Attenuation of pollution arising from acid mine drainage by a natural wetland on the Witwatersrand

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Wetlands are well known to be efficient at sequestering pollutants from contaminated water. We investigated metal accumulation in the peats of the Klip River, a natural wetland that has received contaminated water from gold mining operations in Johannesburg for over 130 years. Previous work conducted in the downstream portion identified the wetland as an important system for sequestering metals. We focused on the upstream section of the wetland, more proximal to the source of acid mine drainage, to provide a better understanding of the pollutant sources and the role of the wetland in pollutant attenuation. Geochemical and mineralogical analyses of peat cores revealed considerable metal enrichments in the peat ash, particularly in Co, Ni, Zn, Pb, Cu and U. Metal concentrations are typically between 4 to 8 times higher than those previously reported for the downstream, more distal portion of the wetland. The distribution of metal accumulation within the peat profiles suggests that contamination arises from a combination of sources and processes. Elevated concentrations in the shallow peat are attributed to the input of contaminated surface water via tributaries that drain the Central Rand Goldfield, whereas enrichments in the deeper peat suggest significant sub-surface inflow of contaminated water through the underlying dolomitic rocks. Metal immobilisation occurs through a combination of mechanisms, which include the precipitation of gypsum, metal sulfides, Fe-Mn oxyhydroxides and phosphates. Our study highlights the environmental and economic importance of natural wetland systems which have the ability to accumulate large quantities of metals and thus remediate polluted waters.

Significance:

- Considerable levels of metal accumulation are observed within the Klip River wetland peats.
- The wetland is effective in remediating highly polluted water emanating from the Witwatersrand Basin.
- The Klip River system is important for the region's future water supply.

Introduction

South Africa is renowned for the diversity and richness of its mineral wealth, the exploitation of which has sustained the economic growth of the country since the mid-1800s. However, this minerals-driven growth has been associated with a number of undesirable environmental impacts. For example, the severe health and consequent social problems arising from mine workers' exposure to asbestos-bearing dust have been well documented.[1] Similar problems were experienced in the gold mining industry as a result of exposure to silica-bearing dust, particularly in the early years of mining.[2] But perhaps the most severe and insidious adverse legacy of the mining industry is acid mine drainage (AMD), especially that arising from coal and gold mining.[3] This problem has resulted in a decline in water quality in the economic heartland of the country and could result in water shortages in the future.

AMD arises from the oxidation of pyrite which is a common gangue mineral in a variety of ore types, and is fairly well understood. AMD arising from gold and base metal mining is invariably enriched in a wide variety of metals, many of which are highly toxic. The gold ores of the Witwatersrand Basin (Figure 1, inset) are no exception and contain elevated concentrations of lead (Pb), copper (Cu), nickel (Ni), cobalt (Co), zinc (Zn) and uranium (U), amongst others. The low pH associated with AMD enhances the mobilisation of these metals, resulting in their dispersion into the ground and surface water. The major source of AMD on Witwatersrand gold mines has been seepage from tailings storage facilities (TSFs)[4-8], although discharge of water from flooded, abandoned gold mines as well as discharge of partially treated water pumped from producing mines has also contributed to the problem in recent years[9-11]. Adverse effects on water quality and the health of natural ecosystems is of growing concern[3,12], with AMD recognised as one of the most significant environmental challenges facing conservation managers and the mining industry in South Africa[13].

Numerous methods for treating AMD have been developed. The most desirable of these are passive treatment methods, two of which – wetlands and carbonate rock drains – are fairly widely used to remediate AMD. Carbonate rock drains serve to raise the pH and thus limit metal solubility in water affected by AMD. Metals continue to be transported in these drains but as insoluble, suspended particulates. However, carbonate rock drains have little influence on the sulfate content of the water. In contrast, wetlands reduce the impact of AMD by creating reducing conditions which cause reduction of sulfate ions to sulfide. The presence of sulfide results in the precipitation of many metals as sulfide minerals. The sulfate content in water is also reduced, partly because of metal sulfide precipitation but also as a result of the release of sulfur in the form of hydrogen sulfide gas. Removal may also occur through the formation of insoluble metal oxides in aerobic zones of the wetland, metal complexation with organic matter, sorption onto particles, and incorporation into the plant biomass.[14] As such, wetlands are particularly efficient in sequestering metals from inflowing waters and highly effective in remediating polluted water. The effectiveness of wetlands in removing metal contaminants from water has resulted in the use of constructed wetlands as low-cost biogeochemical systems for the treatment of AMD.[15,16]

