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An analysis of historical Mussel Watch Programme data from the west coast of the Cape Peninsula, Cape Town

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ABSTRACT

The concentrations of metals in the mussel *Mytilus galloprovincialis* (Lamarck, 1819) prevalent along the west coast of the Cape Peninsula, Cape Town are presented. The mussels were sampled during the routine “Mussel Watch Programme” (MWP) between 1985 and 2008. Levels of Cu, Cd, Pb, Zn, Hg, Fe and Mn at Cape Point, Hout Bay, Sea Point, Milnerton and Bloubergstrand were analysed for autumn and spring and showed consistent similar mean values for the five sites. There was a highly significant temporal (annual and seasonal) difference between all metals as well as a significant difference in metal concentrations between the five sites. The concentrations of Zn, Fe, Cd and Pb were higher than previous investigations and possibly indicative of anthropogenic sources of metals. The results provide a strong motivation to increase efforts in marine pollution research in the area.

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To monitor the health of coastal systems, sentinel organisms such as mussels (bivalves) have been identified as suitable candidates to indicate levels of contaminants in the coastal environment and, as such, have been proposed to be suitable “biomonitors” of pollution (Besada et al., 2011). According to Farrington (1983), bivalves are considered ideal to be used as surveillance tools to monitor coastal pollution because they have a widespread distribution across the world’s coastal waters, are sedentary, concentrate pollutants by factors of a thousand to a hundred thousand, appear to be resistant to pollutants, are commercial products and are consumed extensively in some areas of the world, and hence pose a risk to human health. To monitor the nature and extent of coastal pollution, a Mussel Watch Programme (MWP) was developed by Goldberg (1975) in an attempt to quantify the levels of pollutants in coastal systems. The use of mussels to monitor coastal pollution is now widely accepted and supported by many international organizations (Besada et al., 2011).

Mediterranean blue mussels (*Mytilus galloprovincialis*) are widely used as biomonitors of metal pollution and this is also the case in southern Africa (Wepener and Degger, 2012). Although an invasive species in South Africa (Griffiths et al., 1992), *M. galloprovincialis* is used for biomonitoring metal concentrations along the west and south coast of southern Africa as part of the country’s

MWP. The MWP started in South Africa in 1985 as part of the South African National Committee for Oceanographic Research (SANCOR) and the Marine Pollution Research Programme (MPRP) was initiated by SANCOR as a framework for pollution research (SANCOR, 1985; Wepener and Degger, 2012). Prior to this, similar small scale projects were carried out in South Africa to monitor metals in mussels (Orren et al., 1980) but this was done in isolation from that done in other parts of the world. The intention for the development of the MWP in South Africa was to develop a means of monitoring the health of the coastal environment. The monitoring was intended to provide relevant research and scientific advice to authorities on the management of pollutants (metals) in the marine environment (SANCOR, 1985). The samples have been collected since 1985, but unfortunately publications in accredited sources are lacking. Hence the value and effectiveness of the MWP in South Africa is relatively unknown. Cape Town is one of the most popular tourist destinations in the world (Anon, 2008) and is renowned for its natural and pristine coastal environment. However, since little is known about the status of metal contamination in the region, the aim of this study was to determine the levels of metals in mussels along the west coast of the Cape Peninsula.

Description of the study area and study sites: five sites along the west coast of the Cape Peninsula (Cape Town) were selected (Fig. 1). The sites selected were part of ongoing MWP sampling stations (see Table 1). The Cape Peninsula is largely rocky, mountainous and dominated by the Table Mountain chain (Van Herwerden and Bally, 1989). Historically, urban development has

