Rhizosediments of *Salicornia tegetaria* Indicate Metal Contamination in the Intertidal Estuary Zone

Marelé A. Nel[1,2,3]*, Gletwyn Rubidge[4], Janine B. Adams[1,2] and Lucienne R. D. Human[2,3]*

[1] DSI/NRF Research Chair, Shallow Water Ecosystems, Nelson Mandela University, Port Elizabeth, South Africa,
[2] Department of Botany, Nelson Mandela University, Port Elizabeth, South Africa, [3] South African Environmental Observation Network (SAEON) Elwandle Coastal Node Nelson Mandela University, Port Elizabeth, South Africa, [4] Department of Chemistry, Nelson Mandela University, Port Elizabeth, South Africa

Metal pollution is a well-known anthropogenic impact of highly developed estuaries, with dire consequences to the ecosystem. This study investigated the metal concentrations (Al, Cr, Cu, Fe, Mn, Ni, Pb, Zn) in the sediment colonized by *Salicornia tegetaria*, a dominant salt marsh plant in the lower intertidal zone of the Swartkops Estuary. The samples were collected at five sites along the banks of the middle and lower reaches of the estuary, and analyzed using an Inductively Coupled Plasma –Optical Emission Spectrometer. Metal contamination was determined using established normalized baseline models. It was found that all the sites contained metal enrichment, with the estuary mouth experiencing the least enrichment. *Salicornia tegetaria* holds a substantial amount of anomalous metals within its rhizosediment—providing a valuable ecosystem service to a highly developed Swartkops Estuary.

Keywords: metal pollution, Swartkops Estuary, baseline, coupled plasma optical emission spectrometer, salt marsh

INTRODUCTION

Estuaries are historically convenient places to build industries, as it was deemed a suitable place to dispose of large quantities of urban and industrial waste into the ocean (Forstner and Wittman, 1981). At the time it was judged to be appropriate, as rivers can transport and deposit waste into the ocean, which was considered to be so vast that it is insurmountable. Thus, metal pollution into estuaries is a well-known occurrence. Metals form part of various industrial processes, producing general products for consumers (Crane et al., 2017; Peppicelli et al., 2018). Once the waste and products are discarded, it adds to the naturally occurring metals in the sediment. Metals are commonly adsorbed onto the surface of sediment components, or dissolved in porewater (Basta et al., 2005; Almeida et al., 2008). These characteristics allows the sediment to act as a sink for metals, and mediates the release to the biological environment (Tack and Verloo, 1995; Strawn et al., 2015). The capacity for the sediments to retain the metals are limited to its physical and chemical characteristics, i.e., granulometric fraction, pH, oxidation-reduction potential and organic matter content are all important factors to include when assessing the bioavailability of metals

in sediments (Impellitteri et al., 2001; Navas et al., 2005; Carrillo −Gonzalez et al., 2006; Kabata-Pendias, 2011). However, metal behavior in sediments is far from simple, and these characteristics are not always applicable at the same extent, for other regions with different physico-chemical and biological interactions.

Wetlands play a crucial role in the biogeochemistry of trace elements in estuaries and provide a major sink for these elements (Caçador et al., 2009; Vodyanitskii and Shoba, 2015; Bonanno et al., 2018). The Swartkops Estuary is a very important socio-economic and environmental asset and has high biodiversity importance for in terms of fish, birds and plants (Turpie et al., 2002; Adams, 2020). It has a large intertidal salt marsh area and *Salicornia tegetaria* is a dominant species, but it only earns a botanical importance rating of 41–45 out of 100, due to the modifications to the system brought on by the development (Colloty et al., 2000). The accumulation of metals into the bottom sediments make these habitats particularly vulnerable to the impacts of metal toxicity. This is of concern due to the prevalent trend of environmental problems caused by metal pollution, which turns pristine environments toxic (Forstner and Wittman, 1981; Bonanno et al., 2017). However, some plant species can tolerate seemingly toxic metal levels and concentrate them into their below- or above-ground organs (Williams et al., 1994; Olguín and Sánchez-Galván, 2012). Moreover, some plant species can manipulate the bioavailability of metals in the sediments (Reboreda and Caçador, 2007; Duarte et al., 2010). Several wetland plants can also act as bioindicators of metals (Phillips et al., 2015), and can be used in ecological engineering in environmental management strategies. Estuary habitats are some of the most productive in the world and provide several crucial ecosystem services, namely: (1) nursery areas for marine fish, (2) a path for migratory marine and bird species, (3) habitat for important and endangered wetland ecosystems (saltmarsh, mangroves, seagrass beds), (4) transportation for nutrients and organic materials to coastal habitats, (5) carbon sequestration, and (6) the containment of endemic species dependent on the estuarine ecosystem (Roy et al., 2001; Turpie et al., 2002; Barbier et al., 2011; NBA, 2012; Adams, 2020).

A simple question of potential metal contamination in an area can become complicated without historical baseline data for comparison. Separating the naturally occurring metal concentrations from the contaminants is a challenge. Sediment Quality Guidelines (SQGs) are often used to compare current metal concentrations where historical data are unavailable. However, the SQGs are based on concentrations that are adverse to the ecosystem or human activity (Long et al., 1995), and cannot give an indication of *in situ* metal contamination. Sediment with comparably higher concentrations of metals compared to other areas can also not be assumed to be metal-contaminated. The research by Newman and Watling (2007) used these insights as a means to create geochemical baseline models for geological areas of the south-eastern coast of South Africa, between the Kromme Estuary in Cape St. Francis and the Nahoon Estuary in East London. Geochemical normalization compares the metal concentration with a reference element that follows crustal decomposition (Karageorgis et al., 2009).

The ratio of metal: normalizer is only comparable due to the stability of the normalizer within the area. Aluminum is often used as a normalizer in estuarine and coastal sediment (Kersten and Smedes, 2002). A stable metal will have little increase or decrease in their concentration. Aluminum concentrations are naturally high in sediment, being the third most abundant element in the earth's crust (Turekian and Wedepohl, 1961; Kring, 1997). The normalizer element can only be used when it's anthropogenic input is negligible (Almeida et al., 2008). Aluminum fits these criteria as anthropogenic inputs are not likely to be significant enough to affect its levels (Schropp et al., 1990). Iron (fourth most abundant element in the earth's crust) is often not suitable, due to its close association with manganese, which concentrates iron in the metal surface (Douglas and Adeney, 2000).