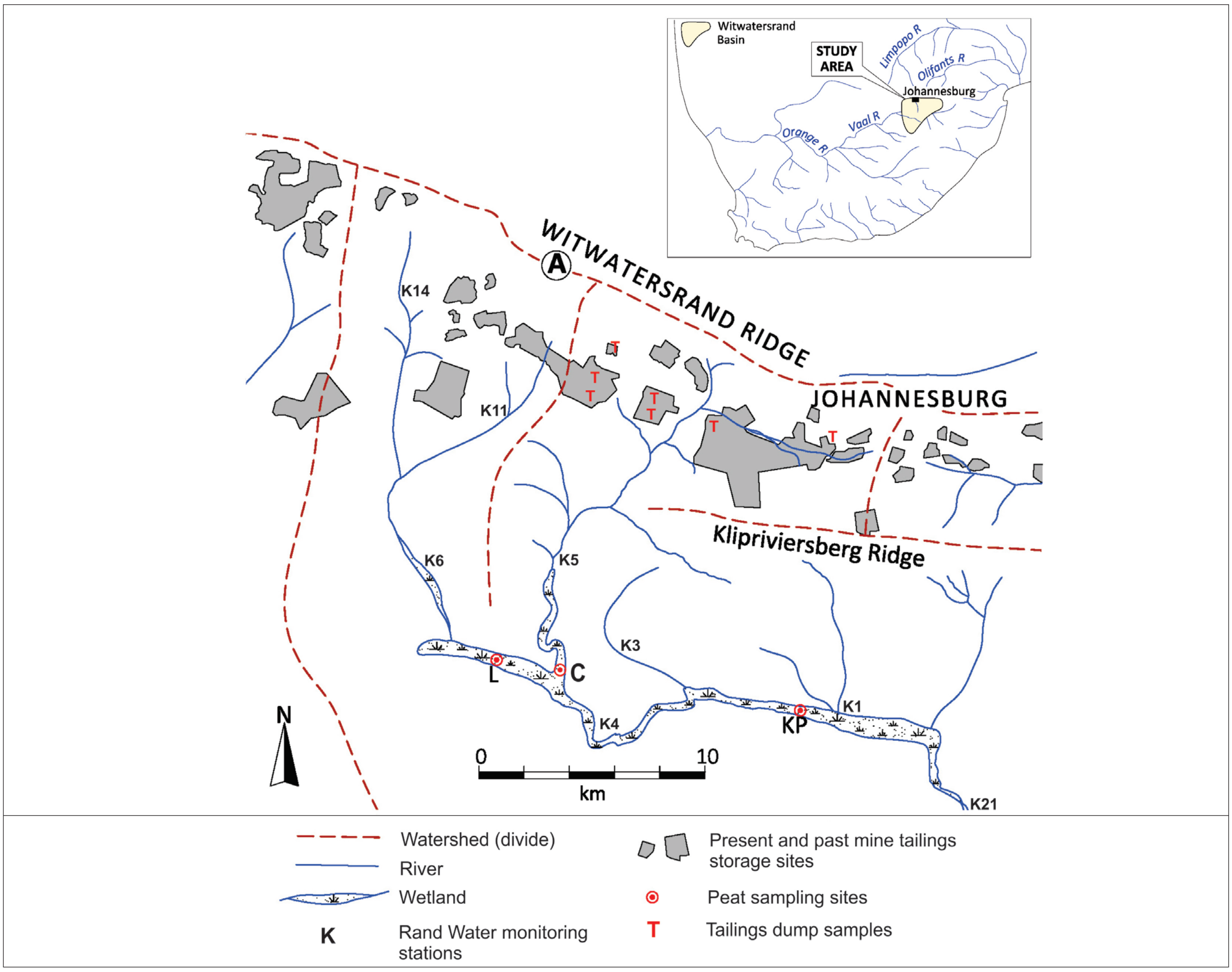


Figure 1: Map of the study area and location of the sampling sites in relation to mining activities in the Johannesburg area.

Groundwater and run-off from the Central Rand Goldfield discharges into extensive wetlands that have developed along the Klip River, the principal drainage of the southern portion of the Johannesburg conurbation. A previous study conducted in the distal, downstream portion of the wetland (Figure 1, Site KP) revealed that peat in the wetland contained elevated concentrations of certain metals as a result of sequestration from polluted water.[17] Contamination was typically confined to the uppermost section (top ~1 m) of the peat, where elevated levels of Co (460 ppm), Ni (1500 ppm), Cu (170 ppm), Pb (60 ppm) and Zn (2300 ppm) were observed in ashed material. These levels represent 15–30 times the natural background and likely arose from a combination of sources including mining, industrial effluent and sewage discharge. The previous study highlighted the importance of this wetland system in sequestering contaminants that would otherwise enter the Vaal River system and cause widespread pollution. Given the valuable function this wetland performs, a more detailed understanding of the pollutant sources, processes leading to pollutant attenuation, and the potential downstream impacts through remobilisation of toxicants is needed. The present study was undertaken in the upstream section of the wetland, more proximal to the source of acid mine drainage, in order to investigate metal sequestration in more detail and to define the sources of metals more clearly.

Study area

The study area is located southwest of Johannesburg in the Klip River valley (Figure 1).

Geology

The gold mines in the Johannesburg area (Central Rand Goldfield) commenced operations in 1886. Over the life of the goldfield, some 7700 tonnes of gold (~246 million oz.) have been extracted from the treatment of approximately 940 million tonnes of rock. The gold was contained in quartz pebble conglomerates, which are hosted in a sequence of siliceous quartzites of the Witwatersrand Supergroup. The deposits are now largely worked out and most mining has ceased. Reworking of TSFs to extract remaining gold as well as small-scale surface and underground operations continue.

The bedrock geology of the region is summarised in Figure 2a. The gold-bearing strata of the Precambrian Witwatersrand Supergroup form an east-west striking belt across the centre of the region and lie unconformably on granitoid basement rocks. Strata dip to the south at between 15° and 30°. Gold-bearing conglomerates are confined to the upper portion of the stratigraphy, which consists largely of quartzites and conglomerates. The bulk of the gold was produced from the Main Reef group of conglomerates. The TSFs are located in close proximity to the outcrop of these conglomerates. The Witwatersrand strata are conformably overlain by basaltic volcanic rocks of the Ventersdorp Supergroup. Both the Witwatersrand and Ventersdorp rocks are in turn unconformably overlain by dolomitic rocks of the Transvaal Supergroup which dip at about 10° to the south. It is these rocks that underlie and host the Klip River wetlands.