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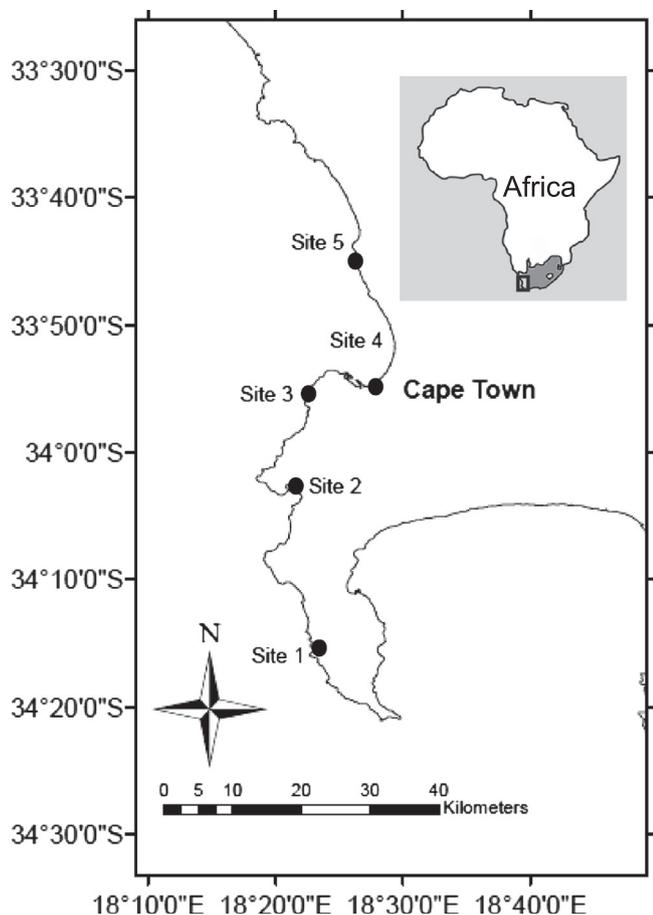


Fig. 1. Map of the Cape Peninsula, Cape Town showing the position of the sampling sites. Site 1 = Olifantsbos and Noordhoek, Site 2 = Hout Bay, Site 3 = Sea Point, Three Anchor Bay and Granger Bay, Site 4 = Table Bay harbour and site 5 = Paarden Island, Milnerton and Bloubergstrand.

centered on the slopes of Table Mountain, initially starting around the safe anchorage of Table Bay, and then gradually spreading southwards, mainly along the eastern sides of the Table Mountain chain. According to Van Herwerden and Bally (1989), the shoreline along the Cape Peninsula is dominated by rocky shores along the mountainous section of the Peninsula, interspersed with pocket beaches of sand or mixed sand and rock. The area falls within a Mediterranean-type climatic region, typified by winter rainfall from successional cold fronts from the west and dry southeasterly winds during the summer. Winter frontal systems cause north and westerly winds. The annual mean temperature in the region is 17 °C (range ± 10 °C). Because it is in a winter rainfall region, the area receives the bulk of its mean annual precipitation of between 500 and 700 mm mainly during the months of April to August (Shannon, 1985).

The main objective of this study was to analyze the MWP data (1985–2008) to ascertain if there were any temporal and spatial changes to metal concentrations in the mussels *M. galloprovincialis* along the western coastline of the Cape Peninsula. Any significant changes in metal concentrations in the mussels would provide valuable information for various agencies responsible for management of pollutants.

Historical data from the Mussel Watch Programme (MWP) in South Africa from 1985 to 2008 were sampled during spring and autumn at spring low tide. Samples of *M. galloprovincialis* were collected and analysed for metals ($\mu\text{g/g}$ dry weight) by the Department of Environmental Affairs and seven metals were analysed for this study (Cd, Cu, Pb, Zn, Hg, Fe and Zn).

Prior to 1995, all MWP samples ($n = 702$, average mussel length = 60.8 mm) were collected and processed according to the methods used by Watling and Watling (1976). In brief, soft tissue of *M. galloprovincialis* were weighed and then dried at 105 °C for 48 h. The tissue was then digested with redistilled, analar-grade nitric acid and the solution was allowed to evaporate. The residue was redissolved in a 4:1 nitric-perchloric acid mixture and the solution dried at about 250 °C. This residue was then dissolved in 10 mL of 0.1 mol/L nitric acid. Metal concentrations in solution were determined by Atomic Absorption Spectrophotometry. The results were expressed as metal concentration in mussel tissue of whole organisms ($\mu\text{g/g}$ dry tissue). Watling and Watling (1976) made no reference to any form of quality control and it is thus assumed that no certified reference material was used.