The Swartkops Estuary is located within the Nelson Mandela Metropolitan, South Africa. The estuary flows through highly urbanized and industrialized developments that began in the first quarter of the 19th century (Theal, 2010). Historical data does not include metal baseline concentrations specific to the area, so it is difficult to assess the impacts of industry and urbanization on the biota. Indeed, "there is a lack of baseline data of pollutants in the sediments and biota in the estuaries of South Africa" (NBA, 2012). Instead, studies have compared the metal concentrations to other datasets available from the 1970s—more than 150 years after the initial developments. Studies agree that the rate of metal accumulation has increased throughout the Swartkops Estuary, in some cases more than 100% for Cr, Mn, Pb and Zn (Binning and Baird, 2001). In 2014 high concentrations were found in the juveniles of popular angling fish, selected invertebrates and in the eggs of gull, exceeding the international food quality guidelines, where applicable (Nel et al., 2015). Other than fishing, the estuary has important recreational and ecological importance, providing numerous essential ecosystem services originating from the diverse salt marsh and seagrass habitats. The estuary has high national botanical importance, because of the large intertidal salt marshes (Colloty et al., 2000; Adams, 2020). The ability of the salt marshes to capture and localize metals and other contaminants is important to maintain a healthy ecosystem. Assessing the extent of metal contamination in the area will provide critical information on how the salt marsh habitats are coping as metal sinks, as well as information for environmental management procedures within the estuary. *Salicornia* spp. is good at localizing metals in their roots, preventing metals from entering the food chain (Smillie, 2015). Little research has been done on *S. tegetaria*, a lower intertidal salt marsh species vulnerable to the effect of sea-level rise (Brown and Rajkaran, 2020). In this study, sediment metal concentrations within monoculture stands of *S. tegetaria*, a dominant halophyte within the Swartkops salt marshes, were assessed. The metals analyzed included Al, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The objective of this paper was to investigate the levels of metal contamination within the salt marsh habitat of the Swartkops Estuary. The sediment characteristics were also determined to ascertain the behavior of metals in the salt marsh. In order to determine whether contamination was influenced by anthropogenic sources, a geochemical (normalization) model created by Newman and Watling (2007) was used. This can

potentially indicate the extent of metal contamination in the marsh, between the approximately 40-year-old datasets used for the models.
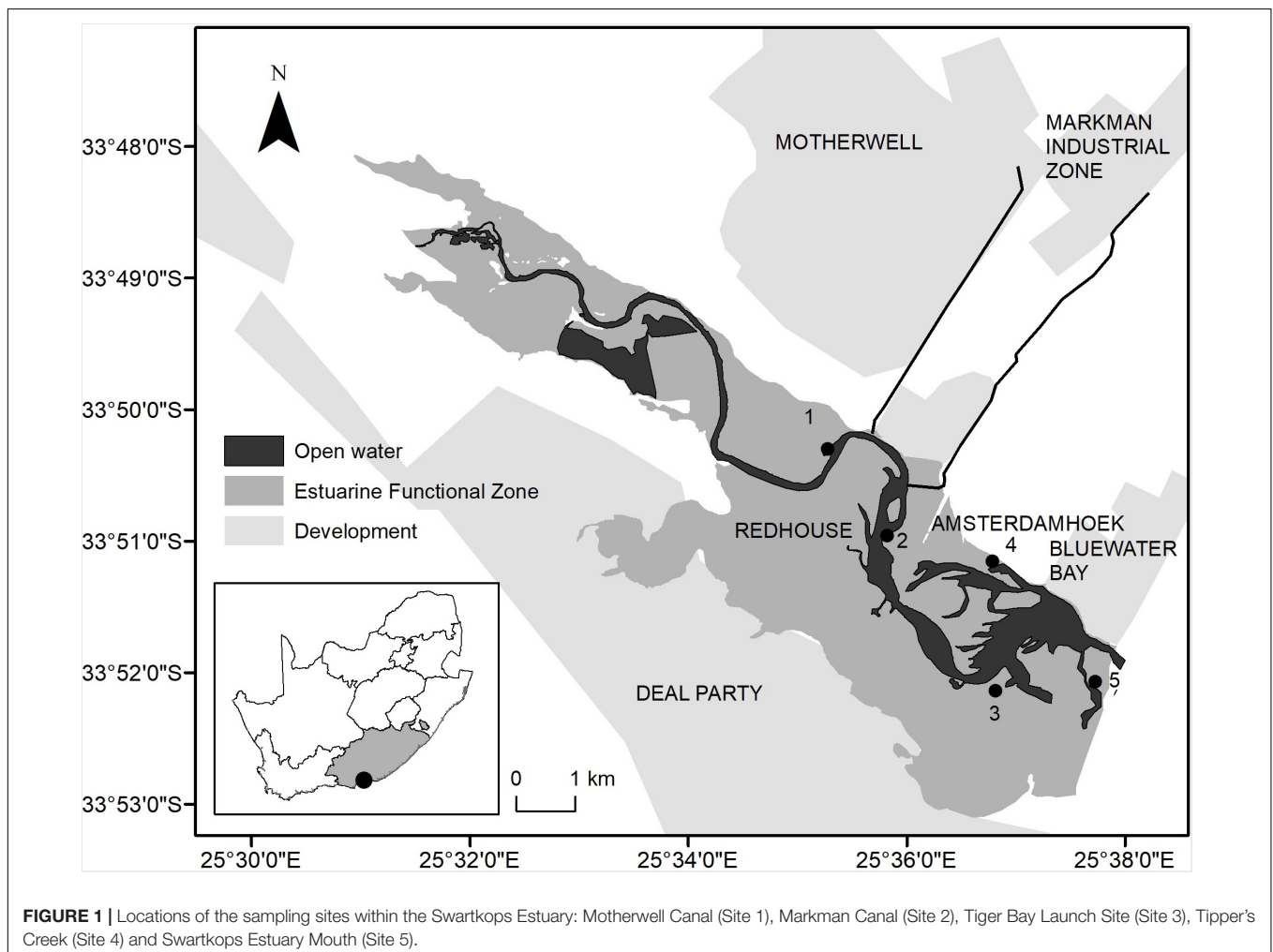
MATERIALS AND METHODS

Study Site and Sampling

Sediment samples were collected on 30 April 2019 and 01 May 2019 from the saltmarsh of the Swartkops Estuary (33°51′11″S; 25°36′53″E), which is a predominantly open warm temperate estuary. Five sites were chosen along the middle and lower reaches of the estuary, according to the distribution of plant species. Point source inputs from surrounding catchment activities occur in close proximity to Motherwell Canal (Site 1), Markman Canal (Site 2), Tiger Bay Launch Site (Site 3), Tipper's Creek (Site 4) and Swartkops Estuary mouth (Site 5) (**Figure 1**). The latter is close to an inactive oyster farm. At each site randomly selected *S. tegetaria* plants were carefully uprooted using a PVC corer (Diameter = 11.2 cm). Sediment samples from the rhizosediment were collected at the surface of the cores and stored in polyethylene jars. Five replicates of the sediment

samples were collected at each site. The samples were transported in a cooled and insulated container, to the laboratory on the day of collection.