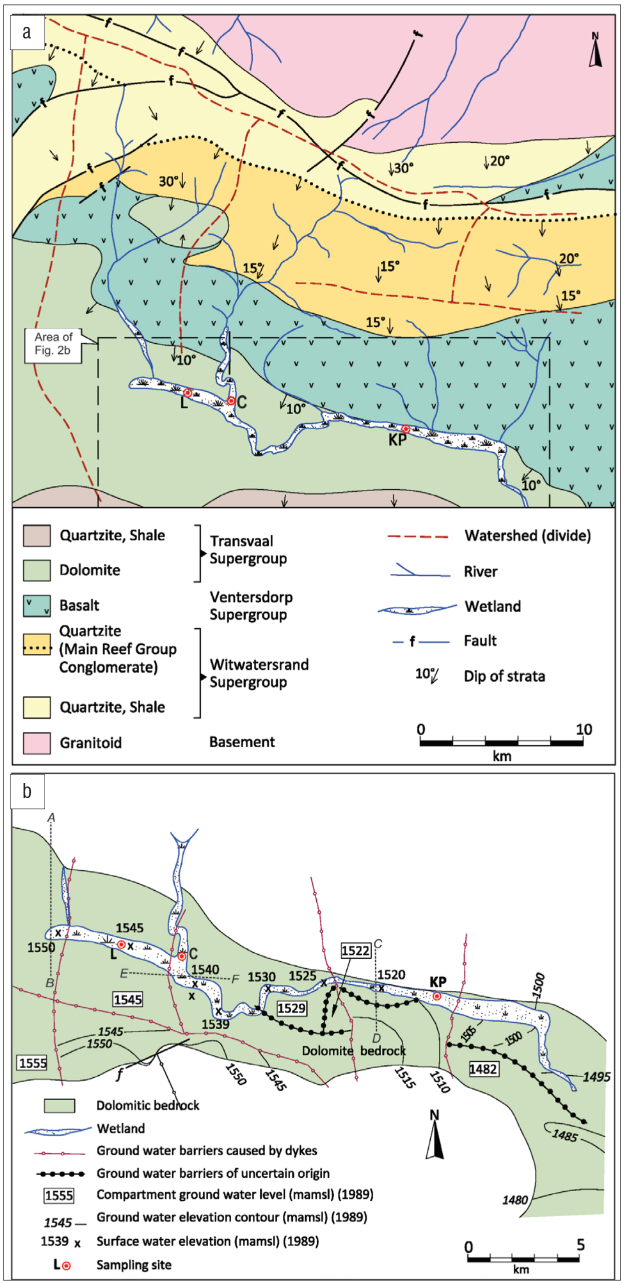


Figure 2: Maps showing (a) the simplified geology in the study area, (b) groundwater elevation and major barriers to groundwater movement in the upper Klip River Basin.[19]

Geomorphology

The primary watershed in the area (A in Figure 1) forms part of the continental divide separating the Vaal and Limpopo drainage basins. The majority of TSFs in the area lie south of this watershed in the Vaal River catchment. Minor watersheds compartmentalise run-off from the dump region (Figure 1), with the run-off arising to the west of Johannesburg entering the upper Klip River reach where study Sites L and C are situated. Tributaries discharging into the wetland further downstream, where the previously studied Kibler Park site is situated, are isolated from the dump area by the watershed associated with the low hills of the Klipriversberg Ridge.

Geohydrology

The dolomite of the Transvaal Supergroup is karstic but is typically divided up into numerous separate compartments by igneous intrusions (dykes), which restrict sub-surface flow from one compartment to the next.[18] Within each compartment, much of the surface water infiltrates into the sub-surface to fill solution cavities in the dolomite. Water typically emerges at springs located on dykes that form the downstream boundaries of compartments and cascades over these into the next lower compartment. These spring sites are host to wetlands. Sinkholes and dolines along water courses across the dolomitic areas similarly host extensive, interlinked wetland systems.

A detailed geohydrological study of the dolomitic rocks in the region of the study revealed that the dolomitic aquifer is divided into several compartments by dykes with slightly different groundwater levels in each compartment[19] (Figure 2b). According to early reports[20], springs abounded along this section of the river flanked by extensive wetlands with dense stands of *Phragmites* reeds growing atop several metres of peat. The age of the deeper peat in the wetland is in excess of 3500 years.[17] Kafri and Foster[19] found that the flow of water from one compartment to the next was largely by surface discharge across bounding barriers and there was evidently no sub-surface connection. The most important dykes that compartmentalise the dolomite in the region belong to the north-northeast-striking Pilanesberg Dyke Swarm[18], which divide the dolomite aquifer into north-south trending compartments. Compartments in the upper catchment are likely subject to ingress of polluted water from the TSFs and surface streams (Figure 3a), whereas groundwater further downstream is uncontaminated (Figure 3b) as this compartment contains no TSFs. The only source of pollution to the downstream portion of the wetland system is via overspill from the upstream compartments and run-off of polluted surface water (Figure 3c).

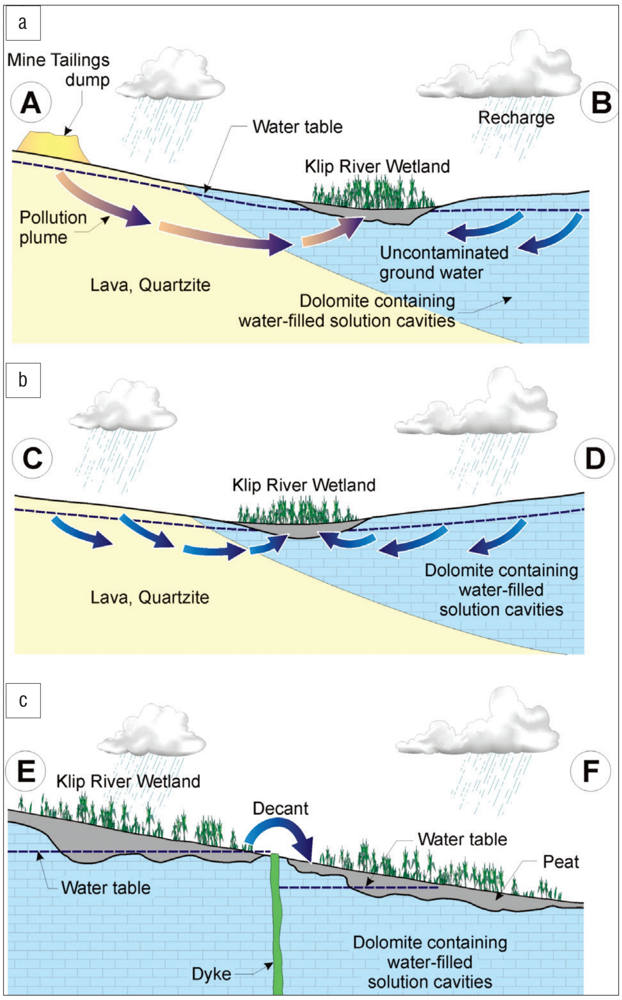


Figure 3: Schematic diagrams showing (a) the ingress of polluted groundwater into the karst-hosted Klip River wetland, (b) the recharge of groundwater in the karst-hosted Klip River wetland and (c) the flow of water from one dolomitic compartment to another across a bounding dyke. The down-channel gradient has been greatly exaggerated in this sketch. See Figure 2b for approximate profile locations.

