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ORIGINAL PAPER

The impact of urban pollution on the metal contamination of the Zandvlei estuary, Cape Town, South Africa

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Abstract

Metal contamination of aquatic systems is a global concern, negatively impacting ecosystems and human health. However, limited information is available on metal concentration levels in South African estuaries, including the Zandvlei estuary in Cape Town, a highly urbanised system with an extensive stormwater drainage network. The objective of this study was to determine spatial and temporal variations of metal concentrations (aluminium, zinc, lead, and copper) in water, sediment, and macroalgae (i.e. *Enteromorpha* spp.) in the Zandvlei estuary. Samples were collected from five sites over four seasons in 2017 and analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), with metal levels were compared to water and sediment quality guidelines. Results revealed significant spatial and temporal variations, influenced by the proximity to pollution sources, physicochemical parameters, river inputs, sediment characteristics, weather conditions, and anthropogenic activities (i.e. industrial activities and urban development). In water samples, metals were most concentrated in the order Al > Zn > Cu > Pb; in sediment and macroalgae, the order was Al > Zn > Pb > Cu. Notably, *Enteromorpha* spp. accumulated higher metal concentrations than water and sediments, and some metal levels exceeded guideline thresholds, indicating contamination risks. These findings highlight the importance of *Enteromorpha spp*. as a biomonitoring tool for metal pollution in urban estuarine environments. This study addresses significant knowledge gaps in South African estuaries, supporting enhanced environmental monitoring and conservation strategies.

Keywords Biomonitoring · Enteromorpha · Estuarine pollution · Macroalgae · Water quality

Introduction

The Zandvlei estuary is a prime example of an estuarine system in the Cape Town Metropole that has been severely affected by urbanisation, industrialisation and population growth. This is evident from the water quality testing results that have been published in various reports by the City of Cape Town over the years and which have led to periodic closures of the estuary for public access. Land uses within the Zandvlei catchment ranges from industry to housing, agriculture and conservation (C.A.P.E., 2010). The estuary supports a variety of recreational activities, including sailing, windsurfing, canoeing and fishing (CoCT 2022). The estuary comprises of an extensive stormwater drainage network which discharges directly into the estuary (WCG 2018). An industrial area located approximately 2 kilometres (km) upstream is adjacent to the Keyser's River, which discharges just downstream into the Zandvlei estuary. Additionally, the estuary is subject to dredging, which occurs occasionally in order to remove large amounts of sediment deposits. This is done in order to improve water circulation and reduce the risk of flooding. Dredging and the manipulation of the estuary mouth are also likely to affect the circulation of water and mobilisation of contaminants. Seasonal environmental conditions such as rainfall, estuarine circulation, river and groundwater discharge, water flow velocities, sediment input and resuspension, as well as physicochemical parameters (i.e. pH, salinity) of the estuary may potentially exacerbate metal pollution within this system, particularly

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since these conditions affect the transportation and fate of metals (De Souza Machado et al. 2016). Human activities such as urban development, industrial activities, dredging and the manipulation of estuary mouth are responsible for the extensive modification of the Zandvlei estuary. These activities have the potential to introduce toxic and persistent contaminants such as metals, which may significantly alter water quality and potentially threaten both aquatic and human life (Wright and Mason 1999).

Unlike most organic contaminants, metals may not necessarily be eliminated from aquatic systems as they do not undergo environmental degradation or other natural processes which may reduce their toxicity or concentration (Tabudravu et al. 2002; Phillips et al. 2015). Metals enter estuaries from both influent rivers and from direct discharges (i.e. stormwater discharge). Once metals are introduced into surface waters, they rapidly become associated with particulates and are found in bottom sediments (Hanson et al. 1993; Wright and Mason 1999; Phillips et al. 2015; CSIR 2015). This results in estuaries being the largest sinks of pollutants as sediments are ultimately transferred to the coastal environment (Szefer et al. 1995; Ryan et al. 2012). Metals are a significant concern, especially with the backdrop of global climate change. Predicted shifts in pH, temperature and oxygen levels may potentially modify their behaviour and release into the environment (Schiedek et al. 2007; Adams et al. 2020). Metals also accumulate in different organisms and move through the different trophic levels of a food chain through bioaccumulation and biomagnification which ultimately affects human beings (Chakraborty et al. 2014; Billah et al. 2017). In light of the above, biological monitoring and analysis of metal concentrations in the Zandvlei estuary is therefore necessary to identify the potential vulnerability of this aquatic ecosystem to pollution as well as to prepare baseline information for monitoring and necessary future management actions.

Macroalgae are found to be reliable indicators of metal contamination because of their ability to accumulate metals (Vlachos et al. 1998). They are described as being sessile and can be used to monitor changes in metal levels over time. Their size makes them readily identifiable, and they are easily handled (Vlachos et al. 1998). Other studies indicate that macroalgae are used as bio-indicators because of their distribution, longevity, and presence at polluted sites. A report by Bryan (1969) indicated that the binding of metals by macroalgae are strong, with only a minimal exchange between bound metals and ambient water. Green algae species such as *Enteromorpha* spp. (Chlorophyceae) are commonly found in cold temperate to tropical waters, including estuaries and oceanic waters (Dawes 1998). Say et al. (1990) also noted that *Enteromorpha* spp. are one of the most commonly found algae in estuaries and are widely distributed in many coastal regions. In South Africa, there are three *Enteromorpha* spp. that were recorded in freshwaters, namely: *E. basiramosa*; *E. gracillima and E. intestinalis* (Joska and Bolton 1993). *Enteromorpha intestinalis* is most commonly found in estuarine and marine environments where large growths are recorded in estuarine systems with high nutrient levels such as the Zandvlei estuary (Joska and Bolton 1993). Their occurrence in aquatic systems is influenced by physical and chemical properties (i.e. salinity, pH, temperature) of environment as they usually occur in areas of relatively higher salinities, alkaline ($pH > 7$) and slow moving waters (Bryan et al. 1985; Joska and Bolton 1993). As algae are widespread, they have been used to measure metal contamination in many parts of the world (Melville and Pulkownik 2006). Observations by Munda (1984) discovered that the *Enteromorpha* spp. absorbed more Zn, Mn and Co at low salinity compared to high salinity. Furthermore, several studies have shown that the levels of Co, Fe, Cd, Mn, Cu and Zn in *Enteromorpha* spp. increased due to increasing water levels as they reduced salinity concentrations (Bryan et al. 1985). One of the advantages of using *Enteromorpha* spp., as reported by Bryan et al. (1985), is their ability to reflect changes in ambient metal levels more rapidly when compared to some other species.

There is very limited information available in South Africa on the use of macroalgae as a biological indicator of metal contamination (Vlachos et al. 1998). In addition, there is little information available in South Africa on the effects of metal pollutants on estuaries (Nel et al. 2015; Adams et al. 2020). The Zandvlei estuary is a highly urbanised system which is fed by three rivers, an extensive stormwater drainage network and which is also located near a residential as well as an industrial area. Therefore, the objectives of this study were to assess spatial and seasonal variations of metals (Al, Zn, Pb, and Cu) in water, sediment and algae samples collected from the Zandvlei estuary in order to understand the levels and patterns of metal concentrations within the system. Furthermore, metal concentrations recorded in this study was also compared with national and international environmental quality guidelines. Another key objective was to assess the effectiveness of *Enteromorpha* spp. as a bioindicator for monitoring metal pollution in estuarine environments, focusing on metal accumulation patterns in the algae compared to surrounding sediments and water. This study was conducted in Cape Town, South Africa, in 2017.

Materials and methods

Study area

Zandvlei is a long, shallow coastal estuarine lake situated on the north-western shore of False Bay (34°05′ S; 18°28′ E) (Fig. 1) about 20 kms south of the Cape Town

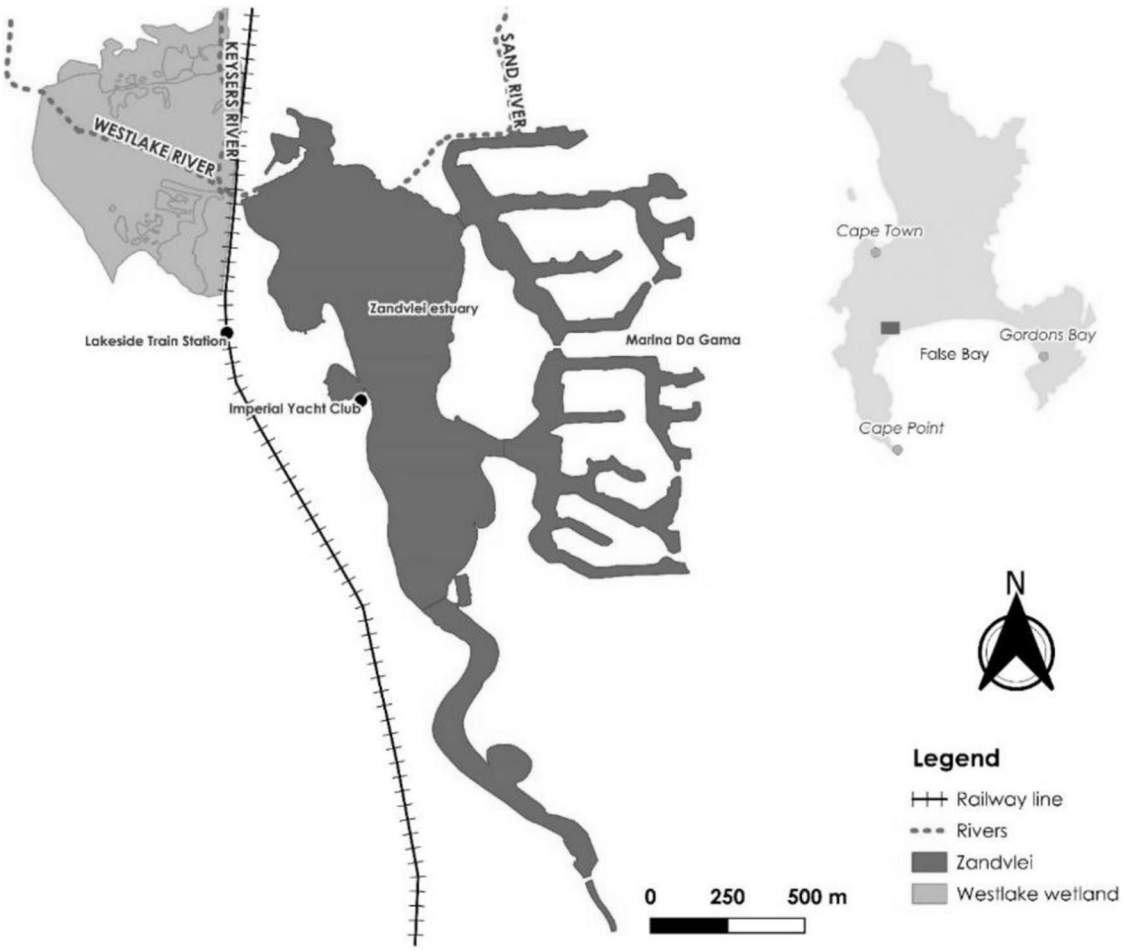

Fig. 1 Map of the Zandvlei estuary and its influent rivers, namely: Westlake, Keysers, and Sand River. The location of the study area is shown with a red rectangle on the City of Cape Town map (green map on the right-hand side) (*Source*: QGIS, Sidondi, L)

central business district (Harding 1994; McQuaid 2013). The estuarine lake forms part of the estuaries located in the Cape Floristic Region and it falls within the cool-temperate biogeographic region in South Africa (Quick and Harding 1994; WCG 2018). The Zandvlei estuary has a sporadic tidal connection to the sea and is classified as a temporarily open/closed estuary (Whitfield and Baliwe 2013). It is also the largest of the eight estuaries situated along the False Bay coast, as it covers about 155 hectares which makes up approximately 80% of the estuarine area in False Bay (Brown and Magoba 2009; McQuaid 2013). Zandvlei is divided into three components (Morant and Grindley 1982; Brown and Magoba 2009), namely: a) the Marina Da Gama (residential area) with a water surface area (WSA) of approximately 32.6 hectares, b) the main vlei (the lake itself) (WSA of approximately 57 hectares), and c) the Westlake wetlands (WSA of approximately 31 hectares). The Zandvlei catchment comprising an area of 9,655 ha is drained by several rivers and streams which include the Little Princess Vlei Stream, Westlake Stream, the Sand River, Diep River, Keyser's Rivers, and Langevlei Canal (C.A.P.E., 2010).