The Motherwell Canal (Site 1) is the furthest site from the mouth and is located just above the actual canal. The canal is connected to 14 stormwater drains and contains a series of litter traps located at regular intervals. The base of the canal is connected to an artificial wetland, which was built to extract the pollutants from the wastewater flowing down the canal. Large volumes of plastic debris and other litter enter the canal from the surrounding developments. The Motherwell township is located along the canal. Approximately 1 km downstream from Site 1 is the Markman Canal, which transports stormwater effluent from a large industrial area. Site 2 is located downstream from the canal, within a large salt marsh. The Tiger Bay Launch Site (Site 3) is located downstream, on the opposite side of the riverbank. It has an interconnected series of creeks, which contains large stands of eelgrass (*Zostera capensis*). The Papenkuils River connects to the Swartkops Estuary close to Site 3. This river is very small but flows through a large section of Port Elizabeth (urban and industrial areas) to reach the Swartkops Estuary. The last 8 km of the Papenkuils river is reinforced with concrete, forming a canal. Site

FIGURE 1 | Locations of the sampling sites within the Swartkops Estuary: Motherwell Canal (Site 1), Markman Canal (Site 2), Tiger Bay Launch Site (Site 3), Tipper's Creek (Site 4) and Swartkops Estuary Mouth (Site 5).

3 is located adjacent to Site 4, on the other side of the estuary, and next to the wastewater treatment works, which treats urban and industrial effluent. A busy national road is located next to Site 3, and can be followed to a dense neighborhood, Amsterdamhoek, adjacent to the riverbank and Tippers Creek (Site 4). The creek contains numerous jetties and a large mudbank. The Swartkops Estuary mouth is predominantly open. The area is subjected to higher flushing rates, due to the strong marine influence in the area, compared to the rest of the estuary. Site 5 is located next to the estuary mouth, where an inactive oyster farm was located. The catchment lacks any large-scale agricultural activities (Bornman et al., 2016).

Metal Determination

Total metal extractions were performed using a conventional HNO_3 (65%, AR, Merck) digestion in 250 ml glass beakers covered with watch glasses (Du Laing et al., 2003; Phillips et al., 2015). The samples were first freeze-dried using a (Vacutec, V-FD12 Series Freeze Dryer), which dries the sediment at $-60°C$. The homogenized and dry sample of sediment was pushed through a 1 mm nylon mesh. Then 1.00 g was digested in 10 ml of the 65% HNO_3 overnight, and afterward on a hotplate for 5 h at $110°C$. After evaporation to near dryness the sample was diluted with 20 ml of 2% (v/v H_2O) nitric acid and transferred to 50 ml volumetric flasks, after filtering with Whatman® glass fiber filters (GF/F, pore size $= 0.7 \mu m$), and diluted to the mark with Milli-Q ultra-pure water.

Extracts were analyzed for the selected metals using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, PerkinElmer®, Avio^{TM} 200) by the aspiration of the sample into an argon generated plasma. The analytical wavelengths used were (in nanometer): Al (396.2), Cr (357.9), Cu (224.7), Fe (302.1), Mn (259.4), Ni (221.6), Pb (217.0) and Zn (206.2). Detection limits for the selected metals (in $\mu g \, L^{-1}$) were directly obtained from the ICP-OES program: Al (28), Cr (23), Cu (7.7), Fe (20), Mn (1.6), Ni (10), Pb (90) and Zn (5.9). Method blanks were prepared by using the same digestion procedure as the samples and were subtracted from the results during analysis. Blanks and concurrent analysis of standards were used to detect possible contamination during analysis. The samples were measured in triplicate and obtained in ppm. Due to the magnitude of Al and Fe, they were reported in mg g^{-1}, whereas the rest of the metals were reported in $\mu g \, g^{-1}$.

Sediment Characteristics

Sediment pH was measured using a handheld Hanna (Hanna® Instruments, HI98121 Tester) *in situ*, on the surface sediment, upon collection. All instruments were calibrated and cleaned according to the manufacturer's specifications. Other sediment characteristics were measured in the laboratory; sediment organic content (%), conductivity (μS) and granulometric size. Organic content of the sediment was measured using the loss on ignition method described in Veres (2002) with 10 g of wet sediment (Eq. 1). The samples were freeze-dried using a (Vacutec, V-FD12 Series Freeze Dryer). Sediment salinity was measured conductometrically by mixing a ratio of 250 g

dried sediment to 100 ml distilled water, or until saturation, according to the specification in Bernard (1990). The mixture was then filtered through Whatman No.1 filter papers and the electrical conductivity was measured using a handheld conductivity meter (CyberScan, HANNA handheld conductivity meter). Granulometric size was also determined with the dry sediment using the sieve method (Wentworth, 1922). All samples were analyzed in triplicate.

$$\% \, TOM \ = \ [(\text{dry mass before combustion}$$
$$- \text{dry mass after combustion})/\text{dry mass}] \ \times \ 100 \quad (1)$$

Statistical Analysis

The analyses of variance (ANOVA, random effects) was used to test for differences in the total concentrations of metals, the percentage total organic matter (TOM), pH and salinity. Tukey's *post hoc* test was then used to compare the means where significant differences were found. The assumptions of normality were verified before analysis with the Shapiro-Wilks test accompanied with the respective histograms. Variables were log transformed (Log[M], where M is the concentration of the selected metal) if the null hypothesis for normality was rejected. Metal enrichment was determined using metal-Al baseline relationships for coastal sediment in the region that included the study site (between the Kromme Estuary and the Sundays Estuary). The regressions were modeled by Newman and Watling (2007). Scatterplots of the metal data were overlain with the straight-line equations provided. Points above the baseline are considered enrichment. Non-metric multidimensional scaling (NMDS) was performed on the metal concentrations and the environmental factors (i.e., the sediment characteristics) were overlain as vectors, to show the degree of influence of the environmental characteristics on the metals and the sites. Statistical processing was performed in RStudio (R version 3.5.1 and 4.0.2), a product of RProject using the R-commander (Version 2.6-2) with the packages Vegan, RColorBrewer, Tidyverse and Geoveg.

RESULTS

Metal Concentrations

Considering the metal concentration in the sediment, Site 4 had the highest concentrations of metals in the sediment with no exceptions, followed by Site 3 (**Table 1**). The lowest concentrations were measured in Site 5, with the exception of Zn, where the lowest value occurred in Site 1. These differences were for the most cases significant ($p < 0.05$), however, Zn concentrations had no statistical difference across all the sites. Other cases where Site 5 did not contain the statistically lowest concentration was: Cr and Cu (Site 1 and Site 2; $p > 0.05$), and Mn (Site 1; $p > 0.05$) Contrastingly, the metal normalizer (Al), showed statistical differences across all sites with the exception of Site 2 and Site 3 ($p > 0.05$).

