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A review of metal pollution in a transformed, urban South African Estuary

Aldwin Ndhlovu [a,c,f,*], Janine B. Adams [b,c], Marele Nel [b,c,d], Brent Newman [e,g], Gavin M. Rishworth [a,c], Lucienne R.D. Human [b,c,d]

[a] Department of Zoology, Nelson Mandela University, Gqeberha 6031, South Africa
[b] Department of Botany, Nelson Mandela University, Gqeberha 6031, South Africa
[c] DSI/NRF Research Chair in Shallow Water Ecosystem, Institute of Coastal and Marine Research, Nelson Mandela University, Gqeberha 6031, South Africa
[d] South African Environmental Observation Network, Elwandle Node, Gqeberha 6031, South Africa
[e] Coastal Systems and Earth Observation research group, Council for Scientific and Industrial Research, Durban 4013, South Africa
[f] Scientific Services, South African National Parks, Sedgefield 6573, South Africa
[g] Institute for Coastal and Marine Research, Nelson Mandela University, PO Box 77000, Gqeberha, 6031, South Africa

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ABSTRACT

Metal pollutants enter coastal water bodies from agricultural, industrial, and domestic wastewater activities amongst other sources. These pollutants are often transported through the food chain to higher trophic levels including organisms such as fish. Ultimately, they may pass to humans that consume contaminated seafoods. As such, it is imperative to understand how metals in estuarine systems are transported across trophic levels. Baseline data on metal concentrations are of crucial importance to evaluate changes over time and amongst areas to inform management and conservation strategies. In this assessment, we compile and discuss a database of metal concentrations recorded in various environmental media in the Swartkops River estuary, as a baseline against which future comparisons can be made. The Swartkops Estuary is subjected to considerable anthropogenic pressure that has led to a deterioration in water quality. We also provide a conceptual model to understand the flow of metals in the estuary. We furthermore identify lines of future research that will address gaps and uncertainties in the existing data and provide recommendations for remediation. Studies on metal concentrations in the water column of the estuary are limited. Studies on metals in sediment suggest that the estuary is not significantly metal contaminated. While studies revealed that plants do accumulate metals and fauna studies show differences in metal concentrations in the tissue of invertebrates and fish. It is difficult to conclude if these fauna are accumulating metals in their tissue compared to historically and if concentrations reflect uptake as a consequence of exposure to metal contaminated water, sediment and food.

1. Introduction

An estimated 45% of the world's population, or ~3 billion people, live within 100 km of a coast. The result is extensive urbanisation and industrialisation of many coastal areas and damage to and extraction of coastal natural resources. Estuaries in particular are under threat (Wepener and Degger, 2012; Zhu et al., 2017) because of the position they occupy in the coastal landscape. Estuaries provide many economic and social benefits (Jasmin et al., 2020; Sink et al., 2012), but often bear the brunt of man's activities. Human derived contaminants are introduced directly or indirectly into estuaries, posing a risk to fauna and flora (Wepener and Degger, 2012) and to humans that extract resources (e.g., fish) from estuaries (Wepener and Degger, 2012; Zhu et al., 2017; Ye et al., 2020; Olisah et al., 2021). Approximately 34% of the total estuarine area in South Africa is under severe pressure from pollution (Van Niekerk et al., 2022).

The Swartkops Estuary in Gqeberha (formally Port Elizabeth) in South Africa is an example of a highly impacted estuary. The surroundings of the lower part of the Swartkops River and much of the estuary are urbanised and this has resulted in numerous pressures on the estuary (Adams et al., 2019; Colloty et al., 2000). Activities that impact on the estuary include saltworks, wastewater treatment works, sand/-clay mining, brickworks, a decommissioned power station, motor vehicle and allied industries, tanneries, marshalling railway yards and depots, and agriculture (Adams et al., 2021, 2019; Baird et al., 1986; Binning and Baird, 2001) (Fig. 1). A summary of sources of potential

* Corresponding author at: Department of Zoology, Nelson Mandela University, Gqeberha 6031, South Africa.
E-mail address: aldwynstav@gmail.com (A. Ndhlovu).

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contaminants to the Swartkops River and estuary was provided by Adams et al., (2019). Numerous canals, such as the Markman and Motherwell Canals and small streams that pass through formal residential, informal residential, and industrial areas discharge surface runoff into the estuary. Water quality in the canals and streams is known to be poor (Adams et al., 2021).

The Swartkops Estuary has been the subject of considerable scientific attention, but this has focussed largely on its ecology and there is relatively little information on metal and other chemical concentrations in water, sediment, fauna, and flora in the estuary. The first studies were performed in the 1970's and 1980's (Connell et al., 1976; Watling and Watling, 1979), after which there was a hiatus in research until 2002 (Binning and Baird, 2002), followed by another hiatus until a series of recent work 2015–2022 added to our understating on metals in the Swartkops Estuary (Nel et al., 2015; Phillips et al., 2015, Nel et al., 2020; 2022).

The purpose of this study is to review available information on metal concentrations in water, sediment, fauna, and flora in the Swartkops Estuary, by drawing and summarising information from unpublished and published studies. Gaps and limitations in available information are identified and recommendations on studies to improve our understanding on metals in the estuary are provided.

1.1. The Swartkops Estuary

The Swartkops Estuary is one of ~290 outlets to the sea in South Africa that fulfil the criteria to be classified a functional estuary (van Niekerk et al., 2022). The estuary is situated on the north-eastern outskirts of Gqeberha (formally Port Elizabeth), on the warm-temperate southeast coast of South Africa. The Swartkops River, which is ~155 km in length, has its source in the Groot Winterhoek Mountains (Reddering et al., 1981). The river has a catchment area of ~1370 km^2. The main tributaries are the Elands River, which joins the Swartkops above Kariega (formerly Uitenhage), the Brak River, and the small Chatty system, which enters the estuary below its tidal limit (Lord and Mackay, 1991). The Swartkops Estuary is classified a medium-large, predominantly open estuary (Van Niekerk et al., 2015). The estuary mouth connects to Algoa Bay in the Indian Ocean ~15 km north of the Port Elizabeth harbour. The estuary mouth is kept open by strong tidal currents, which exceed the average river flow by about sixty times (Baird et al., 1987). A tidal influence extends ~16.4 km into the estuary. The upper reaches of the estuary are narrow (~9 m wide) and channel-like, twisting their way through steep banks of muddy sand, and include a small intertidal area comprising a sandy substratum. The estuary widens slightly and becomes less convoluted between the Bar-None Salt Pans and Brickfields in the middle reaches (Fig. 1). Below Brickfields the steep banks flatten, the estuary broadens considerably (~350 m wide), and there are extensive open mudflats and saltmarshes and supratidal flats. The water temperature varies between ~21–26 °C in summer and ~11–18 °C in winter (Emmerson et al., 1983; Scharler and Baird, 2003). The mean salinity ranges between ~23–34 (Emmerson et al., 1983; Marais, 1984). Hypersaline conditions (up to 42) sometimes occur in the upper part of the estuary during the summer due to high evaporation and low freshwater inflow, while flooding can reduce the salinity to <3 through most of the water column in the upper and middle reaches (Baird et al., 1987; Marais and Baird, 1980). The Chatty River is the largest tributary that flows into the estuary. This river flows through the highly populated townships of Zwide, Veeplaas, New Brighton, Bethelsdorp and Missionvale, where the river collects polluted stormwater runoff, litter, and raw sewage discharge. There Markman and the Motherwell Canals divert surface runoff into the estuary. Markman, an industrial area located on the north bank of the estuary,

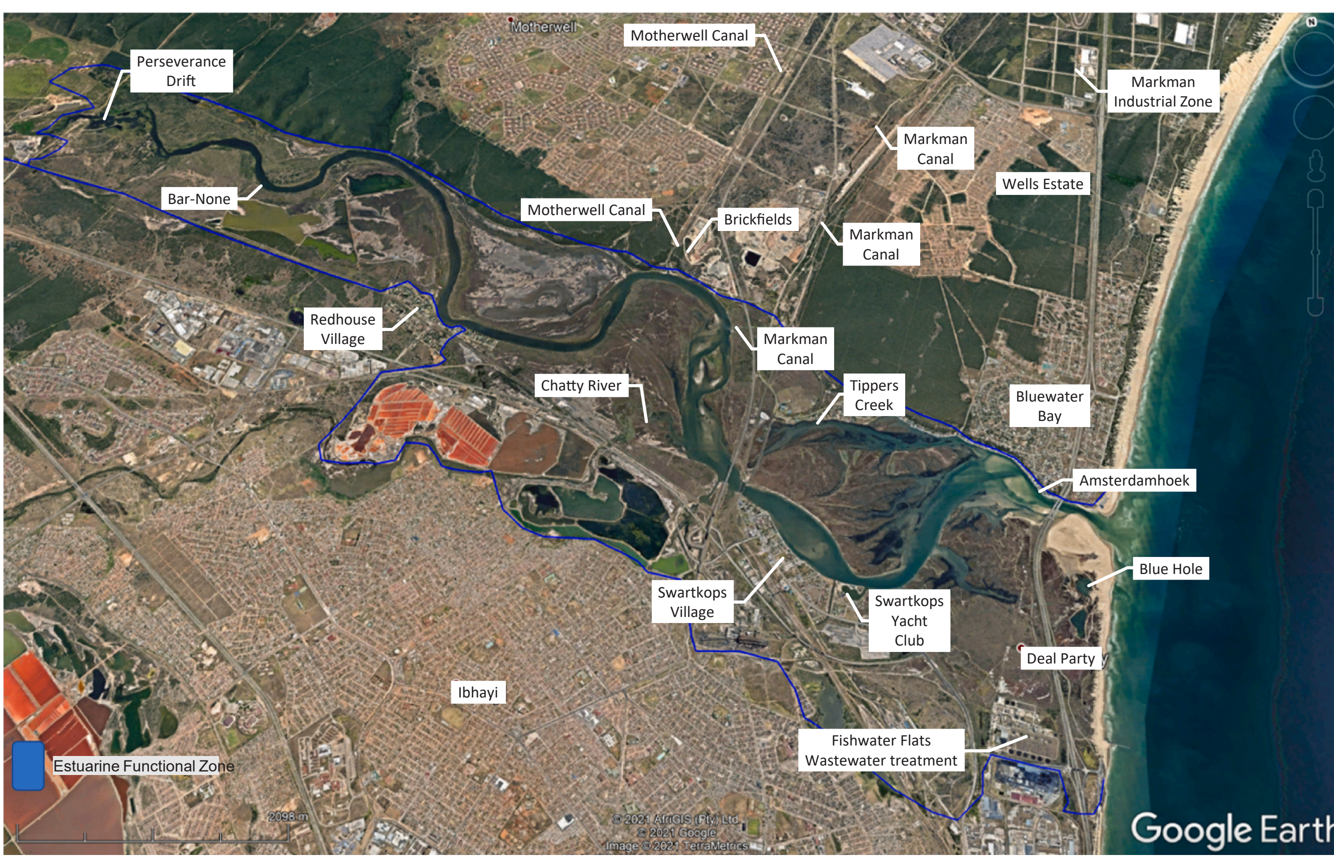

Fig. 1. Google Earth satellite image of the Swartkops Estuary (31–08–2021), showing the extensive development of the estuary surroundings. The blue line delineates the Estuarine Functional Zone (EFZ).

