Green Point (33°54'S, 18°23'E), Milnerton (33°53'S, 18°28'E) and Bloubergstrand (33°48'S, 18°27'E), (Fig. 1). Sampleswere collected at spring low tide, with sampling always commencing at Scarborough, the southern-most site. Mussels of the same size range (45 - 55 mm) were collected randomly at each site and transported in individual plastic bags, in cooler boxes, to the laboratory. Once in the laboratory, the specimens were allowed to depurate gut contents for 24 hours and subsequently frozen at -18ºC until the analyses were done.

Metal analysis

Metal analysis was done according to the method of Odendaal and Reinecke (1999). Frozen mussel samples (n=6) were defrosted and oven dried for 48 hrs at 60° C in a Memmert drying oven. The dried tissue samples were weighed and homogenized per individual mussel with a mortar and pestle. Sub-samples of individual mussels (± 0.2 g) were digested using nitric acid (HNO_3) and stored until further analysis was done.

The concentrations of Mn, Fe, Cu, Zn, Cd andPb

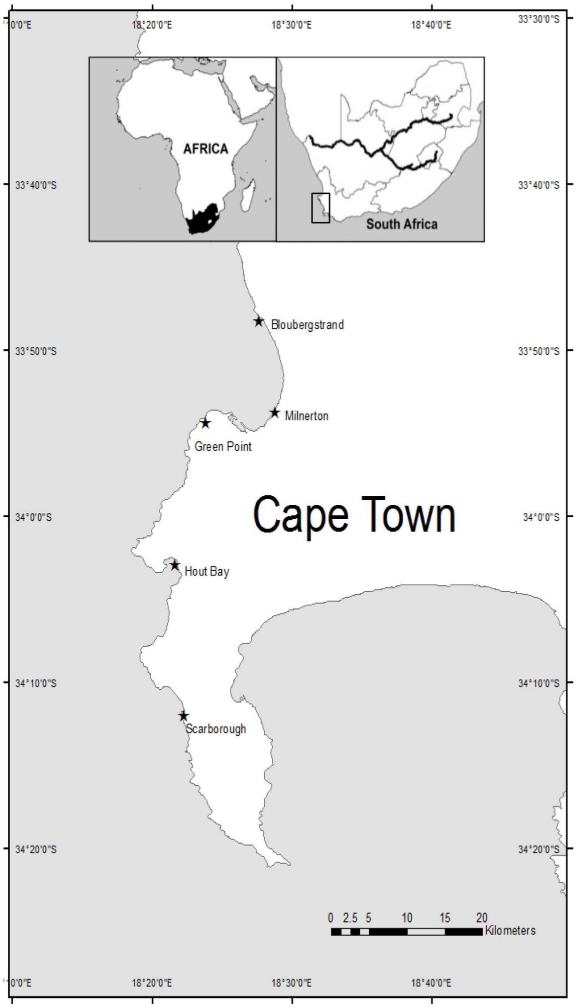

Fig. 1. Map showing the position of the sampling sites in the Cape Peninsula, Cape Town

were analysed at Stellenbosch University at the Central Analytical Facilities laboratory. The laboratory follows the US EPA method 6020A for quality control protocols during analysis and reporting of data. An Agilent 7700x ICP-MS with anOctopole Reaction System was used for metal analysis. A blank accompanied all samples during analysis andstandardsolutions were prepared and applied to serial dilutions of standard stock solutions. The quality assurance of data was a NIST traceable standard and the results presenting certified concentrations/analysed concentrations or % relative standard deviation (RSD) were as follows: Mn (24.68/26.93/0.52%), Fe (24.68/24.17/2.07%), Cu (24.68/24.41/1.10%), Zn (24.68/24.76/0.33%), Cd (9.87/9.80/0.75% and Pb (24.68/24.19/1.99%). All metal concentrations in *M. galloprovincialis* were expressed as µg/g dry weight.

Statistical analysis

All calculations and data analysis were done using SPSS 22 and the data are presented as means with standard error of the mean (±SE). The one way ANOVA was used to determine seasonal and spatial differences in mean metal concentrations in *M. galloprovincialis*. The data were tested for normality and homogeneity of variance using Kolmogorov-Smirnoff and Levene's tests respectively, prior to post hoc comparisons. Non-parametric Spearman rank correlations of metals in *M. galloprovincialis* were determined.

To investigate the similarity in metals at different sites and seasonally, dendrograms representing cluster analysis of the six metals were produced using PRIMER (Plymouth Routines in Multivariate Ecological Research) V6. (Clarke and Gorley, 2006). A multi-dimensional scaling (MDS) ordination of the concentrations of the metals measured in *M. galloprovincialis* was produced. Data were fourth root transformed and Euclidean distance used to produce a resemblance matrix. Dendrograms representing the cluster analysis of samples were produced to illustrate groups of samples that were similar to each other. All data were log x + 1 transformed, normalised and Euclidean distance used to produce a similarity matrix. Transformation of the environmental data was done to justify the Euclidean distance as a dissimilarity measure on normalised data (Clarke and Gorley, 2006).

The efficiency of metal accumulation in *M. galloprovincialis* was evaluated by calculating the biosediment accumulation factor (BSAF). The BSAF is defined as the ratio between the metal concentrations in the organism to that in the sediment (Lau *et al.*, 1998).

RESULTS AND DISCUSSION

The spatial and seasonal mean metal concentrations (±SE) in *M. galloprovincialis* are shown in Table 1. Spatially, the highest average metal concentrations for the study period were recorded at Hout Bay for Fe (190.96 ± 43.60 µg/g) and Mn (6.05 ± 0.48 µg/g), Milnerton for Cu (9.93 ± 1.73 µg/g) and Green Point for Zn (166.11 ± 20.67 µg/g), Cd (19.03 ± 7.61 µg/g) and Pb (4.37 ± 1.80 µg/g). The lowest metal concentrations were recorded at Scarborough for Fe (86.30 ± 9.01 µg/g), Mn (1.50 ± 0.19 µg/g), Cu (3.41 ± 0.66µg/g) and Pb (0.09 ± 0.02 µg/g) and Hout Bay for Zn (58.67 ± 8.58 ug/g) and Cd (1.01 ± 0.14 µg/g).