TABLE 1 | Average metal concentrations (Al, Fe = mean mg g^{-1} ± SD; Cr, Cu, Mn, Ni, Pb, Zn = mean μg g^{-1} ± SD) of the surface sediment at the sampling sites ($N = 15$).

[M]	Site 1	Site 2	Site 3	Site 4	Site 5
Al	8.8 ± 0.2[a]	15.1 ± 0.3[b]	20.3 ± 6.4[b]	42.1 ± 2.8[c]	2.1 ± 0.2[d]
Fe	18.1 ± 6.3[a]	24.8 ± 1.4[a]	30.2 ± 7.1[a]	58.0 ± 4.6[b]	5.1 ± 0.9[c]
Cr	21.7 ± 5.6[a]	26.6 ± 0.3[a,c]	42.3 ± 15.0[a]	99.4 ± 2.2[b]	14.1 ± 2.5[c]
Cu	36.9 ± 7.1[a,c]	39.7 ± 3.9[a,c]	52.0 ± 9.1[a]	85.6 ± 7.6[b]	18.4 ± 3.0[c]
Mn	110.9 ± 55.6[a,c]	283.1 ± 34.3[a,b]	286.6 ± 49.4[a,b]	379.1 ± 103.1[b]	33.9 ± 0.3[c]
Ni	10.3 ± 2.7[a]	10.5 ± 0.7[a]	14.7 ± 3.3[a]	24.4 ± 1.8[b]	2.5 ± 0.3[c]
Pb	48.3 ± 12.9[a]	60.8 ± 2.8[a]	89.3 ± 27.1[a]	187.5 ± 19.1[b]	14.8 ± 1.8[c]
Zn	90.9 ± 20.5[a]	93.4 ± 4.9[a]	104.5 ± 24.9[a]	136.6 ± 16.0[a]	98.6 ± 23.2[a]

Different letters (a, b, c, d) indicate significant differences between values of the same element within the five sites (p < 0.05).

Sediment Characteristics

Figure 2A show the separation of the metal concentrations in Site 5 to the rest of the sites. The NMDS showed a good fit with a stress value <0.05. Similarities occurred between Site 2 and Site 3, seen by the overlap of the diagram in the figure. The sediment characteristics had different degree of influence on the metal concentrations in the sites. Gravel, pH and organic matter showed significant results ($p < 0.05$). The environmental vector representing percentage gravel showed the greatest influence in Site 1, while pH and total organic matter showed the greatest influence in Site 2 and Site 3. The metal concentrations all differed from each other (**Figure 2B**), but according to the environmental vectors do not point directly at the type of metals. The exception is Mn, where the significant vector, total organic matter, is directed to it.

Total organic matter (TOM) was highest at Site 3 (6.32 ± 0.008%) and the lowest at Site 5 (2.89 ± 0.003%; **Figure 3**). These sites also displayed the highest (41.53%) and lowest (1.40%) silt/clay content, respectively. The difference was significant according to statistical processing ($p < 0.05$). The other sites displayed no significant statistical differences in TOM. The grain size distribution was reasonably similar throughout the sites except for Site 3 and Site 5. The latter having a much coarser grain than the other sites. Gravel was not present in Site 1 and Site 2 and was negligible in Site 4 and Site 5 (<0.1%). Site 3 had the highest gravel content but did not exceed 2%.

The pH differed across the sites (**Figure 4A**). The lowest pH was found in Site 4 (7.3 ± 0.1), while the highest was in Site 5 (8.3 ± 0.1) and they differed significantly from each other ($p < 0.001$). The pH of Site 4 was also lower than Site 2 and Site 3 ($p < 0.05$), and Site 5 had a higher pH than Site 1 ($p < 0.05$). The salinity (μS; **Figure 4B**) did not differ significantly between sites according to statistical testing. The lowest salinity was measured in Site 1 (6.6 ± 0.9), while the highest in Site 2 and Site 4 (10.8 ± 0.6 and 10.8 ± 1.3; **Figure 4**).
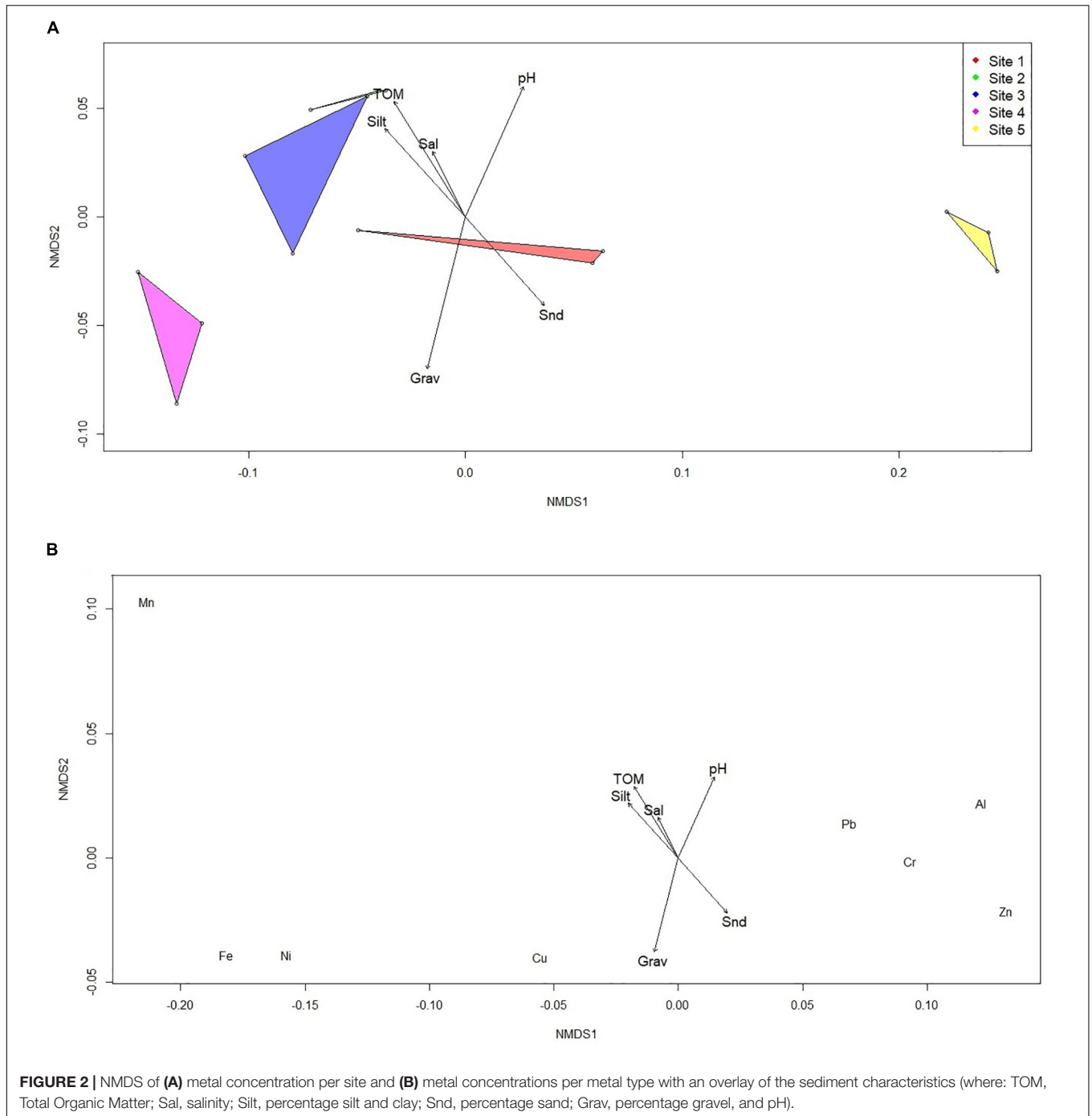
Metal Contamination