The wetlands are sustained predominantly by groundwater, which discharges into the peat from the underlying dolomite (Figure 2a,b). In summer, this discharge is augmented by surface run-off from rainfall, with the Klip River and Klipspruit being the dominant fluvial inputs. The Klip River also receives run-off from a number of informal settlements that flank the banks of the Klip River and Klipspruit, as well as ~500 ML/day in discharge from three sewerage treatment plants, much of which enters the river a short distance downstream of Site C (Figure 1).

Little is known about the hydrochemistry of the Klip River watershed. The Rand Water Board has a number of monitoring points within the Klip River catchment (Figure 1), although data from these sites are sparse. Surface water analyses indicate that major ion concentrations are typically low, but highly variable, with pH varying between 6.0 and 8.1 (Table 1). The low metal concentrations at monitoring sites indicate that surface run-off undergoes rapid dilution upon entering the watercourse. In contrast, Naicker et al.[6] and Tutu et al.[8] found groundwater within the Central Rand mining district to be acidified (pH <4) and contaminated by high sulfate, Fe, Zn, Co and Ni concentrations. The percolation of rain water through mine dumps, creating polluted groundwater plumes, was considered to be the main contribution to contamination.

Table 1: Surface water chemistry data for the Klip River catchment for the period 2010 to 2015 (n=52)

	pH	SO_4 (mg/L)	Mg (mg/L)	Fe (mg/L)	Mn (mg/L)
			Tributaries		
K14	6.6 ± 0.4	32 ± 22	3.9 ± 1.5	0.47 ± 1.0	0.26 ± 0.4
K11	6.5 ± 0.7	97 ± 40	9.6 ± 1.6	0.11 ± 0.1	0.33 ± 0.3
K5	7.5 ± 0.3	164 ± 72	15.1 ± 2.5	0.31 ± 0.4	1.9 ± 0.8
K3	7.7 ± 0.2	57 ± 8	9.5 ± 1.6	0.06 ± 0.06	0.07 ± 0.06
			Klip River		
K6	7.8 ± 0.3	110 ± 20	18.6 ± 2.3	0.08 ± 0.09	0.74 ± 0.66
K4	7.8 ± 0.3	104 ± 30	13.3 ± 1.4	0.08 ± 0.1	0.83 ± 0.6
K1	7.7 ± 0.2	96 ± 22	13.4 ± 1.7	0.15 ± 0.23	1.2 ± 2.5
K21	7.9 ± 0.2	97 ± 17	13.2 ± 1.3	0.10 ± 0.08	0.36 ± 0.18

Source: Rand Water Board

Gold extraction and the formation of pollution sources

The cyanidation process used to process the Witwatersrand ore selectively removed gold and silver. Pyrite and other sulfide minerals together with the gangue minerals (primarily quartz with minor phyllosilicate minerals) reported to the TSFs. During cyanidation, the pH of the pulverised rock was kept above 9 to prevent the formation of hydrogen cyanide. However, the tailings material has a very low buffering capacity because of its high quartz content, and after disposal, oxidation of pyrite in the TSFs leads to the rapid acidification of the material. The elevated water table within the dumps[7] caused by infiltration of rain water has led to the formation of acid plumes which currently discharge from the dumps. The contaminated groundwater locally discharges into streams draining the area around the dumps.[6,8]

Methods

Sampling

Two sediment cores (L1 and L2), ~100 m apart, were collected from the upstream, western section of the Klip River wetland near the town of Lenasia (Site L, Figure 1) and one from further downstream (Site C, Figure 1) . The wetland here is approximately 500 m wide and consists of a reed-covered swamp dominated by *Phragmites australis.* These sites were selected based on examination of historical aerial photography and maps, which indicated that this region of the wetland had remained relatively undisturbed for the last ~80 years[21,22] and thus probably best resembles the hydrological functioning of the system prior to the development of the Witwatersrand mining and industrial complex. Samples were collected using a Russian peat corer, coring until the underlying clay layer was intercepted. Sub-samples for analysis were taken at 20-cm intervals. The pH of the peat was measured by inserting a pH electrode directly into collected samples. Material from several mine TSFs in the upper catchment was also sampled (Figure 1).

Chemical analyses

Sediment samples were dried at 110 °C and milled into homogeneous powders. Organic content was measured by loss on ignition at 450 °C. Ash residues were analysed for major elements by X-ray fluorescence (XRF) using fused glass beads and a PANalytical PW1400. Calibration was performed using a range of international (NIST) and national (SARM) rock standards. Trace metal and rare earth element (REE) analyses were carried out using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The analyses were performed using an Agilent 7700 ICP-MS connected to a Resolution M-50-LR Excimer (Resonetics) laser ablation system (193 nm). Helium was used as a carrier gas with a flow of 0.3 L/min. Analyses were calibrated using a certified BCR glass reference material as an external standard. SiO_2 concentrations (from XRF analyses) were used for internal standardisation. Accuracy, as the relative difference from reference values, was typically better than 10%, and most elements plotted in the range ±5%. Total carbon and sulfur were measured on bulk peat samples using a Euro EA3000 elemental analyser. Material collected from TSFs was analysed for major and minor elements using XRF.

Sequential extractions

To examine the partitioning of metals among various phases, sequential extractions on bulk sediment samples from Core L1 were performed following the modified BCR procedure.[23] Samples were sequentially extracted in four stages to identify metal associated with different fractions, namely acid soluble (exchangeable and carbonates), reducible (Fe-manganese (Mn) oxyhydroxides), oxidisable (organic matter/sulfides) and residual (silicates). The extracts from each step were analysed for selected major and trace elements using an Agilent 7700 ICP-MS in gas and no gas modes where appropriate.

Mineralogy

Mineralogical investigations were performed using X-ray diffraction on un-orientated powder samples using a Bruker D2 Phaser with monochromated CoKα radiation (10–90° 2θ). Scanning electron microscope energy dispersive X-ray (SEM-EDX) analyses were performed on selected minerals within the peat using a FEI Nova 600 microscope. Samples were dispersed in water, mounted onto aluminium (Al) stubs and coated with 10 μm gold-palladium. Peat samples were selected based on bulk geochemical analyses which showed high metal concentrations.