Sample collection

The five sampling sites were located along the western boundary of the estuary (Fig. 2). These sites were located within intervals ranging between 400 and 600 m and were chosen based on access and the ability to easily obtain representative samples. Sites 1 and 2 were located within the upper reaches of the estuary. Sites 3 and 4 were within the middle to lower reaches of the estuary, and site 5 was located near the estuary mouth. Samples (water, sediment and algae) were collected from the five sampling sites using plastic containers. Five replicates were collected for each sample. Surface (0–10 cm) water samples were collected, while sediment samples were collected at a depth of approximately 0–15 cm. Algae samples (*Enteromorpha* spp.) were collected manually. Samples were immediately stored in an icebox for transportation to the laboratory and stored

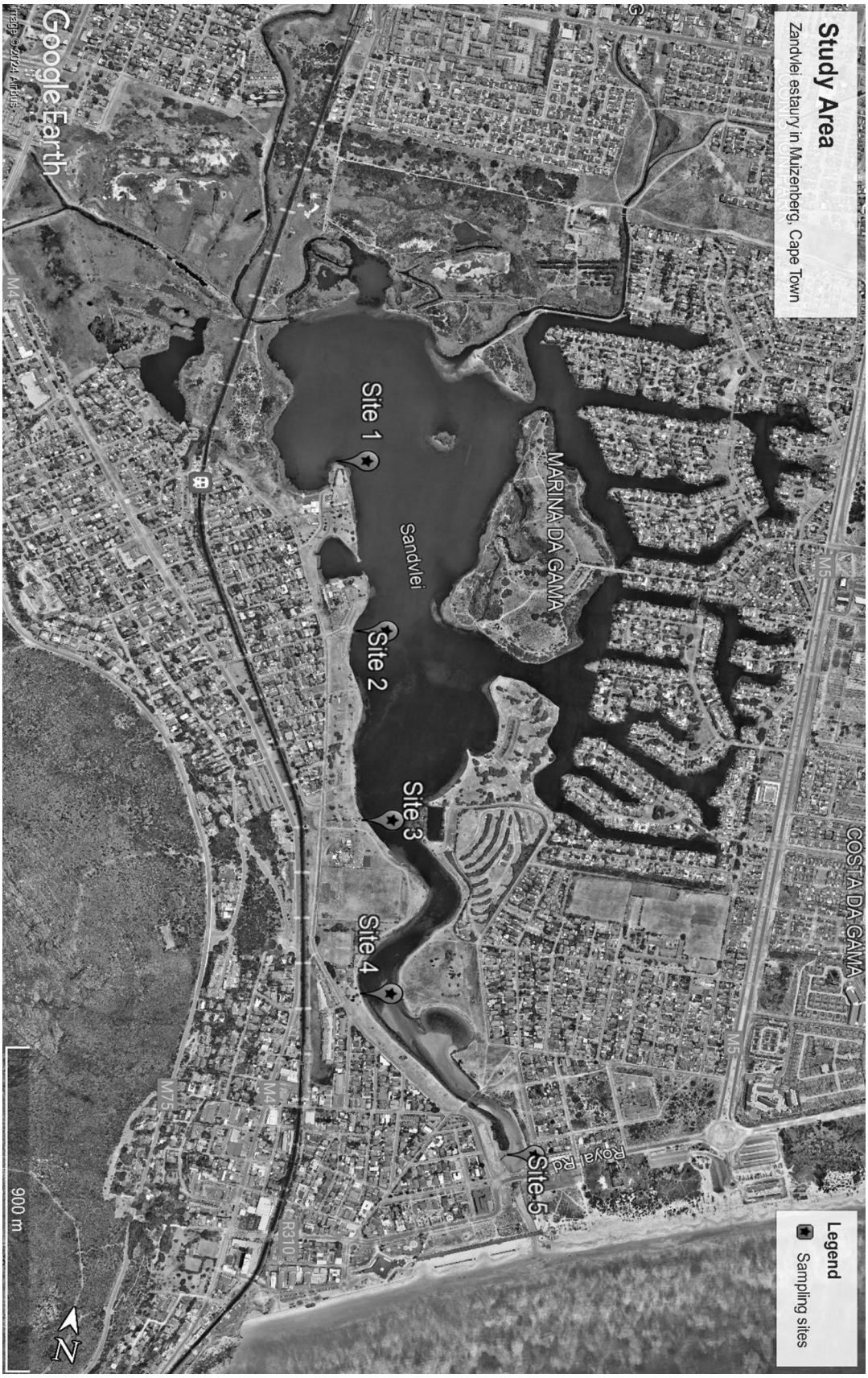

Fig. 2 An aerial view of the sampling sites within the study area (*Source*: Google Earth, 2024)

at – 18 °C for further analysis. Sampling was conducted during wet and dry seasons on four sampling occasions in 2017 [SO1 (January—dry summer); SO2, (April—autumn); SO3, (August—rainy winter); SO4, (November—spring)] to evaluate variation in metal concentrations of environmental samples. A total of 75 samples were collected during each sampling occasion.

Environmental parameters

Selected physical and chemical parameters were measured at each sampling site on each sampling occasion. The physicochemical parameters that were measured included temperature (°C), pH, dissolved oxygen (mg/L), electrical conductivity (µS/cm) and salinity (ppt). These were measured with a YSI ProDDS multi-parameter instrument. The equipment was checked and calibrated according to the manufacturers' specifications. Rainfall data measured in mm was obtained from the South African Weather Services for the sampling period. The recorded monthly average rainfall ranged from 0.3 to 93.1 mm within a 12-month sampling period. The rainfall data for the study area was obtained from the closest weather station, the Rondevlei Nature Reserve station. The estuary mouth opening and closing periods was obtained from the City of Cape Town. It is important to note that due to technical issues, no physicochemical parameters data is available for Sampling Occasion 3.

Acid digestion and metal analysis

Water samples (10 mℓ) were digested with 5 mℓ of 65% nitric acid at 40 °C for 60 min and then at 120 °C for 180 min, using a Grant UBD heating block. Sediment and algae samples were oven dried at 60 °C for 48–72 h. A subsample with an exact mass measured between 0.2 and 0.3 g of the sediment and algae samples was digested in 10 mℓ 65% nitric acid at 40 °C for 60 min and then at 120 °C for 180 min. An acid blank of 10 mℓ of 65% nitric acid was analysed along with all the collected samples to check for possible contamination. After cooling to room temperature, the water, sediment and algae samples were first filtered using Whatman No. 6 (90 mm) filter paper, followed by a second filtration with 0.45 µm cellulose nitrate ultrafiltration membrane filters (Millipore). Metal analyses was carried out using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Metal concentrations in water samples were expressed in mg/L, while those for sediment and algae samples were expressed in mg/kg.

Statistical analysis

The results in this study are averages (±SD) of five replicates from each sampling site. Statistical analysis was conducted using the SigmaPlot (version 14.0) software by SYSTAT Software Inc. Statistical differences between the different sampling sites and sampling occasions for the subject metals were analysed and evaluated using the Kruskal–Wallis, also known as One-Way Analysis of Variance (ANOVA) on Ranks and Student Newman Kuels Method for post hoc tests. In cases where there were missing or unequal datasets, the Dunns Method was utilised for post hoc tests. The condition for the significant differences was set at $p < 0.05$ for all statistical analysis undertaken for this study.

Results and discussion

Physicochemical parameters

The physicochemical parameters measured for each sampling site included temperature, pH, dissolved oxygen, electrical conductivity and salinity. No data is available for SO3 due to technical problems. The recorded temperature during the different occasions ranged from 21.1 to 24.4 °C. As expected, salinity was higher near the estuary mouth and lower upstream near the influent rivers, ranging from 12.01 to 25.45 ppt. The recorded pH was higher upstream and lower near the estuary mouth, ranging from 4.97 to 9.42. Similar to pH, dissolved oxygen was also higher upstream and lower downstream (near the estuary mouth), ranging from 2.42 to 18.51 mg/L (Table 1).

Aluminium

Comparisons of spatial variations in Al concentrations (mg/ℓ) in water showed statistical differences ($p < 0.05$) between sites 2 and 3, and sites 4 and 5 on SO2, as well as between sites 3 and 4 on SO3. The highest mean Al concentration (mg/ℓ) in water was recorded at site 3 (2.0438 ± 2.7055) (SO2) (Table 2). Seasonal variations in Al concentrations in water revealed statistical differences in Al concentrations recorded between SO1 (summer) and SO2 (autumn) on sites 3 and 4. Mean Al concentrations recorded in sediment (mg/kg) showed significant ($p < 0.05$) fluctuations between site 2 and site 5 on SO1. Site 4 (SO2) recorded the highest mean Al concentration (1562.04 ± 923.63) in sediment. Significant differences in Al concentrations were found for algae between the different sampling sites (except site 1) on SO1 (Table 2).