has many stormwater drains that discharge into Markman Canal. Prior to entering the estuary, the canal passes through a small peri-urban village and there are two sewage pump stations that divert domestic sewage and industrial wastewater into the canal. The Motherwell Canal passes through the residential township of Motherwell. This township is serviced by a network of 14 stormwater drains transporting litter, debris, and raw human waste to the canal and eventually the estuary. The estuary is subject to persistent input of nutrient rich baseflow from upstream wastewater treatment works (WWTWs) leading to increased eutrophic conditions (Adams et al., 2021).

The Swartkops Estuary has the third largest saltmarsh area in South Africa, which adds significantly to its botanical importance rating of 99% according to the scheme derived from Coetzee et al., 1997 (Adams et al., 2021; Sink et al., 2012; Turpie et al., 2007). The saltmarsh covers an area of ~1091 ha, with the intertidal saltmarsh covering ~192 ha and supratidal saltmarsh ~359 ha, and ~547 ha being dominated by *Spartina maritima* in the lower reaches (Van Niekerk et al., 2015). *Salicornia* sp. is found higher up the intertidal zone. There are also extensive *Zostera capensis* (seagrass) beds that cover an area of ~54 ha (Adams et al., 2021). The *Z. capensis* beds are important for nutrient and metal cycling and as nursery areas for fish. Intertidal mudflats and the shallow subtidal are colonised by mud (*Upogebia africana*) and sand (*Kraussillichirus kraussi*) prawns, which may be highly abundant in parts of the estuary. The prawns are harvested illicitly and legally by subsistence and recreational fishing communities (Adams et al., 2021; Nel et al., 2022).

The urbanisation and industrialisation of the surroundings has had a major impact on the estuary. Some plant community types have been physically eliminated and the area covered by supratidal and intertidal salt marshes has declined dramatically due to encroachment (Colloty et al., 2000).

In 2013, the estuary was assigned a Present Ecological Status score of 53, or category "D" (Largely modified), due to the "large loss of natural habitat, biota and basic ecosystem function and processes" (Van Niekerk et al., 2013). The estuary was recently assigned a Present Ecological Status score of 47, revealing a deterioration in the overall health of the estuary (Adams et al., 2021). Despite this, the estuary is still highly productive and is ranked 11th in South Africa in terms of fish, bird, and botanical importance (Turpie et al., 2007; Sink et al., 2012; Van Niekerk et al., 2015). An improvement to a Present Ecological Status rank "C" through appropriate management intervention would improve the health of the estuary, but Adams et al., (2021) concluded it is unlikely the estuary will ever return to a "C" rank due to the irreversibility of some impacts, such as the presence of permanent infrastructure in the estuary and catchment and all wastewater inputs would need to be removed and salt marsh habitat restored (Adams et al., 2021).

2. Metal concentrations in water

Metals may be introduced to estuaries from multiple sources (Briffa et al., 2020; Vareda et al., 2019). Most metals will be introduced in solution or bound to suspended particulate matter in water. These metals may remain in solution, where they are available for uptake by plants and animals, or they may be scavenged from the water column to the sediment, where they may be immobilised (Giles et al., 2016; Huang et al., 2020). The primary route of metal exposure for many plants and animals from the water column is when metals are accumulated by uptake across the cell or gill surface (Borgå et al., 2004).

Connell et al., (1976) measured the dissolved concentrations of eight metals in surface water sampled in February 1975 at seven sites between ~0.5 km (Site 1) and 14.5 km (Site 7) from the estuary mouth (Fig. S1, Table S1). The concentrations of five metals were measured in a follow-up survey in December 1975. In the follow-up survey, water was sampled at three of the seven sites sampled in February 1975, at low and high tide. Connell et al., (1976) provided data for an additional site (denoted as Site N2) for the survey in February 1975, but the site position was not given. In April 1977, Watling and Watling (1979) measured the dissolved concentrations of thirteen metals in surface water sampled at sixteen sites between ~1.8 km (Site 15) and 16 km (Site 1) from the estuary mouth (Fig. S2, Table S1). Station 16 was in Blue Hole, a shallow tidally influenced side arm of the estuary that was historically the site of an oyster aquaculture operation. The water was sampled from a vessel by submerging sample bottles beneath the water surface at low tide, starting at the mouth and proceeding upstream, staying ahead of the incoming tide. Seawater was also sampled from the shore at two sites in Algoa Bay near the estuary mouth (Fig. S2). Although the latter sites are not in the estuary, Site 17 is included as it provides a convenient marine end member for measurements made at sites in the estuary. Site 18 was near the Fishwater Flats wastewater treatment works discharge, ~1.8 km south of the estuary mouth. The concentrations of some metals in water sampled at this site reflect the influence of the wastewater discharge and provide a further point for comparison to metal concentrations reported by Connell et al., (1976).

The metal concentrations reported by Connell et al., (1976) and Watling and Watling (1979) are provided in Fig. S3 and Table S1. Connell et al., (1976) reported challenges in the analysis of mercury (Hg) in the first survey and no concentrations were thus reported for this metal. Mercury was found in all samples in the follow-up survey, but the concentrations showed no pronounced spatial or tidal trend apart from the concentration in water sampled at Site 1 near the estuary mouth on the incoming tide, which was far higher than the concentrations measured at low tide and at other sites (Table S1). Mercury concentrations were below the method detection limit in water at all sites sampled by Watling and Watling (1979) (Table S1), which is interesting since the method detection limit was far lower than Hg concentrations reported by Connell et al., (1976). In both studies, sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg) concentrations generally progressively increased from the upper part of the estuary (Site 1) to near the estuary mouth (Site 15) and into the marine environment (Site 17) (Fig. 2, Fig. S2). The concentrations in each study were comparable at similar positions in the estuary (Fig. 2). The increase in the Na, K, Ca, and Mg concentration toward the estuary mouth reflects the gradual mixing of riverine and tidally entrained marine water. The manganese (Mn) and nickel (Ni) concentrations reported by Watling and Watling (1979) generally progressively decreased between Sites 1–13 and then remained comparable at sites nearer the mouth and in the marine environment (Site 18 excluded). The Mn and Ni concentrations are strongly positively correlated to one another ($r = 0.965$, $p < 0.001$) and strongly inversely correlated to Na concentrations (Mn: $r = -0.921$, $p < 0.001$; Ni: $r = -0.905$, $p < 0.001$) (Site 18 excluded), which is used here as a proxy for the mixing of freshwater and seawater as salinity was not measured. The conservative trend for Mn and Ni concentrations also reflects the gradual mixing of riverine and tidally entrained marine water and implies there were no significant sources of these metals in or to the estuary at the time. The concentrations of other metals were not strongly correlated to one another, nor to Na concentrations. The iron (Fe) concentration generally increased between Station 1 and Station 9, decreased sharply at Station 10, and then generally progressively decreased toward the mouth. Although the trend might appear to imply a source of Fe in the upper and middle parts of the estuary this is unlikely since the trends for other metals showed no evidence for metal inputs in these parts. The copper (Cu) concentrations reported by Watling and Watling (1979) varied minimally between Stations 1–6, and apart from a notable increase at Station 10 generally progressively decreased to Station 13 and then remained broadly comparable at sites nearer the mouth and in the marine environment. The lead (Pb) and zinc (Zn) concentrations reported by Watling and Watling (1979) showed no pronounced spatial trend, but the Zn concentrations at Sites 7 and 13 suggest a possible source from discharge of untreated industrial effluents surrounding the industrial area of Markman and upstream suburb of Motherwell. The Cu, Pb, and Zn concentrations reported by Connell et al., (1976) were broadly comparable to concentrations reported by Watling and Watling (1979) at similar positions in the estuary apart

