

Assessment of Toxic Metals and Anionic Surfactants in Agricultural Soils, Crocodile River Catchment

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ABSTRACT

Increasing levels of toxic metals and surfactants in soils due to rapid urbanisation, industrialisation, intensive agriculture, and mining have led to environmental and human health concerns. In developing countries, agricultural soils are particularly vulnerable to contamination due to poor irrigation practices and effluent discharge. This study aimed to assess the levels of potentially toxic metals and anionic surfactants in agricultural soils around the Roodeplaat and Hartbeespoort Dams in the Crocodile River (West) Catchment, South Africa. Soil and water samples were collected from four agricultural sites and three control sites between June 2019 and March 2020. Soil samples were first digested using aqua regia digestion then analyzed using ICP-MS and ICP-AES. The methylene blue active substances (MBAS) assay was used to determine anionic surfactants. Data analysis involved Principal Component Analysis (PCA), the Geo-accumulation Index (Igeo), and Pearson correlation. The findings indicated that metals such as Cr, Fe, As, Pb, and Ni were above the regulatory limits. The Igeo values pointed to moderate to heavy anthropogenic contamination. Anionic surfactants were reported in all the soil samples, but they did not correlate with any of the metals. Contamination patterns between the two study sites could be differentiated by PCA, highlighting potential contamination from anthropogenic sources. Based on the findings, it was concluded that irrigation with polluted dam water was severely compromising the soil quality and raising concerns over crop safety and ecosystem health. Future studies will need to assess the levels of metals in the cultivated crops to investigate risks in the food chain.

Keywords: Agricultural soils, Anionic surfactants, Contamination, Crocodile River Catchment, Toxic metals

INTRODUCTION

One of the biggest challenges in the 21st century is the growing release of pollutants into the environment due to rapid urbanization, industrialization, and intensive agriculture. Recent evidence points to an increase in soil contamination by metal pollutants, thus posing food security, ecosystem integrity, and public health risks (Hou et al., 2025; Rashid et al., 2023). Even though many metals are found naturally in soils through geogenic processes, anthropogenic activities have been elevating their concentrations, thus posing environmental and health risks (Mkhize, 2020; Piwowarska et al., 2024).

Soils are naturally regarded as primary sinks for metal pollutants since they accumulate these contaminants from a variety of sources and determine their movement, bioavailability, and uptake by plants and other media (Wan et al., 2024). In agricultural soils, metals and metalloids are regarded as significant environmental contaminants due to their ability to accumulate and cause negative impacts on crop productivity, soil fertility, and food safety. If not transported through leaching, plant uptake, and remediation, metal pollutants can persist in soils for extended periods (Rashid et al., 2023). Worldwide, metal elements such as chromium (Cr), lead (Pb), mercury (Hg), copper (Cu), cadmium (Cd), zinc (Zn), nickel (Ni), and arsenic (As) are frequently reported among the most common pollutants in agricultural soils (Wan et al., 2024).

Among these, elements such as Hg, Pb, Cd, and As are very toxic even at trace levels and have the potential to accumulate in food crops and pose serious human health risks (Hou et al., 2025; Rashid et al., 2023).

The contamination of agricultural soil by metals has become an important global environmental issue. Anthropogenic activities such as manufacturing, mining, irrigation, wastewater treatment, power generation, use of pesticides and fertilisers, waste disposal, and rapid urbanization are all significantly contributing to the contamination of soils by metals (Rahman et al., 2021; Wan et al., 2024). Other major pathways contributing to metals accumulation in agricultural soils include livestock manure, deposition from the atmosphere, agrochemicals, and sewage sludge (Shapi et al., 2020). Natural geological processes and climatic conditions are also additional factors influencing the movement and accumulation of metals in soils (Shapi et al., 2020).

It is estimated that 14-17% of global croplands are affected by metal pollution (Hou et al., 2025). The problem is particularly prevalent in developing countries due to a lack of regulatory enforcement, environmental monitoring, and awareness of the impacts of toxic metals on human health and ecosystems (Rashid et al., 2023).