Results and discussion

Core profile characteristics and major chemistry

The proportion of organic matter in the samples collected from the Klip River wetland is highly variable. Cores from Site L reveal ~3 m of peat (defined here as organic-rich sediment) underlain by cohesive grey clayey sand. The peat is very fibrous and relatively low in inorganic components, with carbon contents varying between 24% and 48% (Figure 4). Total sulfur concentrations were variable, ranging between 2% and 5.5%, while pH displayed little variation with depth, averaging 6.9. Peat accumulation at Site C is less well developed and generally confined to the upper 40 cm of the profile (Figure 4). The peat is characterised by elevated sulfur concentrations (up to 5%), with pH again showing little variation with depth.

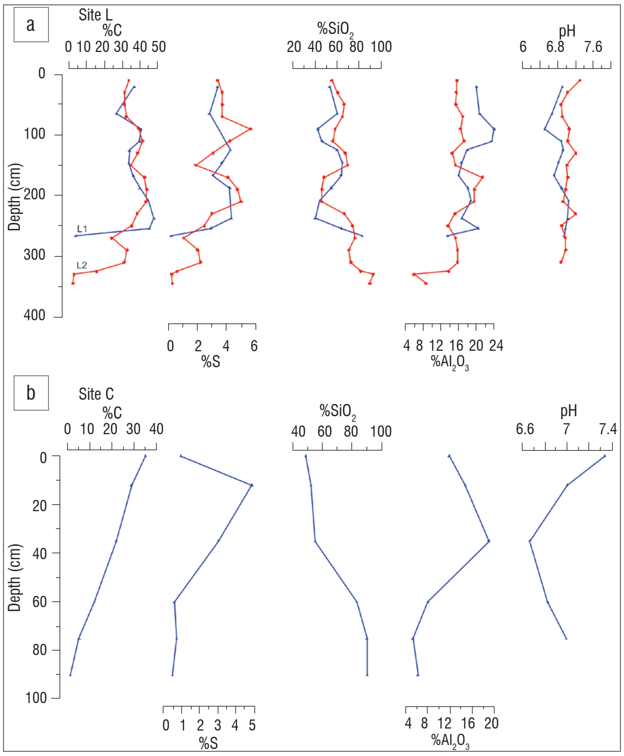


Figure 4: Variation in pH and bulk chemical composition of peat with depth at (a) Site L and (b) Site C.

The inorganic fraction of the peat is largely dominated by SiO_2 and Al_2O_3, which together comprise between 55% and 80% of the ash fraction (Figure 4). The inorganic component is derived predominantly from clastic material in run-off and airborne dust.[17] Plots of Al_2O_3-SiO_2, Fe_2O_3-Al_2O_3 and CaO-Al_2O_3 abundances in the clastic material underlying the peat at Sites L, C and KP and in mine tailings show linear trends reflecting varying proportions of quartz and an iron (Fe)-bearing aluminous clay mineral end member (Figure 5). The peat samples all show departures from the mixing lines as a result of the presence of Fe- and calcium (Ca)-bearing minerals, which are not part of the clastic load. Departure from the mixing line is most clearly observed in samples from Site L, indicating extensive in-situ precipitation and sequestration of chemical components within the peat.

Metal profiles

In order to compensate for the varying proportion of inorganic material contained within the peat and allow for comparison between sediment profiles, metal concentrations were normalised by expressing data relative to $SiO_2+Al_2O_3$, which are primarily of clastic origin. The clay underlying the wetland is characterised by very low metal ratios (Table 2) and provides a baseline level for pre-mining, uncontaminated sediment. In contrast, normalised metal values within the peat from Sites L and C reveal strikingly different downcore variations (Figure 6a,b). At sampling Site L, metals show highly elevated ratios, although enrichments occur in different sections of the peat profiles. Normalised concentration profiles for CaO, Fe_2O_3, Co and Ni show similar downcore trends, with highest enrichment found near the base of the peat sequence (200–250 cm) where Co and Ni in particular are enriched up to 700 and 200 times, respectively, relative to the underlying clay. In contrast, Pb and Cu show pronounced increases in concentration, of about four-fold, over the uppermost metre of the peat profile. Zn values are variable through the profile, although higher enrichments are generally observed in the deeper section of the profiles, particularly between 70 cm and 200 cm, where samples are enriched up to 900 times relative to the underlying clay.

Normalised metal profiles at Site C show similar trends for all metals investigated, revealing increasing enrichment toward the top of the profile (Figure 6b). Co, Ni and Zn are enriched 30–50 times in the surface peat relative to the underlying material. Surface enrichment in metals was also observed at the previously studied downstream Site KP. Here metals within the surface peat (upper 1 m) were enriched 2–10 times relative to the underlying peat material (Figure 6c).

Spatial differences in chemical accumulation

Average metal ratios at Site L are significantly higher when compared to those from Sites C and KP (Table 2). Site L is located ~15 km upstream of Site KP and is in closer proximity to potential surface and groundwater pollution sources (Figures 1 and 2). Higher pollution levels at Site L thus reflect proximity to source and the efficacy of the wetland system in removing metals from solution. Between sampling Sites L and KP, Co, Ni, Cu and Zn ratios decrease by between 75% and 80%, while average Zn and U ratios decrease by ~90% and 96%, respectively.

At Sites KP and C, contamination is confined to the near surface peats, whereas peat from deeper within the profiles (>150 cm) is unpolluted (Figure 6). This result is in contrast to both surface and sub-surface metal enrichments observed at Site L. The strong enrichment in metals in the deepest peat here strongly suggests inflow of contaminated groundwater into the wetland from below. The formation of gypsum crusts observed along the margins of the wetland near Site L indicates that groundwater seeping into the wetland is highly concentrated in Ca and SO_4. Similar groundwater seepage zones associated with surface gypsum precipitate formation were observed along reaches of the Natalspruit drainage network.[6]