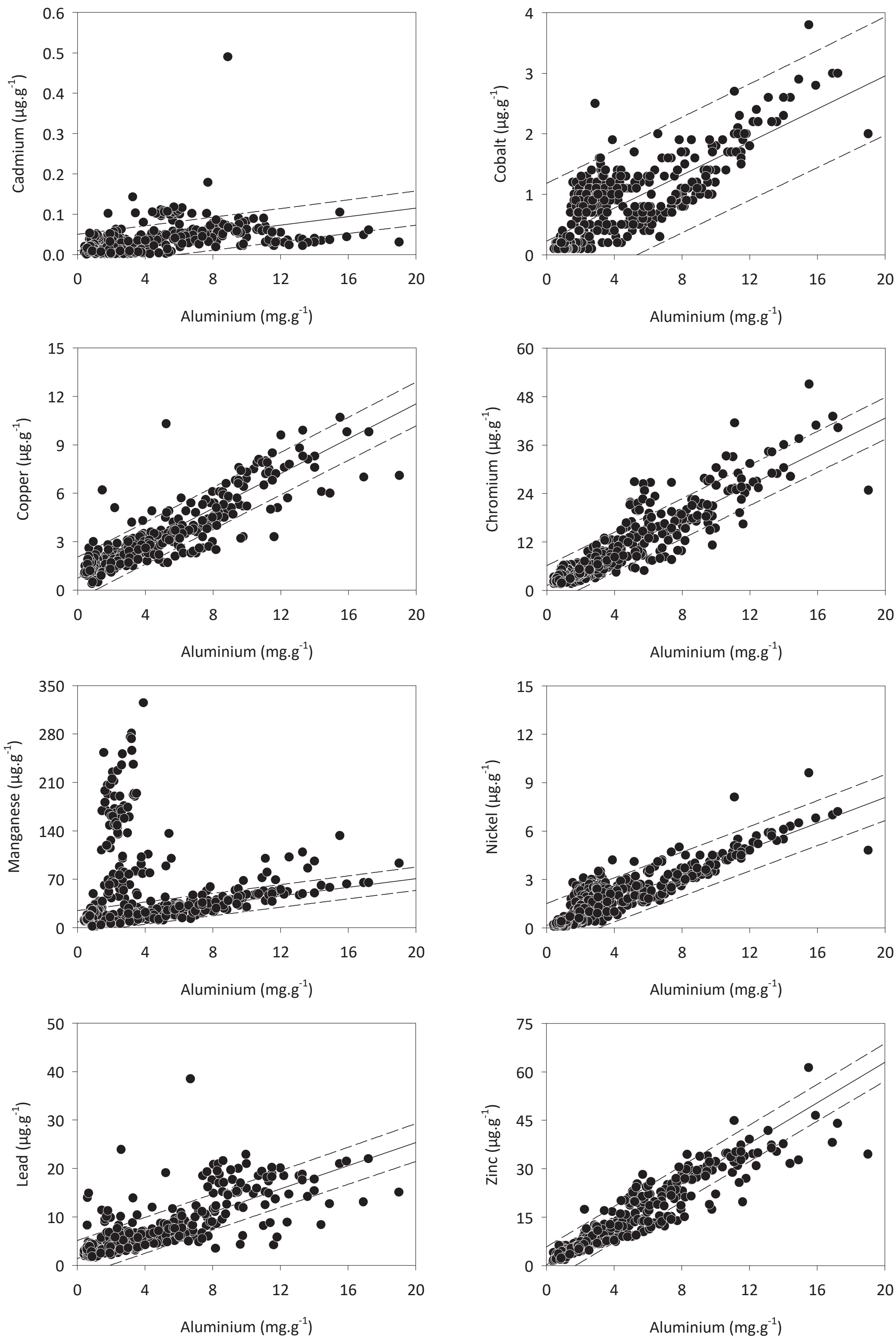

Fig. 2. Aluminium normalised baseline metal concentration models for metals in sediment in the Swartkops Estuary defined using data from Watling and Watling (1979), with metal concentrations measured in all samples superimposed.

from near the estuary mouth, where concentrations reported by Connell et al., (1976) in both surveys were higher than elsewhere. The cadmium (Cd) concentrations reported by Connell et al., (1976) were lower than those measured by Watling and Watling (1979) at similar positions in the estuary apart from near the mouth, where the concentrations in both surveys were often considerably higher (including other sites in the estuary). The Cd concentration reported for Site 18 in Algoa Bay by Watling and Watling (1979) was comparable to concentrations reported near the estuary mouth by Connell et al., (1976).

Although there was some evidence for metal contamination at Redhouse, Swartkops village, and Amsterdam Hoek in the study by Watling and Watling (1979), the concentrations are by no means high apart from those measured on an incoming tide near the estuary mouth by Connell et al., (1976). The metal concentrations were in fact generally low, and Watling and Watling (1979) considered they were of no cause for particular concern at the time. Connell et al., (1976) attributed the high metal concentrations in water sampled near the estuary mouth to the tidal entrainment of contaminated water from the marine environment but did not allude to a source. The metal concentrations reported by Watling and Watling (1979) for Site 18 in Algoa Bay suggest the Fishwater Flats wastewater discharge might have been a source if these waters were advected to the estuary mouth, but the concentrations of several metals were not inordinately different to concentrations at sites in the lower part of the estuary. The concentrations of some metals at an elevated concentration in water sampled near the estuary mouth by Connell et al., (1976) were not particularly high at Site 18. The surveys were not made at the same time and tidal state and strong similarities amongst metals in the samples should not thus be an expectation.

In 2012, Pretorius (2015) analysed total concentrations of eight metals, and dissolved concentrations of Hg and selenium (Se) in surface, and where the water column was deep enough, also bottom water sampled at six sites in the Swartkops Estuary between ~0.4–16.4 km from the estuary mouth. Water was also sampled at a site in each of the Markman Canal, Motherwell Canal, and Chatty River that discharge into the estuary (potential sources of contaminant metals) (Fig. S4). Although Pretorius (2015) analysed total metal concentrations, which will always be higher than dissolved metal concentrations, the concentrations reported for most metals at many, or all sites depending on the metal were markedly high (Table S2, Fig. S5). The concentrations often varied minimally amongst sites in the estuary and for several metals (e.g., Cd, Cu, Zn) were high at a station near the estuary mouth, where the concentration would ordinarily be expected to be amongst the lowest due to dilution with tidally entrained seawater (Table S2, Fig. S5). The concentrations for some metals were in fact markedly higher at sites ~0.4 and 2.2 km from the estuary mouth compared to other sites and raises further suspicions on whether the method used to analyse the saline samples was appropriate. If the concentrations are valid, they can be placed into perspective by using saltwater metal translators recommended by the USEPA. In the case of Cu, the acute translator is 0.83. Copper concentrations in surface water samples would thus range between <LOR to 75 μg. l^{-1}, and none of the quantified concentrations would fall below 8.3 μg. l^{-1}. These would represent an extreme case of contamination. There was no clear evidence that metal concentrations in Markman and Motherwell Canals and Chatty River were consistently higher than in the estuary.

There are no water quality guidelines (WQG) for estuarine water in South Africa. It is thus difficult co compare metal concentrations analysed in the water column to guidelines to develop an idea on the potential ecological risk they posed. However, the concentrations of certain metals (e.g. Cu, Pb) across varying degrees of the estuary were well in excess of freshwater and/or marine WQG's.

The paucity of information on metal concentrations in water in the Swartkops Estuary, and the variation of some measured concentrations, makes it difficult to draw any conclusion on metal contamination of water in the estuary and represents an important gap in understanding.

3. Metal concentrations in sediment

Most metals have a low water solubility and are particle reactive, and when they are introduced to (especially saline) surface waters generally adsorb onto suspended sediment and organic matter and in this way are scavenged from the water column by flocculation, coagulation and sedimentation (De Groot et al., 1976; Förstner and Wittmann, 1979; Olsen et al., 1982; Huh et al., 1992; Schropp et al., 1990; Mwanuzi and De Smedt., 1999; Hatje et al., 2003; Huang et al., 2020). Although diagenic processes in sediment can modify and redistribute metals between solid and dissolved phases, immobilisation by sedimentation dominates for most metals (Hanson et al., 1993). Consequently, the concentrations of metals in sediment and at the sediment water interface usually exceed those in the water column by several orders of magnitude (Horowitz, 1991; Bryan and Langston, 1992; Daskalakis and O'Connor, 1995). Metals generally do not degrade and with continued input and limited sediment redistribution by currents they can accumulate in depositional zones to such high concentrations they exert direct and indirect toxic effects on benthic and epibenthic organisms (Hornberger et al., 2000; Fleeger et al., 2003). Estuaries are generally sheltered environments that are characterised by weak currents, making them susceptible to contaminant accumulation since these conditions facilitate the settlement of suspended particulate matter onto which metals adsorb. Sediments in estuaries thus act as a sink for metals (Akcay et al., 2003; Thevenon et al., 2011), but they can also be a source to the overlying water. Metals can be remobilised from sediment if there are changes in the pH, redox state, or salinity of the water column (Algül and Beyhan, 2020; Ye et al., 2020), through flooding and dredging related disturbance (Hill et al., 2013; Simpson and Batley, 2007), and through bioturbation (Hill et al., 2013; Ye et al., 2020). The remobilisation of metals from sediment leads to secondary contamination (Huang et al., 2020) that may affect ecological receptors.

Several metals, namely Fe, Cd, Cu, Cr, Hg, Pb and Zn were analysed in sediment sampled at the same water six sites discussed above in the Swartkops Estuary in February 1975 by Connell et al., (1976), using a cone dredge (Fig. S6). In 1977, Watling and Watling (1979) sampled surface sediment and collected sediment cores at the same sites in the estuary where water was sampled in the survey discussed above (Fig. S2). Watling and Watling (1979) also collected sediment cores at a few additional sites. Surface sediment was sampled using an aluminium scoop towed behind a vessel. Three tows were made at each site and a composite of the sediment was retained for analysis. Sediment cores of up to 600 mm were collected by forcing a stainless tube with a polyvinylchloride liner into the sediment for its full length or until failure. Sediment was removed from the core at ~2 cm intervals and at obvious sediment boundaries. The sediment was dried and sieved. The sediment that passed through a 210 μm mesh size sieve was retained for analysis. The sediment was analysed for the concentrations of 16 metals, but Na, K, Ca, Mg, and Sr are not considered here as they are usually not (significant) contaminants of sediment.

Connell et al., (1976) concluded that there was evidence for metal contamination of sediment at Site 3 near road and rail bridges that cross the estuary a short distance upstream of Swartkops Village (Fig. S6). Watling and Watling (1979) concluded sediment at Redhouse, near Swartkops village, at Amsterdam Hoek, and near the Brickworks showed evidence for metal contamination, but they did not consider the contamination to be cause for concern and the sediment could not be described as 'polluted in the true meaning of the word'.