On the other hand, surfactants are increasingly being reported in the environment because of their regular use in industries and households. Unique properties such as self-aggregation, interface adsorption, and the ability to lower surface tension have made surfactants popular as detergents (Wo³owicz et al., 2022). Surfactants and metals can persist in water and soil, and their combined effects have not been well studied (Pierattini et al., 2018; Razak et al., 2013). Previous studies such as Razak et al. (2013) have suggested that surfactants react with metals to form complexes, thus making the metals more soluble in water and enhancing their adsorption onto particles (Razak et al., 2013).

The mining sector has been a driving force for the growth of the South African economy for decades. The unfortunate consequence of this extensive history of mining is the thousands of improperly closed and abandoned mines (Oyourou et al., 2019). Vast amounts of waste such as tailings produced during the mining processes contain high levels of toxic metals that end up leaching to contaminate groundwater or contaminating nearby soil. As of today, the mining sector remains a leading contributor to the South African economy, and the mining and processing procedures produce millions of tons of waste that end up contaminating air, soil, and water (Mkhize, 2020).

As the demands for food and agricultural land continue to rise sharply (Frona et al., 2019), promoting and maintaining healthy soils is of vital importance. Regardless, human-induced pollution remains a threat to many agricultural systems, with the Crocodile West irrigation scheme being one prime example (Du Preez et al., 2021). The Crocodile West irrigation scheme is dependent on water derived from the Crocodile West River, which is heavily polluted. This underscores the need to better understand the relationship between water pollution and pollution of agrarian soils in the area (Du Preez et al., 2021).

The Roodeplaat and Hartbeespoort Dams, located in the Crocodile West catchment, are renowned for being heavily polluted by human activities. They receive huge loads of nutrients and other pollutants from industrial and urban discharge, wastewater treatment effluent, mining discharge, and agricultural runoff (Lukhele et al., 2024; Mnyango et al., 2025). Since these dams are primarily used for irrigation, the current study aimed to assess levels of toxic metals and anionic surfactants in soils collected from agricultural fields around these two dams and to assess their suitability for agricultural use. The purpose of the study was to assess the pollution levels and sources of potentially toxic metals and anionic surfactants in soils irrigated with water derived from the Roodeplaat and Hartbeespoort Dams using the Geo-accumulation Index and Principal Component Analysis. The findings are expected to inform long-term pollution control and mitigation in the catchment.

MATERIALS AND METHODS

Site description

The study area was the Hartbeespoort and Roodeplaat Dam sites (Figure 1). The two dams are found in the Crocodile (West) and Marico Water Management Area (WMA). The Crocodile and the Marico are the two main rivers in the WMA. The Hartbeespoort Dam is primarily used for recreation, irrigation, and domestic water supply. The Crocodile River catchment is characterized by dense human settlements and is highly industrialized and thus experiences extreme pollution levels. The overbank part of the Crocodile River, particularly downstream of the Hartbeespoort Dam, is under intensive agriculture and is subject to much irrigation.

The Roodeplaat Dam, on the other hand, is used mainly for potable and irrigation purposes. Activities in the catchment comprise approximately 12%