Zinc

The results showed significant differences in Zn concentrations (mg/ℓ) in water recorded between sites 1 and 2 on SO2. The highest mean Zn concentration (1.1085 ± 0.4763) in water was recorded at site 1 (SO2) (Table 3). Pairwise

Table 1 Physicochemical parameters recorded for each sampling site during the different sampling occasions (SO)

	Site 1	Site 2	Site 3	Site 4	Site 5
SO1					
Dissolved oxygen (mg/L)	5.8	5.48	5.42	4.5	3.71
Temperature (°C)	24.4	23.3	23.4	22.9	23.2
Electrical Conductivity (µS/cm)	24,608	24,765	25,943	30,107	34,678
Salinity (ppt)	15.15	15.63	16.30	19.75	22.67
pH	8.63	8.43	8.01	7.97	7.28
SO2					
Dissolved oxygen (mg/L)	13.84	11.2	6.1	4.97	2.42
Temperature (°C)	23.2	22.7	22.6	21.8	21.1
Electrical Conductivity (µS/cm)	28,812	30,135	31,789	32,803	36,885
Salinity (ppt)	18.65	19.68	20.85	22.3	25.45
pH	8.81	8.63	8.02	4.97	6.8
SO4					
Dissolved oxygen (mg/L)	18.51	14.77	9.91	8.63	6.44
Temperature (°C)	22.0	23.0	23.6	21.6	22.6
Electrical Conductivity (µS/cm)	13,546.50	22,005	22,369	21,671	22,961
Salinity (ppt)	12.46	13.80	12.01	14.05	14.60
pH	9.42	9.23	8.73	8.54	8.14

multiple consecutive comparisons of the different sampling sites showed statistical differences ($p < 0.05$) in Zn concentrations recorded in sediment between sites 1 and 2 on SO1. The highest Zn concentration (5834.36 ± 3788.34) in sediment was recorded at site 2 (SO1) (Table 3). Mean Zn concentrations recorded in algae (mg/kg) showed significant ($p < 0.05$) fluctuations between sites 2 and 3, sites 3 and 4 as well as sites 4 and 5 on SO1. Site 5 (SO1) recorded the highest mean Zn concentration (86.95 ± 186.73) in algae.

Lead

The results showed significant differences ($p < 0.05$) in Pb concentrations (mg/ℓ) recorded between sites 3 and 4 on SO3 in the water samples (Table 4). The highest Pb concentration (0.0261 ± 0.0346) in water was recorded at site 1 (SO1). The results also showed a significant increase in Pb concentrations ($p < 0.05$) in sediment (mg/kg) between sites 1 and 2 on both SO1 and SO2. The highest Pb concentration (37.37 ± 34.62) in sediment was recorded at site 5 (SO4) (Table 4). The results showed significant differences ($p < 0.05$) in Pb concentrations recorded in algae between sites 2 and 3, sites 3 and 4 as well as sites 4 and 5 on SO1. The highest Pb concentration in algae was recorded at site 2 on SO4 (Table 4).

Copper

The results showed no significant differences ($p > 0.05$) in Cu concentrations recorded in water (mg/ℓ) between the different sites on each occasion. However, significant differences were recorded in some of the sampling occasions (from water samples) between the different sampling sites (except for sites 2 and 3) (Table 5). The highest Cu concentration (101.71 ± 211.04) in sediment was recorded at site 1 (SO2). Significant differences ($p < 0.05$) in Cu concentrations in sediment were recorded between sites 1 and 2 on both SO1 and SO4 (Table 5). The results showed statistical differences ($p < 0.05$) between Cu concentrations recorded in algae between sites 1 and 2 as well as sites 3 and 4 on SO2 (Table 5). No significant differences in mean Cu concentrations in algae were recorded between the different sampling sites on SO1, SO3 and SO4 (Table 5).

Discussion

Water

Mean Al concentrations (mg/ℓ) ranged from 0.0000 ± 0.0000 (undected) to 2.0438 ± 2.7055 (Table 2). Spatial variations in Al concentrations revealed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between sites 2 (0.0135 ± 0.0195) and 3 (0.3563 ± 0.2080) as well as sites 4 (0.3938 ± 0.1779) and 5 (0.0309 ± 0.0305) for SO2 (autumn) (Table 2). The increase in Al concentrations ($p < 0.05$) recorded between sites 2 (0.0135 ± 0.0195) and 3 (0.3563 ± 0.2080) for SO2 (autumn) may be due to land-based discharges or urban run-off, particularly since there is a stormwater drainage outlet located close to site 3. Other factors that may have also influenced the recorded Al concentrations include

Table 2 Mean concentrations (±SD) of aluminium on different sampling occasions at five sampling sites

Aluminium	Sampling occasions (SO)			
	SO1 (Summer)	SO2 (Autumn)	SO3 (Winter)	SO4 (Spring)
Water (mg/ℓ)				
Site 1	$^{a}0.0464^{a}$ (±0.0911)	$^{a}0.0228^{a}$ (±0.0511)	$^{a}0.2076^{a}$ (±0.2681)	ND
Site 2	$^{a}0.0325^{a}$ (±0.0726)	$^{a}0.0135^{a}$ (±0.0195)	$^{a}0.2431^{a}$ (±0.2430)	ND
Site 3	$^{a}0.0019^{a}$ (±0.0042)	$^{b}0.3563^{b}$ (±0.2080)	$^{a}0.0788^{c}$ (±0.1179)	ND
Site 4	$^{a}0.0000^{a}$ (±0.0000)	$^{b}0.3938^{b}$ (±0.1779)	$^{b}2.0438^{b}$ (±2.7055)	ND
Site 5	$^{a}0.0000^{a}$ (±0.0000)	$^{c}0.0309^{a}$ (±0.0305)	$^{b}0.0199^{a}$ (±0.0232)	ND
Sediment (mg/kg)				
Site 1	$^{a}986.86^{a}$ (±181.56)	$^{a}1448.81^{b}$ (±246.13)	$^{a}1128.81^{c}$ (±190.29)	$^{a}794.28^{d}$ (±121.12)
Site 2	$^{a}1229.91^{a}$ (±247.36)	$^{a}1399.36^{a}$ (±406.64)	$^{a}1242.21^{a}$ (+297.10)	$^{a}948.86^{a}$ (±106.18)
Site 3	$^{b}606.17^{a}$ (±226.72)	$^{a}901.26^{a}$ (±279.44)	$^{a}979.04^{a}$ (±309.31)	$^{a}1062.32^{a}$ (±156.22)
Site 4	$^{c}923.95^{a}$ (±191.91)	$^{a}1562.04^{a}$ (±923.63)	$^{a}1357.36^{a}$ (±723.22)	$^{b}189.36^{b}$ (±26.21)
Site 5	$^{d}250.55^{a}$ (±66.75)	$^{b}452.96^{b}$ (±88.83)	$^{b}466.32^{b}$ (±48.42)	$^{c}301.32^{c}$ (±40.10)
Algae (mg/kg)				
Site 1	$^{a}1587.81^{a}$ (±960.79)	$^{a}1525.49^{a}$ (±438.18)	$^{a}307.782^{b}$ (±127.12)	$^{a}596.46^{b}$ (±335.08)
Site 2	$^{a}1310.95^{a}$ (±639.94)	$^{a}497.88^{b}$ (±27.88)	$^{a}266.91^{c}$ (±31.08)	$^{a}325.13^{c}$ (±119.27)
Site 3	$^{b}3688.73^{a}$ (±818.35)	$^{a}1302.49^{b}$ (±539.51)	$^{a}999.43^{b}$ (±454.50)	$^{a}713.15^{b}$ (±209.80)
Site 4	$^{c}60.24^{a}$ (±44.13)	$^{b}2662.61^{b}$ (±859.27)	$^{a}2220.69^{b}$ (±1778.35)	$^{a}3548.74^{b}$ (±922.99)
Site 5	$^{d}4517.35^{a}$ (±9620.77)	$^{c}915.03^{a}$ (±879.69)	$^{a}1937.46^{a}$ (±3401.13)	ND

The statistical differences between sites per sampling occasion are indicated by superscripted letters to the left of mean values. The statistical differences between sampling occasions per site are indicated by superscripted letters to the right of mean values. Water, sediment and algae samples were not statistically compared with each other

ND No Data

the gradient of the estuary, the closing and opening of the estuary mouth, and physicochemical parameters. The relatively deeper channels could potentially prevent the movement of metals as water circulation becomes slow or even stagnant, and this could be a reason for elevated concentrations in the central and upper parts of the estuary. The estuary mouth was also closed during SO2 (autumn), and this could have contributed to stagnant waters within the system. According to Sany et al. (2013) elevated metal concentrations in the water column may be linked to an increase in salinity and decrease in pH and redox potential. Toxic effects of Al are usually found over the pH range of 4.4–5.4 with maximum toxicity occurring around pH 5.0–5.2 (DWAF 1996; ANZECC 2000). Salinity concentrations recorded for the study area increased from 19.68 ppt (site 2) to 25.45 ppt (site 5), while the pH decreased from 8.63 (site 2) to 6.8 (site 5) on SO2 (autumn) (Table 1). The increase in salinity and Al concentrations appears to be in line with the findings by Sany et al. (2013). Aluminium is commonly introduced into the environment through industrial processes or product production (i.e., cosmetics, chemicals, etc.), domestic run-off, or agricultural activities (Erasmus 2004). Aluminium is one of the most abundant metallic elements and constitutes about 8% of Earth's crust (WHO 1997). The source of metals in urban run-off is mainly from industries, buildings,

Table 3 Mean concentrations (±SD) of zinc on different sampling occasions at five sampling sites

Zinc	Sampling Occasions (SO)			
	SO1 (Summer)	SO2 (Autumn)	SO3 (Winter)	SO4 (Spring)
Water (mg/ℓ)				
Site 1	^{a}0.1818^{a} (±0.1511)	^{a}1.1085^{b} (±0.4763)	^{a}0.1066^{c} (±0.1341)	ND
Site 2	^{a}0.0801^{a} (±0.0333)	^{b}0.2112^{a} (±0.1610)	^{a}0.0239^{b} (±0.0418)	ND
Site 3	^{a}0.1560^{a} (±0.0676)	^{b}0.1257^{a} (±0.1171)	^{a}0.0388^{a} (±0.0856)	ND
Site 4	^{a}0.1306^{a} (±0.0462)	^{b}0.1015^{a} (±0.0600)	^{a}0.1478^{a} (±0.2620)	ND
Site 5	^{a}0.2026^{a} (±0.0444)	^{b}0.2114^{a} (±0.1391)	^{b}0.4677^{a} (±0.2867)	ND
Sediment (mg/kg)				
Site 1	^{a}1040.01^{a} (±275.52)	^{a}22.70^{b} (±4.01)	^{a}75.74^{b} (±54.61)	^{a}25.77^{b} (±21.19)
Site 2	^{b}5834.36^{a} (±3788.34)	^{a}26.97^{b} (±8.51)	^{a}40.05^{b} (±13.64)	^{a}5.94^{c} (±2.89)
Site 3	^{b}513.45^{a} (±268.67)	^{b}7.03^{a} (±4.17)	^{b}15.55^{a} (±11.80)	^{a}5.90^{a} (±5.59)
Site 4	^{b}1000.95^{a} (±422.36)	^{b}8.40^{b} (±4.89)	^{b}12.50^{b} (±3.75)	^{a}5.87^{b} (±9.16)
Site 5	^{b}400.39^{a} (±106.80)	^{b}7.07^{a} (±9.87)	^{c}14.34^{a} (±6.37)	^{a}37.37^{a} (±34.62)
Algae (mg/kg)				
Site 1	^{a}31.65^{a} (±18.24)	^{a}33.48^{a} (±7.76)	^{a}28.14^{a} (±6.36)	^{a}31.35^{a} (±13.26)
Site 2	^{a}20.08^{a} (±5.61)	^{b}34.33^{a} (±54.20)	^{a}27.10^{a} (±11.47)	^{a}48.31^{a} (±19.89)
Site 3	^{b}52.16^{a} (±12.87)	^{c}6.93^{b} (±3.80)	^{b}15.79^{c} (±6.50)	^{a}26.09^{d} (±9.13)
Site 4	^{c}0.68^{a} (±0.95)	^{c}31.19^{b} (±12.49)	^{b}60.89^{c} (±6.22)	^{a}38.22^{d} (±16.01)
Site 5	^{d}86.95^{a} (±186.73)	^{d}11.32^{a} (±7.90)	^{b}47.11^{a} (±52.71)	ND

