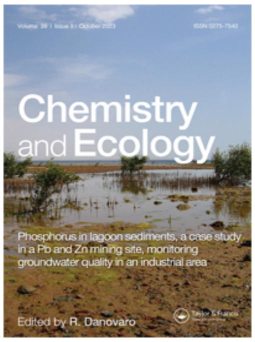

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Metal and non–metal dynamics and distribution in soil profiles across selected pans in the Ramsar declared subtropical within a national protected area

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ABSTRACT

The study investigated the spatial distributions of selected metals, semi–metals and non–metals within a floodplain pan ecosystem in the Ramsar declared Makuleke Wetlands within the Makuleke Contractual National Park, in the northern Kruger National Park (South Africa), along varying soil depths (0–120 cm) at 20 cm intervals. The study identified significant differences in metal concentrations (i.e. Ca, Mn, Fe) and non–metals (i.e. C, S) across sediment depths. Metal and non–metal concentrations in surface sediments (0–40 cm) were generally high. Compared with the sediment quality guidelines, all measured metals were within the 'no effect' level across different sites and depths, except for one site (i.e. Mambvumbvanyi pan). In contrast, enrichment factors showed that K, Ca and Mg were enriched in sediments across all the floodplain pans and depths. Principal component and cluster analyses indicated that various metals originated from different sources. Although a high concentration of metals was found in the topsoil, no potential detrimental effects on the aquatic systems could be observed. Based on the findings, this study provides a baseline overview of sediment metal pollution that can inform effective management of these floodplain wetlands systems.

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KEYWORDS
Floodplain pans; Ramsar wetlands; metals; sediment profiles; geo-accumulation index; enrichment factor

1. Introduction

Floodplain ecosystems are widespread globally and are utilised by diverse fauna, including fish, amphibians, macroinvertebrates and even wild and domesticated mammals [1–4]. They also provide socioecological services such as drought relief, flood attenuation, fodder provision, water storage and purification, and soil protection [5,6].

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Floodplain pans differ from other aquatic ecosystems in that they are subject to seasonal inundation by lateral overflows of rivers, with associated biota adapted to these significant habitat changes related to water level fluctuations [7,8]. These ecosystems are increasingly threatened by river–induced flood regime changes, upstream flow diversions, and river management, often with detrimental implications for the structure, functioning and productivity of floodplain pans [4]. The flood pulse can also result in the import of pollutants, such as metals which are of health concerns but also alter aquatic foodweb structures [9,10]. The Environmental Protection Agency (EPA) has listed most of these non–degradable toxic elements, such as Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper, (Cu), Mercury (Hg), Nickel (Ni), Lead (Pb), and Zinc (Zn) as priority pollutants that require monitoring when they reach the soil medium [11,12]. This suggests a need for monitoring metal accumulation in sediment, especially in important aquatic systems that have conservation value.

Due to extensive human activities on floodplain wetlands, numerous pollutants make their way into these ecosystems [13–15]. These transferred metals are normally in soluble form in water or accumulated in sediments through a number of pathways including atmospheric deposition, sewage, stormwater as well as leachate, which transport metals originated from various places such as residential, industrialised and cultivated areas [16–18]. Natural activities that contribute to metal release into floodplain wetlands include geological processes such as weathering and decomposition of parent rock ore material and volcanic eruptions [19,20]. Therefore, natural metal release dynamics are highly homogenous globally [21]. Since the presence of metals can be natural, indigenous fauna are likely to be largely adapted to deal with metals at natural background levels [22,23]. However, many floodplain ecosystems are now characterised by excessive and non–natural metal deposits [24]. Rivers often accrue pollutants from their contributing catchment area [25] and river floodplains, where flow velocity dissipates, often accumulate such pollutants through deposition [26]. The accumulation of metals in sediments within these aquatic systems can cause various negative implications on living organisms such as fish, amphibians and macroinvertebrates within aquatic environments [27–29].

Accumulation of metals in floodplain pan sediments is a serious problem in these systems due to their toxicity and threats to biota [30,31]. Sediments in aquatic ecosystems are important as they act as natural filters for contaminated water and they potentially act as sinks for contaminants [6,32]. These sediments also provide important habitats for organisms and play an important role in maintaining the health of the environment and reducing carbon [33,34]. In order to quantify metal sediment dynamics in aquatic ecosystems, sediment core sampling/analysis is employed, thereby providing useful information on metal and non–metal composition, sedimentary history and environmental change over time [35,36]. Furthermore, sediment chemistry can provide information about various human activities in a watershed where floodplain wetlands are situated [37,38].

The study of sediment chemistry dynamics in floodplain wetland sediments is important because sediments can potentially indicate the status of contamination and the history in various floodplain pans across different seasons and hydroperiods [39,40]. One of the most crucial properties of metals, which differentiates them from other pollutants, is that they are not biodegradable in the natural environment [41]. In natural aquatic environments, sediments are the main sink for metals, but due to changes in environmental conditions such as pH, electrical conductivity and sediment redox potential, sediments can potentially accumulate high metal concentration leading to contamination of water sources [42–44] and changes in the biological processes within the aquatic systems [45].

The present study focuses on the Makuleke Ramsar floodplain pan wetland system found in the northern Kruger National Park region of South Africa. These pans, while located in a globally significant protected area, also fall within the transboundary Limpopo River basin. The Limpopo arises in the highveld of South Africa and flows through areas characterised by many different land use practices, including industrial, agricultural and mining activities. It is joined by major tributaries arising in the Southern African interior in Botswana and Zimbabwe, before entering the lowlands of Mozambique after having past through the Makuleke wetland floodplain area. However, although the wetlands are impacted by metals [46,47], the detailed distribution characteristics in the pan's sediments have not yet been clearly determined, and so their potential ecological risk is poorly understood. Therefore, this study aimed to (i) to investigate spatial distributions of different metals (i.e. Zn, Mn, Cu, Fe, Na, Ca, K, Mg), non-metals (i.e. C, S) and a semi metal (i.e. B) in sediment cores within selected pans, (ii) investigate distributions of metal, semi metal and non–metal concentrations in relation to sediment depth and identify relationships among sediment and (iii) determine the sediment contamination and toxic risks associated with the identified metals, semi metal and non–metals using pollution indices. We hypothesised that the concentration of metals, semi metal and non–metals will be higher at the sediment surface compared to the subsurface due to the fact that when pans dry up, most of the metals, semi metal and non–metals elements accumulate at the surface layer of sediments.