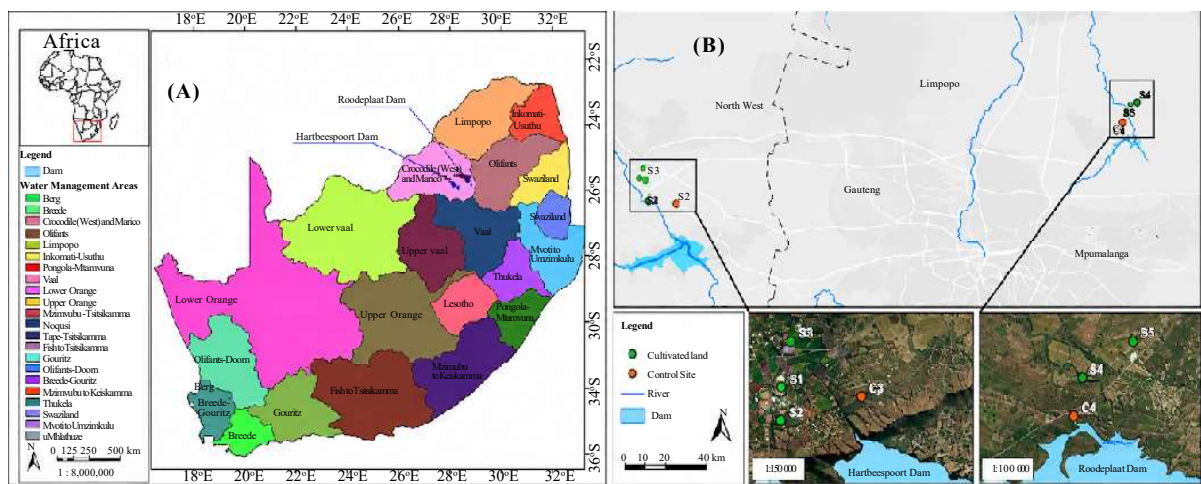


Figure 1. (A) Location of the Crocodile Marico West WMA and the Roodeplaat and Hartbeespoort Dams (B) Location of the sampling points at the two sites: Roodeplaat and Hartbeespoort Dam sites.

urban/industrial, 23% agriculture/cultivated land, and the remaining part grasslands. The three major rivers feeding the Roodeplaat Dam are the Pienaars, Edendalespruit and Hartbeespoort Rivers. Both the dam and its feeding rivers have been described as hyper-eutrophic. The major sources of pollution into the rivers are industrial effluents, urban discharge from households, sewage treatment plants and agricultural run-off emanating upstream of the Roodeplaat Nature Reserve (Marchand et al., 2012).

The study area has a highland subtropical climate characterised by summer rainfall (October to March) and mean annual rainfall of about 700 mm. The area's summer temperatures range from a minimum of 15 °C to a maximum of 30 °C, and winter temperatures range from 5 °C to 25 °C (Ali et al., 2022). The area's geology generally consists of the Chuniespoort group overlain by the Pretoria Group with an intrusion of the Bushveld Complex (Davis, 2017). Typical rocks in the area are the karstic dolomites deposited approximately 2,643 and 2,520 million years ago (Davis, 2017).

Soil and Water samples collection

Sampling was conducted in June 2019, September 2019, February 2020, and March 20. Soil samples were collected from four agricultural sites. Water samples were collected from farm dams adjacent to the selected agricultural fields and tested for pH and anionic surfactants. The sampling sites were named S1, S2, S3, and S4 (S1 & S2 located at the Hartbeespoort Dam site, and S3 & S4 at the Roodeplaat Dam site, Figure 1(B)). Control samples (i.e., from non-cultivated areas) named C1, C2 and C3 were collected a few kilometres away from the

sampled crop fields at the two sites (Roodeplaat and Hartbeespoort).

All sampling containers were thoroughly washed with 10 % hydrochloric acid (HCl) solution, followed by rinsing with deionised water (Milli-Q). This was then followed by another rinsing step with 50 mL of methanol and, lastly, another rinse with deionised water (Milli-Q) before being left to dry. Soil samples for anionic surfactants were collected at 5-10 cm depth and transported in 250 mL glass jars. The glass jars were covered with a methanol-washed aluminium foil on the mouth of the jars, with the soils preserved in a 10 % formalin solution. The tightly closed glass jars were transported to the laboratory in a cooler packed with ice to prevent degradation and contamination of the samples. For the determination of toxic metals, approximately 250 g of soil samples were collected using a plastic hand shovel at a depth of about 10 cm and transported in clear 100 × 150 mm polyethylene plastic bags. The plastic bags with the samples were tightly closed and transported to the laboratory for extraction and analysis.

The water pH was monitored using a Jen-way pH/Cond meter (model 430) (United Kingdom) in situ at the irrigation canals/farm dams at each site. Water samples for anionic surfactant determinations were collected in 100 mL Schott amber bottles. The sampling bottles were dosed with 3 mL of 30 % (v/v formalin) to preserve the water samples and prevent the biodegradation of the anionic surfactants. All samples were collected in triplicate.

Determination of anionic surfactants

Any overlying water in the soil samples in the jars was removed, and the soils were dried in an oven at 60 °C for 24 h. Extraction of the surfactants

from the dried soils was done using a modification of the method by Sanderson et al. (2006). In brief, the extraction was achieved through sonication of the soils in 100 % methanol in a sonication bath at 50 °C. Three sequential extractions of 10 min each with 10 g of the dried soil and 30 mL methanol were conducted in 50 mL centrifuge tubes, and the soils and extracts were separated through centrifugation at 3000 rpm for 30 mins (Hermle Z 366 centrifuge, Wehingen, Germany). The collected methanol supernatant (extracts) was pooled (approximately 90 mL) and dried at 50 °C under a stream of N₂ gas. The dried extract was then reconstituted in 25 mL of deionized water (Milli-Q) for the methylene blue active substances assay (MBAS) analysis.