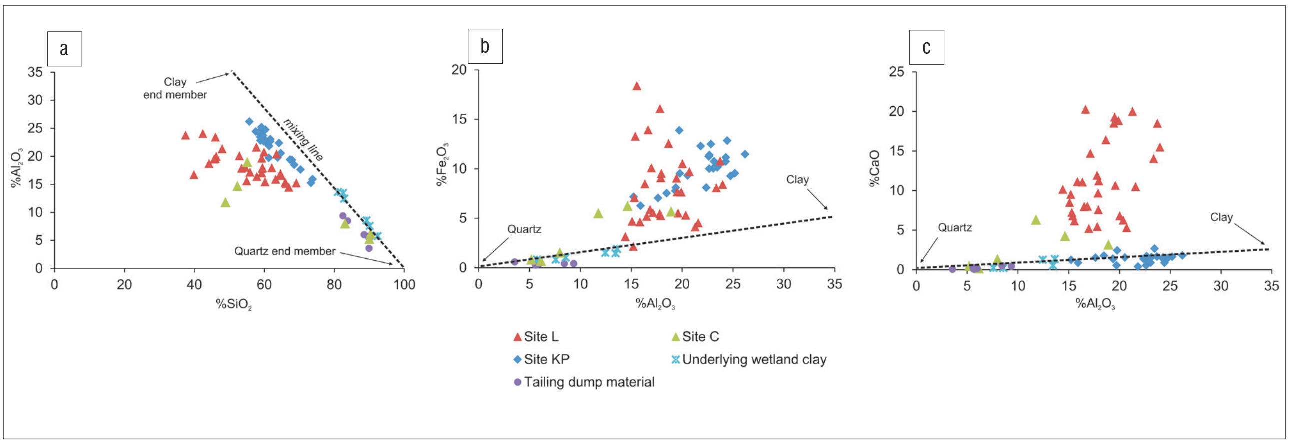


Figure 5: Relationship between (a) SiO_2 and Al_2O_3, (b) Al_2O_3 and Fe_2O_3 and (c) Al_2O_3 and CaO in the underlying wetland clay, tailings storage facilities material, and peat ash at sampling Sites L, C and KP.

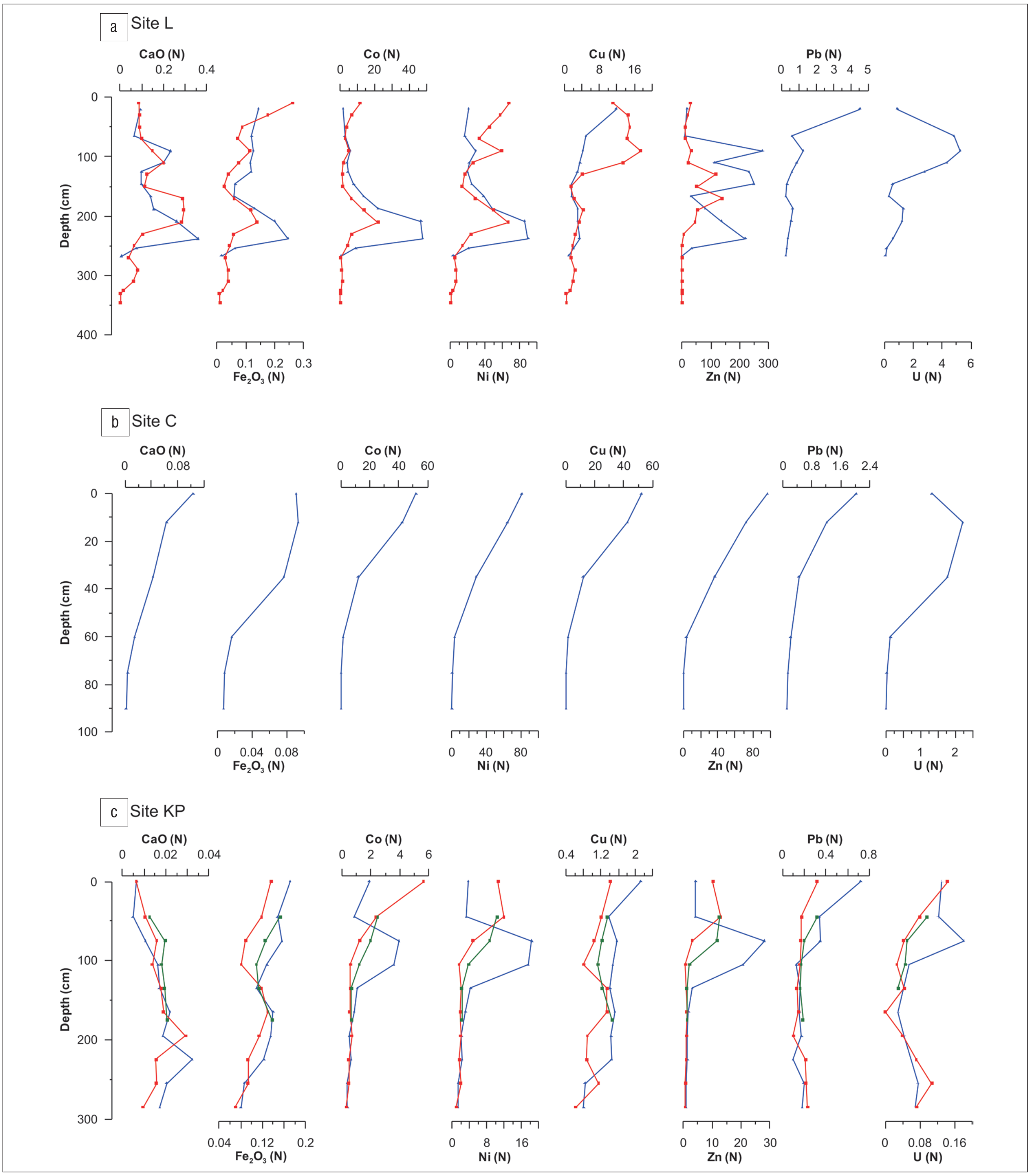


Figure 6: Normalised metal concentration profiles of peat samples from (a) Site L, (b) Site C and (c) Site KB.

Table 2: Average normalised metal ratios within tailings dump material and the inorganic fraction of peat deposits at Sites L, C (this study) and KP.[17] Normalised metal ratios in the clastic layer underlying the peat are given in parentheses.