2. Materials and methods

2.1. Study area

The study area is the Ramsar Convention declared Makuleke Wetlands, in northern Kruger National Park, South Africa (Figure 1). The Makuleke Wetlands are located in the floodplain region at the confluence of the Limpopo and Luvuvhu rivers in the Pafuri region [48,49]. These wetlands received Ramsar recognition status on 22 May 2007, as wetlands of international importance. This area was the first Ramsar site to be owned and co–managed by the community (Makuleke community) and the Kruger National Park in South Africa. The area north of the Luvuvhu River being the Makuleke Contractual National Park. The area has remarkable floodplain features such as flood pans, floodplain grasslands and river channels which are intermittently filled from over–bank flooding and rain. To obtain a variety in study sites, pans were selected according to dominant hydroperiod, in this case greater perenniality than other pans, locality and accessibility.

Three pans in the Makuleke Ramsar site were selected for sampling, namely; Nyavadi (22°21′33.61″S, 31°04′17.68″E), Mambvumbvanyi (22°24′58.10″S, 31°16′22.02″E) and Jachacha (22° 22′ 45.88″S, 31° 13′ 11.56″E) (Figure 1). These pans were selected based on their location, hydroperiod and general biodiversity, for example Nyavadi pan is one of the largest of the Makuleke pans located in an open savanna grassland. Mambvumbvanyi pan has the largest crocodiles, water bird diversity and abundances, and is located

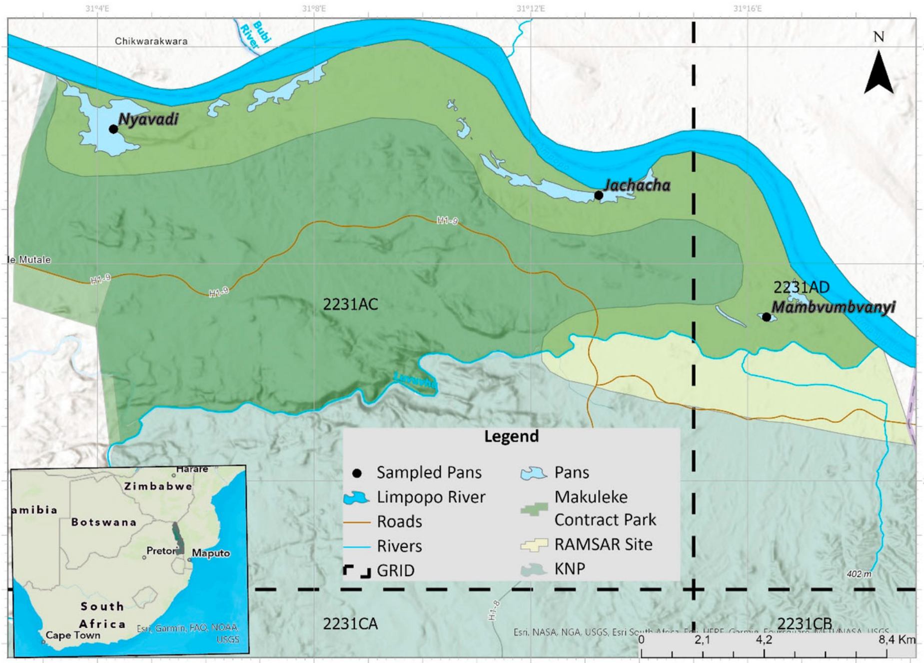

Figure 1. Location of the study sites within the Makuleke Wetlands, northern Kruger National Park, South Africa.

in the fever tree forest (*Vachellia xanthophloea*), and Jachacha pan is one of the permanent pans in the Makuleke Wetlands, whereas the first two are semi permanent. The geology underlying the selected pans is known to be dominated by sedimentary rocks such as sandstone and several acidic, intrusive granites and gneisses of the Sand River formation that underlie the uppermost parts of the Limpopo River sub–catchment [50].

2.2. Sediments collection and processing

Sediments samples were collected in March 2022 from three different pans (i.e. Nyavadi, Jachacha and Mambvumbvanyi) using a 130 cm hand auger. Two replicate samples were collected from each pan along varying soil depth ranges: 0–20 cm, 20–40 cm, 40–60 cm, 60–80 cm, 80–100 cm, and 100–120 cm (2 kg per replicate per depth). Sediment collection sites within a pan were selected randomly from within the deepest points/areas yet to dry out, as these would potentially be areas of high metal accumulation. The samples were then placed separately in clean polyethene Ziplock bags. Collected sediments were transported to the Department of Geography and Environmental Sciences laboratory at the University of Venda, and oven dried at 60°C for 72 h, before being disaggregated in a porcelain mortar and sieved (mesh size 0.05 mm) to remove unwanted plant roots and debris.

In brief, for each sediment core, elements such as K, Mg, Na Ca, Cu, Zn, Mn, B, Fe and S were measured using an Inductively coupled plasma atomic emission spectroscopy instrument (see Rice, 2012 for detailed methodology), while the total nitrogen and phosphorus were analysed using a SEAL AutoAnalyzer 3 high resolution and Bray–2 extract as described by Bray & Kurtz [51]. To estimate the accuracy of this method, a natural standard–certified reference soil, namely SARM–51 (MINTEK) and SL–1 (IAEA), digested and analysed in duplicate, was used for recovery tests. The percentage recoveries of the certified values ranged between 89% and 99% for all metals.

2.3. Data analysis

Data used in the present study were assessed for homogeneity and normality of variance using parametric tests and were found to conform to parametric assumptions. A two–way ANOVA test in SPSS version 28 was used to assess for differences in metals and nutrient concentrations among floodplain pans (i.e. Nyavadi, Jachacha, Mambvumbvanyi) at various sediments depths (i.e. 0–20 cm, 20–40 cm, 40–60 cm, 60–80 cm, 80–100 cm, 100–120 cm). We further employed Tukey's post hoc analyses to assess the comparison for the sites that showed significant differences.