The statistical differences between sites per sampling occasion are indicated by superscripted letters to the left of mean values

The statistical differences between sampling occasions per site are indicated by superscripted letters to the right of mean values. Water, sediment and algae samples were not statistically compared with each other

ND No Data

Table 4 Mean concentrations (±SD) of lead on different sampling occasions at five sampling sites

Lead	Sampling occasions (SO)			
	SO1 (Summer)	SO2 (Autumn)	SO3 (Winter)	SO4 (Spring)
Water (mg/ℓ)				
Site 1	^{a}0.0261^{a} (±0.0346)	^{a}0.0229^{a} (±0.0258)	^{a}0.0015^{b} (±0.0015)	ND
Site 2	^{a}0.0092^{a} (±0.0044)	^{a}0.0043^{a} (±0.0031)	^{a}0.0031^{a} (±0.0032)	ND
Site 3	^{a}0.0139^{a} (±0.0089)	^{a}0.0033^{b} (±0.0025)	^{a}0.0000^{c} (±0.0000)	ND
Site 4	^{a}0.0100^{a} (±0.0050)	^{a}0.0034^{a} (±0.0040)	^{b}0.0120^{a} (±0.0158)	ND
Site 5	^{a}0.0257^{a} (±0.0165)	^{a}0.0047^{b} (±0.0068)	^{b}0.0013^{b} (±0.0009)	ND
Sediment (mg/kg)				
Site 1	^{a}5.46^{a} (±1.85)	^{a}5.42^{a} (±3.08)	^{a}12.92^{a} (±18.11)	^{a}25.77^{b} (±21.19)
Site 2	^{b}29.89^{a} (±14.99)	^{b}32.03^{b} (±32.65)	^{a}9.92^{c} (±3.27)	^{b}5.94^{d} (±2.89)
Site 3	^{c}2.90^{a} (±0.78)	^{b}2.40^{a} (±1.07)	^{b}3.84^{a} (±3.08)	^{b}5.90^{a} (±5.59)
Site 4	^{c}2.69^{a} (±0.42)	^{c}3.74^{b} (±0.89)	^{c}5.81^{c} (±2.77)	^{c}5.87^{d} (±9.16)
Site 5	^{c}3.19^{a} (±0.94)	^{d}1.24^{a} (±0.19)	^{d}2.35^{b} (±0.23)	^{d}37.37^{c} (±34.62)
Algae (mg/kg)				
Site 1	^{a}8.42^{a} (±2.95)	^{a}8.75^{b} (±3.08)	^{a}1.74^{b} (±0.79)	^{a}31.35^{b} (±13.26)
Site 2	^{a}8.94^{a} (±2.54)	^{a}3.95^{b} (±0.53)	^{a}2.22^{c} (±0.50)	^{a}48.31^{c} (±19.89)
Site 3	^{b}14.89^{a} (±2.34)	^{a}5.59^{b} (±2.89)	^{a}3.03^{c} (±1.13)	^{a}26.09^{d} (±9.13)
Site 4	^{c}2.05^{a} (±0.40)	^{a}12.32^{b} (±1.78)	^{a}8.15^{c} (±4.36)	^{a}38.22^{c} (±16.01)
Site 5	^{d}6.35^{a} (±4.43)	^{a}4.19^{b} (±1.27)	^{a}4.36^{b} (±0.47)	ND

The statistical differences between sites per sampling occasion are indicated by superscripted letters to the left of mean values

The statistical differences between sampling occasions per site are indicated by superscripted letters to the right of mean values. Water, sediment and algae samples were not statistically compared with each other

ND No Data

vehicle parts and components, fuel and oils, roofs with metallic elements, and other metal-containing structures (Brown and Peake 2006; Barbosa et al. 2012; Sakson et al. 2018). The study area is characterized by an extensive stormwater drainage network, consisting of stormwater drains that discharge directly into the estuary, some of which discharge into the three rivers that feed directly into the estuary (C.A.P.E., 2010). An industrial area is located approximately 2 km north of the estuary. This area is regarded as a potential source of illegal discharges and contaminated stormwater run-off (WCG 2018).

Seasonal variations revealed that the summer sampling period (SO1) (0.0019 ± 0.0042) had a lower mean Al concentration when compared to autumn (SO2) (0.3563 ± 0.2080) and winter (SO3) (0.0788 ± 0.1179) at site 3 with the highest mean Al concentration at site 3 recorded in autumn (SO2) (0.3563 ± 0.2080) (Table 2). The above may be attributed to changes in anthropogenic load

Table 5 Mean concentrations (±SD) of copper on different sampling occasions at five sampling sites

Copper	Sampling occasions (SO)			
	SO1 (Summer)	SO2 (Autumn)	SO3 (Winter)	SO4 (Spring)
Water (mg/ℓ)				
Site 1	[a]0.1478[a] (±0.1516)	[a]0.0047[b] (±0.0058)	[a]0.1250[c] (±0.1717)	ND
Site 2	[a]0.0461[a] (±0.0072)	[a]0.0170[a] (±0.0202)	[a]0.0847[a] (±0.1157)	ND
Site 3	[a]0.0695[a] (±0.0436)	[a]0.0126[a] (±0.0078)	[a]0.0335[a] (±0.0550)	ND
Site 4	[a]0.0814[a] (±0.0151)	[a]0.0076[b] (±0.0057)	[a]0.0227[b] (±0.0347)	ND
Site 5	[a]0.0860[a] (±0.0254)	[a]0.0026[b] (±0.0027)	[a]0.0586[c] (±0.0444)	ND
Sediment (mg/kg)				
Site 1	[a]1.26[a] (±1.13)	[a]101.71[b] (±211.04)	[a]7.20[b] (±5.08)	[a]0.42[c] (±0.94)
Site 2	[b]8.52[a] (±9.03)	[a]9.50[a] (±5.81)	[a]4.95[a] (±2.45)	[b]5.06[a] (±2.36)
Site 3	[c]0.63[a] (±0.69)	[a]1.97[a] (±1.01)	[a]1.59[a] (±1.72)	[c]1.20[a] (±1.40)
Site 4	[c]0.36[a] (±0.40)	[a]13.94[b] (±15.68)	[a]2.81[b] (±1.90)	[c]0.00[c] (±0.00)
Site 5	[c]0.60[a] (±0.59)	[a]2.01[a] (±1.52)	[a]1.55[a] (±1.07)	[c]0.32[a] (±0.71)
Algae (mg/kg)				
Site 1	[a]15.73[a] (±6.18)	[a]6.12[a] (±2.26)	[a]5.63[a] (±1.32)	[a]7.28[a] (±3.38)
Site 2	[a]10.83[a] (±4.16)	[b]2.53[b] (±0.63)	[a]10.58[c] (±5.91)	[a]6.24[d] (±1.80)
Site 3	[a]9.67[a] (±1.20)	[b]2.34[b] (±1.73)	[a]7.38[b] (±6.75)	[a]8.10[c] (±2.49)
Site 4	[a]8.02[a] (±1.26)	[c]10.37[a] (±4.16)	[a]16.69[a] (±4.69)	[a]7.14[a] (±1.31)
Site 5	[a]12.68[a] (±10.37)	[c]19.69[a] (±20.38)	[a]16.97[a] (±11.63)	ND

The statistical differences between sites per sampling occasion are indicated by superscripted letters to the left of mean values

The statistical differences between sampling occasions per site are indicated by superscripted letters to the right of mean values. Water, sediment and algae samples were not statistically compared with each other

ND No Data

inputs, rainfall levels and physicochemical parameters such as salinity and pH. According to De Souza Machado et al. (2016) elevated rainfall may intensify the adsorption and precipitation processes due to high river flows which ultimately results in less dissolved metals in the water column. This may be the explanation for the relatively low mean Al concentration recorded in winter (SO3) at site 3. Some of the recorded mean Al concentrations within the different sampling sites on each sampling occasion (Table 2) exceeded the recommended water quality guidelines for the protection of aquatic ecosystems as stipulated by the Department of Water Affairs and Forestry (DWAF 1996), the Canadian Council of Resource and Environment Ministers Guidelines (CCREM 1987), and the Australian and New Zealand Environment and Conservation Council (ANZECC 2000) (Table 6). Sites that have exceeded the different water quality guidelines are listed in Table 6. Some of the sites that exceeded guidelines are near stormwater outlets and also not far from the influent rivers. Elevated Al concentrations in surface waters can cause toxic effects in aquatic organisms (ANZECC 2000).