Binning and Baird (2001) used a 6.5 cm diameter and 10 cm long corer to sample sediment at seven sites in the Swartkops Estuary and at seven sites in the Swartkops River in August 1995, December 1995, and March 1996. Binning and Baird (2001) stated that six of the sites in the estuary corresponded to sites where Watling and Watling (1979) collected sediment cores in the intertidal, but many were not especially close based on locations provided in the respective study figures. Binning and Baird (2001) analysed the sediment for concentrations of nine metals, of which seven correspond to metals analysed by Watling and Watling (1979) (strontium is not discussed here). Binning and Baird (2001) concluded that metal concentrations at most sites had increased 'dramatically' since the survey by Watling and Watling (1979), by factors of 0–690% (median = 104%). The conclusion was based on the direct comparison of metal concentrations they measured to metal concentrations measured in the upper parts of sediment cores by Watling and Watling (1979). However, the direct comparison of metal concentrations amongst sediment samples fails to acknowledge that, in a geologically homogenous area, grain size (principally the mud fraction) is the most important factor that controls metal concentrations in sediment. Metal concentrations will thus differ naturally between sediment with a different grain size. Metal concentrations cannot thus be compared directly between sediment samples with different grain size if the purpose is to identify contamination. Since Watling and Watling (1979) provided no information on the grain size of sediment, the direct comparison of metal concentrations to those analysed by Binning and Baird (2001) is misleading (but Fe can be used as a proxy for the mud fraction – see below).

Geochemical normalisation can be used to compensate for the influence of grain size on metal concentrations in sediment. The basis is that in uncontaminated sediment there is usually a strong positive relationship between metal concentrations and the mud fraction, which is the principal natural metal bearing phase of sediment. There is thus also usually a strong positive relationship between metal concentrations in uncontaminated sediment. The relationship between metal concentrations is often stronger than to the mud fraction since analyses are not made on precisely the same samples (split samples present small differences, irrespective of the care taken to minimise differences). In geochemical normalisation, a metal that acts as a proxy for the mud fraction of sediment and that is usually minimally impacted by anthropogenic inputs is used to normalise the concentrations of other metals. Aluminium (Al) or Fe, which are respectively the second and fourth most abundant metals in the earth's crust, are usually used as normalisers, but several other metals are also often used. Linear regression analysis is a common approach for geochemical normalisation, leading to the definition of background models that define the relationship between metal concentrations and the normaliser in uncontaminated sediment. If sediment is sampled in an area where there is an existing anthropogenic influence, geochemical normalisation can be used to define relationships for sediment at relatively uncontaminated sites but in this case the models are more correctly referred to as baseline models since they might include concentrations indicative of low magnitude metal contamination. Baseline models were defined for eight metals analysed in sediment sampled in the Swartkops Estuary by Watling and Watling (1979), using Al as the normaliser. A baseline model could not be defined for Fe since Fe concentrations at numerous sites were anomalous (see Newman and Watling, 2007). A baseline model could also not be defined for Hg since it was analysed in fewer sediment samples per core (5 cm long sections) than other metals and it was not possible to correlate the concentrations to specific Al concentrations in this range. The baseline models were defined by fitting a linear regression and 99% prediction limits to scatter plots of Al and metal concentrations. Metal concentrations falling outside the prediction limits were considered outliers and sequentially trimmed, starting with the concentration with the largest residual, reiterating the regression, and proceeding in this way until all remaining concentrations were within the prediction limits. The baseline models are provided in Fig. 2, with metal concentrations measured in all sediment samples superimposed. Metal concentrations that fall in the baseline model prediction limits are in the baseline range while those that exceed the upper prediction limit are enriched, that is, they are in excess of the baseline. The enrichment may or may not reflect an anthropogenic input (i.e., contamination). Deciding if enrichment reflects contamination requires consideration of ancillary factors, including (bio)geochemical processes that can lead to natural enrichment (e.g. diagenesis), the absolute (vertical) difference between a measured metal concentration and the concentration predicted at a baseline model upper prediction limit, the number of metals at an enriched concentration in a sediment sample, and the proximity of metal enriched sediment to known or strongly suspected anthropogenic sources of metals. The larger the difference between a metal concentration and a baseline model upper prediction limit, the closer an enriched sediment sampling site is to known or strongly suspected anthropogenic sources of metals, and the greater the number of metals enriched in sediment at a sampling site the more likely the enriched metal concentration reflects contamination.

A small proportion of most metal concentrations measured in sediment by Watling and Watling (1979) exceed baseline model upper prediction limits (Fig. 2). A larger proportion of Pb, and especially Mn concentrations exceed baseline model upper prediction limits. Apart from Mn, most of the enriched concentrations slightly exceed baseline model upper prediction limits, indicating minor enrichment that makes it difficult to decide if this reflects contamination. A small proportion of the concentrations for some metals, including Cd, Cu, Pb, exceed baseline model upper prediction limits to such a degree it can be concluded this reflects contamination. The trend for Cd at Site 13 is anomalous since concentrations through the core exceed the baseline model upper prediction limit. Apart from Mn, other metals were rarely enriched in the same sediment within cores and were often enriched in sediment from the deeper parts of cores where contamination is least expected. Manganese enrichment was evident through all or most of the cores at Sites 1, 2, and 3, but was largely or completely absent in other cores. Manganese is not a common contaminant of sediment. The enrichment may be related to the fact Mn is mobile in sediment under certain conditions (e.g., anoxia). Under these conditions, Mn may migrate though sediment porewater and precipitate when contacting oxygen near the sediment surface, leading to its natural enrichment through a process known as diagenetic enhancement. The infrequent and low magnitude enrichment identified for most metals using the baseline models agrees with the conclusion by Watling and Watling (1979) that there was little evidence for metal contamination of sediment in the estuary at the time it was sampled in 1977.

The metal concentrations measured by Connell et al., (1976) are not amenable to baseline model definition due to the small data set. The metal concentrations measured by Binning and Baird (2002) are also not amenable to baseline model definition as they are strongly skewed to low concentrations and there is an often-considerable scatter of concentrations at the few corresponding high Fe concentrations. The baseline models are thus often strongly influenced by metal concentrations at high corresponding Fe concentrations and bear little resemblance to models defined using other metal concentration data.

In 2011, surface sediment was sampled from a vessel using a small stainless steel van Veen grab at 28 sites between ~0.3–11 km from the Swartkops Estuary mouth (Newman, unpublished) (Fig. S8). The concentrations of 14 metals were measured in the sediment. Baseline models for the metals were defined using the same procedure described above, using Al or Fe as the normaliser. The metal concentrations are strongly skewed to low concentrations, reflecting the sandy texture of the sediment at most sites. The skewed metal concentrations result in the linear regressions that define the baseline models having lower coefficients of determination than ideal, but this does not diminish their value for interpreting metal concentrations. The baseline model for Cd is not useful for interpreting concentrations as baseline Cd and Al concentrations are weakly correlated and the linear regression slope is not much different to zero. The weak relationship between Cd (and often Hg) and normaliser concentrations in sediment is not uncommon. Superimposing metal concentrations analysed in all sediment samples onto the baseline models provides no evidence for enrichment for almost all metals, and where there was evidence the enriched concentrations so slightly exceed model upper prediction limits that nothing can be concluded on whether this reflects contamination (Fig. 3). The Mn concentration at four sites in the upper part of the estuary (Sites 23, 26,

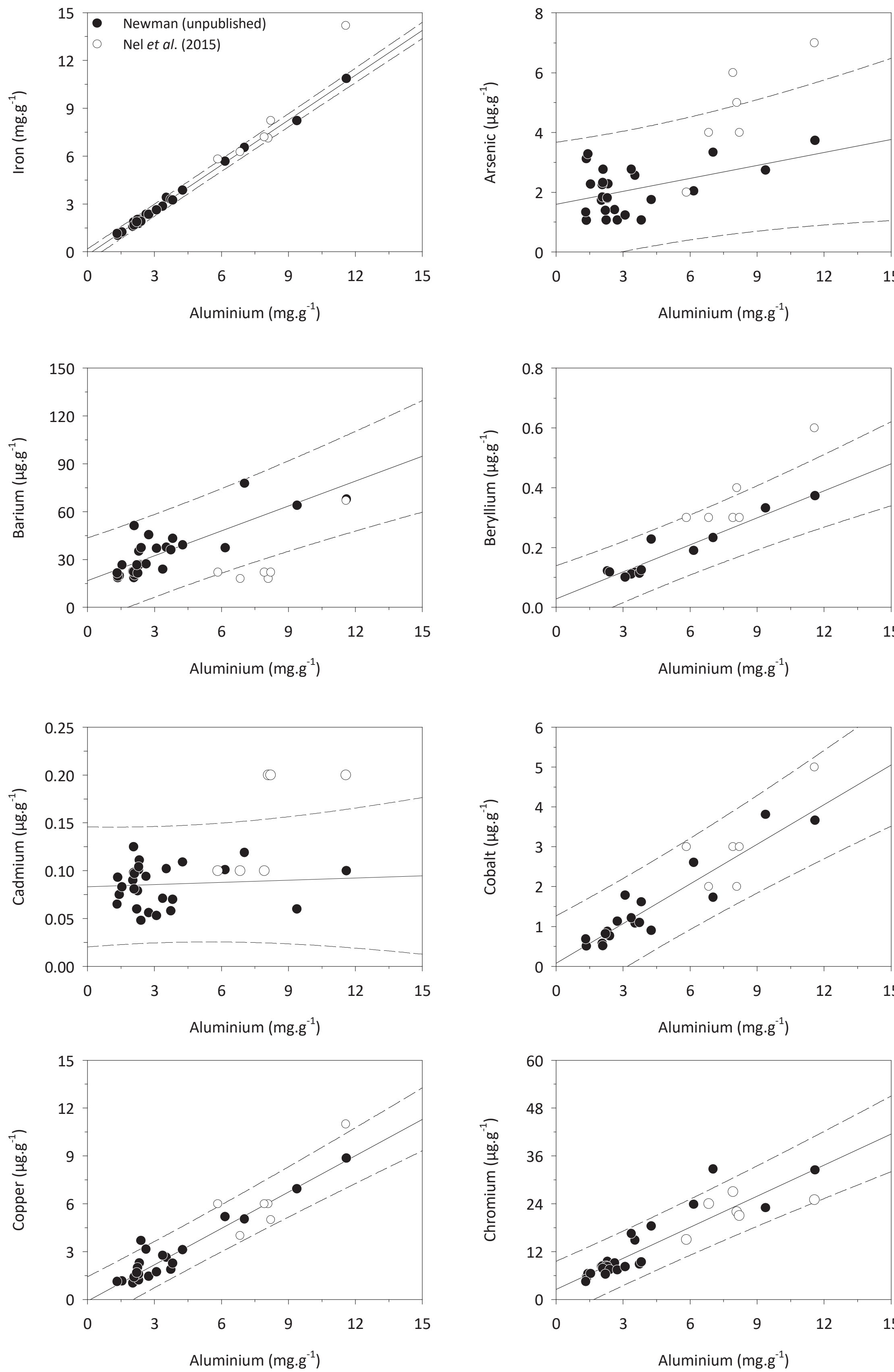

Fig. 3. Aluminium normalised baseline models for metal concentrations measured in sediment sampled in the Swartkops Estuary in 2011 (Newman, unpublished data), with metal concentrations in all samples superimposed. Also superimposed on the baseline models are metal concentrations measured in sediment sampled by Nel et al., (2015).