To determine the metal pollution in the pans of Makuleke concession, selected metal concentrations were compared with international standards of sediment quality guidelines (SQGs) with the aim of evaluating the effects of metals in the aquatic environments. We used the Canadian sediment quality guidelines [52] which comprise two levels, i.e. the low effect level (LEL) and severe effect level (SEL). Sediment metals were assessed based on the effect level across different sites.

2.3.1. Determining enrichment factors (EF)

The assessment of the enrichment degree of heavy metals in sediments was conducted by calculating the enrichment factor (EF), which is an indicator widely used for evaluating the pollution level of artificially imported heavy metals and to discriminate between anthropogenic or naturally geologic inputs of heavy metals [53]. When calculating the EF, a reference element is required to weaken the impact of the effects of the grain size on heavy metal pollution. The present study utilised Fe as the normalisation element. Thus, the EF value for a single metal was calculated as the ratio of the normalisation of all metals by Fe in the sample to the normalisation of all metals by Fe in background values. The specific formula for determining EF is as follows:

$$\mathrm{EF} = \frac{\left(\frac{C_m}{\mathrm{Fe}_{\mathrm{sample}}}\right)}{\left(\frac{C_m}{\mathrm{Fe}_{\mathrm{earth's\ crust}}}\right)}$$

where C_m is concentration of the examined metal in the examined sediment and Fe is the concentration of the reference metal in the examined sediment, where, (Fe = 1.6 mg kg^{-1}). The background values in this study were obtained from the mean environmental background concentrations of sediments selected randomly in the undisturbed soil near to the Makuleke wetland sites, but away from seasonally inundated zones. The collected sediment samples collected from indisturbed areas inside the park were analysed for metals, semi metal and non-metals and results were used as background values to calculate EF. Based on the EF value, the enrichment degree of each heavy metal was then categorised into six groups: (A) EF < 1.5, none; (B) 1.5 < EF < 2, minimal; (C) 2 < EF < 5, moderate; (D) 5 < EF < 20, significant; (E) 20 < EF < 40, very high; and (F) 40 > EF, extremely high [54].

2.3.2. Pollution load index

Pollution severity and its variation along the sites and depths were determined using a Pollution Load Index (PLI). This index is a simple tool to compare the pollution status of different locations. We determined PLI from each pan following the method by Tomlinson et al. [55], where PLI <1, 1 and >1 indicate No pollution, background pollution and deterioration of sediment quality, respectively.

2.3.3. Assessment of geoaccumulation index (Igeo)

Geo–accumulation index (Igeo) was used to assess the individual heavy metal pollution in sediments within each sampling pan. Igeo has also been used previously to assess soil contamination and the degree of metal pollution [56,57] based on 7 Igeo classes. This method can be used to determine the levels of contamination or accumulation of metals in sediments. The formula is mathematically expressed as:

$$Igeo = \log_2\left(\frac{C_n}{1.5 \times B_n}\right)$$

where C_n is the concentration of measured metal in the sediment, B_n is the geochemical background value of the element in the background sample [58], and 1.5 is the background matrix correction factor due to lithogenic effects. For background values, samples were collected randomly from a nearby area that was relatively undisturbed with no known past or present human impacts. According to Müller [59], the seven classes for interpreting the geo–accumulation index are ranged as follows: Igeo ≤ 0, unpolluted; Igeo of 0–1, unpolluted to moderately polluted; Igeo of 1–2, moderately polluted; Igeo of 2–3, moderately to strongly polluted; Igeo of 3–4, heavily polluted; Igeo of 4–5, heavily to extremely polluted; and Igeo ≥ 5, extremely polluted [59].

We tested the relationship between metals concentration found on sediments using the Pearson correlation matrix in SPSS v16.0 for Windows software (SPSS Inc. 2007). To determine the natural and anthropogenic sources of sediment metal across the pans (Nyavadi, Jachacha and Mambvumbvanyi) and depth (0–20 cm, 20–40 cm, 40–60 cm, 60–80 cm, 80–100 cm, 100–120 cm), we employed principal component analysis (PCA) with the varimax rotation method in SigmaPlot (version 10.0). Furthermore, A two–way cluster analysis with Ward's average group was used to identify the different sources of metals within the floodplain pans [60].

3. Results

3.1. Metals vertical distribution in cores

The metal distribution along the sediment cores at three sampling pans are shown in Figure 2. Semi–metal B and non-metal C at a depth of 0–40 cm had similar spatial distribution characteristics with mean average of 1.1 and 1.3 mg kg^{-1} at Mambvumbvanyi and Jachacha, respectively. A very high concentration of Fe (443 mg kg^{-1}) was observed at Mambvumbvanyi pan at the surface layer sediment (0–20 cm) depth (Figure 2). The pan with high metal content was the Mambvumbvanyi with Mn being the one that exhibit highest concentration at all the depth, i.e. 0–20 cm, 20–40 cm, 40–60 cm, 60–80 cm, 80–100 cm and 100–120 cm at 690.5, 552, 488.5, 471, 548 and 525.5 mg kg^{-1}, respectively. The metals Ca and Zn had similar distributions and the content gradually decreased from surface to deep sediment. The content of P, Mg and S were generally high within surface sediments and lower within the deep sedimets. These three elements were mainly concentrated in Nyavadi pan at the depth of 0–20 cm, 40–60 cm, 80–100 cm and 100–120 cm (Figure 2).

Significant differences in metals (i.e. Ca, Mn, Fe) and non–metals (i.e. C, S) concentrations were found ($p < 0.05$) along sediment depths, whereas metals (i.e. Ca, Mg, Na, Cu, Zn, Mn and Fe) were significantly different ($p < 0.05$) across study sites (Table 1). Overall results indicate that metal concentrations decrease as the soil depth increases, except in Mambvumbvanyi pan where metal concentrations (i.e. Na, Cu, Zn, Mn, Fe) and non–metal S increased with depth. The results from pairwise post–hoc comparison indicated that metals such as Ca, Mn and Fe are significantly different ($p < 0.05$) between some study sites (see Table 2).