Mean Zn concentrations (mg/ℓ) ranged from 0.02 ± 0.04 to 1.11 ± 0.48 (Table 3). Spatial variations in Zn concentrations (±SD) recorded in water showed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between sites 1 (1.1085 ± 0.4763) and 2 (0.2112 ± 0.1610) on SO2 (autumn) (Table 3). This may be attributed to the proximity of site 1 to the upstream influent rivers which are likely to carry pollutants from upstream activities. Zinc can occur in both suspended and dissolved forms in natural aquatic environments (CCME 2018). The aqueous zinc ion (Zn^{2+}) is known to be the most toxic (ANZECC, 2000). Zinc (Zn) concentrations recorded between the different sampling sites on each sampling occasion (except for site 2, SO3) exceeded the DWAF (1996) target water quality range (TWQR) value (i.e. chronic and acute effect concentration) of 0.036 mg/ℓ for the protection of aquatic ecosystems. The CCME (2018) water quality guidelines for the protection of aquatic life for dissolved Zn was 0.037 mg/ℓ for short-term exposure and 0.007 mg/ℓ for long-term exposure. The short-term exposure guideline was exceeded by most of the sampling sites (except for site 2 on SO3), while the long-term exposure guideline value was exceeded by all the sampling sites on each occasion (Table 6). The recorded Zn concentrations also exceeded the recommended safe concentration value of 0.0024 mg/ℓ (ANZECC 2000) for the protection of aquatic ecosystems (i.e. for 99% Level of species protection). Temporal (seasonal) variations in mean Zn concentrations showed significant differences ($p < 0.05$) in the pairwise consecutive comparisons between SO1 (summer) (0.1818 ± 0.1511), SO2 (autumn) (1.1085 ± 0.4763) and SO3 (winter) (0.1066 ± 0.1341) at site 1 (Table 3). The results revealed a fluctuation in Zn concentrations between the different seasons at site 1 and this can possibly be attributed to changes in rainfall patterns and river flows which influence the input of metals from catchment areas. The Zandvlei estuary has standing water (Day et al. 2020), which may restrict the movement or distribution of metals, making them readily available for uptake in the water column or by sediments. Changes in anthropogenic inputs (i.e. pollution load), river discharge and estuarine circulation (among other factors), and water quality properties (i.e. salinity, pH, etc.) may be responsible for the statistically lower concentrations

Table 6 Zandvlei estuary sites (in the current study) that have exceeded the recommended safe metal concentrations in freshwater as stipulated by the Department of Water Affairs and Forestry (DWAF 1996), Australian and New Zealand Environment and Conservation Council (ANZECC 2000), Canadian Council of Resource and Environment Ministers (CCREM 1987), and Canadian Council of Ministers of the Environment (CCME, 2001)

Metals		DWAF (1996) Target Water Quality Range (TWQR) (mg/ℓ)	ANZECC (2000) Water quality guideline (mg/ℓ)	CCREM (1987) Water quality guideline (mg/ℓ)[1]	CCME (2001) Water quality guideline for the protection of aquatic life (mg/ℓ)	Zandvlei estuary sites that exceeded water quality guideline concentrations recommended by DWAF (1996)	Zandvlei estuary sites that exceeded water quality guideline concentrations recommended by ANZECC (2000)	Zandvlei estuary sites that exceeded water quality guideline concentrations recommended by CCREM (1987)	Zandvlei estuary sites that exceeded water quality guideline concentrations recommended by CCME (2001)
Al	pH < 6.5	0.005	NGV	0.005	NGV	Site 4 (SO2)	N	Site 4 (SO2)	N
	pH > 6.5	0.01	0.027[i]	0.1	NGV	Sites 1 & 2 (SO1) Sites 1, 3 & 5 (SO2) Sites 1, 2, 3, 4 & 5 (SO3)	Sites 1 & 2 (SO1) Sites 3, 4 & 5 (SO2) Sites 1, 2, 3, 4 (SO3)	Sites 3 & 4 (SO2) Sites 1, 2 & 4 (SO3)	N
			0.055[ii]				Sites 3 & 4 (SO2) Sites 1, 2, 3 & 4 (SO3)		
			0.08[iii]				Sites 3 & 4 (SO2) Sites 1, 2 & 4 (SO3)		
			0.15[iv]				Sites 3 & 4 (SO2) Sites 1, 2 & 4 (SO3)		

Table 6 (continued)

Metals	DWAF (1996) Target Water Quality Range (TWQR) (mg/ℓ)	ANZECC (2000) Water quality guideline (mg/ℓ)	CCREM (1987) Water quality guideline (mg/ℓ)[1]	CCME (2001) Water quality guideline for the protection of aquatic life (mg/ℓ)	Zandvlei estuary sites that exceeded water quality guideline concentrations recommended by DWAF (1996)	Zandvlei estuary sites that exceeded water quality guideline concentrations recommended by ANZECC (2000)	Zandvlei estuary sites that exceeded water quality guideline concentrations recommended by CCREM (1987)	Zandvlei estuary sites that exceeded water quality guideline concentrations recommended by CCME (2001)
Zn	0.036	0.0024[i]	NGV	0.037[c]	Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 3, 4 & 5 (SO3)	Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 2, 3, 4 & 5 (SO3)	N	Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 3, 4 & 5 (SO3)
		0.008[ii]				Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 2, 3, 4 & 5 (SO3)		
		0.015[iii]		0.007[d]		Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 2, 3, 4 & 5 (SO3)		Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 2, 3, 4 & 5 (SO3)
		0.031[iv]				Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 3, 4 & 5 (SO3)		

Table 6 (continued)

Metals	DWAF (1996) Target Water Quality Range (TWQR) (mg/ℓ)	ANZECC (2000) Water quality guideline (mg/ℓ)	CCREM (1987) Water quality guideline (mg/ℓ)[1]	CCME (2001) Water quality guideline for the protection of aquatic life (mg/ℓ)	Zandvlei estuary sites that exceeded water quality guideline concentrations recommended by DWAF (1996)	Zandvlei estuary sites that exceeded water quality guideline concentrations recommended by ANZECC (2000)	Zandvlei estuary sites that exceeded water quality guideline concentrations recommended by CCREM (1987)	Zandvlei estuary sites that exceeded water quality guideline concentrations recommended by CCME (2001)
Pb (A)	0.0002–0.0012	0.001[i]	0.001–0.007	NGV	Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 2, 4 & 5 (SO3)	Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 2, 4 & 5 (SO3)	Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 2, 4 & 5 (SO3)	N
		0.0034[ii]				N		
		0.0056[iii]				Sites 1, 2, 3, 4 & 5 (SO1) Sites 1 (SO2) Sites 4 (SO3)		
		0.0094[iv]				Sites 1, 3, 4 & 5 (SO1) Sites 1 (SO2) Sites 4 (SO3)		
Cu (A)	0.0003–0.0014	0.001–0.0025	0.002–0.004	NGV	Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 2, 3, 4 & 5 (SO3)	Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 2, 3, 4 & 5 (SO3)	Sites 1, 2, 3, 4 & 5 (SO1) Sites 1, 2, 3, 4 & 5 (SO2) Sites 1, 2, 3, 4 & 5 (SO3)	N

[1]The Canadian Council of Ministers of the Environment (1999) water quality guidelines have been withdrawn

[i]99% Level of species protection

[ii]95% Level of species protection

[iii]90% Level of species protection

[iv]80% Level of species protection

[a]Short-term benchmark (CCME 2019)

[b]Long-term guideline (CCME 2019)

[c]Short-term exposure value (CCME 2018)

[d]Long-term exposure value (CCME 2018)

N None (of the sites exceeded the guidelines), *NGV* No Guideline Value

(A) = subject to water hardness (as $CaCO_3$). If the water hardness is unknown, the lowest value is applicable

recorded on SO3 (winter) at both sites 1 and 2 (Table 3) (Sany et al. 2013; De Souza Machado et al. 2016).

Mean Pb concentrations (mg/ℓ) ranged from 0.0000 ± 0.0000 (undected) to 0.0261 ± 0.0346 (Table 4). The results revealed that the highest concentrations were recorded at site 1 on SO1 (summer). However, although the highest concentration was recorded at site 1 (SO1), comparisons of spatial variations in Pb concentrations showed no statistical differences ($p > 0.05$) in the pairwise consecutive comparisons between the different sampling sites on SO1 (summer) and SO2 (autumn) (Table 4). Statistical differences in Pb concentrations ($p < 0.05$) were only recorded in the pairwise consecutive comparisons between sites 3 (0.0000 ± 0.0000) and 4 (0.0120 ± 0.0158) on SO3 (winter) (Table 4). This may be ascribed to estuarine circulation as a result of increased rainfall levels recorded (51.0 mm) in the winter (SO3) months. Local terrestrial inputs or stormwater discharges may also have contributed to the elevated Pb concentration levels recorded at site 4 (SO3), which were statistically higher than the concentrations recorded at site 3 on SO3 (Table 4). According to DWAF (1996) some of the sources of Pb include street run-off, as well as industrial and municipal wastewater discharges. Although South Africa phased out leaded petrol in 2006 and promulgated legislation to control the use of Pb in paint, elevated levels of Pb were still found in soil alongside busy roads compared to that alongside less heavily trafficked roads (Mathee 2014). Some of the mean Pb concentrations recorded at the different sampling sites on each occasion (with a few exceptions) exceeded the recommended water quality guidelines values by DWAF (1996), (CCME 2001), and (ANZECC 2000) (Table 6). This may therefore be an indication of Pb pollution in the study area and it is likely as a result of the abovementioned land uses and activities around the estuary. Elevated Pb concentrations can result in neurological, renal, cardiovascular, haematological, immunological, reproductive, and developmental effects (ATSDR 2020).

Seasonal variations in Pb concentrations showed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between SO2 (autumn) (0.0229 ± 0.0258) and SO3 (winter) (0.0015 ± 0.0015) at site 1 (Table 4). The above statistical differences in concentrations recorded between autumn and winter at site 1 indicated a decline in Pb concentrations and this may be attributed to seasonal fluctuations in weather conditions (i.e. rainfall) and other factors such as physicochemical parameters and anthropogenic inputs. Concentrations of contaminants in aquatic systems have been found to vary widely in temporal scales and this is due to various interacting factors such as flow intensity, tidal and current related effects, and the reoccurrence of contaminating discharges (Phillips and Rainbow 1994). Temporal variations recorded in this study showed that warmer months recorded higher concentrations when compared to concentrations in winter. At site 3, the results revealed SO1 (summer) (0.0139 ± 0.0089) recording a statistically higher Pb concentration when compared to SO2 (autumn) (0.0033 ± 0.0025) and SO3 (winter) (0.0000 ± 0.0000) (Table 4). This may be ascribed to river flow inputs and land-based discharges which affects estuarine circulation, and physicochemical parameters which may ultimately affect the rate of absorption and desorption of metals to and from the water column (Sany et al. 2013).

Mean Cu concentrations (mg/ℓ) ranged from 0.0026 ± 0.0027 to 0.1478 ± 0.1516 (Table 5). Spatial variations in Cu concentrations revealed no statistical differences ($p > 0.05$) in the pairwise consecutive comparisons between the different sampling sites on each sampling occasion. It was noted that most of the recorded mean concentrations exceeded the recommended Target Water Quality Range (TWQR) values stipulated by DWAF (1996) and water quality guideline concentrations recommended by CCME (2001) and ANZECC (2000) (Table 6). This may be an indication of Cu contamination in the Zandvlei. Anthropogenic sources of Cu account for 33–60% of the total global input of Cu to the aquatic environment. These include effluents from wastewater treatment plants and industrial activities, including run-off and corrosion of copper pipes (DWAF 1996). Seasonal (temporal) variations in mean Cu concentrations showed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between the different sampling occasions (SO1, SO2 and SO3) at both sites 1 and 5 (Table 5). The above seasonal variations in the recorded Cu concentrations may be due to seasonal fluctuations or changes in weather conditions between the different seasons as well as physicochemical parameters. Increased salinity intensifies competition between cations and metals for binding sites and this moves metals off into the overlying water through a process known as desorption (Nduka and Orisakwe 2011). A low pH has a similar effect to that of elevated salinity levels in an aquatic system as it also increases competition between metal and hydrogen ions for binding sites which can lead to the release of free metal ions into the water column (Nduka and Orisakwe 2011). Metal concentrations in water samples followed the sequence: Al > Zn > Cu > Pb.