After 1995, mussels ($n = 802$, average mussel length = 62.2 mm) were depurated in tanks filled with flowing sea water for 24 h, whereafter they were freeze-dried for approximately 3 days and metal concentrations determined as above. Quality control of metal concentrations was verified by including blanks and certified reference material (CRM) (DORM-2, dogfish muscle tissue, National Research Council Canada). No data was available regarding recoveries for the entire period but data research reports at the Department indicated that recoveries were within 10% as the institution adheres to stringent quality assurance processes.

All statistical data analysis was done using Statistica v10 (Stat. Soft. Inc.). The effects of time (annually and per season) and location on metal concentration in mussels were analysed and presented as mean concentrations ($\pm\text{SD}$) and further analysis using one-way ANOVA for single factors (year, season or site) and multi-way ANOVA to test the effects of time (year and season) and location (distance from control site) on metals (Cd, Cu, Zn, Pb, Hg, Fe and Zn). Prior to the use of the parametric tests, the data were tested for normality and homogeneity of variances using Kolmogorov–Smirnov and Levene’s tests respectively (Townend, 2002). If the data did not meet the assumptions of the tests, the data were \log_{10} -transformed prior to analysis. For ANOVA analysis, post hoc Tukey tests were done. Error bars in graphs indicate standard error of the mean. Differences between seasonal metal concentrations were done using one way ANOVA and significant differences indicated at $p < 0.05$.

Metal concentrations showed highly variable values when all data per metal were combined (Table 2 – all sites). Metal values ranged from not detected (ND) to 1625.6 $\mu\text{g/g}$ (Zn). The highest mean values recorded were for Zn 186.2 ± 125.6 followed by Fe 129.3 ± 163.3 $\mu\text{g/g}$. The high variability (indicated by the SD values) in Table 2 validated the need to normalise the data and hence supports the \log_{10} transformation that was applied to the data.

The remainder of the mean metal concentrations were below 7 $\mu\text{g/g}$ per metal. There was a highly significant difference between all metals for the entire period of the study 1985–2008 ($p < 0.001$). The decreasing order of metals for all the sites combined was $\text{Zn} > \text{Fe} > \text{Cd} > \text{Cu} > \text{Pb} > \text{Mn} > \text{Hg}$.

The mean concentrations of metals in soft tissue of *M. galloprovincialis* for the period 1985–2008 at all sites are shown per year (Fig. 2) and per season (autumn and spring 2010) (Fig. 3).