The HANNA methylene blue active substances (MBAS) assay/test kits were used to determine the levels of anionic surfactants in both the soils and water. The assay is a colourimetric test that relies on methylene blue to detect the levels of anionic surfactants available in a sample. The assay was carried out following the supplier's manual, and a HANNA HI96769 Anionic Surfactant Portable Photometer (Hanna Instruments, South Africa) was used to give the readings.

Determination of metals

To determine the levels of metals in the soil samples, the samples were first acid-digested using the aqua regia method according to Rashid et al. (2016). Briefly, the oven-dried soils (80 °C for 24 h) were ground to a fine powder using a mortar and pestle and then sieved (particle size <100 µm). Ten grams of the ground and sieved soil sample was then digested with 20 mL of aqua regia (HCl: HNO₃ (3:1) in a 250 mL conical flask. Digestion was conducted by heating at 95°C on a hot plate for 1 h and then allowing the mixture to cool at room temperature. This was followed by filtering the mixture using Macherey-Nagel No.1 filter paper (0.45 µm) (Macherey-Nagel, Germany) and then diluting the filtrate with deionised water (Milli-Q) to the 50 mL mark in a volumetric flask. The diluted samples were kept in a refrigerator at 4°C and later transferred to the Stellenbosch University Central Analytical Facility for analysis of minor & trace elements (combined) using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

Data analysis

Data sorting and management were done in Microsoft Excel (2013), and data analysis was conducted in IBM SPSS version 28.0 for bivariate

correlation analysis, and GraphPad Prism 10 was used for Principal Component Analysis (PCA).

Geo-accumulation index

The geo-accumulation index (I_{geo}) was used to quantify pollution of the toxic metals. This index measures the pollution of each metal against its background levels (Oyebamiji et al., 2024). The geo-accumulation index was calculated according to Müller (1969) using equation 1 below.

$$I_{geo} = \log_2 \frac{C_n}{1.5 \times B_n} \quad (1)$$

Where:

C_n - the concentration of the metal in the sample,
B_n - the concentration of the material in the control/
background sample (Control samples),

1.5 - constant/factor used to limit the possible variances in the background, which might be due to anthropogenic and lithologic changes.

The I_{geo} was interpreted according to Müller (1969), who defined the classes of the I_{geo}, as: I_{geo} < 0 (uncontaminated); 0 ≤ I_{geo} < 1 (uncontaminated to moderately contaminated); 1 ≤ I_{geo} < 2 (moderately contaminated); 2 ≤ I_{geo} < 3 (moderately to heavily contaminated); 3 ≤ I_{geo} < 4 (heavily contaminated); 4 ≤ I_{geo} < 5 (heavily to extremely contaminated); and I_{geo} ≤ 5 (extremely contaminated).

RESULTS AND DISCUSSION

Potentially toxic metals in agricultural soils

Based on the findings in Table 1, the mean levels of Cr in the soils from both dam sites were higher than the guideline limit set by the South African Department of Environmental Affairs (DEA, 2010) for agricultural soils in all four crop fields. The mean levels of Fe, As, and Pb exceeded the U.S. Environmental Protection Agency (2011) and DEA (2010) thresholds in soils collected from the sampling stations at the Roodeplaat Dam site. The mean levels of Ni exceeded the DEA (2010) in soils collected from the two sampling stations at the Hartbeespoort Dam site. Such high levels of metals such as Cr, Fe, As, Ni, and Pb could be attributed to the Cr and Pt mining activities around the Hartbeespoort Dam area, in addition to the hype of industrial, mining, and domestic activities taking place upstream of the Crocodile River. Similar to our findings, Nde and Mathuthu (2018) found that the toxic elements in the water and sediment samples from the Crocodile River catchment were above the limit recommended by the South African Department of Water Affairs

Table 1. Levels of metals in the cropping fields monitored.