The majority of the metals are higher than the baseline (**Figure 5**). Cu, Cr, Fe, Pb, and Zn show enrichment across all the sites. Cr is notably much higher than the baseline in Site 4 compared to the other sites and does not follow the trend of the baseline (**Figure 5B**). Cu, Pb, and Fe plots deviate from the gradients of the

baseline, indicating that the metal concentration increases more steeply with the metal normalizer, than the baseline suggested (**Figures 5A–C**). The majority of the points fall above the baseline for Mn and Ni however, the exceptions occur in Site 1 and Site 4 for Mn and Site 4 for Ni (**Figures 5D,E**). The plots for the latter metal, Ni follows the baseline closely.
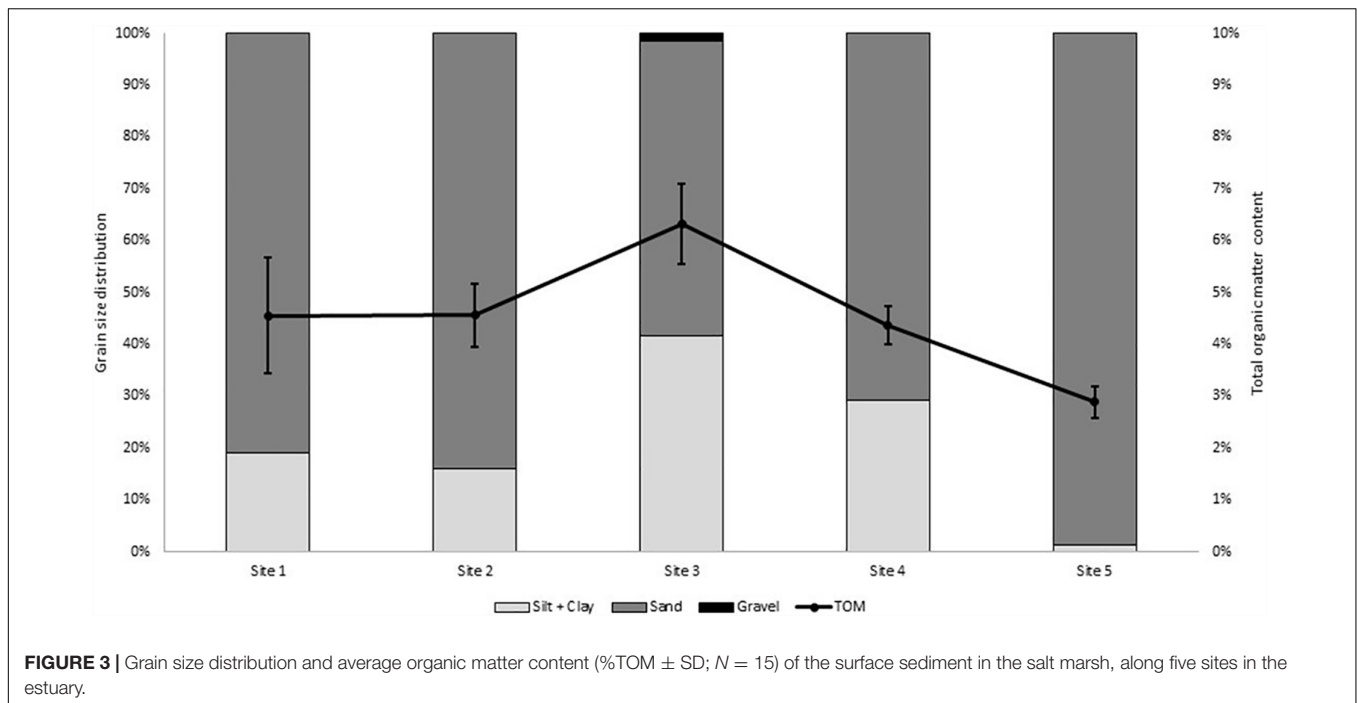
DISCUSSION

This study measured six of the most common metal contaminants in the Swartkops Estuary i.e., Al, Cr, Pb, Mn, Ni and Zn (Strawn et al., 2015). The average metal concentrations in this study follows a decreasing order of Fe > Al > Mn > Zn > Pb > Cu > Cr > Ni (**Table 1**). The five sites within the estuary showed a 46% average increase in metal concentrations (Cr, Cu, Mn, Pb, Zn) over the past 23 years (Binning and Baird, 2001). The same study compared the 1996 dataset with another in 1979, and found an average increase of 149% in metal concentrations between them. Previous authors agree that the anthropogenic activities surrounding the estuary are to blame for the increases (Baird et al., 1986; Binning and Baird, 2001; Phillips et al., 2015). However, metals also occur naturally in the sediment due to the weathering of rock (Kabata-Pendias, 2011). Some metals such as Al and Fe, form a large part of the sediment matrix, and occur in much higher concentrations that the other metals (Newman and Watling, 2007). The Al and Fe concentrations ranged from 2.1–42.1 mg g^{-1} to 5.1–58.0 mg g^{-1} (**Table 1**), respectively. Newman and Watling (2007) established that Fe contamination is prevalent in the Swartkops Estuary. The Al concentrations measured in this study were of a comparable range to previous studies (0–40 mg g^{-1}), which also confirms that no significant Al contamination has occurred in the middle and lower reaches of the estuary (Watling and Watling, 1979, 1982; Newman and Watling, 2007). Gyedu-Ababio (2011) reported much lower Fe concentrations in the sediment of the Swartkops Estuary (1.9 mg g^{-1}–16.42 mg g^{-1}), but is still comparable where sites correspond. Manganese concentrations ranged from 33.9 to 379.1 μg g^{-1} in this study. Iron and Mn oxides play an important role in scavenging other metals such as Cu, Ni, Pb and Zn from solution (Vesper, 2012). Gyedu-Ababio (2011) also found Mn concentrations between 64 and 229 μg g^{-1},