	Fe_2O_3/ (SiO_2+Al_2O_3)	CaO / (SiO_2+Al_2O_3)	Co / (SiO_2+Al_2O_3)	Ni / (SiO_2+Al_2O_3)	Cu / (SiO_2+Al_2O_3)	Zn / (SiO_2+Al_2O_3)	Pb / (SiO_2+Al_2O_3)	U / (SiO_2+Al_2O_3)
Site L	0.11 (0.01)	0.16 (0.002)	10.8 (0.06)	38.9 (0.40)	6.3 (0.33)	84.7 (0.20)	0.9 (0.24)	2.0 (0.06)
Site C	0.05 (0.01)	0.04 (0.003)	18.0 (0.12)	29.6 (0.57)	2.5 (0.20)	35.0 (0.44)	0.7 (0.13)	0.9 (0.02)
Site KP	0.12 (0.07)	0.02 (0.01)	1.45 (0.30)	4.9 (0.94)	1.2 (0.62)	5.1 (0.63)	0.2 (0.23)	0.1 (0.07)
Tailings dump material	0.04	0.002	0.34	0.78	0.47	0.51	0.35	0.25

Table 3: Water chemistry from sampling Site L and typical chemical composition of mine void water (50th percentile) from the Central Witwatersrand Basin[24]

	pH	Electrical conductivity (mS/m)	Mg (mg/L)	Al (mg/L)	Ca (mg/L)	Fe (mg/L)	Mn (mg/L)	SO_4 (mg/L)	Co (ug/L)	Ni (ug/L)	Cu (ug/L)	Zn (ug/L)	Pb (ug/L)	U (ug/L)
Central Basin mine void water (*n*=12)	3.0	397	172	122	279	40	47	2831	4684	10 589	328	9122	28	606
Surface water from Site L (*n*=1)	6.9	62	23	0.04	44	0.01	0.2	–	3.8	5.2	2.9	7.7	0.06	–

Metal distributions within the peat at Site L appear to reflect different sources of water to the wetland, with some trace elements showing increasing abundance in the uppermost metre (e.g. Cu and Pb), whereas Co, Ni and Zn are highly enriched in the deeper peat. AMD-contaminated water from the Central Witwatersrand Basin is highly acidic (pH 3) and remarkably enriched in Co, Ni and Zn (Table 3[24]). The Central Rand is dominated by the numerous mine TSFs which form large footprint plumes within the Klip River catchment.[25] Groundwater entering the wetland thus likely carries high metal loads, which precipitate within the peat under higher pH conditions.

Fe, S and Ca also show some relative enrichment in the deeper peat at Site L, with total Ca concentrations 4–10 times higher when compared to Sites C and KP. The peat at Site L is likewise enriched in REEs. Post-Archaean Australian Shale (PAAS)-normalised REE patterns (Figure 7) indicate that MREEs in particular are enriched relative to both the light (LREEs) and heavy REEs (HREEs). The observed pattern is typical of AMD-affected water and sediments and likely indicates that REEs are fractionated during pyrite oxidation, as has been observed in other studies.[26,27]

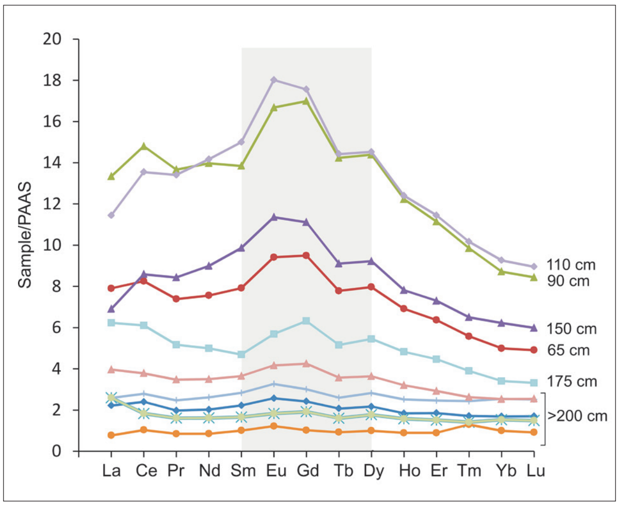


Figure 7: Post-Archaean Australian Shale (PAAS)-normalised rare earth element (REE) patterns of peat samples from Site L. Note that samples from 65 cm to 175 cm show significant medium REE enrichment.

It is clear that the upstream section of the wetland where Site L is located is significantly more impacted by AMD than at Sites C and KP further downstream. Although water discharging from mines on the Central Rand is highly acidic and carries high metal loads, this water is diluted and neutralised as it flows toward the wetland. The presence of dolomite facilitates the infiltration of water and further raises the pH of the water as a result of the presence of carbonate, although the redox potential may still remain low. Flow into the head of the wetland near Site L is therefore likely largely from below, except during heavy rainstorm events. The absence of a pollution signature in the deeper part of the peat at Sites C and KP suggests that groundwater entering the wetland is unpolluted, and that pollutant accumulation in these areas is largely caused by surface water flow and possible atmospheric fallout. Sites C and KP are located in dolomitic compartments in which the groundwater is isolated from pollution plumes from TSFs by dykes (Figure 2b).

Mechanisms of sequestration

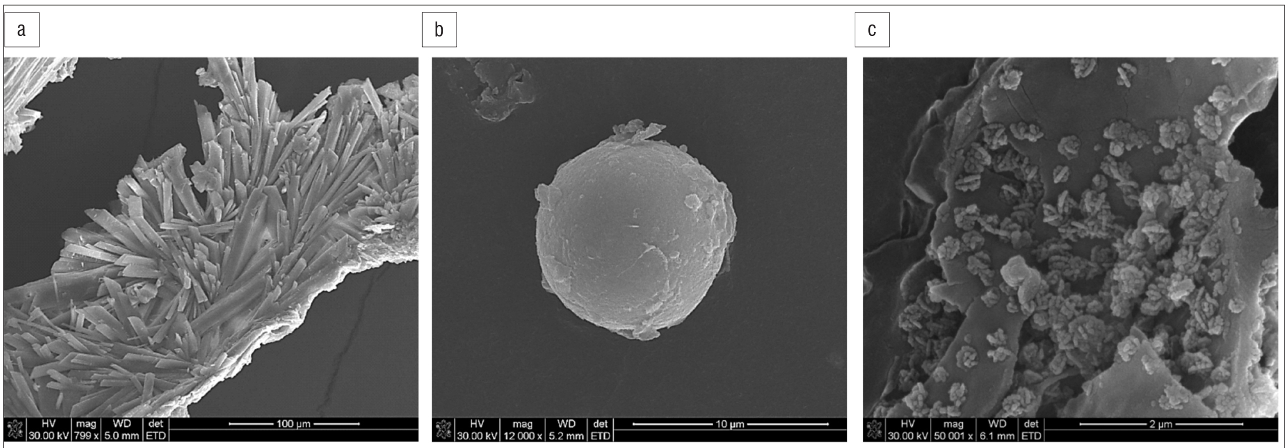
The majority of metal sequestration in the Klip River appears to occur in the upper section of the wetland near sampling Site L. Investigation of the mechanisms involved in the sequestration of metals in the peat therefore focused on core samples from this area.