3.2. Sediment quality guidelines assessment in the sediment cores

We found that most of the metals were within the ‘no effect’ level across different sites and depths, except for one pan (i.e. Mambvumbvanyi). Phosphorus showed ‘low effect

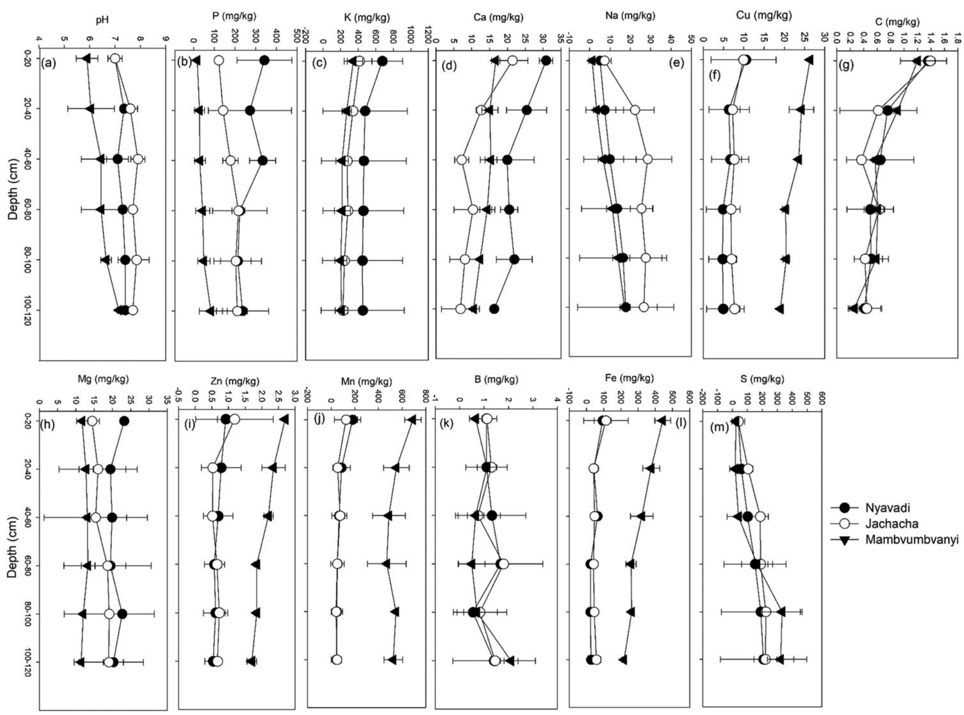

Figure 2. Metals, semi metals and non–metal concentrations (mean ± standard deviation) along sediment depths in three Makuleke Wetlands, Kruger National Park.

Table 1. Two–way ANOVA assessing the differences in metals, semi metals and non–metals concentrations across sites and sediment depths in Makuleke Wetlands, Kruger National Park.

	Depth		Sites		Depth × Sites	
	F	*P*	*F*	*P*	*F*	*P*
PH	2.55	0.065	**25.12**	**<0.001**	0.62	0.777
P	0.14	0.981	**22.69**	**<0.001**	0.68	0.728
K	0.42	0.828	3.11	0.069	0.02	1.000
Ca	**7.52**	**0.001**	**31.81**	**<0.001**	0.88	0.568
Mg	0.07	0.996	**5.00**	**0.019**	0.14	0.998
Na	1.90	0.145	**5.96**	**0.010**	0.20	0.994
Cu	2.27	0.092	**93.68**	**<0.001**	0.26	0.982
Zn	2.27	0.091	**57.69**	**<0.001**	0.48	0.880
Mn	**2.79**	**0.049**	**156.65**	**<0.001**	0.31	0.967
B	1.00	0.444	0.34	0.715	0.45	0.901
Fe	**6.58**	**0.001**	**159.31**	**<0.001**	1.71	0.156
C	**11.38**	**<0.001**	0.16	0.855	0.46	0.894
S	**3.44**	**0.023**	0.26	0.771	0.40	0.927

Note: Bold values indicates significance at $p < 0.05$.

level' (LEL) in two sites, namely, Nyavadi and Mambvumbvanyi at depth of 80–120 cm. Potassium showed a 'no effect level' across all sites and depths, thus indicating low concentrations of K in the study pans and sediment profiles. Metals such as Cu, Zn, Mn, Fe and semi-metal B showed a 'no effect' level across all sediments depths and in two pans (Nyavadi and Jachacha), whereas in Mambvumbvanyi, Cu, Mn and Fe metals resembled LEL from 0–120 cm depth.

Based on the results from the geo–accumulation index, metals (i.e. K, Ca, Mg, Na, Mn, Fe) showed extreme pollution in all sites and depths (Figure 3). This is attested by the Igeo values which were all above class 6 suggesting extremely polluted sediments. The Igeo values for Zn and B indicated no pollution as both were grouped under class 0 with Igeo < 0 in all study sites and depths. For Cu, the Igeo values ranged mostly from class 4 (strongly polluted) to Class 6 (extremely polluted) (Figure 3).

The calculation of enrichment factors showed that K, Ca and Mg were enriched in sediments across all the floodplain pans and along the sediment depth. Magnesium had high EF value among the all metals studied and it has a significant enrichment (mean 5.81). Sodium (mean 0.43) and Cu (mean 0.78) had minor enrichment. Zinc (mean 0.01) and B

Table 2. Pairwise post–hoc comparison of significantly differed variables across the study sites.

Variables	Pairwise comparison		*p*
Ca	Nyavadi	Jachacha	**<0.001**
	Nyavadi	Mambvumbvanyi	**<0.001**
	Jachacha	Mambvumbvanyi	0.136
Mn	Nyavadi	Jachacha	0.887
	Nyavadi	Mambvumbvanyi	**<0.001**
	Jachacha	Mambvumbvanyi	**<0.001**
Fe	Nyavadi	Jachacha	0.769
	Nyavadi	Mambvumbvanyi	**<0.001**
	Jachacha	Mambvumbvanyi	**<0.001**
C	Nyavadi	Jachacha	0.864
	Nyavadi	Mambvumbvanyi	0.998
	Jachacha	Mambvumbvanyi	0.895
S	Nyavadi	Jachacha	0.764
	Nyavadi	Mambvumbvanyi	0.869
	Jachacha	Mambvumbvanyi	0.979

Note: Bold indicates sites with significant differences at $p < 0.05$.