Sediment

Mean Al concentrations (mg/kg) recorded in sediment at the different sampling sites within the Zandvlei estuary ranged from 189.36 ± 26.21 to 1562.04 ± 923.63 (Table 2). Spatial variations in Al concentrations revealed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between sites 2 (1229.91 ± 247.36) and 3 (606.17 ± 226.72), sites 3 (606.17 ± 226.72) and 4 (923.95 ± 191.91) as well as sites 4 and 5 (250.55 ± 66.75) on SO1 (summer) (Table 2). This may be due to several environmental factors such as

salinity, pH, anthropogenic inputs, redox potential, and sediment grain size distribution (Davies et al. 1991). The fluctuating mean Al concentrations between the different sampling sites on each occasion may also be due to different levels of anthropogenic inputs from the various stormwater drainage outlets. Physicochemical factors such as salinity, density, flow velocity, and suspended matter composition also influence the distribution and fate of metals in estuaries (De Souza Machado et al. 2016). Chapman and Wang (2001) noted that the partitioning of contaminants between sediments and overlying water is controlled by salinity. This is because the water chemistry and ionic strength, which both affect the movement of metals in estuaries, is influenced by salinity (Benoit et al. 1994; De Souza Machado et al. 2016).

The results showed statistical differences in Al concentrations ($p < 0.05$) recorded between sites 4 (1562.04 ± 923.63) and 5 (452.96 ± 88.83) on SO2 (autumn), as well as sites 4 (1357.36 ± 723.22) and 5 (466.32 ± 48.42) on SO3 (winter) (Table 2). The relatively high concentrations recorded at site 4 may be attributed to a combination of factors such as physicochemical parameters, rainfall, sediment grain size distribution and a local source of contamination such as nearby stormwater drainage outlets. Elevated rainfall on both SO2 (autumn) (24.2 mm) and SO3 (winter) (51.0 mm) may have contributed to the above spatial variations between sites 4 and 5 on SO2 and SO3 (Table 2). It was noted that site 5 mostly recorded concentrations that were lower than the other sites which could have been due to the location of the site (as it was further away from influent rivers), or it could have also been due to sediment grain size distribution, as well as anthropogenic load inputs, river flow, estuary gradient and the closing and opening of the estuary mouth. Izegaegbe et al. (2020) also recorded lower metal concentrations at a site located near the estuary mouth in the Mhlathuze estuary in KwaZulu Natal, South Africa, which was attributed to strong tidal currents that prevent the deposition of fine sediments, limiting the accumulation of metals in sediment. Both CSIR (2015) and Maurer (2019) studies noted that the upper parts of the Zandvlei estuary were characterised by muddy/fine sediments and the lower parts by coarse/sandy sediments. According to Nduka and Orisakwe (2011) fine sediments have a significant capacity to retain metals and as a result can adsorb an increased concentration of metals.

Seasonal variations in Al concentrations showed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between the different sampling occasions at site 1 (Table 2). The results showed elevated Al concentrations in both autumn (SO2) and winter (SO3) as compared to other seasons at site 1 (Table 2). This may be ascribed to increased fluvial and other land-based discharges due to elevated rainfall. Site 1 is located close to the influent rivers, which are heavily impacted by upstream anthropogenic activities. Sewer overflows and the dumping of waste and litter in the stormwater drainage network (WCG 2018) may also have resulted in elevated metal concentrations in the estuary. The results showed a significant decline ($p < 0.05$) in mean Al concentrations between winter (SO3) (1357.36 ± 723.22) and spring (SO4) (189.36 ± 26.21) at site 4 (Table 2). The relatively high concentration recorded in winter could be due to elevated rainfall which transports metals and particulate matter. The comparison of seasonal variations in mean Al concentrations revealed that the dry seasons (spring [SO4] and summer [SO1]) recorded low mean Al concentrations when compared to the wet season (autumn [SO2] and winter [SO3]). This may be attributed to rainfall, which increases land-based run-off and river discharges, which are polluted by contaminants such as Al, among others. However, some researchers (Lim et al. 2006; Li et al. 2009) argue that rainwater causes increased mobility and dilution, which decreases metal concentrations in sediments. This was not the case for this study as the recorded mean Al concentrations (Table 2) were higher during the wet season. The mean Al concentrations recorded in this study were compared to those recorded for the Mhlathuze estuary, South Africa (Izagaebe et al. 2020), since there are no sediment quality guidelines for Al from South Africa's Department of Water Affairs (DWAF) (1996), Canadian Sediment Quality Guidelines (CCME 2001) as well as the Australian and New Zealand Environment and Conservation Council (ANZECC 2000) (Table 7). Concentrations recorded for Al in the Mhlathuze estuary (12,668 ± 6958 mg/kg) were much higher than those recorded in the current study (911.5875 ± 243.857 mg/kg). This may largely be attributed to the fact that Mhlathuze is in close proximity to a vast industrial and shipping complex as compared to the Zandvlei estuary, which is located within a residential area with some upstream industrial and other activities within its surroundings.

Mean Zn concentrations (mg/kg) recorded in sediment ranged from 5.87 ± 9.16 to 5834.36 ± 3788.34 (Table 3). Spatial variations in Zn concentrations showed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between sites 1 (1040.01 ± 275.52) and 2 (5834.36 ± 3788.34) on SO1 (summer) (Table 3). The elevated Zn concentration recorded at site 2 (SO1) may be attributed to urban run-off from the nearby stormwater drainage outlet, the parking area and yacht club. Sediment grain size and physicochemical parameters may have also influenced the recorded concentrations between the above sites. The gradient of the estuary where dense growth of *Stuckenia pectinata* (pondweed) is often found (i.e. site 2), comprises of deeper channels with standing or stagnant water (WCG 2018; Day et al. 2020). The results showed significant differences ($p < 0.05$) in Zn concentrations recorded between sites 2 (26.97 ± 8.51) and 3 (7.03 ± 4.17) on SO2 (autumn) (Table 3). This may be due to the proximity of the sites to

Table 7 Zandvlei estuary sites (in the current study) that have exceeded the recommended safe metal concentrations in sediment as stipulated by the Australian and New Zealand Environment and Conservation Council (ANZECC 2000), and Canadian Council of Ministers of the Environment (CCME 1999)

Metals	ANZECC (2000) sediment quality guidelines (mg/kg)	CCME (1999) sediment quality guidelines for the protection of aquatic life (mg/kg dry weight)	Zandvlei estuary sites that exceeded sediment quality guideline concentrations recommended by ANZECC (2000)	Zandvlei estuary sites that exceeded sediment quality guideline concentrations recommended by CCME 1999)
Al	NGV	NGV	N	N
Zn	200[a]	124[i]	Sites 1, 2, 3, 4 & 5 (SO1)	Sites 1, 2, 3, 4 & 5 (SO1)
	410[b]	271[ii]	Sites 1, 2, 3 & 4 (SO1)	Sites 1, 2, 3, 4 & 5 (SO1)
Pb	50[a]	30.2[i]	N	Site 2 (SO2) Site 5 (SO4)
	220[b]	112[ii]	N	N
Cu	65[a]	18.7[i]	Sites 1 (SO2)	Sites 1 (SO2)
	270[b]	108[ii]	N	N

[i] Interim sediment quality guidelines (ISQGs) for metal in estuarine/marine environment

[ii] Probable effect levels (PELs) for metal in estuarine/marine environment

[a] Default guideline values (DGVs)

[b] Upper / higher guideline values (GV-high)

N None (of the sites exceeded the guidelines), *NGV* No Guideline Valu

pollution sources, sediment characteristics as well as the gradient of the estuary. Mean Zn concentrations recorded in this study were in line with the expectation relating to decreasing grain size and increasing metal concentrations as there were higher Zn concentrations recorded in the upper parts of the estuary and lower Zn concentrations recorded in the lower parts of the estuary. Zinc concentrations decreased significantly from site 2–3 on SO3 (winter) (Table 3) and this may be linked to sediment grain size distribution, as described above. It may also be due to rainfall as rainwater was found to increase mobility and dilution which decreases metal concentrations in sediment (Lim et al. 2006; Li et al. 2009).

Seasonal variations in Zn concentrations revealed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between SO1 (summer) (1040.01 ± 275.52) and SO2 (autumn) (22.70 ± 4.01) at site 1 (Table 3). The elevated concentrations recorded on SO1 may be linked to changes in anthropogenic inputs/activities over time, such as the establishment or closure of industrial and construction activities, which can lead to temporal variations in metal concentrations. Sampling occasion 1 received the least amount of rainfall (5.2 mm) of all the sampling occasions. Since the estuary is classified as a standing water system (Day et al. 2020), less rainfall further reduces estuarine circulation or water flow within the system, resulting in stagnant water areas which may contain metals that can be deposited on sediment when conditions are favourable. At site 2, statistical differences ($p < 0.05$) in Zn concentrations were recorded in the pairwise consecutive comparisons between SO1 (summer) and SO2 (autumn) as well SO3 (winter) and SO4 (spring) (Table 3). Sampling occasion 1 (summer) recorded a statistically ($p < 0.05$) higher concentration than SO2 (autumn) at both sites 2 and 4 (Table 3) and as discussed above, this may be attributed to factors such as rainfall, estuary gradient, anthropogenic inputs (i.e. stormwater, urban run-off, etc.) and physicochemical properties (i.e. salinity, organic content, pH, amongst others. Zinc concentrations recorded between the different sampling sites on SO1 exceeded the CCME (1999) recommended safe sediment quality guideline concentration (124 mg/kg), while Zn concentrations recorded at all sites during SO2 (autumn), SO3 (winter) and SO4 (spring) were below the recommended sediment quality guideline by CCME (1999). Zinc concentrations recorded at the different sampling sites (except site 5) on SO1 exceeded the high guideline value recommended by ANZECC (2000) and the low guideline value by ANZECC (2000) was exceeded by all the sites on SO1 (summer) (Table 7). However, it is important to note that all the other sampling sites on the other sampling occasions (i.e. SO2, SO3 and SO4) were below the guideline values by ANZECC (2000) and CCME (1999) (Table 7).