Table 1. Concentrations of metals in *M. galloprovincialis* (ìg g^{-1} dry weight) (± SE, n = 6) from the west coast of the Cape Peninsula sampled from autumn 2010 to autumn 2011

Site	Season	Fe	Mn	Cu	Zn	Cd	Pb
Scarborough	Autumn 2010	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Winter 2010	117.49 ± 15.25	1.93 ± 0.21	3.39 ± 0.19	71.52 ± 9.61	4.65 ± 0.56	0.23 ± 0.05
	Spring 2010	122.15 ± 10.26	0.98 ± 0.32	3.82 ± 2.21	140.29 ± 26.91	6.53 ± 0.42	0.22 ± 0.05
	Summer 2010	73.30 ± 7.02	2.27 ± 0.24	3.81 ± 0.60	46.51 ± 5.15	2.11 ± 0.12	0.04 ± 0.02
	Autumn2011	104.16 ± 4.65	2.35 ± 0.15	6.02 ± 1.92	172.13 ± 23.18	8.97 ± 0.58	<0.01
	Mean	86.30 ± 9.01	1.50 ± 0.19	3.41 ± 0.66	86.09 ± 13.50	4.45 ± 0.61	0.09 ± 0.02
Hout Bay	Autumn 2010	627.93 ± 66.13	9.05 ± 0.53	7.80 ± 0.83	148.27 ± 18.59	2.48 ± 0.19	5.54 ± 0.30
	Winter 2010	175.85 ± 20.83	8.46 ± 0.74	10.07 ± 0.46	69.43 ± 3.88	0.59 ± 0.09	0.85 ± 0.06
	Spring 2010	52.35 ± 12.32	5.24 ± 0.70	6.71 ± 1.78	12.88 ± 4.63	0.42 ± 0.02	0.22 ± 0.02
	Summer 2010	46.22 ± 6.31	3.27 ± 0.38	3.89 ± 0.32	31.53 ± 3.22	0.61 ± 0.05	0.16 ± 0.03
	Autumn2011	52.43 ± 3.71	5.23 ± 0.50	5.98 ± 0.62	61.09 ± 3.03	1.19 ± 0.07	<0.01
	Mean	190.96 ± 43.60	6.05 ± 0.48	6.86 ± 0.56	58.67 ± 8.58	1.01 ± 0.14	1.13 ± 0.36
Green Point	Autumn 2010	2.31 ± 0.32	2.43 ± 0.61	1.86 ± 0.34	6.70 ± 1.18	105.14 ± 27.64	25.21 ± 8.00
	Winter 2010	244.05 ± 16.17	4.57 ± 0.15	9.11 ± 0.40	187.81 ± 50.29	3.13 ± 0.65	2.72 ± 0.85
	Spring 2010	245.30 ± 35.14	1.60 ± 0.25	2.12 ± 0.60	199.02 ± 43.86	4.09 ± 0.17	1.33 ± 0.14
	Summer 2010	124.03 ± 11.32	1.95 ± 0.13	3.19 ± 0.10	212.02 ± 36.22	4.92 ± 0.29	1.02 ± 0.12
	Autumn2011	130.16 ± 16.32	1.93 ± 0.17	6.46 ± 1.18	171.86 ± 29.53	6.58 ± 0.25	<0.01
	Mean	159.66 ± 18.38	2.50 ± 0.24	4.74 ± 0.61	166.11 ± 20.67	19.03 ± 7.61	4.37 ± 1.80
Milnerton	Autumn 2010	197.36 ± 6.72	5.62 ± 0.63	4.42 ± 0.20	116.78 ± 19.43	1.57 ± 0.16	0.99 ± 0.10
	Winter 2010	30.29 ± 0.96	1.48 ± 0.07	21.00 ± 2.71	7.31 ± 0.44	<0.01	0.26 ± 0.04
	Spring 2010	345.70 ± 28.76	6.94 ± 0.78	10.69 ± 5.27	90.77 ± 12.89	3.36 ± 0.28	1.32 ± 0.04
	Summer 2010	141.03 ± 9.80	2.24 ± 0.27	2.90 ± 0.30	162.08 ± 24.04	3.41 ± 0.24	0.53 ± 0.08
	Autumn2011	239.59 ± 14.78	4.44 ± 0.43	8.81 ± 1.07	243.92 ± 45.14	5.16 ± 0.54	<0.01
	Mean	190.33 ± 21.90	4.04 ± 0.45	9.93 ± 1.73	124.70 ± 18.95	2.78 ± 0.37	0.55 ± 0.09
Bloubergstrand	Autumn 2010	316.29 ± 11.46	4.25 ± 0.60	5.07 ± 0.32	164.03 ± 20.47	3.41 ± 0.33	1.92 ± 0.11
	Winter 2010	31.44 ± 3.36	1.11 ± 0.12	19.39 ± 3.66	4.73 ± 0.63	<0.01	0.25 ± 0.03
	Spring 2010	202.90 ± 12.91	2.30 ± 0.28	2.57 ± 0.29	348.44 ± 91.03	5.75 ± 0.55	1.14 ± 0.11
	Summer 2010	39.65 ± 3.69	2.53 ± 0.30	2.60 ± 0.19	31.19 ± 3.17	1.74 ± 0.20	0.09 ± 0.03
	Autumn2011	59.41 ± 13.00	3.93 ± 0.39	6.66 ± 1.03	57.02 ± 3.78	1.92 ± 0.36	<0.01
	Mean	123.51 ± 20.90	2.78 ± 0.26	7.33 ± 1.41	119.60 ± 30.01	2.54 ± 0.39	0.60 ± 0.13
Season	Autumn 2010	256.16 ± 53.52	3.90 ± 0.69	3.73 ± 0.62	82.92 ± 16.40	19.01 ± 9.01	5.92 ± 2.19
	Winter 2010	119.83 ± 16.42	3.51 ± 0.53	12.59 ± 1.50	68.16 ± 15.59	1.68 ± 0.38	0.86 ±0.24
	Spring 2010	193.68 ± 20.91	3.41 ± 0.48	5.18 ± 1.27	158.28 ± 28.70	4.03 ± 0.42	0.85 ± 0.10
	Summer 2010	84.85 ± 8.30	2.45 ± 0.14	3.28 ± 0.17	96.66 ± 16.26	2.56 ± 0.29	0.37 ± 0.07
	Autumn2011	117.15 ± 13.47	3.58 ± 0.28	6.79 ± 0.55	141.20 ± 17.28	4.77 ± 0.56	<0.01
	Mean	150.09 ± 11.93	3.34 ± 0.20	6.42 ± 0.52	110.74 ± 9.22	5.88 ± 1.57	1.33 ± 0.38