FIGURE 2 | NMDS of **(A)** metal concentration per site and **(B)** metal concentrations per metal type with an overlay of the sediment characteristics (where: TOM, Total Organic Matter; Sal, salinity; Silt, percentage silt and clay; Snd, percentage sand; Grav, percentage gravel, and pH).

previously in the estuary. The concentrations reported by this author are also lower for Mn, but is again comparable where the sites correspond.

Lead concentrations in this study ranged from 14.8 to 187.5 μg g^{-1} of sediment, showing a 47% increase from 1996 (**Table 1**). High loads of Pb were associated with the stormwater originating from high density, low-income settlements in entering False Bay, South Africa (MacKay, 1994). This may be the case in the Swartkops Estuary, as stormwater and effluent

from the Wastewater Works enters the system. Another source of Pb contamination is the highway, as automobile exhaust gas is a well-known source of Pb aerosol (Mielke et al., 2010). Site 4 was the only site in which Pb concentrations exceeded Zn concentrations—owed to its proximity to an urban roadway. Lead concentrations in this study were much higher than that reported by Phillips et al. (2015)—maximum concentrations differed by approximately 60 μg g^{-1} (or 16%) of sediment. In both these cases, the maximum concentrations were located close

FIGURE 3 | Grain size distribution and average organic matter content (%TOM ± SD; $N = 15$) of the surface sediment in the salt marsh, along five sites in the estuary.
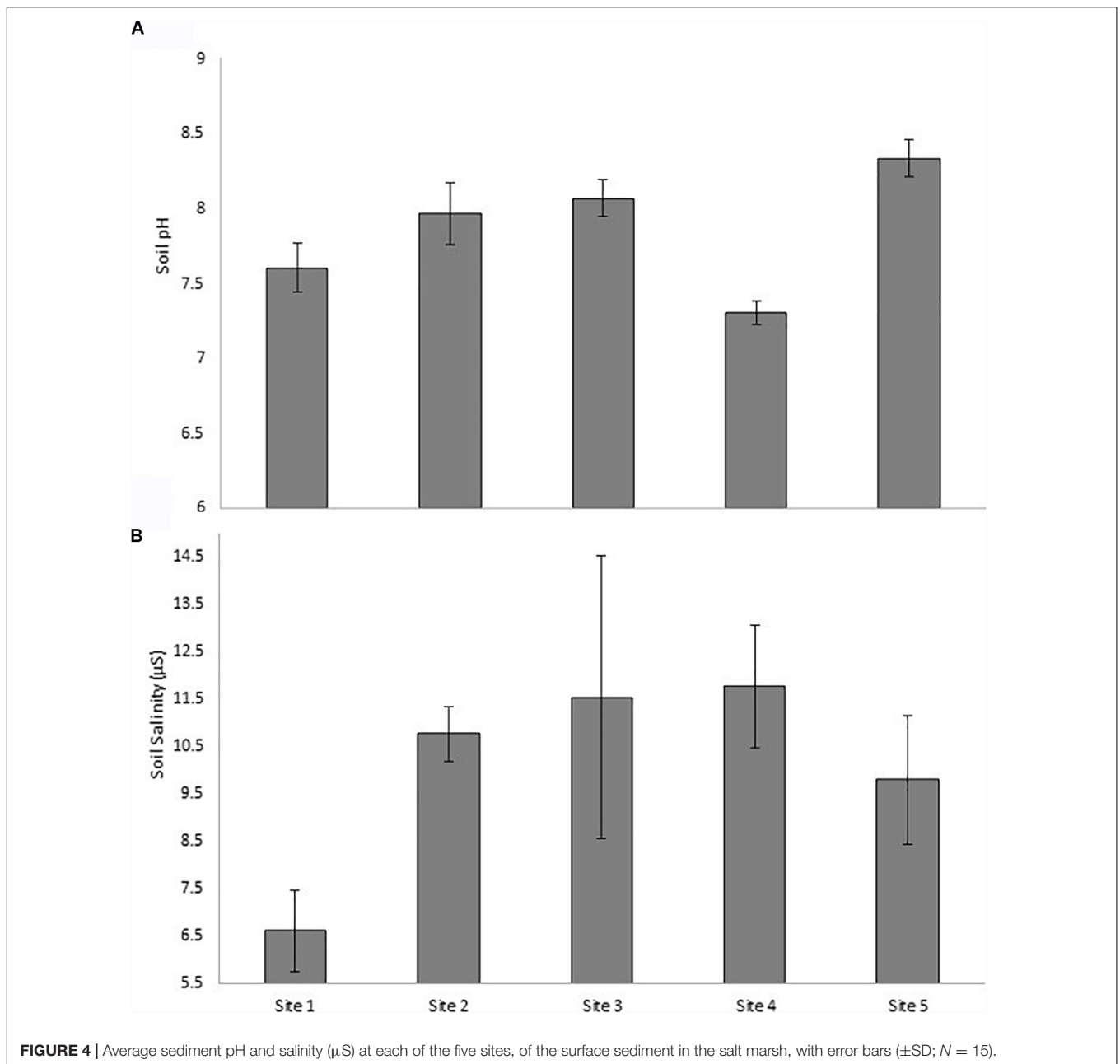
to highways and roads, that is; Redhouse and Tippers Creek (Site 4; **Figure 1** and **Table 1**). Copper, Pb, Ni and Zn are the most commonly measured metals in the estuary. Copper and Zn concentrations ranged from 18.4–85.6 µg g^{-1} to 93.4–136.6 µg g^{-1}. Binning and Baird (2001) indicated that Cu and Zn pollution enters the system in the freshwater reaches, from the industries in Uitenhage (**Figure 1**). Phillips et al. (2015) found their highest Cu and Zn concentrations (51.5 µg g^{-1} and 112.9 µg g^{-1}, respectively) in the Upper Markman Canal, which carries effluent from industries into the estuary.