Parameter (mg kg ⁻¹)	Site			
	S1	S2	S3	S4
Al	28683.72±18720.00	30671.01±20800.00	10176.03±5951.60	10647.31±6943.10
	2520.00–48617.00	2271.00–56742.00	701.50–15612.00	1331.50–20687.00
B	3.66±2.60	3.10±2.38	2.65±0.97	2.26±0.87
	1.37–8.70	0.93–7.47	1.11–3.61	1.17–3.61
Cr	185.433±50.372	149.779±78.082	144.221±76.192	144.907±63.101
	111.07–229.30	91.51–320.29	83.30–307.96	87.90–273.49
Mn	496.90±228.99	812.88±347.60	1263.41±890.16	1804.58±1148.00
	244.79–881.01	269.43–1137.00	770.02–3254.10	752.20–3475.90
Fe	16534.47±10259.00	17075.82±11339.00	27139.54±14194.00	28228.92±14728.00
	1507.00–25826.00	1387.00–28766.00	3155.50–42523.00	3526.00–41291.00
Ni	85.31±11.43	85.85±16.95	41.46±23.91	44.46±21.46
	70.68–104.46	66.10–111.50	24.07–91.50	23.32–88.02
Cu	22.11±8.79	25.06±8.72	32.23±18.44	33.95±16.70
	15.31–41.20	14.20–36.90	18.22–72.21	20.15–69.57
Zn	36.22±7.07	46.64±16.51	60.03±22.76	49.51±13.97
	28.34–49.97	24.96–74.44	29.91–92.30	33.33–73.12
As	0.80±0.33	2.83±3.21	9.70±4.31	9.43±4.41
	0.52–1.32	0.44–9.30	5.33–18.49	4.10–17.26
Cd	0.05±0.01	0.06±0.02	0.04±0.02	0.04±0.02
	0.03–0.06	0.03–0.09	0.02–0.08	0.02–0.06
Hg	0.09±0.12	0.09±0.11	0.10±0.12	0.10±0.14
	0.01–0.27	0.01–0.26	0.02–0.27	0.01–0.34
Pb	4.44±3.08	6.41±2.41	20.29±13.30	24.16±10.41
	1.88–9.88	4.14–11.52	7.50–46.94	16.20–46.15
Anionic	3.00±1.47	3.33±3.70	3.10±1.60	2.54±0.96
Surfactants	1.72–5.13	0.91–8.73	1.36–5.17	1.84–4.63

Values represent mean ± standard deviation & Min – Max; [†]US Environmental Protection Agency (2011).

N.B: Figures in bold exceed the stipulated guidelines.

and Forestry (DWAf) and the United States Environmental Protection Agency (USEPA).

The Igeo results in Table 2 show that the Igeo values for Cd, Fe, Pb and Zn were below zero, thus suggesting no contamination of the cropping fields by these metals. The Igeo class for Cr, Cu and Mn were between 0 and 1, indicating no contamination to moderate contamination at all four sampled sites. Differences in the two areas (Hartbeespoort and Roodeplaat) were noted for metals like Ni, which showed moderate contamination for Hartbeespoort sampling sites compared to no contamination/moderate contamination for Roodeplaat sites. Whereas, As had a higher Igeo (moderate contamination) at the Roodeplaat sites and a low Igeo (no contamination) at the Hartbeespoort sampling sites. Higher Igeo values, showing

moderate contamination, were reported for Hg in all four cropping fields, and moderate to heavy contamination was reported for Al at the two Hartbeespoort sampling sites. The high Igeo values in Table 2 for As for the Roodeplaat sites and Ni for the Hartbeespoort sites confirm their exceedance of the set limits for agricultural soils in Table 1. Inasmuch as metals such as Hg and Al did exceed the set guidelines in Table 1, their high Igeo values for these metals based on Müller's (1969) classification suggest heavy contamination from anthropogenic sources.

Contrary to our findings, Nde and Mathuthu (2018) studied sediments in the same study area (upper Crocodile River catchment) and found the Igeo values for Cu, Pb, Cd, Zn, As, Mn and Al to be less than zero (uncontaminated). Whilst the Igeo

Table 2. Soil contamination assessment for soil samples collected at various agricultural sites.