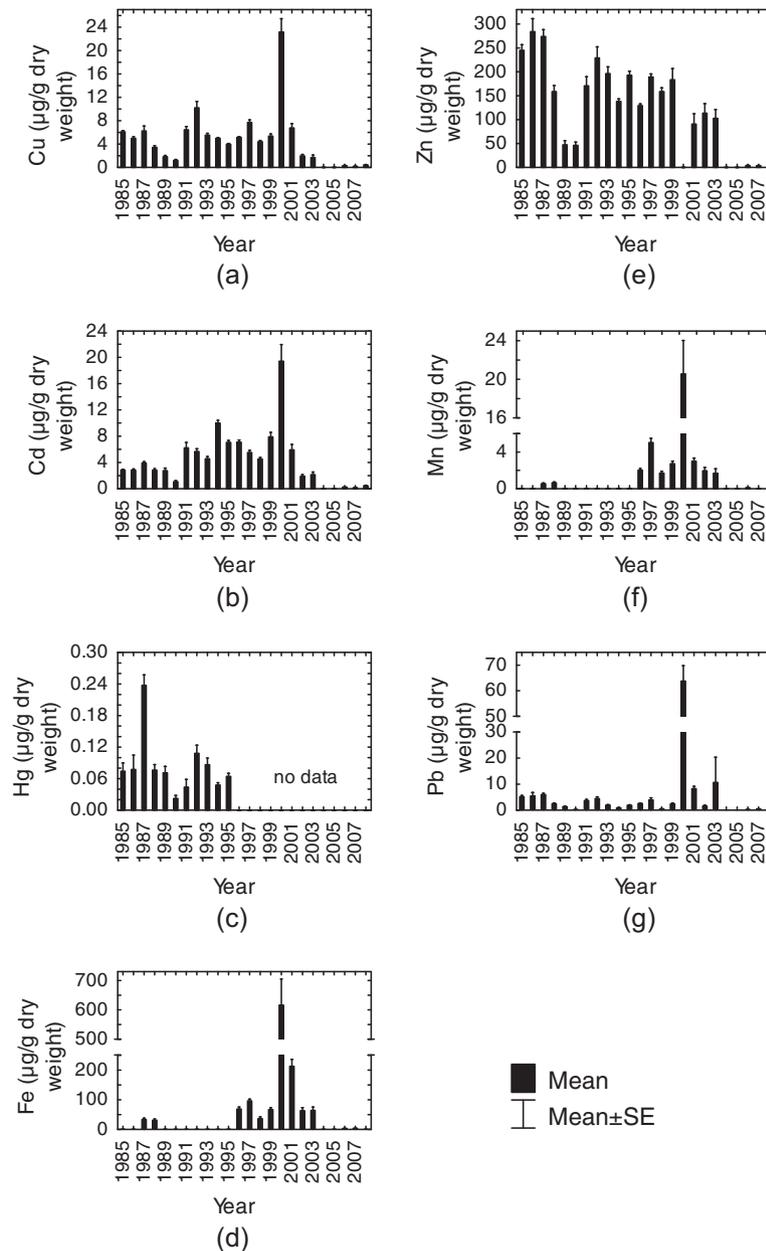
Table 1

Site and station information of samples collected during the Mussel Watch Programme.

Name	Stations	Number of MWP stations
Site 1	Olifantsbos, Noordhoek	2
Site 2	Hout Bay	5
Site 3	Sea Point, Three Anchor Bay, Granger Bay	3
Site 4	Table Bay	4
Site 5	Milnerton, Paarden Island, Bloubergstrand	3

Table 2Mean metal concentration ($\mu\text{g/g}$ dry weight) of Cd, Cu, Pb, Zn, Hg, Fe and Mn along the west coast of the Cape Peninsula for the study period 1985–2008.

	All sites		Site 1		Site 2		Site 3		Site 4		Site 5	
	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max
Cd	6.2	39.1	6.6	21.9	5.6	35.4	6.9	39.1	5.2	32.5	7.5	26.5
Cu	5.6	43.9	4.8	27.2	5.5	43.9	6.7	37.5	5.8	21.9	5.4	29.1
Pb	5.1	427.6	2.9	76.4	4.6	427.6	7.3	88.0	5.6	79.6	4.4	85.4
Zn	186.2	1625.6	159.2	1625.6	181.0	932.0	221.9	1306.6	221.0	668.0	159.3	575.3
Hg ^a	0.2	0.9	0.1	0.4	0.2	0.9	0.2	0.9	0.1	0.3	0.1	0.2
Fe	129.3	1309.0	127.5	976.5	102.7	873.0	162.0	1309.0	170.4	1057.5	133.0	1013.5
Mn	4.2	64.7	4.3	64.7	3.4	55.8	4.3	21.3	5.1	31.5	5.8	64.7

^a Indicates data from 1985 to 1995 only.**Fig. 2.** Mean (\pm SE) annual Cu (a), Cd (b), Hg (c), Fe (d), Pb (e), Mn (f) and Zn (g) ($\mu\text{g/g}$ dry weight) concentrations in *M. galloprovincialis* for all sites combined from 1985 to 2008. No Hg data was collected from 1995 to 2008.