There are multiple point sources in the Swartkops Estuary, and most prominent is the effluent from the Markman (industrial) Canal, the stormwater from the Motherwell Canal, treated effluent from the Fishwaterflats Wastewater Treatment Works, and contaminated water from the Papenkuils River. However, the data indicates that the highest metal concentrations were measured in Site 4 (Tippers Creek), which is downstream from the two point-sources mentioned first. Site 3, also downstream from the two main point sources, contained the second highest metal concentrations in the estuary. The Papenkuils River connects to the Swartkops Estuary at this site. Watling and Emmerson (1981) found higher concentrations of Cu, Zn, Cr and Pb in the Papenkuils than in the estuary. Both sites are located within creeks and between two motorway bridges, that carry heavy traffic. The bridges are one of the factors that cause heavy sediment accretion in Site 3 and Site 4 (Esterhuysen and Rust, 1987). Sediment accretion in Site 4 is further enhanced by the jetties, which also trap sediment and creates a large sand bank against the concrete wall, adjacent to the urban area, Amsterdamhoek (**Figure 1**). The obstructed flow of water entering the creek is therefore trapped between the artificial concrete bank with the jetties and the large sand bank in the
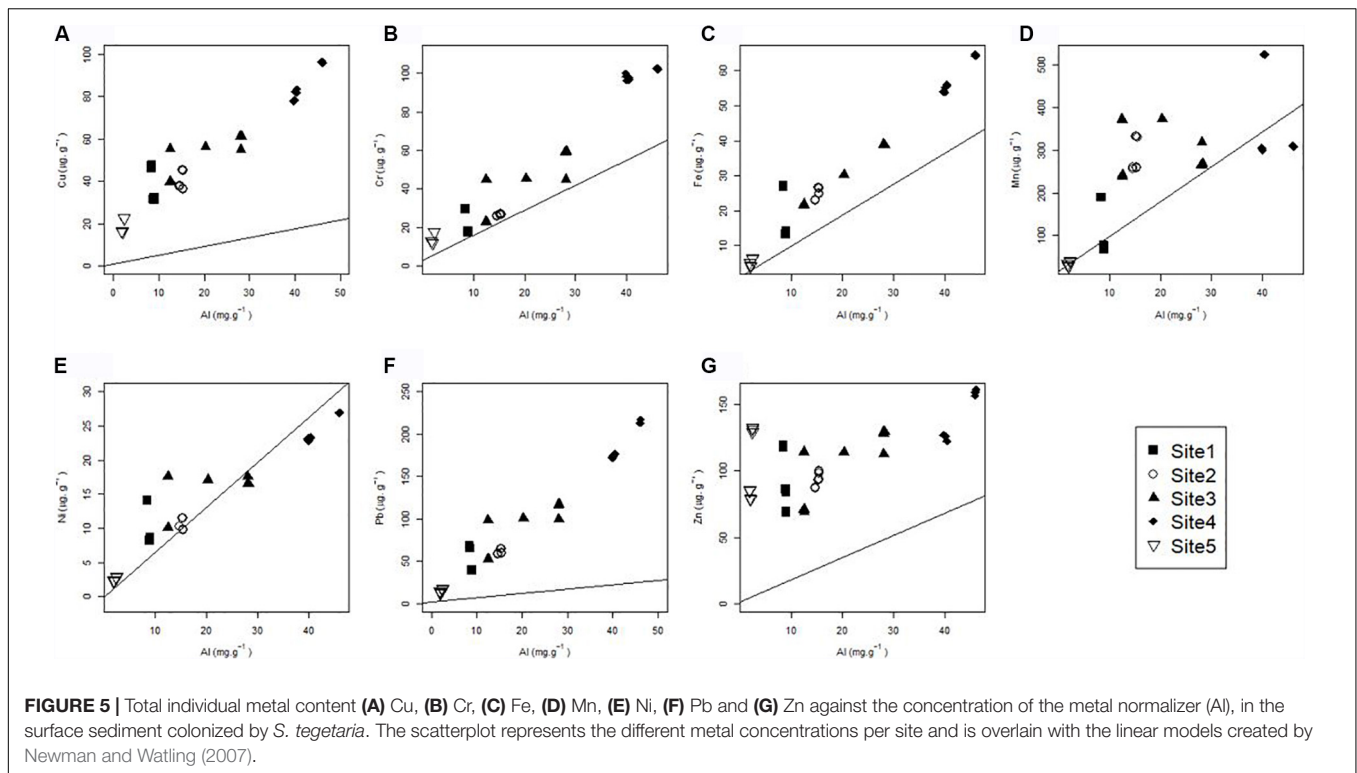
middle of the estuary. According to Esterhuysen and Rust (1987), both Site 3 and Site 4 are conducive to trapping sediment and other particles that flow downstream. These conditions make the sites favorable to trap particles containing metals, as well as capturing soluble metals from the overlaying water column. The extensive root system of *S. tegetaria* can also trap sediment particles that flow down river, creating an ideal environment to act as a metal sink. The metals trapped within the creeks may most likely originate from the Motherwell Canal and the Markman Canal, which transports effluent from low-income settlements and large industries, respectively. Indeed, Watling and Watling (1982) and Nel et al. (2015) both formed the conclusion that pollutants transported into Tippers Creek (Site 4) may be incompletely flushed by tidal action and may have resulted in its build-up over time. Adams et al. (2019) recommended Tippers Creek as a long-term metal monitoring site.

Each of the five sites sampled in the estuary show distinct differences, and general similarities (**Figure 2A**). Metal concentrations in Site 2 and Site 3 are the most similar, depicted by the overlap in **Figure 2A**. Site 4 is distinctly dissimilar from Site 2 and Site 3, just emphasizing the extremely high metal concentrations found here. The lowest metal concentrations in Site 5 can also distinctly be seen, as the diagram is far removed from the other sites. The sediment characteristics of the given sites largely affect the capacity of the sediment to accumulate metals. Contrastingly, it also dictates the potential for leaching (or flushing) and the bioavailability (or mobility) of the metal to plants and other biota. Authors are still debating which sediment characteristics are the most important determinant of the element's form (Kabata-Pendias, 2011), however, pH, carbonates and Fe and Mn oxides greatly influence the behavior

FIGURE 4 | Average sediment pH and salinity (μS) at each of the five sites, of the surface sediment in the salt marsh, with error bars (±SD; *N* = 15).

of chemical elements (Shine et al., 1995; Li et al., 2013). Others suggest that it is pH, redox potential and organic matter that are the most important in sediments (Hermann and Neumann-mahlkau, 1985; Strawn and Sparks, 2000). In this study, the gravel content, pH and organic matter content had the most significant effect on the metal behavior. Copper and Pb did not form a close association with the total organic matter content as would be expected (**Figure 2B**; Duarte et al., 2010; Wyatt and Stevenson, 2010; Human et al., 2020), but metal behavior in sediment is complex, and the other characteristics and unmeasured factors cannot be ignored. The pattern of the environmental vectors in **Figure 2B** would suggest that the sediment characteristics play a dynamic part in the metal form.