Seasonally, highest metal concentrations were recorded during autumn 2010 for Fe (256.16 ± 53.52 μg/g), Mn (3.90 ± 0.69 μg/g), Cd (19.01 ± 9.01) and Pb (5.92 ± 2.19 μg/g), winter for Cu (12.59 ± 1.50 μg/g) and spring for Zn (158.28 ± 28.70 μg/g), with lowest seasonal metal concentrations recorded during summer for Fe (84.85 ± 8.30 μg/g), Mn (2.45 ± 0.14 μg/g) and Cu (3.28 ± 0.17 μg/g), winter for Zn (68.16 ± 15.59 μg/g) and Cd (1.68 ± 0.38 μg/g) and autumn 2011 for Pb (< 0.01 μg/g).

Metal concentrations were correlated using non-parametric Spearman Rank Order correlations and the results are provided in Table 2. Only Pbwas significantly ($p < 0.05$) negatively correlated with season, suggesting that metal concentrations decreased from autumn 2010 to autumn 2011. There were no significant relationships between metals and site.

An MDS (multi-dimensional scaling) of seasonal data for all the sites and metals combined (stress = 0.11) showed that there were overlaps between the seasonal samples. However, autumn 2010 and winter samples showed two groups whereas spring data were scattered (Fig. 2). Both summer and autumn 2010 data were closely grouped. The MDS

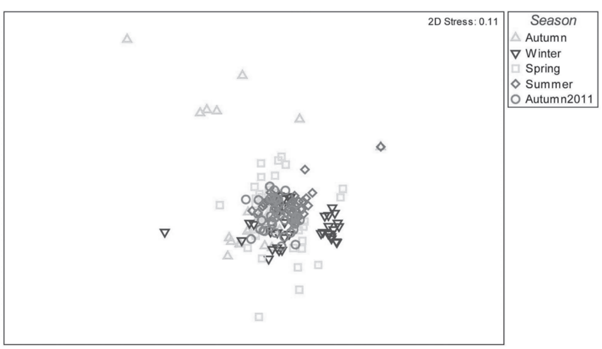

Fig. 2. MDS ordination of the seasonal data sampled using all metal data. The data were log x+1 transformed and normalised. Euclidean distance was used to plot the samples

of spatial data (per site) (stress = 0.11) indicated that Hout Bay and Green Point were the most scattered (Fig. 3). Milnerton and Bloubergstrand indicated that two groups (with some overlap) were present at these sites. Scarborough data were closely grouped. Generally there was an overlap of data at all sites, suggesting that the data were closely associated, albeit that the clusters were not sharply defined. An Analysis of Similarity (ANOSIM) between the seasons showed that there was no significant difference between seasonal metal concentrations (Global $R = 0.24$, $p > 0.05$). An ANOSIM between the five sampling sites also indicated no significant difference between sites and metal concentrations (Global $R = 0.156$, $p > 0.05$).

The results of the seasonal similarity percentages (SIMPER) analysis (Table 3) showed that during autumn 2010 and winter, most metals (except Cu during autumn 2010) were responsible for the similarity at all sites. During spring, all metals, except Cd and Pb, were responsible for the similarities within the mussel metals concentrations. The results of the spatial SIMPER analyses (Table 4) indicated that all metals, except Pb were responsible for the similarity at Scarborough and Milnerton. At Hout Bay, Fe, Zn and Pb were responsible for similarities. At Green Point, Pb and Cd were the largest contributors to similarities. At Bloubergstrand, Fe, Cu, Zn and Cd were the main contributors to similarity.

Although the MDS showed some separation between seasonal and spatial metal data, these results were not conclusive (Fig. 3 and 4). Adendrogram representing the cluster analysis of metals between the different sites suggested that there was some segregation of the metal data with samples from Scarborough being more distinct than the rest of the sites. A dendrogram for seasonal cluster analyses revealed poor grouping of data and

Table 2. Results of the non-parametric Spearman Rank Order Correlations between all environmental variables measured showing r values. * indicates significant r-values at $p < 0.05$.

Site	Season	Fe	Mn	Cu	Zn	Cd	Pb
Site							
Season							
Fe	0.122	-0.114					
Mn	0.097	0.052	0.454				
Cu	0.193	-0.003	0.143	0.448*			
Zn	0.116	0.254	0.772*	0.238	-0.005		
Cd	-0.051	0.274	0.484*	-0.002	-0.178	0.700*	
Pb	0.190	-0.731*	0.530*	0.151	-0.051	0.193	0.077

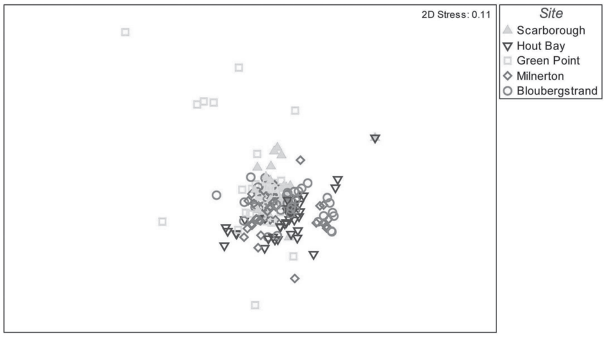

Fig. 3. MDS ordination of the site data sampled using all metal data. The data were log x+1 transformed and normalised. Euclidean distance was used to plot the samples

high variability, suggesting that metal contamination was not influenced by seasonal variations.