(mean 0.03) exhibited the lowest EF values among metals studied and had no enrichment across all study sites and depths (Figure 4).

Results of the present study show that all the sediments across the floodplain pans and sediment depths are subjected to very high pollution and this indicates deterioration of sediment quality (Figure 5). The PLI showed a variation in pollution load across sites and depths, however, Mambvumbvanyi exhibited very high pollution load values across all the sediment depths (Figure 5). The values of the Pollution Load Index were found to be generally high (>1) in all the studied pans suggesting deterioration of sediment quality. The difference in indices results is due to the difference in sensitivity of these indices towards the sediment pollutants.

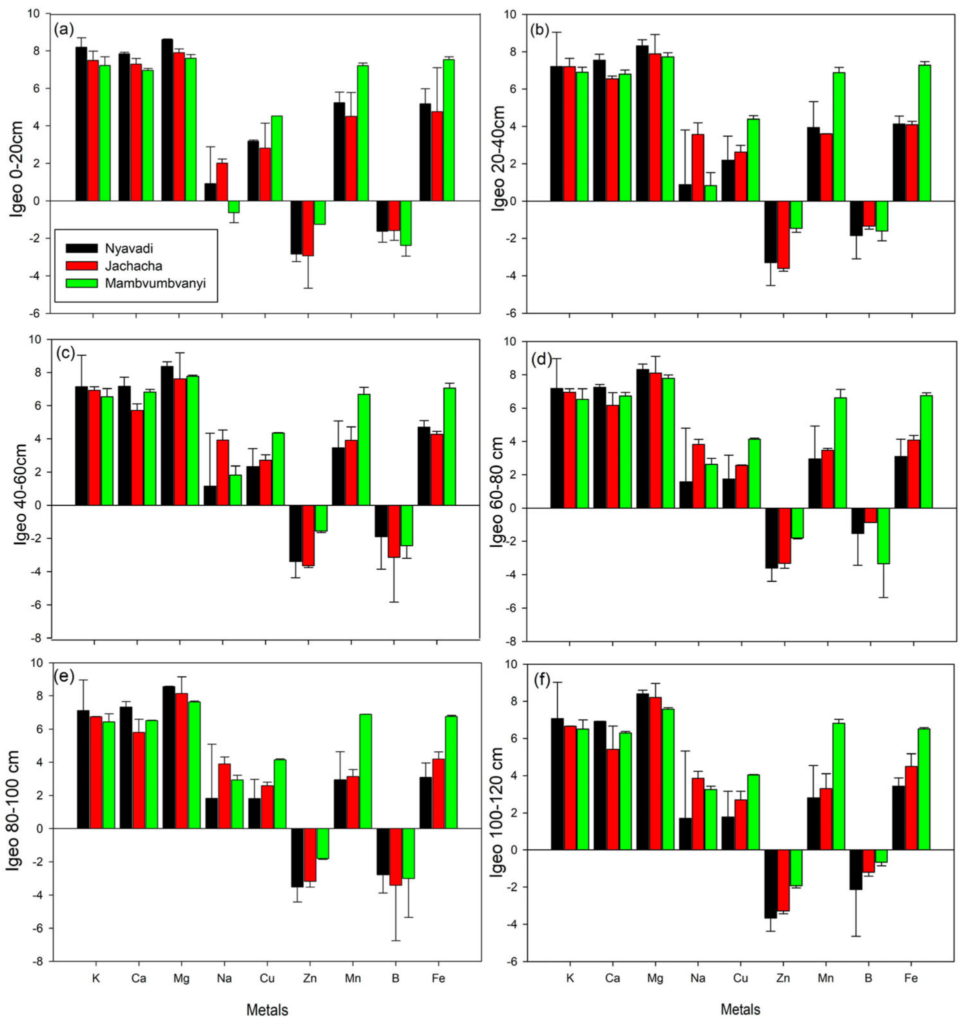

Figure 3. Geo–accumulation indices (Igeo; mean ± standard deviation) across different floodplain pans and sediments depth for various metals and non–metals.