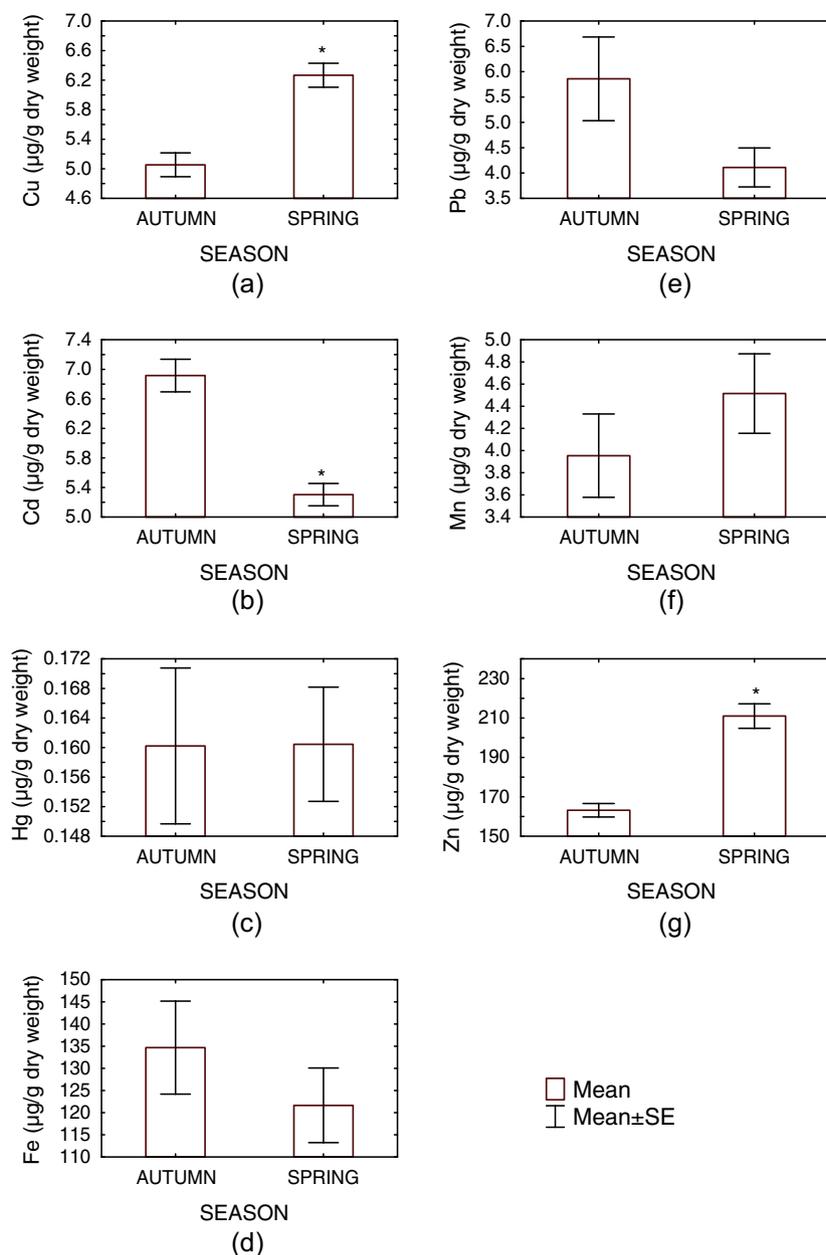


Fig. 3. Mean (\pm SE) seasonal Cu (a), Cd (b), Hg (c), Fe (d), Pb (e), Mn (f) and Zn (g) ($\mu\text{g/g}$ dry weight) concentrations in *M. galloprovincialis* measured at all sites from 1985 to 2008. * indicates significant differences using one way ANOVA ($p < 0.05$).

Copper concentrations were low but variable, with one peak in 2000 ($23.2 \mu\text{g/g}$) (Fig. 2a). The values ranged from nd (2004–2005) to $101 \mu\text{g/g}$ with a mean of $4.4 \pm 5.0 \mu\text{g/g}$ (Supplementary data Table 3). The concentrations for all the stations were generally below $10 \mu\text{g/g}$. There was a highly significant difference in Cu concentration between years ($p < 0.001$) and a significant difference in Cu concentrations between of 2010 ($p < 0.05$) (Fig. 3a). Cadmium levels ranged between nd and $39.1 \mu\text{g/g}$. Mean Cd concentrations were low for most of the study period ($6.17 \mu\text{g/g}$). There were highly significant differences in Cd concentrations between years and between autumn and spring ($p < 0.001$) (Fig. 3b).