Metal	S1		S2		S3		S4	
	Igeo	[†] Igeo Class	Igeo	[†] Igeo Class	Igeo	[†] Igeo Class	Igeo	[†] Igeo Class
Al	2.157	4	2.254	4	0.240	2	0.305	2
Cr	0.342	2	0.034	2	0.822	2	0.829	2
Mn	0.029	2	0.739	2	0.060	2	0.574	2
Fe	-0.529	1	-0.482	1	-0.287	1	-0.231	1
Ni	1.065	3	1.074	3	0.550	2	0.650	2
Cu	0.015	2	0.195	2	0.275	2	0.350	2
Zn	-1.083	1	-0.718	1	-0.299	1	-0.577	1
As	-2.459	1	-0.636	1	1.409	3	1.368	3
Cd	-0.694	1	-0.336	1	-1.043	1	-1.242	1
Hg	1.624	3	1.647	3	1.524	3	1.607	3
Pb	-2.925	1	-2.397	1	-0.731	1	-0.479	1

[†]Igeo Class: 1=uncontaminated; 2= uncontaminated to moderately contaminated; 3=moderately contaminated; 4=moderately to heavily contaminated; 5=heavily contaminated; 6=heavily to extremely contaminated; 7=extremely contaminated

values for Cr indicated no contamination to moderate contamination in all four sites sampled here, Nde and Mathuthu (2018) found moderate contamination in all the land uses they investigated. All the potential toxic metals, such as Ni, As, Hg, Cu and Cr, found to be moderately contaminating the agricultural soils in the study area are known to be found in the natural environment, but are elevated by human activities such as agriculture, industry and mining (Martinez-Guijarro et al., 2021). Aluminum (Al) levels in soils are also known to be elevated by anthropogenic activities such as mining and geological activities (Hýzlý et al., 2023).

Toxic metal contamination of soils and sediments in areas dominated by anthropogenic activities such as agriculture, mining, and human settlements is a common feature in the South African context. Addo-Bediako et al. (2021) found high levels of Cr and Ni in sediments collected on the banks of the Spekboom River, in Mpumalanga Province of South Africa. Addo-Bediako et al. (2021) attributed these elevated levels of Cr and Ni to anthropogenic activities like agriculture, mining, and industrial activities, resulting in toxic metal pollution to the river ecosystem. Ouma et al. (2022) also attributed toxic metal pollution in many South African river catchments to mining activities and the release of toxic metals such as Pb, Hg, Zn, and As. Similar to our findings, Duncan et al. (2018) found high levels of Pb and Cr in the Pra mining Basin in Ghana. In addition to Pb and Cr, Duncan et al. (2018) also found high levels of Cd and attributed this to illegal mining taking place in the area.

Anionic surfactants & water pH

Over the sampling duration, the mean anionic surfactant levels in agricultural soils ranged from 2.54 ± 0.96 to 3.33 ± 3.70 mg kg⁻¹. In this study, anionic surfactants were recorded in all agrarian soils sampled, ranging from 0.91 to 8.73 mg kg⁻¹. In comparison, Ekmekyapar and Celtikli (2014), found higher levels of the anionic surfactant linear alkylbenzene sulfonate (5.84 to 19.6 mg kg⁻¹) in agricultural soils in Istanbul, Turkey. Anionic surfactants were deemed important to monitor in this study since they are known to increase the levels of metals in soils, since they act as chelates for metals in soil solution (Hernandez-Soriano et al., 2008). Anionic surfactants are also known to promote soil organic matter solubility and thus increase the solubility of metals attached to organic matter (Hernandez-Soriano et al., 2008).

The Pearson correlation findings in Table 3 showed no correlation between anionic surfactants (in both water and soil samples) and any of the metals monitored. However, a study by Razak et al. (2013) reported a correlation of surfactants in a lake's microlayer with metals like Pb, Zn, Cd, and Ni, thus indicating that the co-existence of surfactants and metals in the surface microlayer may enhance metal availability in the water.

As with many hypertrophic water bodies, the water pH from these two dams is alkaline; the current study reported water pH values above 9 for both dam sites. The study's findings in Table 3 showed that the water pH did not correlate with any of the

Table 3. Pearson correlation matrix of the parameters monitored.