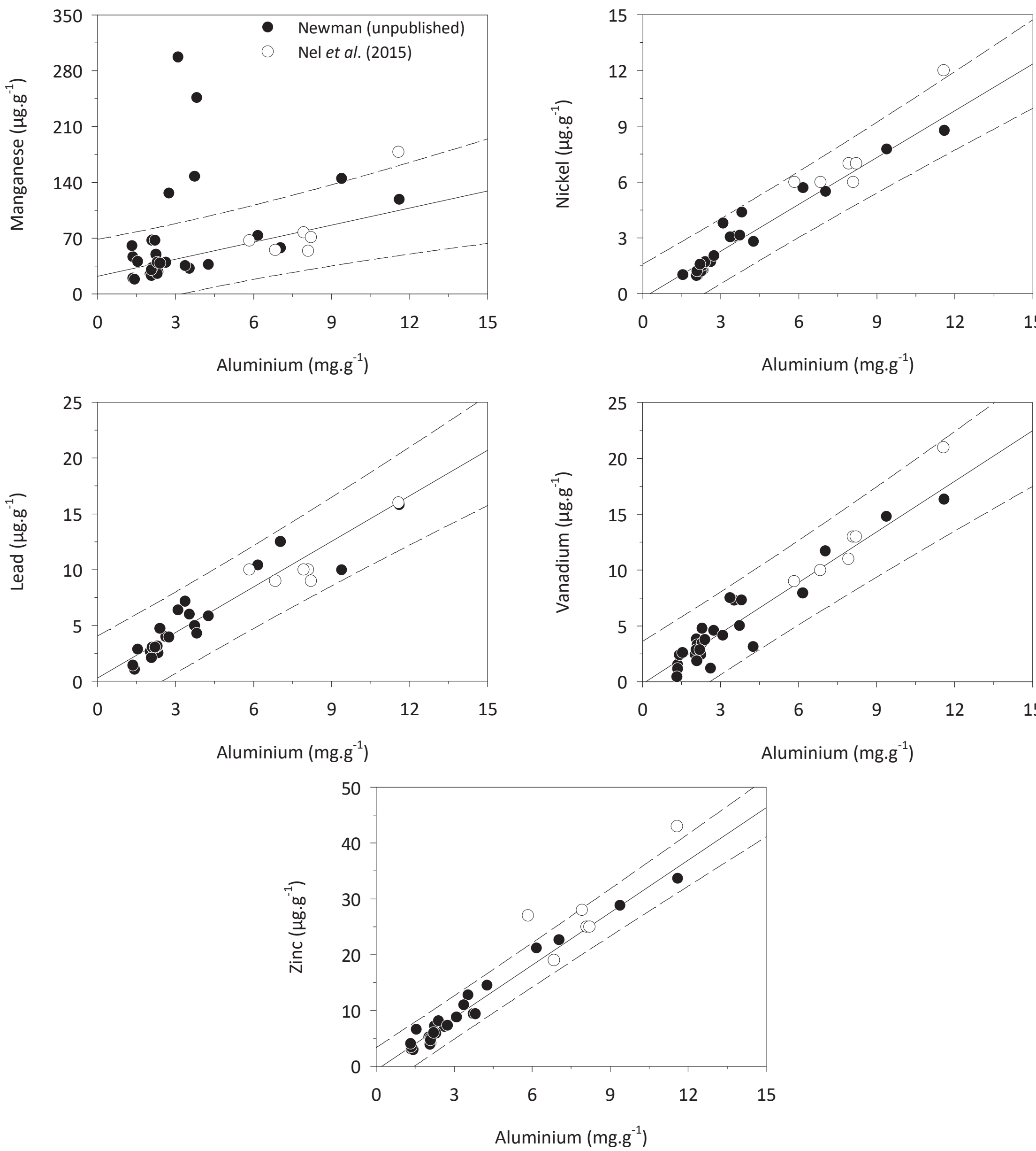

Fig. 3. (*continued*).

27, 28; see Fig. S8) considerably exceeds the baseline model upper prediction limit.

The definition of baseline models using Fe as the normaliser for metal concentrations analysed by Newman (unpublished) allows the interpretation of metal concentrations measured by Connell et al., (1976) and Binning and Baird (2001). The metal concentrations measured by Connell et al., (1976) are anomalous. Apart from Zn and to a lesser degree Cu, all other metal concentrations exceed baseline model upper prediction limits, often substantially (Fig. S9; Table S3), implying the sediment at all sites is contaminated by at least two but usually more metals. The sediment at two sites was clearly comprised of relatively coarse sand, as concluded from the low Fe concentrations, yet the Cd and Pb concentrations were high. This is anomalous since sandy sediment has a low capacity for metal adsorption. The findings also contrast to those of other studies.

The metal concentrations in most estuarine sediment samples analysed by Binning and Baird (2001) fall in or near the baseline model prediction limits (Fig. S10). This implies no, or relatively low magnitude metal enrichment of sediment at most sites. A few concentrations for most metals do considerably exceed baseline model upper prediction limits and imply contamination. The contamination was most pronounced for sediment at the Swartkops Yacht Club (Site K) and Perseverance Drift (Site G) (see Fig. S8). However, the magnitude of enrichment at some sites varied widely amongst surveys, suggesting considerable small-scale variability in the enrichment. For example, at Site G at Perseverance Drift the sediment was highly enriched by Cu, Mn, Pb, and Zn in one survey, but the concentrations of the metals in other surveys fall in or very baseline model prediction limits (see highlighted data in Fig. S10). Although the sediment at some sites sampled by Binning and Baird (2001) is identified as metal contaminated using the baseline models, the contamination was not as pervasive nor significant as concluded by Binning and Baird (2001). As a point of interest, sediment sampled in the Swartkops River was more often, and often more significantly enriched by Cu, Pb, and Zn than sediment in the estuary (Fig. S10).

In 2012, Nel et al., (2015) sampled intertidal sediment at six sites between Tippers Creek and Redhouse using a stainless-steel corer. Five cores were collected per site and a composite was retained for analysis.

Comparison of metal concentrations measured in the sediment to Al normalised baseline models defined using metal concentrations analysed by Newman (unpublished) shows the concentrations usually fall in or near the baseline model prediction limits (Fig. 3). There is thus little evidence that the sediment sampled by Nel et al., (2015) was contaminated apart possibly from Site 5 near Motherwell Canal, which showed evidence for low magnitude enrichment by several metals and may thus reflect contamination (Table S4).

In 2014, Phillips et al., (2015) analysed metal concentrations in sediment sampled to a depth of ~30 cm in three quadrats in the root-zones (rhiszosediment) of the emergent macrophytes *Phragmites australis*, *Typha capensis* and *Spartina maritima*, at three sites along the banks of the middle to lower parts of the estuary, at two sites in canals that direct surface runoff from urban areas into the estuary, in an artificial wetland in one of the latter canals, and in a natural freshwater wetland at Redhouse (Fig. S11, Table S5). The sites in the canals, while not in the estuary, are included as they are sources of metals to the estuary. Phillips et al., (2015) did not analyse Al or Fe in the sediment, and it is not thus possible to compare the metal concentrations to the baseline models discussed above. Phillips et al., (2015) report extremely high average (mean± standard error) Cd concentrations in sediment in Markman Canal (22.97±0.06 μg. g^{-1}), in the artificial wetland in Motherwell Canal (35.93±4.83 μg. g^{-1}), and at the confluence of Motherwell Canal and the estuary (14.61±13.51 μg. g^{-1}). The Cd concentration in sediment at the Motherwell Canal confluence was clearly highly variable, as evident in the wide standard error. The Cd concentrations are indicative of severe contamination. The Cd concentration in sediment at other sites was far lower, between 0.61±0.13–1.55±0.06 μg. g^{-1}. The lowest Cd concentration reported by Phillips et al., (2015) exceeds the highest concentration reported by Watling and Watling (1979) (0.6 μg. g^{-1}), Newman (unpublished) (0.109 μg. g^{-1}), and Nel et al., (2015) (0.2 μg. g^{-1}), but some concentrations reported by Connell et al., (1976) are higher (maximum = 1.84 μg. g^{-1}). The highest Cu, Pb and Zn concentrations reported by Phillips et al. (2015) were in sediment in the canals or wetlands. The highest average Cu, Pb and Zn concentrations at sites in the estuary were lower, at 10.86±0.59, 37.93±3.91, and 43.73±5.08 μg. g^{-1} for Cu, Pb, and Zn respectively. The sediment in canals and wetlands was thus evidently contaminated by most metals. Metal concentrations in sediment at sites in the estuary are within the range reported in other studies.

Nel et al., (2022) sampled rhizosediment seasonally at Motherwell Canal, Markman Canal, Tiger Bay launch site, Tippers Creek, and Blue Hole in 2019 and 2020 (Fig. S12). At each site, five sediment samples were collected by excavating the rhizosphere in homogenous stands of *Z. capensis, S. maritima,* and *S. tegetaria*. Unvegetated sediment nearby was also sampled at two sites. The range of Al concentrations analysed in sediment by Nel et al., (2022) is far wider than the range reported in other studies. Al normalised metal concentrations thus deviate substantially from Al normalised baseline models defined using metal concentrations analysed by Newman (unpublished). The range of Fe concentrations analysed by Nel et al., (2022) is also wider than the range reported in many other studies, but not to the same degree as Al concentrations. The Fe normalised metal concentrations show a reasonable correspondence to Fe normalised baseline models defined using metal concentrations analysed by Newman (unpublished) but do tend toward being slightly lower than the baseline models apart from Co and Zn concentrations, which tend to fall slightly above the baseline models. The differences might reflect the different method (TXRF spectrometry) used to analyse metals by Nel et al., (2022) compared to other studies (usually ICP spectrometry) (Table S11).