The present study has shown, compared to the MWP data reported by Sparks *et al.,* (2014), that all the metals investigated, except Fe and Cu, have lower mean concentrations than MWP data collected from 1985 to 2008 for the same area. The order of mean concentrations (µg/g dry weight) of metals (for all sites combined and for the entire sampling period) in *M. galloprovincialis* was Fe (150.09µg/g) > Zn (110.744 µg/g) > Cu (6.42µg/g)>Cd (5.88µg/g) > Mn (3.34µg/g)>Pb (1.33µg/g). The spatial and temporal variations of metal concentrations of this study were difficult to interpret due to high variability, but generally, metal concentrations in the tissue of *M. galloprovincialis* were lowest at Scarborough, with the lowest significant ($p<0.05$) concentrations recorded in winter. Given that the study was conducted in a winter rainfall area, the low concentrations recorded is indicative of either flushing of the system or that the area is not influenced by anthropogenic sources of metals. Metals such as Fe, Cu, Zn and Mn are considered essential elements for the biological functioning of organisms (Cevik *et al.,* 2008). In order to minimise the effects of metals, various authorities have set metal contamination guidelines/standards for mussels to indicate

Table 3. SIMPER (Similarity Percentage) of the seasons using all metal variables. A resemblance matrix using Euclidean distance was used in the analysis. The following table represents the average similarity between the seasonal groups. The values in bold represent the metals which contribute most to the similarity within each group.

Season Average squared distance Environmental factor	Autum 2010 14.09 % contribution	Winter 2010 4.33 % contribution	Spring 2010 5.58 % contribution	Summer 2010 1.92 % contribution	Autumn 2011 1.69 % contribution
Fe	25.02	9.38	12.06	23.71	14.06
Mn	14.38	22.79	23.39	18.79	24.68
Cu	6.50	14.27	29.96	11.21	19.90
Zn	13.04	17.82	31.42	24.47	12.81
Cd	20.57	14.14	5.79	14.97	28.55
Pb	20.49	20.60	4.08	6.84	0

Table 4. SIMPER (Similarity Percentage) of the sites using all metal variables. A resemblance matrix using Euclidean distance was used in the analysis. The following table represents the average similarity between the five sampling sites. The values in bold represent the metals which contributed the most to the similarity within each group.

Season Average squared distance Environmental factor	Scarborough 6.54 % contribution	Hout Bay 2.57 % contribution	Green Point 8.10 % contribution	Milnerton 2.88 % contribution	Bloubergstrand 3.47 % contribution
Fe	19.80	28.55	18.33	19.84	15.42
Mn	20.44	9.61	5.66	17.27	7.59
Cu	25.54	7.32	7.83	20.57	15.27
Zn	18.29	35.42	13.64	19.09	33.94
Cd	12.80	4.12	20.29	20.53	22.68
Pb	3.13	14.98	34.26	2.69	5.10

whether they are contaminated (Table 5). Consumption of essential elements such as Fe and Cu is permissible, but only to certain concentrations. However, metals such as Pb and Cd are non-essential, as they are toxic even at trace concentrations (Matta *et al.*, 1999; Cevik *et al.* 2008).

Sediments are considered to be contaminant sinks of pollutants and can remain in areas for lengthy periods (Schiff, 2000). As such, metals that accumulate in sediments, can over time, be transferred to and potentially accumulate in marine organisms. According to Rainbow and Phillips (1993), marine organisms have the ability to accumulate high levels of metals from their environment, in particular from sediment. Although most sediment-adsorbed contaminants are not readily available to aquatic organisms, variability within the water may result in the release of metals back into the water, making sediments an important source of pollution in certain environmental conditions (Rainbow and Phillips, 1993; Burger and Gochfeld, 2006). Metal concentrations in mussels are known to correlate with metal levels in proximate sediments (Puente *et al.*, 1996). Hence data concerning metal concentrations in sediment is essential to assess their potential to accumulate in marine organisms (Joksimovic *et al.*, 2011).

Table 5. Concentrations of metals in mussels that is indicative of contamination (μg/g dry weight). Values for South Africa are permissible legal limits for shellfish.

Metal	Global (FAO, 1983)	Black Sea (Cantillo, 1998)	South Africa (South Africa, 1994)
Fe	-	-	-
Mn	-	-	-
Cu	50-150	10	50
Cd	10	3.7	3
Zn	200-500	200	300
Pb	5-30	3.2	4

Data from sediment samples (Sparks *et al.*, 2017) were correlated with metal concentrations in mussels sampled from the same site (Table 6). Spearman rank correlations indicated significant (weak) positive correlations between Fe, Mn and Pb concentrations between sediments and mussels sampled. These results suggested that there is no uniform accumulation of metals in mussels from the surrounding medium and levels of metals within mussels are subject to the bioavailability of metals and these in turn are influenced by the mussel's physiology to take up the metals (Eisler, 1981; Bayne, 1986; Almeida *et al.*, 2007).

Metal bioavailability has traditionally been defined to include the availability of metals to organisms as well as the availability of metals to tissues within organisms once inside the organism (Peakalland Burger, 2003). According to Mountouris *et al.*, (2002) metal bioavailability results in high concentrations of the corresponding metal in biota through a bioconcentration process. Bioconcentration is the process by which a chemical species is accumulated into organisms from its surrounding medium (Mountouris *et al.*, 2002) and is calculated using the BSAF (also termed the bioconcentration factor). Bioavailability is affected by sediment characteristics (Mountouris *et al.*, 2002) such as: the concentration of iron, manganese and aluminium oxides (Bendell-Young and Harvey, 1991; Shea, 1988), levels of organic carbon (Mahoney *et al.*, 1996) and acid volatile sulphide (Chapman *et al.*, 1998). Bioavailability is also dependent on several environmental factors: physical (grain size of the sediment and suspended particulate materials), chemical (solubility, reactivity of compounds, complexing agents), and biological (benthic or pelagic organisms, modes of exposure) (Geffard *et al.*, 2003). The uptake of metals is also highly dependent on geochemical factors such as

Table 6. Summary of Spearman rank correlations for combined metal concentrations in the sediment (S) (mg/g dry weight) and mussels (M) (μg/g dry weight) sampled along the west coast of the Cape Peninsula. Values in bold are statistically significant at $p < 0.05$ level

	M Fe	M Mn	M Cu	M Zn	M Cd	M Pb
S Fe	0.348					
S Mn		0.314				
S Cu			-0.145			
S Zn				-0.061		
S Cd					-0.115	
S Pb						0.338

temperature, pH and dissolved oxygen (Lu *et al.*, 2005).