The BCR sequential extraction data reveal similarities in the partitioning of Pb, Ni and Zn, with Fe-Mn oxyhydroxides the predominant phase for sequestration (Table 4). Metal associated with Fe-Mn oxyhydroxides are expected given the pH of the peat (pH 6.5–7) which favours the precipitation of Fe and Mn minerals and has also been noted in the AMD-affected Blesbokspruit wetland.[28] The oxidisable fraction becomes an increasingly important phase for Co (43%), Ni (37%) and Cu (75%) below 150 cm, indicating that the sequestration of these metals in the deeper peat is likely associated with sulfides and/or organic matter. Highly chalcophile metals such as Ni and Co are thus expected to precipitate with FeS_2 in the deeper peat where sulfur is present in the reduced S^{2-} form. Scanning electron microscopy investigations of the deeper peat reveal the presence of pyrite spheres that are enriched in Ni and Co (Figure 8), as well as Zn sulfide clusters. Cu is predominantly found within the oxidisable fraction, likely associated with sulfides. The partitioning data suggest that changes to pH or redox could result in the remobilisation of metals, particularly Pb, Ni, Zn, Co and Cu which are held predominantly in potentially available forms.

Peat samples showed evidence of extensive gypsum precipitation (Figure 8). Correlation between Ca and total S (R^2=0.62) suggests that this is likely the dominant phase for these two elements. Ca is precipitated as gypsum likely in response to evapotranspiration which leads to saturation in Ca minerals. The formation of gypsum crusts observed along the margins of the wetland near Site L indicates that groundwater seeping into the wetland is highly concentrated in Ca and SO_4. Kafri and Foster[19] also reported elevated sulfate in the groundwater. Gypsum precipitates are likely important adsorption sites for trace metals. Analysis of gypsum crusts from the Natalspruit wetland revealed high concentrations (2000–5000 ppm) of several metals, including Co, Ni, and Zn.[6] The BCR partitioning data indicate that gypsum adsorption could account for 12–18% (acid soluble fraction) of the total Co, Ni and Zn sequestered within the peat at Site L.

Implications and conclusions

Mining operations over the last ~130 years on the Witwatersrand have released high levels of acid and metals into surface and groundwater, with abandoned mines continuing to produce acid and contaminated water. The considerable enrichment in metals observed within the Klip River peats reflects exposure to contaminated water since the establishment of mining operations on the Witwatersrand and demonstrates the value of this wetland system in sequestering metals from polluted water. The wetland system therefore performs a vital ecosystem service in the environment by trapping metals that would otherwise enter the Vaal River system downstream.



	Weight %	Atomic %
O	56.8	74.3
Mg	1.1	0.9
Si	0.5	0.4
S	20.9	13.7
Ca	20.7	10.8

	Weight %	Atomic %
O	8.2	18.6
Si	0.5	0.7
S	47.0	53.5
Fe	34.7	22.7
Co	2.1	1.3
Ni	2.6	1.6

	Weight %	Atomic %
Al	3.5	6.1
S	28.1	42.2
Ca	3.3	4.1
Zn	64.9	47.6

Figure 8: Scanning electron microscopy images and elemental results indicating various forms in which pollutants are sequestered within the peat: (a) precipitation of gypsum crystals (at 100 cm), (b) precipitation of Co- and Ni-enriched pyrite spheres (at 250 cm) and (c) formation of Zn sulfide clusters (at 250 cm).

Table 4: Partitioning of metals in Core L1, defined using the BCR extraction procedure. Data are reported as averages (*n*=12) with the predominant fraction shown in bold.

%	Acid soluble	Reducible (Fe-Mn-oxyhydroxides)	Oxidisable (organic matter /sulfides)	Residual	Potentially available[†]
Al	0.9	26	8	**65**	35
Fe	0.2	8	28	**64**	36
Pb	10	**63**	25	8	75
Ni	12	**42**	25	21	74
Zn	13	**54**	7	28	64
Co	18	25	**31**	23	68
Cu	5	30	**57**	15	92

[†] *The potentially bioavailable fraction is considered to be the sum of metal concentrations in the acid soluble, reducible and oxidisable fractions.*

This occurs through a complex combination of metal sequestration mechanisms, which include mineral precipitation, co-precipitation and adsorption. Reducing wetland conditions and sustained groundwater discharge from the underlying dolomite produce biogeochemical conditions that favour metal sequestration, creating a natural passive treatment system.

The Klip River case study highlights the importance of natural wetlands as vital biogeochemical systems that have a substantial ability to accumulate large quantities of metals and thus remediate polluted waters, particularly those affected by acid mine drainage.

Although the Klip River peats are an important sink for contaminants, the accumulation of a large chemical reservoir presents a possible future source of pollutants. Pollutant metals are associated with relatively unstable phases, potentially susceptible to chemically or biologically mediated release into interstitial waters. This emphasises the importance of conserving the Klip River system as degradation, particularly in the most proximal region, would likely cause the wetland to become a source of contamination.[22] It also highlights the need for future research focused on a better understanding of metal sequestration within the peat and the potential for remobilisation. In addition, an increase in chemical loading within the system may ultimately result in a decrease in metal retention efficiency over time. The Klip River peats are therefore unlikely to act as an infinite metal sink and an increase in contaminated discharge into the system could have devastating consequences for both the wetland and the region's water supply.

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Authors' contributions

M.S.H. and T.S.M. collected the samples and interpreted the data. All authors contributed to writing the manuscript.

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