Mean Pb concentrations (mg/kg) recorded in sediment ranged from 1.24 ± 0.19 to 37.37 ± 34.62 (Table 4). Comparisons of spatial variations in Pb concentrations showed statistical differences ($p < 0.05$) in Pb concentrations recorded between sites 1 (5.46 ± 1.85) and 2 (29.89 ± 14.99) as well as sites 2 (29.89 ± 14.99) and 3 (2.90 ± 0.78) on SO1 (summer) (Table 4). The above differences may be attributed to several factors such as stormwater run-off, land-based discharges, sediment grain size, estuary gradient, month manipulation, as well as physicochemical parameters. Site 2 is located opposite a yacht club, a parking area as well as a stormwater

drainage outlet. Discharges from the stormwater outlet and street run-off from the nearby parking area may have resulted in the elevated levels of Pb recorded at site 2 on SO1 (summer). Lead enters the aquatic environment in various ways, such as precipitation, lead dust fall-off, street run-off as well as industrial and municipal wastewater discharges (DWAF 1996). The influent rivers such as the Keysers River that discharges into the Zandvlei estuary may have also been contaminated with Pb from the industrial area located along its banks. Deeper channels in the estuary are caused by the continuous removal of pondweed that have been found to exacerbate flooding, limit light penetration, restrict current flow and thus increase stagnation (WCG 2018). The estuary mouth was also closed on SO1. Similar spatial variations were observed between the different sampling sites on other sampling occasions, and this may be ascribed to sediment grain size, estuary gradient, anthropogenic inputs and river flow. According to Davies et al. (1991) the accumulation of metals in sediment is dependent on several external factors such as anthropogenic input, pH, Eh, ionic strength and grain size distribution. It is important to note that majority of the recorded mean Pb concentrations were well below the interim sediment quality guidelines (ISQGs) for marine/estuarine ecosystems (30.2 mg/kg) (CCME 1999a) (Table 7) except for Pb concentrations recorded at site 2 (SO2) (32.03 ± 32.65) and site 5 (SO4) (37.37 ± 34.62) (Table 4). The standard deviations recorded in both sites 2 (SO2) and 4 (SO4) were high and this seems to be an indication of concentrations that varied widely across the different sites. The above which exceeded the CCME guidelines may also be an indication of some lead pollution in autumn (SO2) and spring (SO4) in the Zandvlei estuary. However, it is important to note that the recorded mean Pb concentrations in this study were well below the recommended sediment quality guidelines by ANZECC (2000) (Table 7).

Seasonal variations in Pb concentrations revealed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between SO3 (winter) (12.92 ± 18.11) and SO4 (spring) (25.77 ± 21.19) at site 1 (Table 4). This may be attributed to changes to pollution load inputs from the influent rivers and rainfall. Sampling occasion 3 (winter) recorded a monthly average rainfall of 51.0 mm as compared to the monthly average rainfall of 27.8 mm recorded for SO4 (spring). According to Lim et al. (2006) and Li et al. (2009) precipitation increases metal mobility and dilution which decreases metal concentrations in sediments. This may be one of the reasons why SO3 (winter) recorded statistically lower Pb concentrations than SO4 (spring) at site 1 (Table 4). Statistical differences ($p < 0.05$) in Pb concentrations were recorded in the pairwise comparisons between the different sampling occasions at both sites 2 and 4 (Table 4). The results showed both SO1 (summer) and SO2 (autumn) recording statistically higher Pb concentrations when compared to SO3 (winter) and spring (SO4) at site 2. This may be attributed to seasonal fluctuations in weather conditions as well as physical and chemical properties of the estuary. The estuary mouth was closed on SO1 (summer) and SO2 (autumn) and this could have contributed to the higher concentrations recorded on both occasions, especially since the estuary is characterised by deeper channels (WCG 2018) and standing water (Day et al. 2020) in the central and northern parts. Another possible cause for elevated Pb concentrations on SO1 (summer) and SO2 (autumn) is an increase in anthropogenic activities due to favourable weather conditions (i.e. less rainfall).

At site 4, SO2 (autumn) recorded statistically higher concentrations when compared to SO1 (summer) and this could be linked to an increase in rainfall which increases land-based discharges and stormwater run-off. However, according to Sany et al. (2013) increased metal concentrations may be linked to an increase in salinity, decrease in pH and redox potential. The recorded salinity concentration for SO1 (summer) and SO2 (autumn) at site 4 was 19.75ppt and 22.3ppt, respectively, whilst the pH was 7.97 for SO1 (summer) and 4.97 for SO2 (autumn). The high salinity and low pH values recorded on SO2 (autumn) may have therefore contributed to the temporal variations recorded between SO1 and SO2 at site 4 (Table 4). Temporal variations in Pb concentrations further revealed statistical differences ($p < 0.05$) in the pairwise comparisons between SO2 (autumn) (1.24 ± 0.19) and SO3 (winter) (2.35 ± 0.23) as well as between SO3 (winter) and SO4 (37.37 ± 34.62) at site 5. This may be ascribed to seasonal fluctuations in weather conditions and changes to pollution load from anthropogenic sources. River discharge coupled with seasonal and tidal currents as well as other sediment resuspension events also play a significant role in relation to the partitioning and bioavailability of metal contaminants in estuarine sediments (Chapman and Wang 2001; Sany et al. 2013).

The recorded mean Cu concentrations (mg/kg) ranged from 0.00 ± 0.00 (undetected) to 101.71 ± 211.04 (Table 5). Spatial variations in mean Cu concentrations (mg/kg) showed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between sites 1 and 2 as well as sites 2 and 3 on SO1 (summer) and SO4 (spring) (Table 5). Site 2 recorded statistically higher Cu concentrations when compared to the other sampling sites on both of the above-mentioned sampling occasions (Table 5). Site 2 is located near a stormwater drainage outlet which may be responsible for the discharge of Cu into the estuary. Site 2 is also located near a parking area and a yacht club. Furthermore, influent rivers feeding into the estuary may also have been responsible for the elevated levels of Cu at site 2. The gradient of the estuary at site 2 as well as the closing of the estuary mouth may have also contributed to the higher concentrations at site 2 on SO1 and SO4 (Table 5). It is important to also note

that Cu may emanate from various anthropogenic sources such as industrial activities, wastewater treatment plants as well as run-off and corrosion of copper pipes, among others (DWAF 1996). The above activities do occur within the vicinity of the study area. The recorded Cu concentrations appear to be in line with the grain size of the sediment in the estuary as statistically higher mean concentrations were recorded in fine-grained sediment (i.e. mud) and statistically lower concentrations were mostly found within the coarsely grained sediment (i.e. sand). All the recorded mean Cu concentrations (except for site 1, SO2) were well below the sediment quality guidelines recommended by CCME (1999b) and ANZECC (2000) (Table 7). Temporal variations in Cu concentrations showed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between SO1 (summer) and SO2 (autumn), as well as SO3 (winter) and SO4 (spring) at sites 1 and 4. Both summer (SO1) and spring (SO4) recorded statistically lower Cu concentrations when compared to autumn (SO2) at both sites 1 and 4. This may be attributed to seasonal fluctuations and changes to anthropogenic load input (Sany et al. 2012). However, SO2 (autumn) also recorded a high standard deviation value at both sites 1 and 2 (Table 5) and this reflect a wide variation of Cu concentrations. Metal concentrations in sediment followed the sequence: Al > Zn > Pb > Cu.

Algae

Mean Al concentrations (mg/kg) recorded in *Enteromorpha* spp. ranged from 60.24 ± 44.13 to 4517.35 ± 9620.77 (Table 2). Spatial variations in Al concentrations showed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between sites 2 (1310.95 ± 639.94) and 3 (3688.73 ± 818.35), sites 3 and 4 (60.24 ± 44.13) as well as sites 4 and 5 (4517.35 ± 9620.77) on SO1 (summer). The recorded variations may be attributed to local and seasonal environmental conditions which influence the growth and morphology, life span of the algae species as well as the interactions among metal ions resulting in competition for binding sites (Villares et al. 2002; Chakraborty and Owens 2014). According to Zbikowski et al. (2006), metal concentrations in algae may be affected by various environmental conditions including the concentrations of metals in water, light intensity, pH and salinity, among other factors. Physicochemical parameters such as salinity and pH seem to have had little effect on the spatial variations recorded on SO1 (summer). Site 5 (SO1) recorded the highest Al concentration (4517.35 ± 9620.77). However, the recorded standard deviation was also very high which demonstrates that the Al concentrations recorded at site 5 varied considerably. Similar variations were recorded between the different sites on SO2 and this may be due to reasons such as those indicated above, which include (but is not limited to) the location of sampling sites, metal concentrations in solution, the interaction between metals and other elements, dilution of metal concentrations due to growth (metabolic factors), and physicochemical parameters such as pH and salinity (Villares et al. 2002). Zbikowski et al. (2006) noted that it is difficult to clearly pinpoint the main factors that could influence the accumulation of metals in algae because of the different factors (i.e. pH, salinity, temperature, etc.) interacting with each other.

Seasonal variations in Al concentrations recorded in this study revealed significantly higher mean concentrations in the dry seasons as compared to the wet season except for site 4 (Table 2). Some researchers have found concentrations of chemical elements in algae generally lower in the warmer months. This was attributed to the metabolic activity of algae, which is usually high in summer and results in the dilution of the accumulated metals whereas in winter, after slowing down of metabolic processes, the element content is usually higher (Hou and Yan 1998; Villares et al. 2002).

The abovementioned impact of the metabolic activity of algae on metal concentrations did not correlate with the findings of this study, as there were concentrations that were relatively high in both summer and winter months (Table 2). Villares et al. (2002) also notes that the metabolic activity of algal species could not explain all the variation in their study. A study conducted by Wright and Mason (1999) recorded higher concentrations of metals in winter for *Enteromorpha* spp. and noted a similar pattern in metal levels in sediments and in various invertebrates. The above findings indicate that seasonal variation appears to be largely influenced by environmental factors, such as physicochemical parameters and discharges into the estuary, to name a few. These factors seem to play a greater role than the metabolic and reproductive nature of macroalgae.

Mean Zn concentrations (mg/kg) ($\pm$SD) in algae (*Enteromorpha* spp.) ranged from 0.68 ± 0.95 to 86.95 ± 186.73 mg/kg (Table 3). Spatial variations in Zn concentrations showed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between sites 2 and 3, sites 3 and 4 as well as sites 4 and 5 on SO1 (summer) (Table 3). The high standard deviation recorded at site 5 (SO1) reflected a wide variation of bioaccumulated Zn concentrations in macroalgae. The variations recorded on SO1 may be due to changes in growth and metabolic rates of macroalgae (i.e. dilution of metal due to algal growth), which are influenced by local and seasonal environmental conditions (i.e. physicochemical parameters), interactions among metal ions resulting in competition for binding sites in macroalgae, as well as species lifespan and morphology (Villares et al. 2002; Ryan et al. 2012; Chakraborty and Owens 2014). Zinc at low concentrations is regarded as an essential micronutrient to support algae growth. However, at elevated concentrations, Zn may adversely influence the physiological

and biochemical processes of algal growth (Trzcińska and Pawlik-Skowrońska 2013). Sampling occasion 2 also recorded similar fluctuations in Zn concentrations between the different sites. Sites 1 and 2 for SO2 (autumn) recorded statistically ($p < 0.05$) higher concentrations when compared to sites 3 and 5 (Table 3) and this may be attributed to elevated anthropogenic inputs from influent rivers and stormwater discharges or run-off.