The efficiency of metal accumulation in *M. galloprovincialis*, as evaluated by calculating the biosediment accumulation factor (BSAF), is indicated in Table 7 and can be indicative of the bioavailability of the metals sampled. The orders of BSAF were: Cd > Zn >Cu>Pb> Mn > Fe. The results indicated that Cd, Zn, Pb and Cu had the highest mean BSAF, as the metal concentrations were higher in the mussels than the sediment, suggesting that these metals were bioavailable for uptake. The BSAF values in the present study are considerably higher than that reported by Abdallah and Abdallah (2008). An understanding of the bioavailability of metals is important to consider when investigating whether *M. galloprovincialis* in the Western Cape are ideal biomonitoring tools of metal pollution. Viarengo and Canesi (1991) found that *M. galloprovincialis* was able to rapidly eliminate Cu from its system, but was less able to expel Cd. These results could therefore explain the higher mean Cd BSAF values recorded in the mussels as they were not able to eliminate Cd effectively. However, there are various factors pertaining to *M. galloprovincialis* that affect the bioavailability of metals they are exposed to. Such factors can be defined by attributes of the individual mussel, groups of mussels or the species as a whole that can influence the amount and degree of metal exposure, uptake, absorption, biokinetics, susceptibility and toxicity (Burger *et al.*, 2003). According to these authors, such factors include age, gender, size and weight, nutritional status, genetics and behaviour.

Orren *et al.*, (1980) reported low Fe concentrations in Bloubergstrand from samples collected in 1980 and suggested that a contributing factor to the higher sources of Fe was increased anthropogenic sources of runoff from urban and industrial sources. However, the low BSAF value for Fe (0.18) suggests that *M. galloprovincialis* is either able to control the levels of Fe in its tissue or the metal is not bioavailable. Iron is an essential trace metal that is required for development and its uptake is known to be highly specialised due to complex chemical speciation linked to intracellular homeostasis (Worms *et al.*, 2006). According to these authors, most bioavailable iron in the natural environment is strongly associated to poorly characterise organic ligands. Furthermore, studies have indicated that iron complexes and colloidal iron are accessible to organisms and that bioavailability is enhanced by both chemical and biological mechanisms (Allison *et al.*, 1998; Peakalland Burger, 2003; Worms *et al.*, 2006).

The mean Cu concentration in *M. galloprovincialis* for the study period (2.35 µg/g) was below the legal limit of 50 µg/g for Cu allowed in shellfish in South Africa (South Africa, 1994). According the results of this study, none of the sites reported Cu concentrations above this limit. Copper is a naturally occurring element and essential for cellular metabolism. The uptake of Cu is hence variable, dependant on the kinetics of uptake and excretion (Philips, 1976). The low Cu concentrations in *M. galloprovincialis* recorded in the present study could be indicative of *M. galloprovincialis* not accumulating Cu in its soft tissue because Cu was either not bioavailable or that the mussel was able to regulate Cu. The BSAF (2.35) suggests that the mussel was able to regulate Cu and that Cu was bioavailable. Allison *et al*. (1998) reported that Cu concentrations in the faeces of *M. edulis* was significantly lower than in the particulate matter it was fed, reflecting a net loss of Cu from particles in the mussel gut. It was suggested that changes to the digestive physiology of mussels (increase in the proportion of food sent to the digestive gland and increase in gut passage time) compensated for lower digestion rates. These alterations increased the net release of particulate Cu and hence the bioavailability of Cu to the mussel. According to Cevik *et al.* (2008) Cu is a critical element to measure when analysing pollution of an area as it is both an important trace element for physiology but can also affect the health of organisms if available to bioaccumulate.

The mean Zn concentrations (spatial and

Table 7. Mean concentration of metals in the sediment and *M. galloprovincialis* as well as mean biosediment accumulation factor (BSAF). Sediment data from Sparks et al (submitted)

	Fe	Mn	Cu	Zn	Cd	Pb
Sediment	835.69	9.25	2.73	14.26	0.29	1.89
M. galloprovincialis	150.09	3.34	6.42	110.75	5.88	1.32
BSAF	0.18	0.36	2.35	7.77	20.28	0.69

temporal) for the study period (110.75 µg/g) were below the recommended level (200 µg/g) suggested by Cantillo (1998). However, concentrations > 200 µg/g were recorded in summer at Green Point and Milnerton (summer)as well as at Bloubergstrand in spring (Table 1). The legal limit of Zn allowed in shellfish is 300 µg/g (South Africa, 1994) and. Zn concentrations in the soft tissue of mussels from Bloubergstr and were above the permissible concentrations during spring. According to Cevik *et al.* (2008), Zn is a critical element to measure when analysing pollution of an area.