Apart from Mn, the metal concentrations measured by Nel et al., (2022) show a strong positive relationship to co-occurring Al and Fe concentrations. The metal concentrations were used to define Fe normalised baseline models. Superimposing metal concentrations measured in all sediment samples onto the baseline models provides little evidence for metal enrichment of sediment apart from Mn, but where there is evidence the magnitude of the enrichment is low (Fig. 4). A considerable proportion of the Mn concentrations exceed the baseline model upper prediction limit. The enriched concentrations were largely restricted to sediment sampled in the *S. tegetaria* zone at Sites 1, 2, 3, and 4. Mn was not enriched in sediment at Blue Hole (Site 5). As stated previously, Mn is not a common contaminant of sediment, at least not on its own. The Mn enrichment probably represents contamination, but it might also reflect a modification of the rhizosphere by *S. tegetaria* leading to enrichment. The metal concentrations are presently being analysed with other measurements made on the sediment and on plants (including metal concentrations) to identify possible causes of the enrichment.

The potential biological implications of metals in sediment in the estuary are uncertain since there have been no studies that have attempted to relate metal (and other contaminant) concentrations in sediment to the status of benthic macrofaunal communities, nor any toxicity testing of the sediment. Sediment quality guidelines (SQGs) are often used to screen metal concentrations in sediment from a biological perspective. The South African government has not defined SQGs apart from an Action Lits that is used to regulate the open water disposal of sediment dredged in South African ports (Government Gazette, 2012). The guidelines were derived by comparing baseline metal concentrations to SQGs defined for other parts of the world (principally North America). None of the metal concentrations exceeds an SQG, which suggests they are not having a major adverse impact on benthic macrofauna.

4. Metal concentrations in fauna and flora

All living organisms contain metals in their tissue. Some metals, such as Cu and Zn, are necessary for the normal physiological functioning of biological tissue, but only in trace amounts. Other metals, such as Hg and Pb, have no known physiological function. If fauna and flora are exposed to high metal concentrations in water, sediment, or food, they may take up metals at a rate faster than they are able to detoxify and excrete them and thus accumulate the metals in their tissue. The accumulated metals may present a toxic risk to the fauna and flora, including mortality. Metals assimilated by fauna and flora are transferred to the next level of a food web, known as dietary accumulation (Ali and Khan, 2019). However, only a few metals, such as some forms of arsenic (As), and Hg have a propensity to biomagnify, that is, to increase in concentration through successive trophic levels. Most organisms have mechanisms to detoxify and depurate metals from their tissue provided metal concentrations are not persistently high in their surroundings. If metals accumulate to a high concentration in organisms consumed by humans, they may present a health risk (Wepener and Degger, 2012; Zhu et al., 2017).

4.1. Flora

Phillips et al., (2015) sampled emergent macrophytes *Phragmites australis*, *Typha capensis* and *Spartina maritima* at the same sites discussed above where sediment was sampled. Root, rhizome, stem, and leaf tissue of plants from replicate quadrats was analysed for Cd, Cu, Pb and Zn. Metal concentrations were compared amongst the tissues of plant species and to rhizosediment concentrations to determine if the plants are suitable bioindicators of metal contamination. Overall, Cd and Pb concentrations declined in the order sediment > roots > rhizomes/stems/leaves. For Cu and Zn, concentrations were higher in roots than in sediment and declined in the order roots > sediment > rhizomes > stems > leaves (Table S6). Pb and Zn concentrations in sediment were reflected in plant organs, particularly the roots. Cd and Cu concentrations did not, in contrast, appear to differ in response to concentrations in sediment. *P australis* and *T capensis* had a stronger root accumulating ability compared to *S. maritima*. There was little difference in metal concentrations in the plants amongst sites. Phillips et al., (2015) concluded each plant can be used as a bioindicator of Pb and Zn

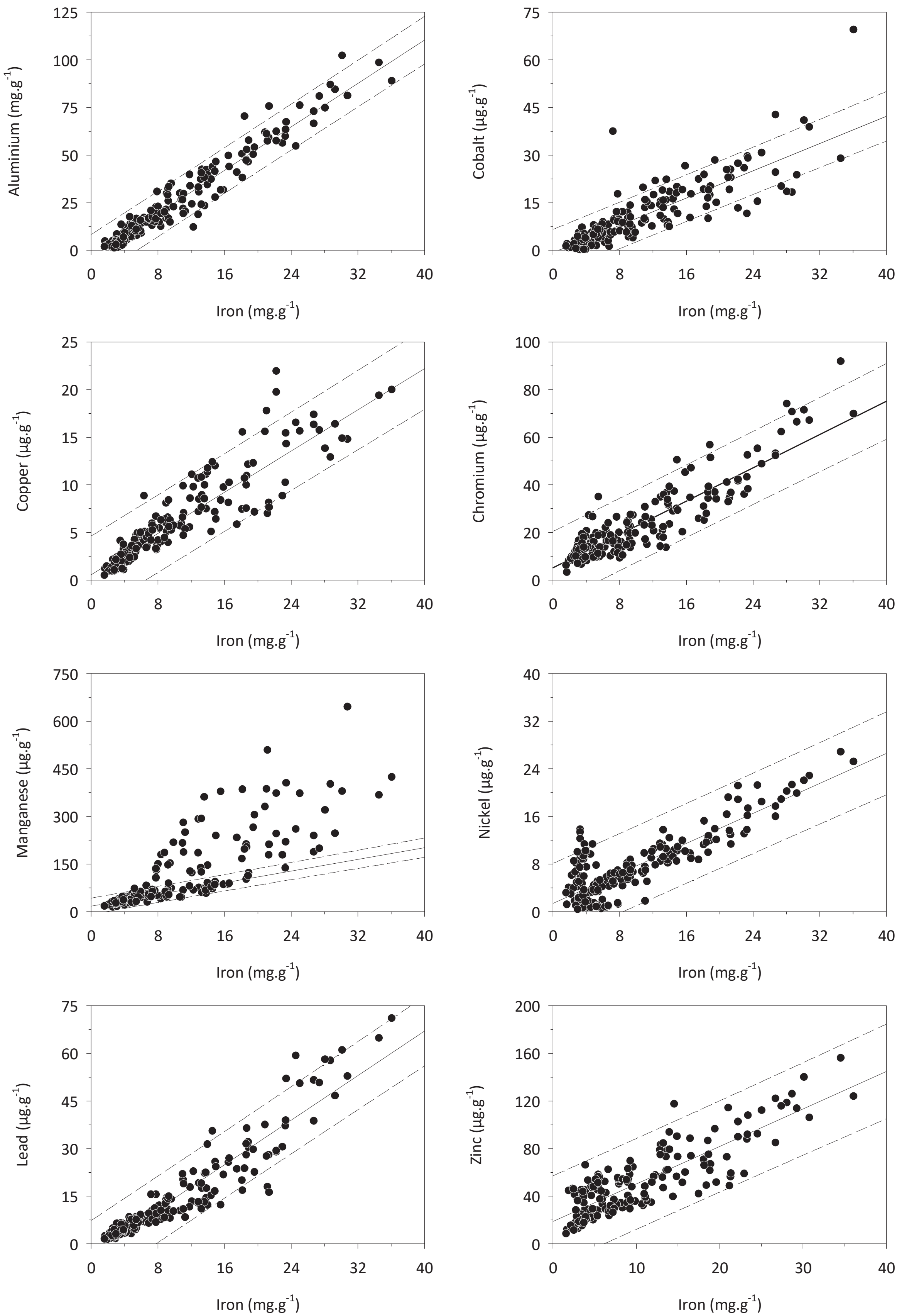

Fig. 4. Iron normalised baseline models for metal concentrations measured in sediment sampled in the Swartkops Estuary using data from Nel et al., (2022), with metal concentrations measured in all sediment samples by Nel et al., (2022) superimposed.

contamination of sediment in the estuary, but not Cd and Cu.

Nel et al., (2022) sampled salt marsh (*Spartina maritima* and *Salicornia tegetaria*) and seagrass (*Zostera capensis*) rhizosediment, and compared the metal concentrations (Cr, Cu, Fe, Mn, Ni, Pb, Zn) to adjacent bare sediment, in Winter 2019. The samples were taken at the Markman Canal (Site 2) and Tipper's Creek (Site 4) (Figure S12). Tipper's Creek is a depositional site that is incompletely flushed and, therefore, accumulates high amounts of particulate organic matter and sediment, while the Markman Canal is a point source that carries stormwater into the estuary. Samples were compared to identify if the rhizosediment contained higher metal concentrations than bare sediment under similar hydrodynamic conditions and metal deposition. They found that metal concentrations in the rhizosediment decreased as follows: *S. tegetaria* > *S. maritima* > *Z. capensis* > bare sediment. Metal accumulation in the bare sediment was similar between the two sites, but the rhizosediment showed much higher metal concentrations at both sites. The rhizosediment tended to accumulate more organic matter and have finer grained sediment, which metals adsorb onto, and increased with intertidal range i.e., *Z. capensis* < *S. maritima* < *S. tegetaria*. This indicated that rhizosediment acts as a metal sink, due to depositional effects of tidal movement, but also by capturing and containing metal-rich particles from the water column.

Nel et al., (2022) sampled the salt marsh (*Salicornia tegetaria, Spartina maritima*) and seagrass (*Z. capensis*) biomass and rhizosediment at 5 sites in the middle and lower reaches of the estuary (Figure S12). The plants were sectioned into three for metal analysis (Cr, Cu, Fe, Mn, Ni, Pb, Zn) i.e., below-ground biomass (roots and rhizomes), shoots or tillers, and leaves. They found that the salt marsh species, *S. maritima* and *S. tegetaria*, accumulated metals within the below-ground biomass and showed little translocation to the shoots and leaves (regardless of the type of metal). This indicates that the plants are good accumulators and potential phytostabilisers of metals. Contrastingly, in the seagrass *Z. capensis,* there was a high translocation to leaf tissue (Transfer factor (TF) = 1 – 8; Mn, Zn, Cr, Pb, Ni, Cu). The seagrass displayed potential as a bioindicator of Cu, Ni and Cr in its below-ground biomass. Metal stocks in the plants were lowest in spring and highest in autumn (*Z. capensis*) and winter (*S. maritima* and *S. tegetaria*). The authors concluded that metal storage was unique between genera and uptake cannot be compared between similar life forms or genera.