Mercury measurements were only done from 1985 to 1995 and ranged from nd to $0.89 \mu\text{g/g}$, with the mean concentration being $0.2 \pm 0.1 \mu\text{g/g}$ dry weight. Mercury concentrations were variable (Fig. 2c) with a threefold increase in 1987. There was a highly significant difference in Hg between years ($p < 0.001$) but no significant differences between autumn and spring (Fig. 3c). Iron was

recorded in mussels from 1987 to 1988 and then again from 1996 to 2003. There was an increase in Fe concentrations from 1996 until 2001 and thereafter Fe concentrations decreased. Fe concentrations ranged from nd to $1309 \mu\text{g/g}$. Mean Fe values for the study period was $129.3 \pm 163.5 \mu\text{g/g}$. There was a highly significant difference between annual Fe measurements ($p < 0.001$) (Fig. 2d).

Lead measurements were variable as values ranged from nd to $427.6 \mu\text{g/g}$ (Fig. 2e). The mean Pb concentrations in mussels were $5.1 \pm 16.5 \mu\text{g/g}$. There was highly significant interannual Pb variations ($p < 0.001$) but no significant differences between autumn and spring (Fig. 3e). The Mn concentration in mussels ranged from ND to $64.7 \mu\text{g/g}$ with an average of $4.2 \pm 6.1 \mu\text{g/g}$. The concentrations of Mn from 1996 was very low with only one spike ($>20 \mu\text{g/g}$) recorded in 2000. There was a significant difference between annual Mn concentrations ($p < 0.001$) but no significant difference between autumn and spring concentrations (Fig. 3f).

Zinc had relatively high concentrations from the start of the MWP (>200 µg/g) and then gradually decreased until 2003 (Fig. 2g). The mean Zn concentration for the study period was 186.2 ± 125.6 µg/g with the highest value being 1625.6 µg/g. Inter-annual Zn concentrations were highly variable and significantly different ($p < 0.001$) (Fig. 2g). Spring Zn concentrations were significantly higher than autumn ($p > 0.05$) (Fig. 3g).

The effects of pollutants (including metals) on living organisms can be evaluated at different levels of organization (molecular, cellular, individual, population and community) (Viarengo and Canesi, 1991). Good interpretation of the data can be obtained by studying the effects of pollutants in individuals, with the aim of understanding and eventually predicting the possible consequences at higher levels (Bayne, 1986). The Mussel Watch Programme (MWP) was established to monitor the concentrations of pollutants (metals in the case of South Africa).

The results of this investigation indicated that the levels of metals in mussels for the western coastline of the Cape Peninsula were approximately the same for the MWP sites sampled (Table 2). For all data combined, the mean order of decreasing metal concentrations were: $Zn > Fe > Cd > Cu > Pb > Mn > Hg$ (indicates non-essential metals). The order of concentrations was similar to that reported by Watling and Watling (1976) and it is in this order that the metals will be discussed.

According to Eisler (1981), the highest concentrations of Zn in the marine environment are found in filter-feeding molluscs. The relatively high Zn concentrations recorded in mussels during the MWP therefore supports this as the Zn concentrations were significantly higher than the other metals recorded ($p < 0.001$). The source of Zn may be from anthropogenic sources although this is unlikely to be the case at site 1 as this site is far (>10 km) from major sources of anthropogenic Zn. According to Moore (1981), however, Zn uptake is mainly from prey rather than from sea water. The high levels of Zn were therefore more likely to be from zoo- and phytoplankton sources as the continental shelf is very narrow in this area (Shannon, 1985). The mean levels of Zn detected at site 1 (134.2 µg/g) were below the maximum limits allowed in foodstuff as set by the South African Bureau of Standards (SABS) of 300 µg/g (South Africa, 1994). What is of concern though is that for site 1, the maximum levels recorded exceed the SABS maximum limit (1625 µg/g was recorded in 1999). Furthermore, there are no local comparative studies to illustrate whether the current Zn values are higher than normal. However, median Zn values recorded along the Cape Peninsula (131 µg/g) is similar to the median World MWP value (130 µg/g) (Cantillo, 1998). According to Cantillo (1998), Zn concentrations above 200 µg/g are indicative of contamination. Zinc values higher than 200 µg/g accounted for 21% of the Zn values at site 1. The Zn values are higher than that of Henry et al. (1986), who recorded Zn values of 0.6 and 0.4 µg/g in mussels in Granger Bay and Green Point, respectively (site 3), but they used different mussel species. The source of the zinc is thus uncertain and needs further investigation.