Seasonal variations in mean Zn concentrations showed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between the different sampling occasions at sites 3 and 4 (Table 3). The concentrations recorded in summer (SO1) was the highest when compared to those recorded in autumn, winter and spring at site 3. It is important to note that there may be different reasons for the recorded seasonal differences, including but not necessarily limited to physicochemical factors such as salinity and pH, metabolic factors, interactions between metals and other elements, and differences in metal concentrations in solution (Villares et al. 2001). Concentrations recorded in this study fluctuated between the different seasons with no particular pattern that could be attributed to a single factor like algae growth. This may be an indication of the interaction of the different environmental factors, as well as interaction between metals and other elements (Zbikowski et al. 2007).

Mean Pb concentrations (mg/kg) recorded in macroalgae (*Enteromorpha* spp.) ranged from 1.74 ± 0.79 to 48.31 ± 19.89 (Table 4). Comparisons of spatial variations in Pb concentrations showed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons recorded between sites 2 and 3, sites 3 and 4 as well as sites 4 and 5 (Table 4). Site 3 recorded the highest mean Pb concentration when compared to other sites on SO1 (summer) and this may be due to stormwater run-off, riverine, and atmospheric inputs. Site 3 is located close to a stormwater drainage outlet which could potentially be a source of Pb. Say et al. (1990) formulated some form of a guideline concentration value ranges for Pb in *Enteromorpha* spp. and these were categorised based on the extent or degree of contamination within estuaries. The above-mentioned concentration ranges are: < 20 mg/kg for relatively "clean or unpolluted" sites, 20–60 mg/kg for "moderate" contamination and > 60 mg/kg for "high" contamination. Applying the above concentrations as a "guideline" to the current study, it was found that all sampling sites on SO1 (summer), SO2 (autumn) and SO3 (winter) recorded concentrations that were below the "moderate" contamination category. However, mean Pb concentrations recorded in the different sampling sites on SO4 (spring) were within the "moderate" contamination category. The concentrations recorded on SO4 are significantly higher as compared to concentrations recorded on other occasions and this may be attributed to a local anthropogenic source of contamination such as the nearby industrial area, including disposal of household products, stormwater run-off and other land-based discharges (C.A.P.E., 2010).

Statistical differences ($p < 0.05$) in Pb concentrations were also recorded between SO1 (summer) and SO2 (autumn) as well as between SO2 (autumn) and SO3 (winter) at site 2 (Table 4). Many studies have reported higher metal concentrations during the winter period when the metabolic processes of algae have slowed down, resulting in an increase of metal content, while lower concentrations were usually recorded in warmer months when there is high metabolic activity resulting in dilution of metals (Hou and Yan 1998; Brown et al. 1999; Ryan et al. 2012; Villares et al., 2002; Zbikowski et al., 2007). The current study found higher metal concentrations during growth periods (i.e. warmer months) as recorded between SO1 (summer), SO2 (autumn) and SO3 (winter) at sites 2, 3 and 5 (Table 4). This may potentially be attributed to the existence of higher rates of photosynthesis and respiration during the summer period, which may support the accumulation of metals (Zbikowski et al., 2007). Comparisons of temporal variations in Pb concentrations further showed statistical differences ($p < 0.05$) between the different sampling occasions at site 3 (Table 4). The results revealed higher mean Pb concentrations in the summer (SO1) (14.89 ± 2.34) and spring season (SO4) (26.09 ± 9.13) as compared to autumn (SO2) (5.59 ± 2.89) and winter season (SO3) (3.03 ± 1.13) at site 3 (Table 4) and this could be attributed to the level of contaminants in water because of land-based discharges during the summer period (Villares et al., 2002). There is limited movement of water within the estuary during the summer period due to low rainfall levels and an abundance of macroalgae due to high salinities (Muhl 2003). According to Karsten and Kirst (1989), the photosynthetic and growth rate of algae is reduced by low salinities. High rainfall and low temperatures in winter usually results in low salinities while low rainfall and high temperatures usually result in high salinities in estuaries. Villares et al. (2002) argues that the reduction in solar radiation and temperature is responsible for slowing down metabolic activities in algae. The low mean Pb concentrations largely recorded in the winter season may potentially be attributed to the fact that *Enteromorpha* spp. is not abundant in the Zandvlei estuary in winter (Muhl 2003) and therefore, the collected biomass may have had limited capacity to accumulate metals as the collected samples were in relatively small amounts, especially towards the influent rivers. Statistical differences ($p < 0.05$) in Pb concentrations were recorded in the pairwise consecutive comparisons between SO1 (summer) and SO2 (autumn) at site 5 (Table 4). This may potentially be attributed to the existence of higher rates of photosynthesis and respiration during the summer period, which may support the accumulation of metals (Zbikowski et al. 2007).

Mean Cu concentrations (mg/kg) (± SD) in algae (*Enteromorpha* spp.) ranged from 2.34 ± 1.73 to 19.69 ± 20.38 mg/kg (Table 5). Spatial variations in the recorded mean Cu concentrations showed statistical differences ($p < 0.05$) in the pairwise consecutive comparisons between sites 1 and 2 as well sites 3 and 4 on SO2 (autumn) (Table 5). A fluctuation in mean Cu concentrations was noted between the above-mentioned sites on SO2 (Table 5). Site 1 (SO2) recorded a statistically significantly higher mean concentration (6.12 ± 2.26) than site 2 (SO2), which recorded a mean concentration of 2.53 ± 0.63 (Table 5). This may be due to the proximity of site 1 to the influent rivers, which are responsible for discharging and transporting of stormwater and urban effluents from upstream and neighbouring activities. Copper concentrations in *Enteromorpha* spp. from sites considered as uncontaminated, ranged between 6 and 12 mg/kg whereas concentrations from sites known to be contaminated ranged from 20 to 70 mg/kg (Brown et al. 1999). The recorded concentrations in this study seem to suggest (when compared to the above guidelines) that the estuary was, to some extent, contaminated with Cu although majority of the recorded Cu concentrations were within the "uncontaminated" concentration range. The physicochemical parameters recorded on SO2 may have potentially influenced the bioavailability and accumulation of metals in algae (Zbikowski et al. 2006). The recorded salinity levels on SO2 ranged from 18.65 ppt (site 1) to 25.45 ppt (site 5) (Table 1). Dissolved oxygen decreased from site 1 (13.84 mg/ℓ) to site 5 (2.42 mg/ℓ) on SO2 (Table 1). The pH also decreased, ranging from 8.81 (site 1) to 6.8 (site 5) (Table 1). Temperature which also appears to play an important role in the metabolic and growth of algae and which directly affects the accumulation of metals in macroalgae (Sany et al. 2013), ranged between 23.2 °C (site 1) and 21.1 °C (site 5) (Table 1). During sample collection on SO2, the estuary mouth was closed, and this may have also contributed to the accumulation of metals at the sites in the lower/southern parts of the estuary.

Seasonal variations showed statistical differences ($p < 0.05$) in Cu concentrations recorded between the different sampling occasions at site 2 (Table 5). Copper concentrations fluctuated between the different sampling occasions at site 2. Sampling occasion 1 (summer) recorded the highest concentrations when compared to other sampling occasions at site 2 (Table 5). This may be due to a combination of several factors, such as the concentration of metals in water, salinity, pH, interactions between different metals, light intensity, and metabolic factors such as dilution of metal contents due to algae growth (Zbikowski et al. 2006). Since there are various factors which affect the bioaccumulation of metals in algae, some researchers have found it difficult to determine explicitly the main factors affecting seasonal changes in metal accumulation in algae as this may be caused by the interactions between the various factors (Vasconcelos and Leal 2001; Szefer 2002; Zbikowski 2006). Elevated anthropogenic inputs from nearby stormwater drainage outlets and low salinity may result in increased metal concentrations in macroalgae (Munda 1984; Wang and Dei 1999) and this may be one of the reasons why SO1 (site 2) recorded a higher concentration than SO2 (site 2). Statistical differences ($p < 0.05$) in Cu concentrations were also recorded in the pairwise consecutive comparisons between SO1 (summer) and SO2 (autumn) as well as between SO3 (winter) and SO4 (spring) at site 3 (Table 5). Sampling occasion 1 (summer) recorded statistically higher concentrations when compared to the other sampling occasions at both sites 2 and 3 (Table 5). The low rainfall (5.2 mm) and slightly high salinities recorded at both sites 2 (15.63 ppt) and 3 (16.30 ppt) on SO1 (summer) (Table 1) may have contributed to the recorded concentrations in summer. However, the slowing down of metabolic processes of algae (i.e. growth) was expected to increase the uptake of metals during the winter period (Hou and Yan 1998; Villares et al. 2002; Zbikowski 2006). However, the winter period (SO3) in this study (at both sites 2 and 3) recorded lower concentrations when compared to SO1 (summer) (Table 5). Therefore, the above expectation in relation to a higher uptake of metals due to slow metabolic processes was not realised in this study and this may have been due to high rainfall which decreases salinity and macroalgae growth in Zandvlei (Muhl 2003), which ultimately affects bioaccumulation as there is less tissue available or may have been due to a combination (or the interaction) of the different factors that affect the bioaccumulation of metals in macroalgae (Vasconcelos and Leal 2001; Szefer 2002; Zbikowski 2006). Metals in macroalgae followed the sequence: Al > Zn > Pb > Cu.

Conclusion

This study assessed the spatial and seasonal variations of metal concentrations (Al, Zn, Pb, and Cu) in water, sediment, and algae (*Enteromorpha* spp.) samples from the Zandvlei estuary, providing insights into the levels and patterns of metal concentrations within this urbanised ecosystem. The findings revealed that aluminium consistently exhibited the highest concentrations across all matrices (i.e., water, sediment, and algae), while zinc, lead, and copper concentrations frequently exceeded both national and international water quality guidelines, indicating potential risks to aquatic health.

The comparison of metal concentrations with established environmental guidelines highlighted areas of concern, particularly regarding zinc, lead, and copper levels in sediment. These elevated metal concentration levels suggest localised sources of contamination, potentially linked to industrial activities and stormwater runoff. The findings of this study

underscore the necessity for ongoing monitoring to better understand and mitigate the impacts of metal pollution in the estuary and its influent rivers.

Furthermore, the use of *Enteromorpha* spp. as a bioindicator demonstrated its effectiveness in tracking metal accumulation. This algal species demonstrated higher concentrations of metals compared to surrounding water and sediment, affirming its role in reflecting the ecological health of the estuarine environment. The metal concentrations in *Enteromorpha* spp. appeared to reflect time-integrated metal bioavailability, further validated by existing literature indicating its rapid responsiveness to changes in ambient metal levels. The comparative analysis of metal levels in *Enteromorpha* spp. and the surrounding matrices reinforces its value as a reliable indicator for monitoring metal pollution in similar ecosystems.

Overall, this study contributes to a greater understanding of metal contamination dynamics in the Zandvlei estuary and highlights the importance of biological indicators in environmental monitoring efforts. Future studies should continue to explore these relationships and assess long-term trends in contamination to inform effective management strategies for preserving the ecological integrity of urban estuarine systems.

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Declarations

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