4.2. Fauna

Connell et al., (1976) measured Hg, Cu, Cd, Pb, Zn and Fe concentrations in several invertebrates and fish sampled in the Swartkops Estuary in February 1975 (Table S7). Connell et al., (1976) did not provide the positions where the fauna were sampled. In some fish, muscle and liver tissue was analysed, but only muscle tissue in others. Connell et al. (1976) concluded that metal concentrations in the fauna (Table S7) tended to confirm the Swartkops Estuary was relatively uncontaminated at the time, even though Cd, Cu, Hg, and Pb concentrations in the oyster *C. margaritacea*, sandprawn *C. kraussi*, and mudprawn *U.* africana were somewhat higher than concentrations found in these organisms elsewhere. Although Connell et al., (1976) did not comment on this, the Cu concentration in *C. margaritacea*, *C. kraussi*, *U. africana*, and the crab *S. serrata* was far higher than in the tissue of fish apart from the liver of grunter *P. commersonnii* (Table S7). Copper is an important constituent of haemocyanin in the haemolymph of crustaceans and is bound to enzymes in their muscle tissue (Bryan, 1968; Depledge and Bjerregard, 1998; Devescovi and Lucu, 2003) and this undoubtedly accounted for the high Cu concentrations in the crustaceans. Oysters are known to accumulate high concentrations of certain metals in their tissue, but the Cu concentration reported in *C. margaritacea* by Connell et al., (1976) is higher than Cu concentrations reported in *C. margaritacea* sampled in the estuary a few years later (see below). At low concentrations, many metals are essential to life, they are essential for various biochemical and physiological functions but can be toxic when present in excess (Sparks, 2005; Briffa at al., 2020). (Briffa et al., 2020; Sparks, 2005)High concentrations of Mn and Fe include chromosomal aberrations (Grazuleviciene et al., 2009) and toxic effects of Cd and Pb include chromosomal abnormalities; damage and dysfunction of the liver, spleen, blood and carcinogenic effects (Sobhanardakani, 2017). Metal pollutants have been shown to affect genetic diversity (Bickham et al., 2000; Belfiore and Anderson, 2001; Van Straalen, 1999; Van Straalen and Timmermans, 2002; Maes et al. 2005). Population genetic studies have shown that when organisms are exposed to metals, they lead to adaptive genetic changes of the affected organisms (Maes et al. 2005; Morgan et al., 2007). Organisms exposed to long term pollution stress can adapt to their environment by optimizing fitness and ensuring that genes or traits favoured are inherited by their offspring (Morgan et al., 2007). Thus, it is important to monitor the genetic patterns of organisms exposed to metal pollutants or genetic ecotoxicology and this can be achieved using by using environmental DNA (eDNA). Environmental DNA metabarcoding is a novel method of assessing biodiversity which can be used to describe genetic material present in environmental samples e.g., sediment, water, air (Ruppert et al., 2019). eDNA enables the detection and classification of species in environmental samples (Ficetola et al., 2008; Barnes and Turner, 2016; Ruppert et al., 2019). Since metal pollutants can affect individual organisms and lead to changes in populations, eDNA studies can be conducted to determine which species are affected by metal pollution to help assess the severity of metal pollution by monitoring population genetics using eDNA in areas exposed to metal pollution such as the Swartkops Estuary.

In 1977, Watling and Watling (1979) transplanted six-month-old oysters *Crassostrea gigas* and *Crassostrea margaritacea* from an oyster aquaculture operation in the Knysna Estuary to two sites at an oyster aquaculture operation at Blue Hole in the Swartkops Estuary (the latter operation has since ceased). The concentrations of nine metals were measured in the oysters at the time of transplant (April) and in transplanted oysters harvested four (August) and seven months (November) later. Metal concentrations were measured in similarly aged oysters grown in the Knysna Estuary for the same period for comparative purposes. The Cd concentration in transplanted oysters decreased over time (Fig. S13, Table S8). *C. gigas* accumulated considerable concentrations of Zn, Pb, Cu and Ni in their tissue after seven months. *C. gigas* in the Knysna Estuary had similar concentrations of Cu and Zn in their tissue at these times and there was thus only evidence for the significant accumulation of Ni and Pb by oysters transplanted to the Swartkops Estuary. Watling and Watling (1979) suggested the increase in Cu and Zn concentrations reflected a seasonal phenomenon. *C. margaritacea* accumulated Cu, Ni, Pb, and Zn to higher concentrations in their tissue than oysters remaining in Knysna Estuary. Watling and Watling (1979) concluded that the metal concentrations accumulated by *C. margaritacea* in the Swartkops Estuary reflected their exposure to greater than normal amounts of metals in water, presumably derived from the Swartkops Estuary.

Nel et al., (2015) measured metal concentrations in the mudprawn *Upogebia africana*, estuarine round herring *Gilchristella aestuaria*, Knysna goby *Psammogobius knysnaensis*, flathead mullet *Mugil cephalus*, garrick *Lichia amia*, dusky kob *Argyrosomus japonicus*, and spotted grunter *Pomadasys commersonnii*. Mudprawns were sampled at four sites using a hand operated suction pump (Fig. S12). Six to nine prawns sampled at each site were retained for analysis. Fish were sampled by cast netting, seine netting, and rod and reel. Metal concentrations were measured in muscle, liver, and fat tissue lining the stomach of *L. amia*, *A. japonicus*, and *P. commersonnii*, but only in the muscle tissue of *M. cephalus* and whole body (as composite samples) of *G. aestuaria* and *P. knysnaensis* due to their small size.

In *U. africana*, Hg, Cu, Zn, and Fe concentrations were comparable, but Cd and Pb concentrations analysed by Connell et al., (1976) were considerably higher than concentrations reported by Nel et al., (2015) (Tables S7 and S9). It is difficult to compare these findings since it is unknown if the concentrations reported by Connell et al., (1976) are for a single individual or composite sample of mudprawns.

The concentrations of metals were usually considerably higher in the liver than muscle and stomach lining fat in *L. amia*, *A. japonicus*, and *P. commersonnii* analysed by Nel et al., (2015) (Table S10). The lowest concentrations were generally found in the muscle tissue of *M. cephalus*. Although *G. aestuaria* and *P. knysnaensis* are small fish, the Cu and especially Zn and Fe concentrations in their tissue were higher than in other fish (Fig. 5, Table S10).

In the muscle tissue of the same fish species, Hg, Cd, and Pb concentrations were usually higher in fish analysed by Connell et al., (1976), Cu and Fe concentrations were higher in fish analysed by Nel et al., (2015), while Zn concentrations were broadly comparable (Fig. 5). Cu, Cd, Zn, and Fe concentrations in liver tissue were higher, and the Zn concentration lower in fish analysed by Nel et al., (2015) (Fig. S14). The Hg concentration was broadly comparable, although tending to lower in fish analysed by Nel et al., (2015) (Fig. S14). At face value, the concentrations of some metals increased over time in fish, while others decreased or remained broadly comparable. This is contrary to what would be expected in the presence, or absence of contamination, but there are few data against which comparisons can be made to resolve the issue. Newman et al., (2015) measured metal concentrations in *P. commersonnii* and *M. cephalus* sampled in Durban Bay and the uMngeni Estuary in KwaZulu-Natal in 2013. Where differences in metal concentrations amongst the studies are evident, the concentrations reported by Connell et al., (1976) and Newman et al., (2015) are more similar apart from Cd and Pb (Fig. 5), but caution should be exercised when making such comparisons since Newman et al., (2015) sampled fish in Durban Bay, which is not only in a different geological area and hence may have different background metal concentrations that will reflect in the fish but is also known to be contaminated by numerous metals.

Nel et al., (2015) compared Cd, Hg, and Pb concentrations in *U. africana* to limits prescribed by the European Union for these metals in crustacean muscle tissue destined for human consumption (Cd = 0.5 $mg.kg^{-1}$, Pb = 0.5 $mg.kg^{-1}$, Hg = 0.5 $mg.kg^{-1}$; all for wet tissue), noting that mudprawns are not known to be targeted for consumption. The Pb concentration in mudprawns sampled at each site equalled or exceeded the limit, but not the Cd and Hg concentrations. Nel et al., (2015) also compared the concentrations of Cd, Hg and Pb in fish muscle tissue to limits prescribed by the European Union for fish destined for human consumption (Cd = 0.05 $mg.kg^{-1}$, Pb = 0.3 $mg.kg^{-1}$, Hg = 0.5 $mg.kg^{-1}$; all for wet tissue). Cadmium in the liver of *P. commersonnii*, *L. amia*, and *A. japonicus*, and in the muscle of *M. cephalus* exceeded the limit. Lead in the liver of *P. commersonnii* and *L. amia* exceeded the limit. Mercury concentrations did not exceed the limit.

Nel et al., (2015) did not provide a conclusion on the risk posed by metals in fish apart from noting concentrations in the muscle tissue of fish were often well below limits prescribed for the sale of fish products in some parts of the world and were thus not cause for concern. Nel et al., (2015) did note that while metal concentrations in fish were generally low, they may pose a risk to subsistence fishers that consume large amounts of fish and recommended the analysis of metal concentrations in larger fish than those analysed to improve the understanding of the risk, since concentrations in fish often increase with size.

5. Conclusions and roadmap

The Swartkops Estuary is subjected to considerable anthropogenic pressure that has led to a deterioration in water quality and ecological functioning of the estuary (Adams et al., 2021). As such, we develop a conceptual model to show the flow of metals across all trophic levels in estuarine systems as a toll to aid in identifying areas where further research is required (Fig. S15). This study only refers to metals, but other contaminants, including organophosphate pesticides and organochlorine pesticides (Olisah et al., 2022), have also been recorded in the estuary.