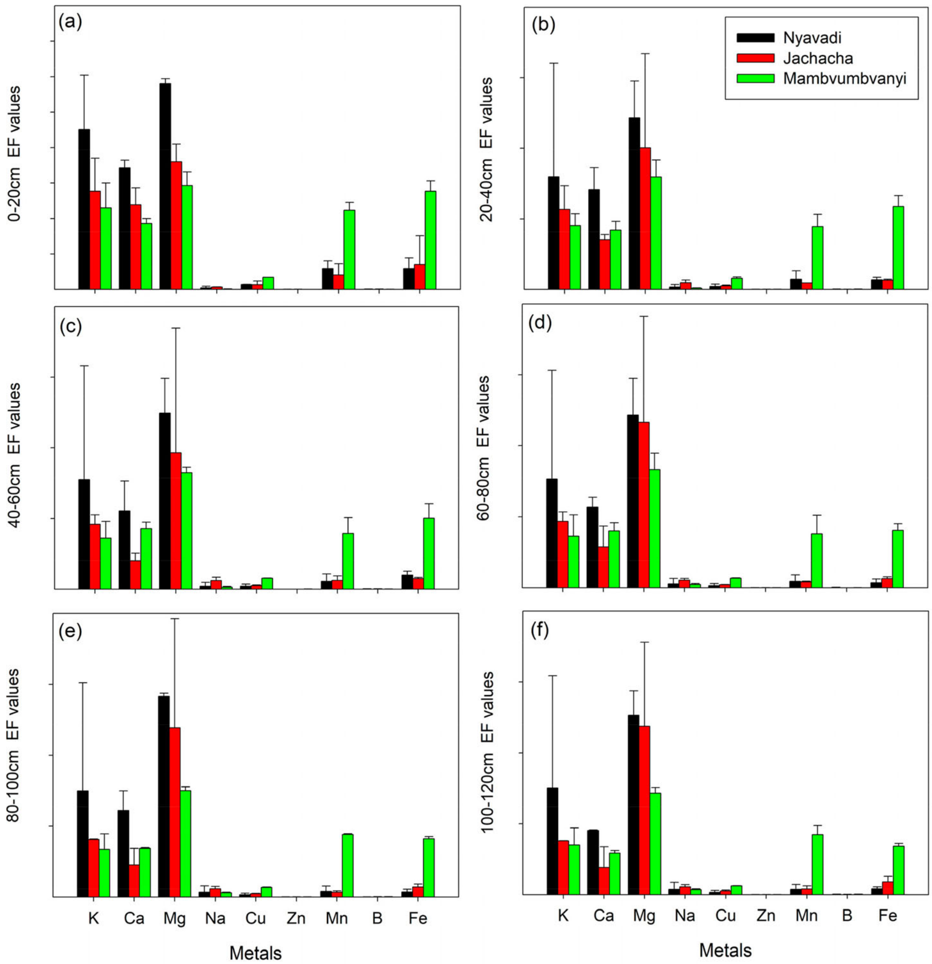

Figure 4. Enrichment factors (EF; mean ± standard deviation) of metals, semi metal and non–metals from the Makuleke Wetlands in Kruger National Park across different study sites and sediment depth. The EF for K, Ca and Mg should be multiplied by 1000.

3.3. Assessing the relationships among pollutants in various sampling pans

According to the Pearson correlation coefficient, a significant correlation was detected between multiple variables studied. Specifically, a significant correlation exists between Ca, Mg, Na, Cu, Zn, Mn, B and Fe, indicating a strong positive correlation (Table 3). Phosphorus was significantly correlated with all other metals analysed, except for C and S, because P can immobilise these other metals though forming the precipitation of phosphate within a water column [61]. Also, this suggests that these metals and P might have a common source. In this study, significant positive correlations were also observed between K and metals (i.e. Ca, Mg) and non–metals (i.e. B, C). Sediment pH was significantly positively correlated with metals (i.e. Na, Zn, Mn, Fe) and non–metals (i.e. C and S) (Table 3) as fine sediment particles adsorb metals [62,63]. Conversely, K and Ca were

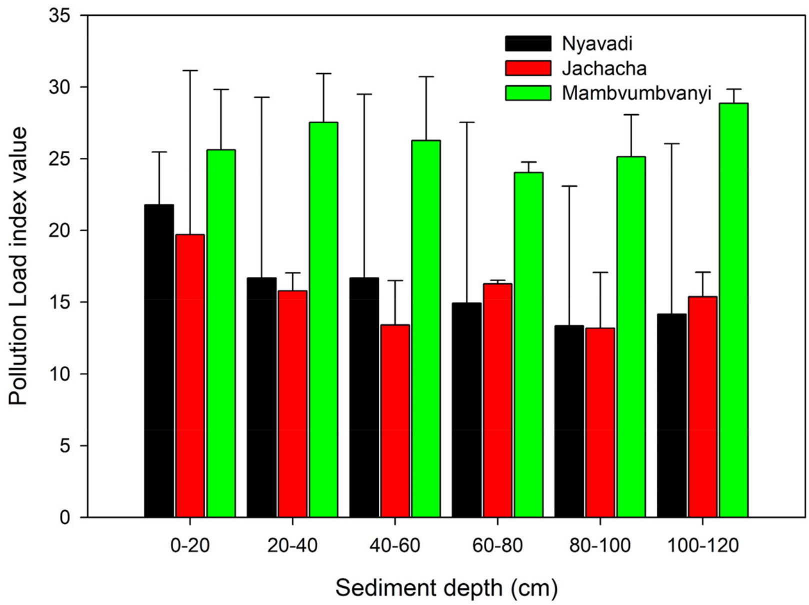

Figure 5. Pollution Load index values (means ± SE) for different sites and sediment depth measured in Makuleke Wetlands, Kruger National Park.

significantly negatively correlated with metals (Cu, Zn, Mn and Fe) (Table 3). This also suggests that these metals might originate from the same natural source. Na was significantly positively correlated with S ($p < 0.01$, Table 3), whereas no significant correlations were observed between sediment pH and K, Ca, Mg and B ($p > 0.05$, Table 3).

3.4. Sources of heavy metals and non–metal categorisation

Principal component analysis was conducted using the varimax rotation method. According to the PCA ordination technique, PC1 and PC2 indicates 44.1% and 22.6% of the variance, respectively, with the total principal component (PC) cumulative variance of 66.8% (Table 4). The PCA results further classified metals into three groups, where *group 1* consisted of K and Ca, *group 2* had Na, B and S and *group 3* had Mg, Cu, Zn, Mn and Fe (Table 4). However, the two–way cluster analysis results identified two major groups; *group 1* consisted of Cu, Zn, Mn and Fe which is clearly separated from *group 2* with metals such as K, Ca, Mg, Na, and non**–**metals such as B and S (Figure 6).

Moreover, the two–way cluster analysis further grouped the metals according to their depth. As shown in Figure 6, three main groups can be clearly identified, whereby *group 1* consist of sediment depth metal concentrations from Mambvumbanyi pan (all depths from 0–120 cm), *group 2* consist of sediment depth in Jachacha and Banyini pans (all depth except 0–20 cm and 20–40 cm in Jachacha pan, and 0–20 cm in Banyini pan), whereas *group 3* consists of sediment depth in two pans i.e. Banyini and Jachacha with all depths (0–120 cm) in Banyini and except 20–40 cm, 40–60 cm, 60–80 cm, 80–100 cm and 100–120 cm in Jachacha pan (Figure 6).