Iron had the second highest concentration reported for the study period and the mean concentrations of Fe for all sites reported in this study (129.3 µg/g) is lower than that reported in other investigations where mussels were sampled (Shiber and Shatila, 1978; Kavun et al., 2002). According to Giarratano et al. (2010), changes in marine Fe concentrations may be related to continental sources of Fe, as the major contributor to Fe is from rock weathering as a result of continental rainfall. Potential anthropogenic sources of Fe are from fertilizers, industry wastes, atmospheric deposition, solid waste disposal units and run-off from urban areas (Pergram and Görgens, 2001). The Fe tissue values recorded in the present study suggest that there are no major anthropogenic sources of Fe other than from urban run-off and the main source of Fe is postulated to be as a result of rock weathering

due to higher rainfall in autumn (Fig. 2d). According to Giarratano et al. (2010), Fe concentrations reported from their study came from natural sources, as human activities were not responsible for Fe input into the system.

Cadmium concentrations (mean = 6.2 µg/g) were similar to that of Cu for the study period 1985–2008 along the west coast of the Cape Peninsula. However, the Cd levels recorded in this study are higher than the recommended SABS of 3.0 µg/g (South Africa, 1994). The values are higher than Cd values for mussels that were indicative of contamination (3.7 µg/g) set by Cantillo (1998). The levels for Cd were also higher than the 2.48 µg/g recorded by Henry et al. (1986) for Table Bay (sites 3–5). Cadmium occurs at high levels in the environment due to anthropogenic sources (Chiffoleau et al., 2001). Cadmium reactions cause various geochemical processes such as the solubilization of Cd on freshwater particles when these reach sea water. As a result, Cd becomes available to molluscs living close to fresh water sources (Chiffoleau et al., 2001). This phenomenon could account for the higher levels of Cd at sites 2–5 as there are potential freshwater inputs such as river mouths and stormwater pipes, although a study on metal concentrations from Diep River (freshwater input into Milnerton) showed low Cd concentrations in both water and sediment (Shuping, 2008). This cannot, however, explain the high values in site 1. The postulated reason for high Cd values at site 1 could be due to site 1 being a combination of two stations, where the mean Cd concentration in Noordhoek was 7.7 µg/g and in Oli-fantsbos was 6.0 µg/g. Noordhoek is a coastal area that could have substantial input of freshwater due to high levels of urbanisation. An alternative explanation is that the sources of Cd were not from anthropogenic sources but from upwelled waters (Reyes, 1995). The shelf edge along the west coast of the Cape Peninsula is narrow and at the southern end of the Benguela upwelling system (Shannon, 1985). Whether the Cd was from anthropogenic or natural sources needs further investigation.

Of the sites sampled, Cd concentrations were the highest at sites 3 (7.0 µg/g) and 5 (7.5 µg/g). Both these sites are at the shoreward end of open coasts and could hence have been influenced by Cd from up-current and stormwater outflow pipe anthropogenic sources. According to Chiffoleau et al. (2001), Cd levels in organisms could be related to domestic and industrial effluents. Sites 3 and 5 are in close proximity to both domestic and industrial sources of effluents that could be a source of Cd at those sites.

Copper is an essential element in mussels as it forms part of blood proteins (Phillips, 1977). There was a significant difference in Cu concentrations between years as well between different sites. Similar results were reported by Adler-Ivanbrook and Breslin (1999), where metal concentrations differed between sites and over time. According to Cantillo (1998), the reproductive process requires high levels of Cu in the tissue to facilitate effective reproduction. Copper concentrations were low for all sites (Table 2) and there were significant differences ($p < 0.05$) between seasonal Cu concentrations for all sites combined (Fig. 3a). The mean levels of Cu recorded for the entire study area (5.6 µg/g) were below the maximum limits allowed in foodstuff as set by the SABS of 50 µg/g (South Africa, 1994). According to Cantillo (1998), Cu concentrations above 10 µg/g in marine mussels are indicative of contamination. The results therefore suggest that the Cape Peninsula is not contaminated with Cu in the coastal environment. The tissue values are similar to those recorded by Mdzeke (2004) for False Bay where 5 µg/g at Kleinmond was recorded for the period winter 2000 to winter 2001. The data of the MWP were, however, higher than that recorded by Henry et al. (1986) for Table Bay (2.5 µg/g).