Studies on metal concentrations in the water column of the Swartkops Estuary are limited. The studies by Connell et al., (1976) and Watling and Watling (1979) were made at a time when pollution in the estuary was becoming a cause for concern, but the degree of concern was by no means as high as is now the case. Neither of these studies provided evidence for significant metal contamination of the water column at the time. The metal concentrations reported by Connell et al., (1976) and Watling and Watling (1979) may have little relevance to contemporary conditions, and this represents a major gap in our understanding on whether metals are important contaminants of the water column in the estuary.

Studies on metal concentrations in sediment in the Swartkops Estuary suggest sediment in most parts of the estuary was historically not significantly metal contaminated. Where contamination was evident, it was usually restricted to small parts of the estuary and of a low magnitude. Metal concentrations were below SQG's, suggesting they posed a low risk to sediment-dwelling organisms. Metal concentrations reported by Phillips et al., (2015) in sediment sampled in canals that direct surface runoff to the estuary, and in freshwater wetlands reveal high concentration by Cd and highlights the importance of the canals as sources of metals to the estuary.

There appears to be some evidence that metals are accumulating in certain plants in the Swartkops Estuary, but none of the studies provide conclusive or convincing evidence of excessive accumulation. Metal concentrations reported in the tissue of invertebrates and fish in the Swartkops Estuary vary widely, making it difficult to conclude if these fauna are accumulating excessive metal concentrations in their tissues.

The multitude of potential metal sources in the Swartkops Estuary catchment and known water quality problems in the estuary due primarily to excessive wastewater inputs, would ordinarily lead to the conclusion that various environmental matrices in the estuary would be metal contaminated. Although this appears to be the case to some degree, as discussed above, the extent and magnitude of the contamination appears less widespread and significant than might be expected. Although this might reflect the fact that metals are not major contaminants in most parts of the estuary, the fragmented and piecemeal approach to research performed to date has contributed to these uncertainties. This can only be resolved through hypothesis driven research. There are enumerable studies that can be performed in this context, ranging from basic studies on metal concentrations in water, sediment, and fauna and flora to identify spatial and temporal trends that can be linked to possible metal sources and to identify human and ecological risks, to more complex studies on metal speciation and metal cycling amongst water, sediment, and biota. Research to provide this information need not be performed sequentially or in isolation, but at this time it is recommended that research in the immediate future focus on surveys to identify spatial and temporal trends that can be linked to (possible) metal sources. Contaminant metals will largely have their source in systems outside the estuary and research must thus be performed at the catchment scale. Metals are one of many possible (and likely) contaminants of water, sediment, fauna, and flora in the estuary and may be of lesser ecological and/or human health concern than other contaminants. Studies on metals should thus not be viewed in isolation nor be prioritised above other possible contaminants.

Possible research on metals in the estuary are outlined below.

1. Metal concentrations in the water column provide fundamental information toward understanding threats facing estuarine ecosystems. However, since the physico-chemistry of the water column is highly variable, the periodic analysis of metal concentrations in water is of limited value. Dissolved and total metal concentrations should thus be analysed at least quarterly, but ideally more frequently for at least 24 months in water sampled at positions along the Swartkops River and estuary, to identify key metal sources to the river and estuary. Water should be sampled in surface runoff canals and near known point sources of metals to the estuary, in addition to

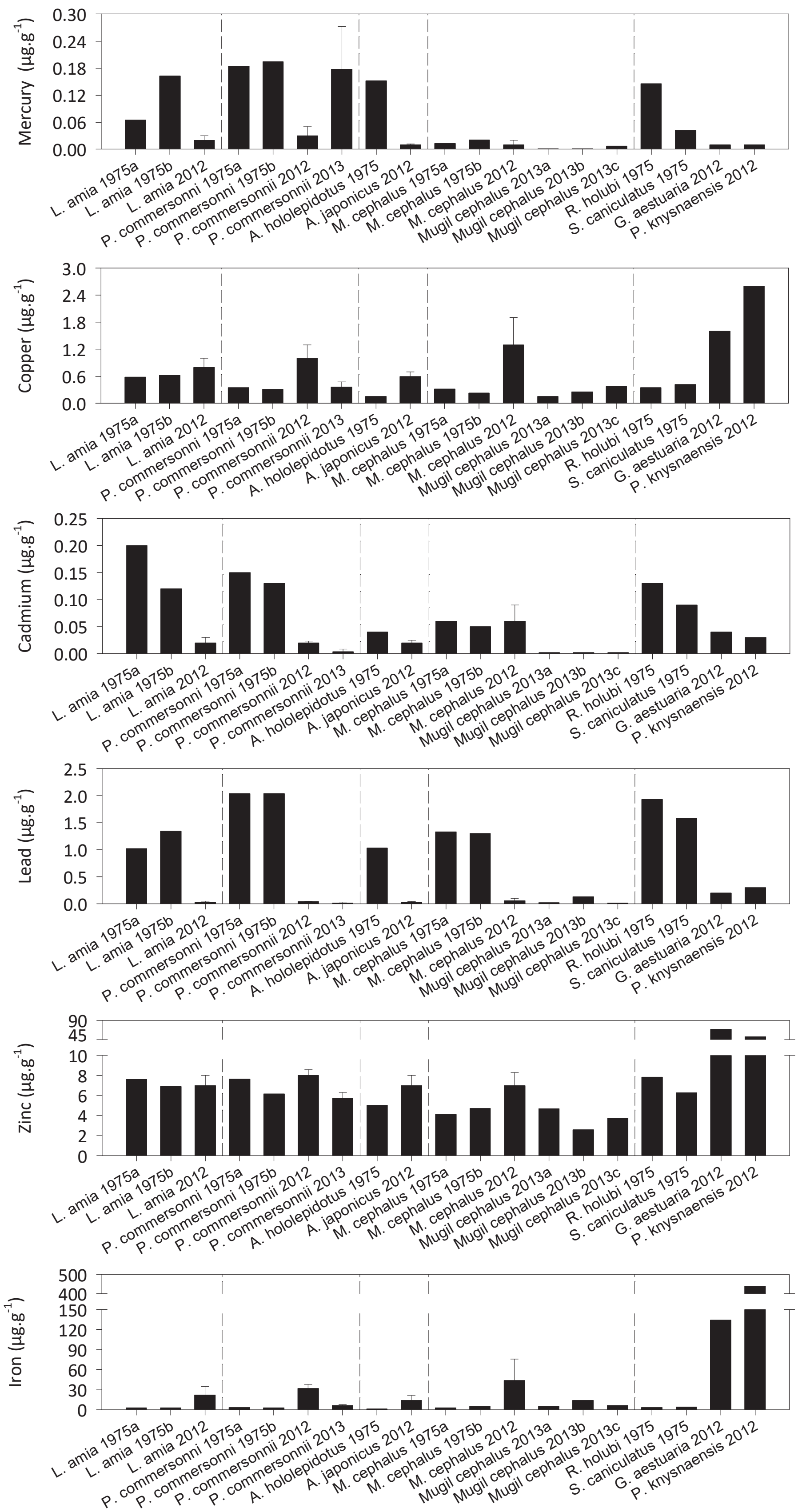

Fig. 5. Metal concentrations (µg. l-1) measured in the muscle tissue of fish sampled in the Swartkops Estuary in 1975 by Connell et al., (1976) and in 2012 by Nel et al., (2015), and in fish sampled in Durban Bay in 2013 by Newman et al., (2015).

positions in the estuary. Sampling in the estuary should ideally be performed on an outgoing tide. The relationship between metal concentrations and salinity should be used to identify if metals are behaving conservatively or are being added to or scavenged from the water column in the estuary. The need for, and frequency of further monitoring can be decided based on the findings.

2. As stated above, studies to date provide evidence for the contamination of sediment in the estuary by some metals, but the contamination is not significant nor widespread. Sediment sampled at a high density of sites along the Swartkops River and Estuary in surface runoff canals and near known point sources of metals to the estuary should nevertheless be analysed for metals. Since sediment provides a conservative indicator of metal contamination, studies of this type need only be performed at three-year intervals, and possibly at a longer interval depending on the findings.
3. High concentration of metals can have deleterious effects on microbes. To survive increased metal concentrations, microbes have evolved a few defence mechanisms that include the metabolisation and transformation of metals into less hazardous forms and at the same time induce the formation of metal resistant microbes. Microbes develop extracellular polymeric substances and resistance genes against metal pollutants. Thus, there is need to consider the influence metal pollution on microbes and the potential role of played by microbes in bioremediation to reduce metal pollutants in contaminated sites along the Swartkops Estuary.
4. Wetland plants may act as sinks for metals through their active and passive uptake, promoting phytostabilization, where plants immobilize metals and store them below ground in roots and/or soil, or phytoextraction, where metals are stored in aboveground tissues. Plants hold much promise for rehabilitating the estuary and limiting the input of contaminants (e.g. artificial wetlands). The role played by wetlands and salt marshes as phytoremediators thus constitutes an important line of future research.
5. The Swartkops Estuary is important for subsistence and recreational fishing communities. The risk posed by metals in the tissue of fish targeted by these communities must thus be evaluated. Research on metals in fish must thus be supplemented by studies on the fish consumption habits and patterns of subsistence and recreational fishing communities in the estuary, to provide site relevant information for risk assessment (e.g., size of meals, frequency of consumption, species consumed). The required frequency of fish tissue analysis and associated risk assessment should be decided based on the findings of an initial comprehensive study.

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Author contributions

AN led the writing of the manuscript. JBA, GMR, MN, BN, LRDH contributed critically to the drafts and gave final approval for publication.

CRediT authorship contribution statement

Aldwin Ndhlovu: Writing – review & editing, Writing – original draft. **Lucienne RD Human:** Writing – review & editing. **Gavin M Rishworth:** Writing – review & editing. **Brent Newman:** Writing – review & editing. **Marele Nel:** Writing – review & editing. **Janine Barbara Adams:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Ethical approval

All applicable international, national, and/or institutional guidelines for the care and use of animals were followed. Research Ethics was issued by Nelson Mandela University for related work, although these data are not presented: Ref: [A21-SCI-ZOO-002 / Approved].

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.rsma.2024.103588.

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