Table 3. Pearson correlation matrix of variables across the Makuleke Wetlands.

	pH	P	K	Ca	Mg	Na	Cu	Zn	Mn	B	Fe	C	S
pH	1	**0.001**	0.253	0.384	0.112	**<0.001**	**<0.001**	**<0.001**	**<0.001**	0.093	**<0.001**	**0.034**	**0.045**
P	**0.54**	1	**<0.001**	**0.029**	**<0.001**	**0.028**	**<0.001**	**<0.001**	**<0.001**	**0.008**	**<0.001**	0.578	0.225
K	0.20	**0.71**	1	**<0.001**	**0.032**	0.056	0.629	0.831	0.367	**0.001**	0.197	**0.003**	0.163
Ca	−0.15	**0.37**	**0.59**	1	0.249	**0.011**	0.630	0.923	0.774	0.927	0.653	**<0.001**	**0.018**
Mg	0.27	**0.68**	**0.36**	0.20	1	0.982	**0.004**	**0.005**	**0.004**	0.279	**0.003**	0.501	0.591
Na	**0.70**	**0.37**	0.32	−**0.42**	0.00	1	0.091	**0.040**	**0.031**	**0.004**	**0.006**	0.051	**<0.001**
Cu	−**0.73**	−**0.61**	−0.08	−0.08	−**0.47**	−0.29	1	**<0.001**	**<0.001**	0.838	**<0.001**	0.096	0.981
Zn	−**0.74**	−**0.58**	−0.04	0.02	−**0.45**	−**0.34**	**0.98**	1	**<0.001**	0.702	**<0.001**	**0.040**	0.751
Mn	−**0.68**	−**0.65**	−0.15	−0.05	−**0.47**	−**0.36**	**0.94**	**0.92**	1	0.582	**<0.001**	0.187	0.947
B	0.28	**0.44**	**0.54**	0.02	0.19	**0.47**	−0.04	−0.07	−0.09	1	0.292	0.635	**0.001**
Fe	−**0.82**	−**0.70**	−0.22	−0.08	−**0.48**	−**0.45**	**0.96**	**0.95**	**0.92**	−0.18	1	0.080	0.360
C	−**0.35**	0.10	**0.48**	**0.56**	0.12	−0.33	0.28	**0.34**	0.23	0.08	0.30	1	0.058
S	**0.34**	0.21	0.24	−**0.39**	0.09	**0.70**	0.00	−0.05	−0.01	**0.53**	−0.16	−0.32	1

Note: Bold values indicates $p < 0.05$ (greyed cells represent r–value and white cells represent P values). Bold values indicate $p < 0.05$.

Table 4. Principal component analysis (PCA) results for metal, semi metals and non–metal concentrations for the entire study area.

Variables	PC1	PC2
Eigenvalue	4.41	2.26
Variance (%)	44.12	22.63
Cumulative Variance (%)	44.12	66.75
Metals	**Factor Loading**	
K	0.32	−0.37
Ca	0.05	0.37
Mg	**0.58**	0.11
Na	**0.52**	**−0.72**
Cu	**−0.93**	−0.30
Zn	**−0.93**	−0.24
Mn	**−0.93**	−0.23
B	0.30	**−0.71**
Fe	**−0.97**	−0.11
S	0.25	**−0.85**

Note: Factor loadings >0.5 are highlighted in bold.

4. Discussion

Generally, the concentrations of metals in the assessed profiles were higher in surface sediment than in deeper sediment which is consistent with our hypothesis. Additionally, we noticed that generally, Mambvumbvanyi pan tended to be more polluted (at a depth of 0–20 cm) than Nyavadi and Jachacha pans (Figure 2). From the latter, high surface sediment metal concentrations are likely be due to plant debris in surface soils [64], plant cycling [65], pan drying as a subject of seasonal changes and soil deposition, through floodplain inundation waters arising from outside the park that contains metals and non-metals from sources such as industries and sewage plants, respectively. Furthermore, we observed that pollution load by metals is varied slightly across the studied floodplain pans and sediment depth due to either over centuries/millenia – or in more recent decades as result of catchment development upstream. The latter may include laundry washing in the river by local communities, washing of cars directly in rivers or discharge

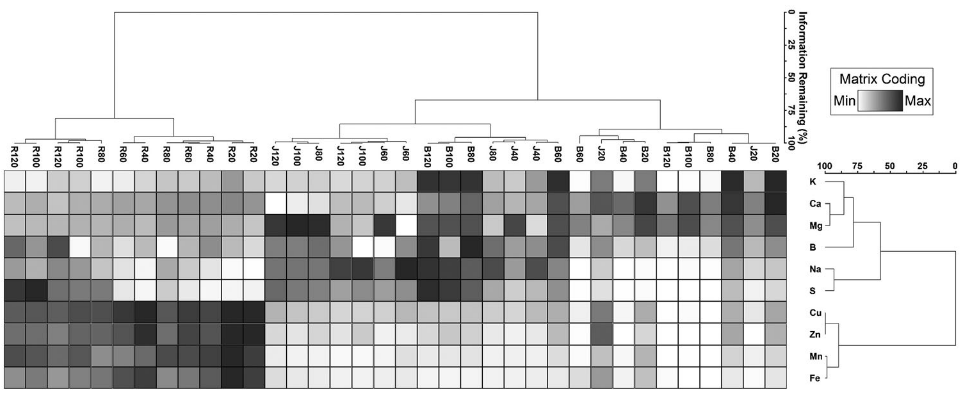

Figure 6. Two–way cluster analysis for metals. The floodplain pans (J–Jachacha, B–Nyavadi and R–Mambvumbvanyi) are indicated in the columns which show metals, semi metals and non–metals concentrations according to sediment depths (i.e. 0–20 cm, 20–40 cm, 40–60 cm, 60–80 cm, 80–100 cm and 100–120 cm).

of metal-rich effluents from wastewater treatment plants, agricultural lands or mining activities [66]. Our observations were similar to Dalu et al. [6] who found that the vertical distribution of metals concentration (e.g. K, Ca, Mg, Na, Cu, Zn) was higher at the surface than those in the bottom layer of the Nylsvlei Ramsar declared wetlands soil profiles. However, this will be expected anyway as the Nyl River is a headwater system and has a significantly smaller contributing catchment than the Makuleke floodplains, these being closer to the outlet of the entire Limpopo River basin and thus one would expect exponentially larger loadings. In addition, parameters such as hydrodynamic conditions have been reported before to affect sediment texture and their ability to withhold metals [67], and the sediment texture of the three pans can thus be partly explained by differing hydrodynamic conditions of the pans and floodplain regimes/hydroperiods.