The mean Cd concentrations from the present study (5.88 µg/g) were above the recommended value (3.7 µg/g) proposed by Cantillo (1998). The high mean concentration was influenced by very high Cd concentrations recorded at Green Point during autumn 2010 (>100 µg/g). The permissible concentration of Cd in mussels is 3.0 µg/g (South Africa, 1994). Possible reasons for the high Cd concentrations are attributed to high ambient Cd concentrations in the sediment and water and the source of it was probably from the adjacent dense residential area and storm water pipe close to the sampling site. The results indicate the bioavailability of Cd for mussels, and could explain the high levels of Cd accumulated in the organism as evident by the BSAF of 20.28. Cadmium concentrations above 3.0 µg/g were recorded at Scarborough, Green Point and Bloubergstrand Table 1). A study by Topping (1973) reported higher concentrations of Cd in the hepatopancreas of arthropods than in mussels. The origins of the Cd were uncertain but it was proposed that the dominant pathway of Cd for the arthropods was via food rather than sea water. Since mussels are filter feeders and their food obtained from the sea water, mussels obtained their sources of Cd from both the sea water and prey within the sea water. A considerable amount of particulate cadmiumcomes from the burning of plastics products, pigments and rubber goods (Schroeder, 1974) but the high Cd levels recorded in the present study could not be indicative of burning of plastic and rubber products at Green Point, MilnertonorBloubergstrand as such activities do not occur in these area.

Irrespective of the source of Cd, it is its bioavailability and uptake that is important. Pan and Wang (2004) studied the influences of dissolved organic carbon (DOC) and colloidal organic carbon on the bioavailability of Cd in *Pernaviridis*. These authors found that DOC from decomposed diatoms resulted in linearly increasing of Cd with increasing DOC content. The west coast of the Western Cape is situated in a major upwelling centre and has a narrow continental shelf (Shannon, 1985). Upwelling intensifies in spring, with further upwelling events in autumn. The upwelling events during late summer and autumn results in algal blooms and in some cases the blooms result in red tides (harmful algal blooms) (Branch *et al.,* 2010) which in turn may provide DOC from decomposing diatoms. The extraordinary high Cd concentrations in *M. galloprovincialis* at Green Point (105 µg/g dry weight) could have been from elevated diatoms present in the area. The mechanism underlying the increase of Cd uptake with increasing DOC is not known, but the origins of DOC could have substantial influence on DOC-metal interaction in mussels (Pan and Wan, 2004).

The mean Pb concentrations in *M. galloprovincialis* for the entire study period (1.32 µg/g) was below the recommended contamination limit (3.2 µg/g) suggested by Cantillo (1998) and the legal limit for shellfish in South Africa (4.0 µg/g) (South Africa, 1994). Higher concentrations than the permissible limits for human consumption of Pb were recorded in autumn 2010 at Hout Bay and Green Point. Giarratano *et al.* (2010) noted high Pb concentrations in mussels during their study and attributed it to Pb contamination from heavy shipping activity. This proposed reason could apply to Hout Bay, given that it has shipping traffic and shipyard activities. It is however unlikely to be the case that shipping activity be responsible for high Pb concentration in Green Point. The high Pb concentrations also correspond to high Pb concentrations in sediment at the same site (Sparks *et al.,* 2017) suggesting that the Pb was bioavailable for uptake by mussels. It is however more probable that stormwater runoff be the main contributor of Pb at Hout Bay and Green Point as Boyden (1977) suggested that higher Pb recorded in mussels was from estuaries (hence areas with fresh water input).

CONCLUSION

Biomonitoring can show temporal changes and the spatial distribution of local metal contamination. Mussels with higher concentrations of Cd, Zn and Cu in the soft tissue were found in areas with high metal loads in the sediment, especially at Hout Bay and Green Point. Generally however, metals concentrations in mussels along the west coast of the Cape Peninsula, Cape Town, are lower than recommended concentrations for shellfish, suggesting that mussels at the sites sampled were not contaminated with metals (except for Cd). The results presented here indicate that it is important to conduct biomonitoring in the coastal regions of South Africa to as certain the status of contamination.

ACKNOWLEDGEMENTS

The research was funded by the Cape Peninsula University of Technology (CPUT)(University Research Fund). We thank the technical staff at CPUT for assistance with collecting samples and laboratory analysis.

REFERENCES

Abdallah, M.A.M. and Abdallah, A.M.A. 2008. Biomonitoring study of metals in biota and sediments in the South Eastern coast of Mediterranean sea, Egypt. *Environ. Monit. Assess.* 146 : 139-145.

Allison, N., Millward, G.E. and Jones, M.B. 1998. Particle processing by *Mytilusedulis*: effects on bioavailability of metals. *Jnl. Exp. Mar. Bio. Ecol*. 222 : 149-162.

Almeida, E.A., Bainy, A.C.D., de MeloLoureiro, A.P., Martinez, G.R., Miyamoto, S., Onuki, J., Barbosa, L.F., Garcia, C.C.M., Prado, F.M., Ronsein, G.E., Sigolo, C.A., Brochini, C.B., Martins, A.M.G., de Medeiros, M.H.G. and Di Mascio, P. 2007. Oxidative stress in *Pernaperna* and other bivalves as indicators of environmental stress in the Brazilian marine environment: Antioxidants, lipid peroxidation and DNA damage. *Comp. Biochem. Phys. A*. 146 : 588-600.

Anon. 2008. *Investment Destinations: Cities, towns, metropolitan councils* and *municipalities*. South African Business Guidebook.

Ansari, T.M., Marr, I.L. and Tariq, N. 2004. Metals in Marine Pollution Perspective-A Mini Review.*Jnl. Appl. Sci.* 4 (1) : 1-20.

Bayne, B.L. 1986. Measuring the effects of pollution at the cellular and organism level. In: G. Kullemberg (ed). *The Role of the Oceans as a Waste Disposal Option.* New York, Riedel.

Beaumont, N.J., Austen, M.C., Atkins, J.P., Burdon, D., Degraer, S., Dentinho, T.P., Derous, S., Holm, P. T. Horton, E., van Ierland, A.H., Marboe, D.J. Starkey, M. Townsend and Zarzycki, T. 2007. Identification, definition and quantification of goods and services provided by marine biodiversity: Implications for the ecosystem approach. *Mar. Pol. Bull.* 54 : 253-265.

Bendell-Young, L. and Harvey, H.H. 1991.Metal concentrations in chironomids in relation to the geochemical characteristics of surficial sediments. *Arch. Environ. Contam. Toxicol.* 21: 202-211.