The study sites are dominated by the larger grain sizes, sand (Avg% sand > 50%; **Figure 3**). Bradley and Morris (1990), who studied salt marshes across the Eastern United States of America, also found that the salt marshes tend to be dominated by sand. This agrees with previous assessments of the middle and lower reaches of the Swartkops Estuary (Reddering et al., 1981; Els, 2020). Reddering et al. (1981) indicated that the sand originates by tidal transportation from the sea. Large grain size (sand) in sediments usually present lower levels of metal accumulation (Williams et al., 1994; Zhang et al., 2001). Contrastingly, higher percentages of the finer particles (clays and silt), increases the metal binding capacity of cationic metals onto the negatively charged surfaces (Ujeviæ et al., 2000). The binding capacity of

FIGURE 5 | Total individual metal content **(A)** Cu, **(B)** Cr, **(C)** Fe, **(D)** Mn, **(E)** Ni, **(F)** Pb and **(G)** Zn against the concentration of the metal normalizer (Al), in the surface sediment colonized by *S. tegetaria*. The scatterplot represents the different metal concentrations per site and is overlain with the linear models created by Newman and Watling (2007).

smaller sediment particles are so significant due to the high specific surface area creating more binding sites for metals (Lin et al., 2003). In this study, the estuary mouth (Site 5) had the highest sand content at 97%, while Site 3 had lowest at 57% followed by Site 4 at 82% (**Figure 3**). Site 3 and Site 4 contained the only silt and clay content above 17%; that is 41.5 and 33.8%, respectively (**Figure 3**). This may indicate a higher degree of fluvial sediment in-put in at these sites, previously established as trapping sediment and other particles flowing downstream. High sand content in the estuary increases the potential of metals to be leached to the water column and transported downstream. This may occur in Site 1 and Site 2 (% sand >80%), where two of the point sources occur (Motherwell Canal and Markman Canal). The metals may thereafter be captured and accumulated by the higher silt/clay content in Site 3 and Site 4.

The organic content of sediments in this study is very low but followed a similar pattern as the grain sizes. The highest value is 6.3% at Site 3 and the lowest value is 2.9% at Site 5 (Estuary Mouth). The organic matter content in Site 4 fell just below the average at 4.4%. Bradley and Morris (1990) indicated that these values are natural, as they found organic matter ranges from 2 to 16% in salt marshes. A recent study in the Swartkops Estuary found similar organic matter content (Els, 2020). Organic matter plays a significant role in metal accumulation. Low organic matter content in sediments usually presents lower levels of metal accumulation (Williams et al., 1994). Higher percentages of organic matter increases the metal binding capacity of cationic metals by forming insoluble complexes with the metals (Ujeviæ et al., 2000). Copper and Pb in general prefer to bind to sediment organic matter, creating complexes with the humic acids that

form part of sediment organic matter (Duarte et al., 2010; Wyatt and Stevenson, 2010; Human et al., 2020). Although, Cu and Pb's association with sediment organic matter is strong, other metals also form bonds with it due to the high specific surface area provided by the sediment organic matter (Lin et al., 2003).

Lastly, the pH and salinity in the rhizosediment of the salt marsh ranged between 7.3–8.3 and 6.6–11.8 μS, respectively (**Figure 4**). The highest pH was found at the mouth (Site 5) and the lowest at Site 4, though the latter is not quite acidic. Acidity increases the mobility of cationic metals—creating conditions conducive to the leaching of these metals into the water column (Williams et al., 1994). It is due to the adsorption and desorption mechanisms onto sediment surfaces that are largely controlled by pH (Li et al., 2013). However, Eh (redox potential) also has an important relationship with metal mobility, and in cases where pH is alkaline and Eh is highly positive, metals can become immobile before reverting to a mobile anionic metal species (Hermann and Neumann-mahlkau, 1985; Kabata-Pendias, 2011). The pH requirements to form an ionic Cu species ($Cu_2O_2^{2-}$) is above 12 and did not occur in this dataset (Hermann and Neumann-mahlkau, 1985). The salinity remained fairly constant within the sites, however, Site 1, being the uppermost site showed significantly lower salinity. Fritioff et al. (2005) found that metals become more bioavailable for submersed plants (like *S. tegetaria*) with decreasing salinity and increasing temperature. Lower salinity and high sand content in upper sites, close to the point sources (Motherwell Canal and Markman Canal), creates conditions that enhance metal mobility, and therefore its transport to the lower reaches of the estuary.

For this study, the baseline models indicate that all the sites are metal enriched—where metal concentrations fall above the baseline (**Figure 5**). The exceptions are for Mn (Site 4 and Site 1), and Ni in Site 4 and Site 2 (**Figures 5D,E**). Copper, Pb and Zn in particular show high enrichment throughout all the sites, with the exception of Pb, which had low concentrations at the mouth (**Figures 5A,F,G**). The sites with the highest concentrations, Site 3 and Site 4, show anomalous Cu, Cr, Fe, Pb and Zn levels. The mouth (Site 5), which contained the lowest metal concentrations, show enrichment in Cu, Cr, Fe, Ni, Pb and Zn. Some of these data points fall close to the baseline, which may indicate that the enrichment in Site 1 is not that large, however, Cu and Zn are of particular concern (**Figures 5A,G**). An outfall, located 1 km SSW from the estuary mouth is a source of contamination, and waste is transported to Site 5 through the connected bay (Emmerson et al., 1983). The outfall contains treated urban and industrial effluent from the wastewater treatment works. However, with the presence of sediment characteristics conducive to leaching and the marine turbulence at the mouth, the contamination at the mouth has not reached critical levels. The same cannot be said for the middle and lower reaches (Site 1–Site 4) that have metal concentrations far exceeding the baseline.

CONCLUSION

This study investigated the levels of metal contamination within the salt marsh habitat of the Swartkops Estuary. From the baseline models it is clear that the pollution is of anthropogenic origin and the estuary is highly enriched by metal contamination resulting from the vast array of urban and industrial settlements, which releases effluent into the estuary. It follows that the gravel content, pH and organic matter content had the most significant effect on the metal behavior. Considering the above observations, it can be concluded that the rhizosediment of *S. tegetaria* acts as a metal sink and localizes the contamination of metals to a large extent thereby performing an important ecosystem service.

Management practices are crucial at this stage of development as high concentrations of metals leading to metal enrichment can restrict some recreational activities, in and around the estuary.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

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