According to the results of the sediment vertical distribution profiles based on international standards, the surface to midsurface sediments (depth 0–80 cm) were significantly more contaminated than subsurface soils (depth 120–140 cm) suggesting recent decadeal deposition. However, overall results showed that the sediment quality complied with Canadian requirements for acceptable sediment quality [52]. This was especially correct for metals such as Ca, Cu, Mn, Fe and Zn where only in few sites and depths were above the 'no effect' level, although B and S concentrations were most frequently enhanced at shallow depths. The pans that surpassed the acceptable limits, however, have been identified for further monitoring efforts. As sediments aggregate and textures vary with depth and sites, the changes in concentration dynamics were likely impacted by variations in metal settling ability within which their transport medium behaves. According to Zhang et al. [68], metals spatial variation in concentration is influenced by sediment particle size, and this is in line with the present study, where surface sediments in the pans were mostly clay and subsurface sediments were loam and sand.

Based on the geo–accumulation results, the top to middle sediments (0–60 cm depth) were generally polluted when compared to subsurface sediments (80–120 cm). However, when the concentration of metals within sediments is compared with the Canadian sediment guideline was found to be within the acceptable levels throughout the cores [52]. Metals such as Cu, Zn, Mn, and Fe and non–metal B showed a 'no effect' level across all sediment's depths and in two pans (Nyavadi and Jachacha), whereas in Mambvumbvanyi, metals resembled LEL in metals (i.e. Cu, Mn and Fe), from 0–120 cm depths, suggesting that pans such as Nyavadi and Jachacha have not been contaminated and their health status is good. However, the LEL of metals in Mambvumbvanyi suggests an input of metal constituents from the overflow of the Luvuvhu River and some constituents from animal movements within the park. Nonetheless, the Mambvumbvanyi has been identified as one of the pans that need further monitoring efforts of its accumulation of metals. From our observations, all studied pans had a surface soil type of clay, with varying types of subsurface soil and higher concentrations of metals were found in topsoils. Therefore, according to Simpson & Batley [69], soil type and texture has the potential to influence the accumulation capacity of metals within a site, thus it can be concluded that clay has the higher potential to accumulate metals than other soil types. It can also be noted that according to Wang et al. [54] and Chen et al. [70], not only the soil type can influence metal accumulation but also the flood events and wind events that occur from time to time which can carry contaminants from one area to the other causing uneven distribution of metals across sites and depths.

It should be noted that the Igeo results suggest that sediments within the Makuleke Wetlands were generally unpolluted. However, PLI showed a variation in pollution load across sites and depths with Mambvumbvanyi pan resembling a higher pollution load. This may be associated with reliance of Mambvumbvanyi pan on allochthonous sources such as leaf litter and detritus from the terrestrial environment [71]. Furthermore, Mambvumbvanyi pan possesses heterotrophic characteristics, and its high PLI may also be associated with a high abundance of riparian vegetation surrounding the pan, such as fever and mopane trees, as well as other terrestrial plants, supplying allochthonous inputs to these pans through leaf litter and debris [71]. Therefore, we suggest that the potential risks posed by K, Ca, Mg, Na, Mn and Fe in the sediments from Mambvumbvanyi should raise more attention with possible loadings from Luvuvhu River, especially to benthic organisms. Elements such as Zn and B were evaluated and were found to be at very low concentration (Igeo) and these were referred to as unpolluted levels and not likely to cause adverse biological effects (far below or slightly beyond EF values). The principal components analysis has also proved to be an effective tool for a better understanding of the sources of heavy metals [72,73].

According to Francouría et al. [74], there are two main explanations for why these metals are connected to PCAs: anthropogenic inputs and geological materials. Zn, Mn, B and Fe, are well–known to be geogenic, and are strongly correlated with K, Ca, Mg, Na and Cu, suggesting that K, Mg, Ca and B may have a common source as attested by Pearson correlation matrix. A positive correlation between heavy metals in these sediments suggests that metals possess common sources of pollution, mutual dependence and identical behaviour during transport and accumulation [53]. Three different sources were potentials identified for the metals based on the PCA analysis, with elements such K and Ca potentially coming from agriculture, Na, B and S elements from urban developments and the remaining metals (i.e. Mg, Cu, Zn, Mn, Fe) being potentially from natural sources.

5. Conclusion

This present study assessed the concentrations, distributions and risks of K, Ca, Mg, Na, Cu, Zn, Mn, B, Fe and S in sediments of freshwater ephemeral wetlands (floodplain pans) ecosystems. The mean concentrations of both metals, semi metal and non–metals were found to be generally higher in all three pans as alluded by the geo–accumulation index and enrichment factor results. These indicate that the pans are still in their natural state except for minimal contamination from natural processes such as animal deposits, dead plant deposits and weathering of rocks leading to marked shifts of metal dynamics in the pans. In general, metals such as K, Ca, and Mg in the floodplain pans should be closely monitored to prevent potential ecotoxicity to the wildlife in Kruger National Park. These results provide foundational information for the Makuleke Wetlands in relation to metal contamination; however, further studies are required to comprehensively understand metal behaviour within the floodplain pans. Moreover, studies to investigate the sources of metal contaminants that accumulate in the pans will be critical for wetlands management within the Kruger National Park. Furthermore, there is a need to determine the spatio–temporal analysis of metal accumulation within the pans. These findings offer baseline data for the Makuleke Wetlands in terms of sediment metal pollution, but additional research is needed to properly comprehend metal dynamics within these systems that are not anthropogenically contaminated to sustain conservation status of these pans.

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Data availability statement

All the data collected during this research is presented in the manuscript.

Credit authorship contribution statement

LFM: Conceptualisation, Investigation, Data curation, Formal analysis, Writing – original draft, review & editing. **LM:** Investigation, Data curation, Supervision, Writing – review & editing. **RJW**: Supervision, Conceptualisation, Resources, Writing – original draft, review & editing. **FD:** Conceptualisation, Investigation, Resources, Data curation, Writing – original draft, review & editing. **CK:** Investigation, Writing – review & editing. **ER:** Permits, Data curation, Investigation, Writing – review & editing. **TD**: Conceptualisation, Investigation, Resources, Data curation, Formal analysis, Supervision, Writing – original draft, review & editing.

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