Besada, V. Andrade, J.M., Schultze, F. and Gonzalez, J. 2011. Monitoring of metals in wild mussels (*Mytilus galloprovincialis*) from the Spanish North-Atlantic coast.*Cont. Shelf Res.* 31 (5) : 457-465.

Boyden, C.R. 1977. Effects of size upon metal content in shellfish. *J. Mar. Biol. Ass. UK*. 57: 675-714.

Branch, G.M., Griffiths, C.L., Branch, M.L. and Beckley, L.E. 2010. *Two Oceans: A guide to the marine life of southern Africa*. Cape Town:Struik Nature.

Burger, J. and Gochfeld, M. 2006. Locational differences in heavy metals andmetalloids in Pacific Blue Mussels *Mytilus [edulis] trossulus* from Adak Island inthe Aleutian Chain, Alaska. *Sci. Total Environ*. 368(2-3): 937-950.

Burger, J., Diaz-Barriga, F., Marafante, E., Pounds, J. and Robson, M. 2003. Methodologies to examine the importance of host factors in bioavailability of metals. *Ecotox. Environ. Safety*. 56 : 20-31.

Cajaraville, M.P., Bebianno, M.J., Blasco, J., Porte, C., Sarasquete, C. and Viarengo, A. 2000. The use of biomarkers to assess the impact of pollution in coastal environments of the Iberian Peninsula: a practical approach. *Sci. Total Environ.* 247 : 295-311.

Cantillo, A.Y. 1998. Comparison of Results of Mussel Watch Programs of the United States and France with Worldwide Mussel Watch Studies. *Mar. Poll. Bull.* 36 (9): 712-717.

Cevika, U.Damla, N., Kobya, A. I., Bulut, V.N., Duran, C., Dalgic, G. and Bozaci, R. 2008. Assessment of metal element concentrations in mussel (M. Galloprovincialis) in Eastern Black Sea, Turkey.*Jnl. Hazard. Mat.* 160: 396-401.

Chapman, M.P., Wang, F., Janssen, C., Persoone, G., Allen, E.H. 1998. Ecotoxicology of metals in aquatic sediments: binding and release, bioavailability, risk assessment, and remediation. *Can. Jnl. Fish.Aquat. Sci*. 55 : 2221-2243.

Clarke, K.R. and Gorley, R.N. 2006. *PRIMER v6: Used Manual/Tutorial*. Plymouth: PRIMER-E Ltd.

Du Plessis, A.J. 1977. Larval Development, settlement and growth of the black mussel, Choromytilusmeridionalis in the Saldanha Bay region.*Trans. Roy. Soc. S. Afr*. 42 (3): 303-316.

Eisler, R. 1981. *Trace metal concentrations in marine organisms*. New York, Pergamon Press.

Forget, J. Beliaeff, B. and Bocquené, G. 2003. Acetylcholineesterase activity in copepods (*Tigriopusbrevicornis*) from the Vilaine River estuary, France, as a biomarker of neurotic contaminants. *Aquat. Toxicol.* 62 : 195-204.

Geffard, O., Geffard, A., His, E. and Budzinski, H. 2003. Assessment of the bioavailability and toxicity of sediment-associated polycyclic aromatic hydrocarbons and heavy metals applied to *Crassostreagigasembryos* and larvae. *Mar. Poll. Bull*. 46 : 481-490.

Giarratano, E., Duarte, C.A. and Amin, O.A. 2010. Biomarkers and metal bioaccumulation in mussels transplanted to coastal waters of the Beagle Channel. *Ecotoxicol.* and *Environ. Saf.* 73 : 270-279.

Giarratano, E., Duarte, C.A. and Amin, O.A. 2010. Biomarkers and metal bioaccumulation in mussels transplanted to coastal waters of the Beagle Channel. *Ecotoxicol.*and *Environ. Saf.* 73 : 270-279.

Goldberg, E.D. 1975. The mussel watch: a first step in global marine monitoring. *Mar. Poll. Bull.* 6 : 111-132.

Goldberg, E.D. 1986. The Mussel Watch Concept. *Environ. Mon.* and *Assess.* 7 : 91-103.

Goldberg, E.D. and Bertine, K.K. 2000. Beyond the Mussel Watch – new directions for monitoring marine pollution. *Sci. Total Env*. 247: 165-174.

Goldberg, E.D. and Bertine, K.K. 2000. Beyond the Mussel Watch – new directions for monitoring marine pollution. *Sci. Total Env*. 247: 165-174.

Goldberg, E.D., Koide, M., Hodge, V., Felgal, A. and Martin, J. 1983. U.S. Mussel Watch: 1977-1978 Results on Trace Metals and Radionuclides. Estuarine, *Coast. Shelf Sci.* 16: 69-93.

Griffiths, R.J. 1981. Population dynamics and growth of the bivalve *Choromytilusmeridionalis (Kr.*) at different tidal levels.*Est. Coast. Shelf Sci.* 12: 10I-118.

Joksimovic, D., Tomic, I., Stankovic, A.R., Jovic, M., and Stankovic, S. 2011. Trace metal concentrations in Mediterranean blue mussel and surface sediments and evaluation of the mussels quality and possible risks of high human consumption. *Food Chem.* 127: 632-637.

Joksimovic, D., Tomic, I., Stankovic, A.R., Jovic, M., and Stankovic, S. 2011. Trace metal concentrations in Mediterranean blue mussel and surface sediments and evaluation of the mussels quality and possible risks of high human consumption. *Food Chem.* 127: 632-637.

Lau, S., Mohamed, M., Tan Chi Yen, A., and Suut, S. 1998. Accumulation of metals in fresh water molluscs.*Sci. Total Environ.* 214: 113-121.

Lu, X.Q., Werner, I. and Young, T.M. 2005. Geochemistry and bioavailability of metals in sediments from northern San Francisco Bay.*Environ. Intern*.31: 593- 602.

Mahony, D.J., Di Toro, M.D., Gonzalez, M.A., Curto, M., Dilg, M., De Rosa, D.L., et al. 1996. Partitioning of metals to sediment organic carbon. *Environ. Toxicol. Chem*. 15 (12): 2187-2197.