	B	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Hg	Pb	SS	Water pH
Al	.638**													
Cr	-0.046	-0.004												
Mn	-0.279	-0.293	0.131											
Fe	0.353	0.346	-0.356	0.141										
Ni	0.242	.451*	.536**	-0.049	-.544**									
Cu	-0.336	-0.229	.414*	.758**	-0.179	0.201								
Zn	-0.178	-0.347	-0.296	0.305	-0.108	-0.161	.411*							
As	-0.221	-.553**	0.282	.654**	0.149	-0.332	.629**	0.371						
Cd	0.107	0.240	-0.093	0.098	-.399*	.523**	0.289	.524**	-0.171					
Hg	.586**	0.165	-0.185	-0.191	0.284	-0.094	-0.241	-0.196	0.083	-0.139				
Pb	-0.173	-.440*	0.242	.800**	0.147	-0.225	.735**	0.252	.898**	-0.095	0.151			
SS	-0.215	.386*	-0.057	-0.024	0.253	0.041	0.200	0.105	-0.226	0.078	-.444*	-0.237		
Water pH	0.012	0.125	-0.249	-0.146	0.295	-0.202	-0.337	-0.120	-0.228	-0.118	-0.126	-0.278	0.193	
SW	-0.158	0.184	-0.057	0.000	0.180	-0.015	0.174	0.163	0.028	0.018	-0.328	-0.055	.706**	-0.097

** Correlation is significant at the 0.01 level (2-tailed); * Correlation is significant at the 0.05 level (2-tailed). SW=Anionic surfactants in water; SS= Anionic surfactants in soil.

metals in the sampled soils. Previous studies, such as Abiye et al. (2015), have reported similar pH for the Hartbeespoort Dam. Even though none of the metals correlated with the water pH, Davis (2017) postulated that the high pH levels in the Hartbeespoort Dam water are likely to elevate the solubility index of the water and increase the likelihood of metals forming salts in the irrigated soils.

Compositional relation

It is evident in Figure 2 (Bii) that locality plays a significant role in metal element levels and

distribution as expressed by the PCA. Figure 2 (bii) shows that the positive side of PC1 was explained by soils from the Roodeplaat site, whereas the negative side of the same PC (PC1) was explained by Haartbeespoort site soil samples. Metals that exceeded the set guidelines, such as Cu, As, Pb, and Zn, were dominant in PC1 (Figure 2(A). Table 3 and Figure 2(A) acknowledge the interactions and correlations between the monitored parameters produced by Pearson correlation and PCA. For example, the strong positive correlations of B & Al; B & Hg; Cr & Ni; Mn & Cu; Mn & As; Mn & Pb;