High levels of Pb are found in the tissue of shellfish that occur near sewer outfalls, heavy traffic, industrialized or densely populated urban areas (Pergram and Görgens, 2001). The mean Pb levels recorded along the west coast of the Cape Peninsula (5.1 µg/g)

were above the maximum limits allowed in foodstuff as set by the SABS of 4.9 µg/g (South Africa, 1994). According to Cantillo (1998), Pb concentrations above 3.2 µg/g are indicative of contamination. Values higher than 3.2 µg/g were recorded at sites 2 (4.6 µg/g), 3 (7.3 µg/g), 4 (5.6 µg/g) and 5 (4.4 µg/g). Site 2 represents Hout Bay and sites 3, 4 and 5 are in the northern part of the study area and represent Table Bay. Table Bay has a major port (and Hout Bay to a lesser extent) and is highly urbanised. The high level of Pb prior to 2000 could therefore be indicative of Pb in motor fuel and hence the runoff from vehicle emissions. This postulation is supported by other studies of lead levels in the environment where Henry et al. (1986) recorded Pb levels of 28.8 and 14.3 µg/g in Granger Bay (close to site 3) and the Black River mouth (close to site 4), respectively. The levels of Pb in mussels of the MWP decreased after 2000 (Fig. 2e). According to Yan et al. (1997), mussels are not able to regulate the levels of Pb and, as a result, Pb tends to accumulate in mussel tissue and may reach very high concentrations when ambient Pb concentrations are high. This provides evidence of using mussels as biomonitors of metal concentrations, given that they are able to accumulate the metals in their tissue.

Manganese is an element found in all animal tissue and is required as an enzyme cofactor or activator of a number of metabolic reactions (Cotzias, 1958). Although the metal is important in trace amounts, exposure to high concentrations could result in accumulation to toxic levels in tissue. There are no tissue standards in South Africa for maximum concentrations for MWP data for Mn. The data collected for this study (4.2 µg/g) was, however, much lower than other studies on Mn accumulation in mussels collected in Europe (Regoli and Orlando, 1994; Swann et al., 1998) and therefore it is concluded that Mn has probably not bioaccumulated in *M. galloprovincialis* in the Western Cape to levels that would be toxic to these animals.

Mercury measurements in mussels were only done until 1995. The mean Hg levels recorded along the west coast of the Cape Peninsula (0.05 µg/g) was below the maximum limits allowed in foodstuff set by the SABS of 1.0 µg/g (South Africa, 1994). Cantillo (1998) noted that Hg concentrations above 0.2 µg/g were indicative of contamination. However, none of the sites recorded Hg values higher than either of these guideline values.

Multivariate analysis (MANOVA) of the MWP data along the west coast of the Cape Peninsula revealed significant effects of year and site including the interaction between year and site (Supplementary data Table 4) for all the metals analysed except for the effect of site on Fe and Mn. This suggests that both temporal and spatial effects can influence the level of metals in mussels. This needs to be taken into consideration when implementing a bio-monitoring system and careful consideration needs to be taken in site selection and timing (periodicity and frequency) of data collection.

Metal concentrations in mussels have been measured in *M. galloprovincialis* since 1985 as part of the MWP. The monitoring programme is important as it provides some indication of bioavailable metals in the coastal environment.

In summary, this study focussed on metal concentrations in mussels along the western coastline of the Cape Peninsula and the results have indicated that the levels of metals have been highly variable within the mussels over the study period. The results indicated that metal concentrations in *M. galloprovincialis* did not increase over the study period and that for some metals, the level of metals decreased. The significant differences between years and seasons suggest that the MWP is providing useful information about the levels of metals in the tissue of the organisms. However, the sources of the high levels of contaminants need further investigation. Furthermore, other potential toxicants could also be affecting the organisms and it is proposed here that the

MWP considers broadening the scope of contaminants (e.g. PAH) as these might be having considerable impact on the health of the coastal marine ecosystem, in addition to the impact of metals.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.marpolbul.2014.07.047>.

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