Matta, J., Milad, M., Manger, R. and Tosteson, T. 1999. Metals, lipid prexidation, and cigateratoxicity in liver of the Caribben barracuda (*Sphyraena barracuda*). *Biol. Trace Elem. Res*. 70 : 69-79.

Morse, J.W., Presley, R.J., Taylor, R.J. Benoit, G., and Sautschi, P. 1973. Trace metal chemistry of Galveston Bay: Water, sediment and biota. *Mar. Environ. Res*. 36 : 1-37.

Mountouris, A., Voutsas, E. and Tassios, D. 2002. Bioconcentration of heavy metals in aquatic environments: the importance of bioavailability. *Mar. Poll. Bull*. 44: 1136-1141.

O' Donoghue, S. and Marshall, D. 2003. Marine pollution research in South Africa: a status report. *S. Afr. J. Sci*. 99 : 349-356.

Odendaal, J.P., Reinecke, A.L 1999. The sublethal effects and accumulation of cadmium in the terrestrial isopod *Porcelliolaevis*Latr. (Crustacea, Isopoda). *Arch. Environ. Contam.Toxicol.* 36 : 64-69.

Orren M.J., Eagle G.A., Hennig H.F-K.O. and Green A. 1980. Variations in trace metal content of the mussel *Chromomytilusmeridionalis (*Kr.) with season and sex. *Mar. Pollut. Bull.* 11 : 253-257.

Pan, J., and Wang, W. 2004. Influences of dissolved and colloidal organic carbon on the uptake of Ag, Cd, and Cr by the marine mussel *Pernaviridis*. *Environ. Poll*. 129 (3): 467-77.

Peakall, D. and Burger, J. 2003. Methodologies for assessing exposure to metals: speciation, bioavailability of metals, and ecological host factors. *Ecotoxicol. Environ. Saf*. 56 : 110-121.

Philips, D.J.H. 1976. The common mussel Mytilusedulis as an indicator of pollution by zinc, cadmium, lead and copper. I. Effects of environmental variables on uptake of metals. *Mar. Biol*. 38 : 59-69.

Preston, B.I. 2002. Indirect Effects in Aquatic Ecotoxicology: Implications for Ecological Risk Assessment. *Environ. Man.* 29 (3): 311-323.

Puente, X., Villares, R., Carral, E. and Carballeira, A. 1996. Nacreous shell of *Mytilusgalloprovincialis* as a biomonitor of heavy metal pollution in Galiza (NW Spain). *Sci. Total Environ*. 183(3): 205-211.

Rainbow, P.S. and Phillips, D.J.H. 1993.Cosmopolitan biomonitors of trace metals. *Mar. Poll. Bull*. 26 (11): 593-601.

Regoli, F. 1998. Metals and antioxidant enzymes in gills and digestive gland of the Mediterranean mussel *M. galloprovincialis*. *Arch. Environ. Contan.Toxicol*. 34: 48-63.

Sarki, M.K., Casterberry, D.T., May, T., Martin, B.A., and Bullard, F. N. 1995.Copper, cadmium and zinc concentrations in aquatic food chains from the Upper Sacremento River (California) and tributaries. *Arch. Environ. Contam.Toxicol.* 24 (4): 484-491.

Schiff, K.C. 2000. Sediment chemistry on the mainland shelf of the SouthernCalifornia Bight. *Mar. Poll. Bull*. 40 (3): 268-270.

Schroeder, H. 1974. *The poisons around us.* Bloomington, Indiana University Press.

Shannon, L. 1985. The Benguela ecosystem part I. Evolution of the Benguela, physical features and processes. *Oceanogr. Mar. Bio. Ann. Rev.* 23 : 105–182.

Shea, D. 1988. Deriving sediment quality criteria. *Environ. Sci. Tech*. 22 : 1256-1261.

Shulkin, V.M., Presley, B.J. and. Kavun, V.I. 2003. Metal concentrations in mussel Crenomytilus*grayanus* and oyster *Crassostreagigas* in relation to contamination of ambient sediments. *Environ. Intern.* 29 : 493– 502.

South Africa. 1994. Government Notice No. R. 1518 of 9 September 1994.

Sparks, C., Odendaal, J. and Snyman, R. 2014. An analysis of historical Mussel Watch Programme data from the west coast of the Cape Peninsula, Cape Town. *Mar. Pollut. Bull*. 87 : 374-380.

Sparks, C., Odendaal, J. and Snyman, R. 2017. Metal concentrations in intertidal water and sediment along the west coast of the Cape Peninsula, Cape Town, South Africa. *Water SA*. 43 : 17-24.

Topping, G. 1973. Metals in shellfish from skittish waters. *Aquaculture.* 1: 379-384.

Ünlü, S., Topçuoðlu, S., Alpar, B., Kýrbaþoðlu, C. and Yýlmaz, Y. 2008. Metal pollution in surface sediment and mussel samples in the Gulf of Gemlik. *Environ. Monit. Assess.* 144: 169-178.

Viarengo, A. and Canesi, L. 1991. Mussels as biological indicators of pollution. *Aquac.* 94: 225-243.

Watling, H.R. and Watling R.J. 1976.Trace Metals in *Choromytilusmeridionalis. Mar. Poll. Bull*. 7: 91-94.

Williams, M.R., Millward, G.E., Nimmo, M. and Fones, G. 1998. Fluxes of Cu, Pb and Mn to the north-eastern Irish sea: the importance of sediment and atmospheric inputs. *Mar. Poll. Bull.* 36(5): 366-375.

Wong, C.K.C., Cheung, R.Y.H. and Wong, M.H. 2000. Metal concentrations in green-lipped mussels collected from ToloHarbour and markets in Hong Kong and Shenzhen. *Environ. Pollut.* 109: 165–171.

Worms, I., Simon, D.F., Hassler, C.S. and Wilkinson, K.J. 2006. Bioavailability of trace metals to aquatic microorganisms: importance of chemical, biological and physical processes on biouptake. *Biochimie.* 88: 1721-1731.

.