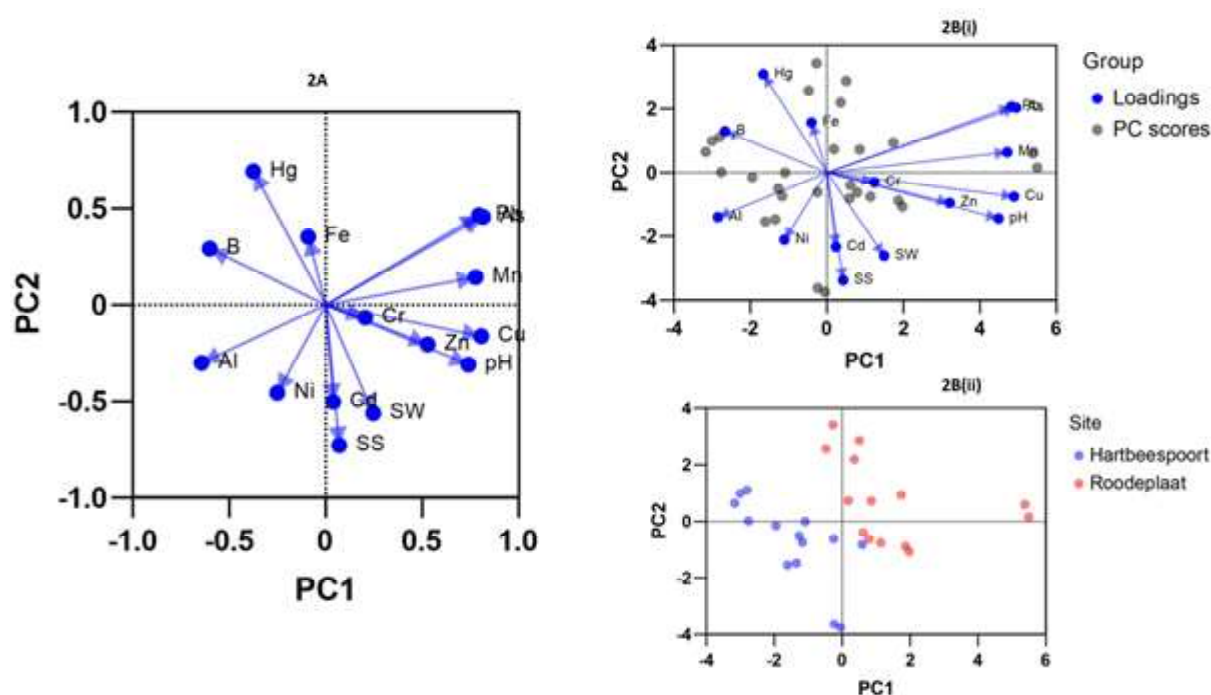


Figure 2. Results of the Principal Component Analysis (PCA) carried out on the metals, water pH, and anionic surfactants monitored in the soils at the different sites throughout the study.

Ni & Cd; Cu & As; Cu & Pb; Zn & Cd; As & Pb and Surfactants in water & Surfactants in soil and strong negative correlations between Al & As and Fe & Ni were reported by both Pearson correlation and PCA loadings (in Table 3 and Figure 2A).

Principal components

The results of the principal components analysis are summarised in Figure 2. The PCA used the data for the levels of the metals and anionic surfactants found in the soils and the water pH to help characterise the patterns and groups formed. The first principal component, as given Figure 2, is largely positively contributed by Mn, Cu, Zn, As, Pb, and water pH. The second PC, PC2, is mainly positively contributed by Hg, Pb, As, and Fe. What is apparent in Figure 2 is that metals such as Hg, Al and Ni, which showed high Igeos in Table 2, dominated the negative side of PC1, thus supporting the assumption that their presence at elevated levels in the sampled soils could be heavily attributed to the same source, which is anthropogenic activities.

Human activities such as agriculture and industrial and mining activities could contaminate the soils with metals. The Hartbeespoort and Roodeplaat Dams receive water from rivers like the Crocodile River. The Crocodile River catchment has for decades been extensively used for industry, agriculture, urban use, and mining (Nde & Mathuthu, 2018) and thus receives a considerable number of pollutants from these anthropogenic activities, which end up contaminating the two dams and the soils through irrigation and run-off.

Figure 2A shows the interactions and correlations between the toxic metals as found in the Pearson correlation matrix of the parameters monitored (Table 3). The bi-plot and PC map (Figure 2B) differentiate the two sampling sites (Hartbeespoort and Roodeplaat) with respect to the metal elements in the soils. The PC1 coordinates on the positive side largely represent the Hartbeespoort site, characterized by high loadings of metals such as As, Pb, Mn, Cu, Zn, and water pH. The negative side of PC1 isolates the Roodeplaat site largely and is mainly characterized by metals such as Al, B, Ni, and Hg.

Such findings can help find potential sources of metal contaminants in the study area since it is characterized by high anthropogenic activities such as industries, mining, agriculture, and urban settlements. The negative side of PC1 can be attributed to human activities such as industrial, mining, and agricultural activities that could result in soil contamination with metals such as Al, Hg and

Ni, which demonstrated high Igeo values. The positive side of PC1 with high loadings of Mn, Pb, Cu, Zn mainly represents metals which demonstrated low Igeo values, thus representing their presence mainly due to their background presence in the area under study.

CONCLUSION

This study reports elevated levels of human-induced pollution of agrarian soils in the Crocodile River (West) Catchment. The elevated levels of toxic metals and anionic surfactants reported pose a threat to environmental integrity and human health. Both the PCA and elevated Igeo values point to a common pollution source potentially linked to irrigation derived from the Hartbeespoort and Roodeplaat dams. Despite the lack of regulatory guidelines for anionic surfactants, their presence in the soils could be exacerbating the uptake of toxic metals by crops. Such findings highlight the need for urgent and strict control measures to abate regional pollution. Future studies looking at the levels of toxic metals in the crops grown in the study area and their fitness for animal and human consumption are recommended.

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